A. Z. Aris · T. H. Tengku Ismail
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From Sources to Solution

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Chapter 1
Enterococci Concentrations in Tropical Coastal Beaches in Malaysia Correlate Better With Pathogen Levels and Other Water Quality Indicators than Faecal Coliforms

Asmat Ahmad, Ayokunle Christopher Dada, Gires Usup and Heng Lee Yook

Abstract There is currently no bacteriological beach quality monitoring (BQM) program in place in Malaysia. To initiate cost-effective, sustainable bacteriological BQM schemes for the ultimate goal of protecting public health, policy decision makers need to be provided robust, indigenous empirical findings that validate appropriate water quality parameters for inclusion in such monitoring programs. This is the first study that assesses the validity of *enterococci* as an ideal indicator for bacteriological BQM in Malaysia using a multivariate approach. Beach water and sand samples from seven beach locations were analyzed for a total of twenty-one microbial and non-microbial water quality parameters. A multivariate approach incorporating cluster analyses (CA), principal component analyses (PCA), and factor analysis (FA) was also adopted. Apart from the weak correlations of *Staphylococcus aureus* with concentrations of *Vibro* species ($r = 0.302$, $p = 0.037$) and total coliforms ($r = 0.392$, $p = 0.006$) in seawater, no correlation existed between *S.aureus* concentration and other parameters. Faecal coliforms failed to correlate with any of the tested parameters. *Enterococci* also correlated with more quality parameters than faecal coliforms or any other indicator. PCA/FA clearly delineated *enterococci* and faecal coliforms as parameters that weighed

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strongly for BQM while *Staphylococcus aureus*, faecal coliforms and *enterococci* weighed strongly for beach sand quality monitoring. On the whole, higher correlations of *enterococci* level with other parameters than was observed for faecal coliforms suggest that the former be considered a preferred parameter of choice for BQM in Malaysia.

Keywords *Enterococci* · Indicator · Recreational Beaches · Bacteriological quality monitoring · Multivariate Approach

Highlights

- *Enterococci* presented with stronger weightings for BQM in Factor Analysis.
- *Enterococci* also correlated with more quality parameters than any other indicator.
- *Enterococci* may be considered a preferred indicator choice for BQM in Malaysia.

Introduction

In Western nations, beach water and sand quality monitoring has attracted significant attention in recent years owing to improved legislation. The situation may be particularly worrisome in less economically developed countries where legislative standards do not exist as a result of frail institutions and tight budgets. In such cases, a prevailing absence of surveillance schemes may allow in beaches undetected pollution from stormwater, domestic sewage and industrial effluents. The situation is exacerbated as less developed nations are often at a loss on how to develop workable standards for the purpose of beach water quality monitoring. Usually, relevant authorities consider water quality statistics and take a decision on what proportion of failures they think can be accepted based on a consideration of political factors, economic factors and suggested minimum action levels (MAC) that are hinged on available empirical data. In cases where there are no indigenous studies that present empirical findings which suggest epidemiologically proven action levels or maximum admissible concentrations that made a case for the initiation of a beach water bacteriological quality monitoring (BQM) program, a worst case scenario of political inaction and negligence might ultimately become observable. With a more or less generalist approach, a surveillance program is currently in place for marine water quality that lays emphasis on levels of faecal coliform (*E. coli*), oil and grease, total suspended solids and selected heavy metals. Public recreational beaches are however, apparently left out of these surveillance schemes. Recent review articles have highlighted potential impacts of tourism

activities, shipping, refinery effluent, land reclamation and coastal zone property development on recreational water quality in Malaysia has previously been highlighted (Dada et al. 2012; Praveena et al. 2011). This study aimed at generating correlations between *Enterococci* and other water quality parameters used in water quality monitoring. Second objective was to explore the use of multivariate techniques in validating an *Enterococci*-based indicator organism paradigm for use in bacteriological BQM in Malaysia.

Materials and Methods

Beaches considered were Pantai Irama, Senuk, Sabah, Cahaya Bulan, Kuala Besar, Sri Tujuh and Tok Bali. Physico-chemical parameters were measured on site using a YSI 556 hand-held multi-probe. *Enterococci* were recovered from beach water and sand via membrane filtration method using Slanetz and Bartley agar. Counts of *Staphylococcus aureus,* total viable bacteria, total/faecal coliforms and *Salmonella* were enumerated using mannitol salt agar, NaCl supplemented nutrient agar, chromogenic coliform agar and Salmonella-Shigella agar respectively. Geometric mean-based correlation analyses were conducted to explore relationships between *Enterococci* and other microbial and non-microbial parameters measured in the study. Following confirmation of goodness-of-fit using Kolmogorov–Smirnov (K–S) statistics, data obtained were z-scale transformed prior to further analysis. Significant PCs were extracted from the PCA and varimax rotated to generate verifactors (VFs) in Factor Analysis (FA) (Abdul-Wahab et al. 2005).

Results and Discussion

From Pearson correlation analysis, it was observed that *Enterococci* concentrations significantly correlated to more parameters than any other microbial or non-microbial parameter analyzed in this stud. Both seawater and sand concentrations of *Enterococci* correlated in varying strengths to the concentration of *Salmonella typhi* in water ($r = 0.445$, $p = 0.002$ and $r = 0.739$, $p = 0.000$ respectively). The correlation between *Enterococci* concentration in sand and the concentration of pathogens in seawater as was observed in this study supports the position of other studies that suggested beach sand can be a source of faecal indicator bacteria and pathogens to adjacent waters (Oshiro and Fujioka 1995). The correlation of *Enterococci* in seawater however was inversely correlated to temperature ($r = -0.590$, $p = 0.000$), salinity ($r = -0.386$, $p = 0.009$) and dissolved oxygen ($r = -0.537$, $p = 0.000$). The negative correlation of water temperature to *Enterococci* antagonizes the concerns that indicator organisms may grow in the environments as argued by a previous study that observed positive correlations between the two parameters in temperate locations (Goodwin et al. 2012). This

study was conducted in a tropical setting with typically high day temperature reaching up to 35 °C. This might have significant implications on population dynamics of the microorganisms studied.

Enterococci concentration in beach sand correlated inversely but in stronger terms with dissolved oxygen levels in seawater. Apart from the weak correlation of *Staphylococcus aureus* concentration in seawater with *Vibro* species ($r = 0.302$, $p = 0.037$) and total coliforms ($r = 0.392$, $p = 0.006$) in seawater, no other correlations existed between *Staphylococcus* concentration and other parameters. Similarly, concentration of *Staphylococcus aureus* in beach sand correlated weakly with those of *Vibro* species ($r = 0.360$, $p = 0.012$) and total coliforms ($r = 0.595$, $p = 0.000$) in beach sand. This observation questions the adoptability of *S. aureus* for use as beach water quality indicator in the considered location. Notwithstanding, findings from this study are in concert with El-Shenawy (2005) that reported that *S. aureus* did not correlate with various other indicators. Notably, faecal coliform concentration in seawater did not correlate with any of the parameters tested apart for inverse correlations with *Vibro cholerae* ($r = -0.436$, $p = 0.02$) in seawater. This observation presents a shadow of doubt on the appropriateness of faecal coliform concentration for seawater quality monitoring in the studied location. Interestingly also, faecal coliform concentration in sand also did not correlate with any of the tested beach sand quality parameters. On a general note, the results of the correlation analysis apparently indicate that *Enterococci* concentrations seem to be a preferred choice indicator bearing in mind that it correlated more and better with other microbial parameters. This observation is in concert with a previous report (WHO 2003).

All 21 variables of normalized data sets for the four different spatial regions obtained from hierarchical cluster analysis (CL1-4) in this study were used for principal component analysis (PCA). PC1-PC6 were retained as they had eigenvalues higher than 1 and were responsible for 86.3 % of the variance or information contained in the original data set. Following verimax rotation of significant PCs, the first six VFs retained spanned 80.3 % of the variance as opposed to 86.3 % as explained by the same number of PCs. For beach sand delineated parameters; *Staphylococcus aureus* (SAS), faecal coliforms (FCS), *enterococci* (ES) and total plate count (TPCS) emerged with strong positive loadings significantly contributing to the variance following verimax rotation in factor analysis (Fig. 1.1). On the other hand, delineated parameters which weighed strongly for beach water were e*nterococci* (EW) and faecal coliforms (FCW) (Fig. 1.1). However, *enterococci* concentration in seawater (EW) weighed strongly in the first verifactor which was responsible for 28.9 % of the total variance unlike faecal coliforms (FCW) which weighed strongly only in the second verifactor responsible for a lesser amount of variance (15.8 %). Barrell et al. (2000) argued that although faecal coliforms were also independently associated with illness in some studies, the apparent superiority of *enterococci* as indicators of health risk in both drinking and bathing waters remains undisputed.

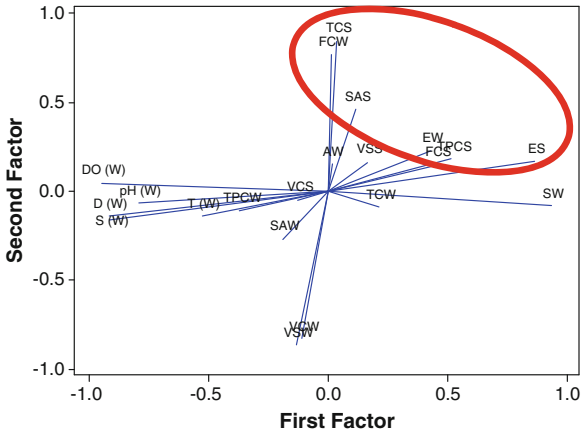

Fig. 1.1 Loading plots based on output from FA (1) *TPCS* total heterotrophic plate count of beach sediment samples (BSS) (2) *EW Enterococci* concentration in beach water samples (BWS) (3) *ES Enterococci* concentration in BSS (4) *SW Salmonella typhi* concentration in BWS (5) *SAW Staphylococcus aureus* concentration in BWS (6) *VCW Vibro cholerae* concentration in BWS (7) *VCS Vibrio cholerae* concentration in BSS (8) *VSW Vibrio* spp concentration in BWS (9) *VSS Vibrio* species concentration in BSS (10) *TCW* Total coliform count of BWS (11) *TCS* Total coliform count of BSS (12) *FCW* Faecal coliform count of BWS (13) *FCS* Faecal coliform count of BSS (14) *AW Aeromonas hydrophila* concentration in BWS (15) *EW Enterococci* concentration in BWS (16) *SAS Staphylococcus aureus* counts of BSS (17) *T* BWS temperature in °C (18) *D* Dissolved oxygen in % air saturation (19) *DO* Dissolved oxygen in mg/L (20) *pH* measure of the activity of the hydrogen ion concentration of BWS (21) *S* Salinity (in ppt) of BWS

Conclusion

Findings from this study provide meaningful evidence for policy direction particularly as it relates to the correlation of *Enterococci* with pathogens and other non-microbial parameters. *Enterococci* counts in beach water samples (EW) emerged with strong loadings and better correlations in our analysis, thus signifying its appropriateness for use as indicator in bacteriological BQM in Malaysia.

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Chapter 2
An Application of Artificial Neural Networks for the Prediction of Surface Ozone Concentrations in Malaysia

Negar Banan, Mohd Talib Latif, Liew Juneng and Md. Firoz Khan

Abstract In this study, an artificial neural network (ANN) was used to extract the complex relationships among divergent parameters that have the capabilities to predict O_3 concentrations which serve as an input to meteorological conditions and precursor concentrations. The ANN was trained using samples of daily maximum data provided by the Malaysian Department of the Environment (DOE) over a period of 9 year (2003–2011) in the towns of Gombak and Shah Alam in Malaysia. Furthermore, surface O_3 concentrations from the two locations (Gombak and Shah Alam) were estimated using surface meteorological variable as predictors for the ANN. Based on the results, it can be deduced that the relationship between the parameters and the O_3 concentrations are highly complex and non-linear. Analysis of the regression based model results between Gombak and Shah Alam were evaluated using the ANN. Based on the sample results it was confirmed that Shah Alam has the highest regression result of $R = 0.64$ in comparison with Gombak station. The inference drawn from this study shows that neural network model consistently gives superior predictions.

Keywords Artificial neural network · Surface ozone · Meteorological factors · Regression

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Highlights

- Artificial neural network model successfully predicts O_3 concentration.
- O_3 precursors and meteorological factors influenced predicted O_3 concentration.
- The proposed algorithm exhibits a high accuracy model.

Introduction

Ozone (O_3) is a major constituent of smog because it is readily released into the atmosphere as a result of photochemical oxidation and hence, a heavy air pollutant. Many studies have shown that the high presence of O_3 is capable of causing severe health respiratory disease (Huang et al. 2012; Neidell and Kinney 2010). Furthermore, it has been proved that there is a positive correlation between exposure to O_3 and decrease in lung function (Highfill and Coasta 1995). At high O_3 concentration, vegetation and forests are affected because of the phytotoxic nature of O_3. Higher concentration above 40 ppbv can be suggested to be harmful to the plants yield, biomass production, vitality and stress tolerance of forest trees (Fuhrer et al. 1997). It has been suggested that excessive level of O_3 may affect the ability of the forest to seize carbon in an event of excess of CO_2 in the future (Banan et al. 2013).

Modeling of O_3 concentrations is not a trivial procedure due to the intrinsic relationship between pollutants and meteorological variables (Sousa et al. 2007). However, different regression approaches have been adopted for forecasting surface O_3 with the predictor parameters varying from a few to a large sample inputs. Studies conducted by Wang et al. (2003) using statistical characteristics of O_3 to enable selection of appropriate predictors of daily maximum O_3 levels and highlighted the inclusion of parameters that affect both photochemical production and atmospheric accumulation of O_3 when forecasting O_3 levels. In this paper, ANN is used for the prediction of the daily maximum O_3 concentration in urban areas using the precursors and meteorological variables.

Materials and Methods

This experiment is carried out with two datasets collected from the air quality monitoring sites at the Department of the Environment (DOE) in Malaysia, which is managed by a private company, Alam Sekitar Sdn Bhd (ASMA). The daily maximum concentration of air pollutants such as; O_3, NO, NO_2, NO_x, CO, PM_{10} and NMHC and daily maximum meteorological variables (Ambient temperature (AT), Humidity (H), Wind speed (WS) and wind direction (WD)) were used. The logarithm of daily maximum O_3 concentrations of two stations, namely Gombak

Table 2.1 Characteristics of the datasets

Datasets	No. of attributes	Training set 70 %	Testing set 20 %	Validation set 10 %
Gombak	10	1019	291	146
Shah Alam	10	1732	495	247

and Shah Alam stations, that are located in Klang Valley in the middle of the Malaysian Peninsula, were derived and used for modeling. The concentration data were sourced from a 9-year period data samples (2003–2011). All the data were used to evaluate the predicting performance of the modeling data. The characteristics of the datasets used are summarized in Table 2.1.

ANN Model for Air Quality Prediction

The model of employed ANN is shown in Fig. 2.1. It comprises of three layers of neurons namely; input, hidden, output layers. The input layer is the first layer of neurons. Each input neural represents a separate attribute in the train/test datasets station (for example from NO to WD). The number of the inputs is equal to the number of attributes in the dataset. The number of nodes for other hidden layers is equal to the half of the number of nodes in the previous layer.

There has been recommendation that the input data be normalized between slightly offset values such as 0.1 and 0.9. One way to scale input and output variables in the interval [0.1, 0.9] as $P_n = 0.1 + (0.9–0.8)\ (P - P_{min})/(P_{max} - P_{min})$ (Xu et al. 2007).

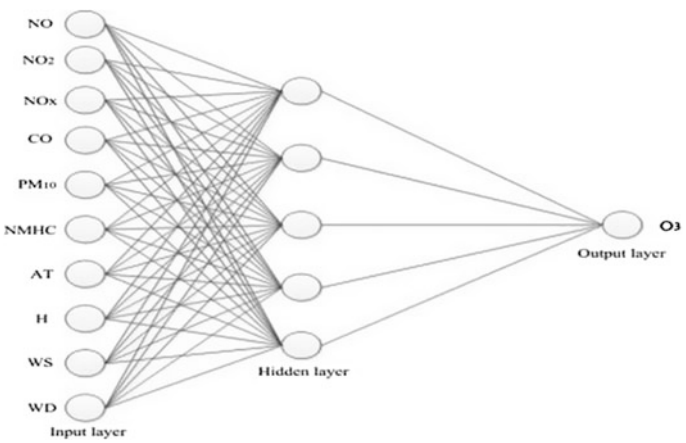

Fig. 2.1 Schematic of a neural network

Results and Discussion

In this study, artificial neural network was applied with input and targeted values normalized in the range of [0.1 and 0.9] before processing the data. The weights and biases were adjusted based on gradient-descent method in the training phase. The correlation coefficient (R) was chosen as the statistical criteria for measuring of the network performance. The result values were shown in Table 2.2.

Figure 2.2 depicts the network performance versus the number of epochs. At initialization of the network, the first values of the epochs were large due to training. Subsequently, the weights are adjusted to minimize this function which resulted in values decreasing. Meanwhile, a black dashed line is plotted which represents the best validation performance of the network. The training is stopped when the green line which represents the validation training set (network performance) cut-across with the black line.

In order to validate our hypothesis, regression analysis was performed to investigate the correlation between the actual and predicted results based on the value of correlation coefficient (R). There was a perfect fit value of R equal to 1 between the training data and the produced results. Figure 2.3 depicts the regression analysis plots of the network structure. From the regression graph, the perfect fit depicts that there is positive correlation between the predicted and targets as indicated by the solid line. The dashed line indicates the best fit produced by the algorithm.

Table 2.2 Correlation coefficient

Datasets	Correlation coefficient (R)
Gombak	0.62945
Shah Alam	0.63819

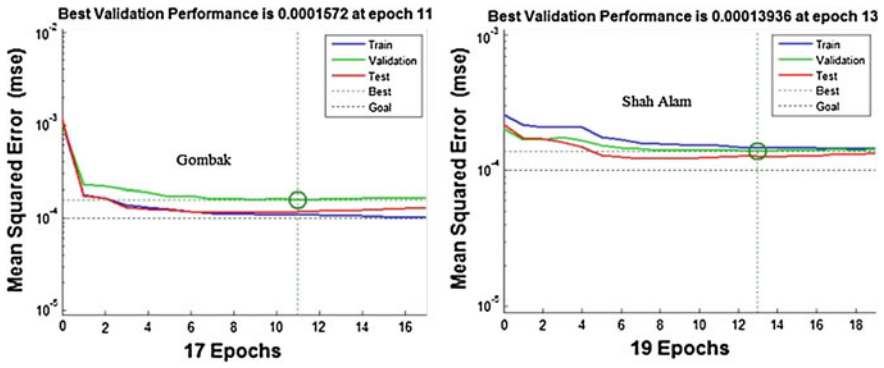

Fig. 2.2 Performance function of the network during training network structure, 10-5-1

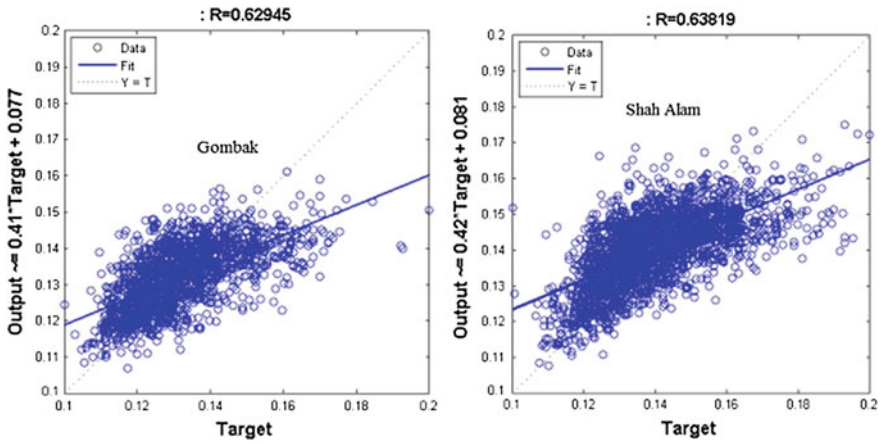

Fig. 2.3 Regression plot analysis network structure, 10-5-1

From Table 2.2, it can be seen that the model with network structure 10-5-1 is the optimal model for the air quality prediction as it yields the highest values of correlation coefficient (R). As depicted in Fig. 2.3, there is a match between predicted and measured values based on the value of correlation coefficient (R).

Conclusion

The input data to ANNs as used to forecast the O_3 concentrations is dependent on meteorological conditions and precursor concentrations. The network was trained using daily maximum data that were extracted from the Malaysian department of the Environment (DOE) during a 9-year period (2003–2011) in Malaysian towns of Gombak and Shah Alam. During the project under review, the surface O_3 concentrations were forecasted using surface meteorological variable as predictors for the artificial neural network on four experimental sites in Malaysia. The experimental results revealed that the proposed algorithm exhibits a high accuracy in predicting the O_3 concentrations. Additional study is hence needed to validate that the ANN algorithm can be used for the purpose of predicting O_3 concentrations with inputs from meteorological conditions and precursor concentrations during monsoon season.

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Chapter 3
Exposure to Indoor PM_{10} and Volatile Organic Compounds and Its Association with Respiratory Health Among Preschool Children from Urban and Rural Areas in Selangor

Nur Arasyi Yahaya and Juliana Jalaludin

Abstract Epidemiological studies have provided evidence that indoor exposure to particulate matter (PM_{10}) and Volatile Organic Compounds (VOCs) may decrease lung function among children. In this study, 96 respondents from both urban and rural areas were selected. Personal and socio-demographic background, and other related information were collected from standardized questionnaire adopted from the American Thoracic Society. Personal air sampling pumps and PbbRAE Portable VOC Monitor were used to measure indoor PM_{10} and VOCs in the respondents' houses. Lung function was measured using Chest Graph Spirometry. Results revealed that indoor PM_{10} level at home is higher in the urban area with mean (76.61 ± 17.53 μg/m3) compared to the rural area (48.37 ± 8.33 μg/m3) ($p < 0.001$). Indoor concentration of VOC indicate a significant difference ($p < 0.001$) between urban 0.083 ppm and rural area 0.035 ppm. Lung function; FVC % and FEV1 % were significantly higher in the rural area compared to the urban area ($p < 0.001$). The prevalence of an abnormal of FVC % was 75 % among the urban group and 37.5 % among the rural group. An abnormal FEV1 % was found in 75 % and 33.3 % of respondents in the urban and rural groups respectively. Respiratory symptoms which include cough ($p < 0.001$), phlegm ($p < 0.001$) and wheezing ($p < 0.001$) were significantly higher among children in the urban area compared to those in the rural area. There was significant association between PM_{10} concentration with cough ($p < 0.033$) and chest tightness ($p < 0.022$). However, there was no significant association between respiratory symptoms and VOCs concentration. PM_{10} does affect lung function and is associated with increased respiratory symptoms among studied population.

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Keywords Children · Lung function · PM_{10} · VOCs · Respiratory symptoms

Highlights

- Indoor PM_{10} level at home is higher in the urban area.
- Indoor VOC indicate a significant difference between urban and rural area.
- Lung functions were significantly lower in the rural area than in the urban area.
- No significant association between respiratory symptoms and VOCs concentration.

Introduction

Indoor air quality (IAQ) as defined by the Environmental Protection Agency (EPA) is a term referring to the air quality within and around buildings and structures, especially as it relates to the health and comfort of building occupants (EPA 2012). It is now known that indoor air pollution likely has equal or even greater impact on children's health when compared to that of outdoor pollutants where it may be vulnerable to pollutants including particulate matters and Volatile Organic Compounds (VOCs) (Sousa et al. 2012).

Materials and Methods

A cross-sectional comparative study design was conducted to compare the respiratory health of preschool children exposed to indoor air pollutants in urban and rural residential areas in Selangor. A total of 96 preschoolers aged between 4 and 6 years of Malaysian nationality and free from respiratory diseases were selected.

Personal and socio-demographic background, and other related information were adopted from the American Thoracic Society, for children. Personal air sampling pumps and PbbRAE Portable VOC Monitor were used to measure indoor PM10 and VOCs in the respondents house for 24-hour. Lung functions were measured by using Chest Graph Spirometry.

Results and Discussion

Statistical analysis, median (IQR) for indoor particulate matter (PM10) at house indicates that there was a significant difference at $p < 0.001$ between the urban 118.00 μg/m3 and the rural 71.50 μg/m3 area. Sources of PM10 is believed to be

the shelf areas and ceiling fans. On contrary, the concentration of volatile organic compounds (VOCs) was not significantly different between the urban area (0.081 ppm) and the rural area (0.099 ppm).

Indoor PM10 reading at home was significantly higher in the urban area 71.47 μg/m3 compared to the rural area 47.06 μg/m3 ($p < 0.001$). For VOCs, indoor concentration at the urban area 0.083 μg/m3 was higher compared to the rural area 0.035 μg/m3. School children in urban area were exposed to more particulate matter emitted by indoor activity (Chalaulakou et al. 2003).

Children in the urban area have highest complains on coughing (79.2 %) followed by phlegm (77.1 %), wheezing (75.0 %) and chest tightness (12.5 %). In the rural setting, children complained more coughing (14.6 %) as well as phlegm (14.6 %). Analysis from this study showed that there is significant association between level of PM10 and coughing ($p < 0.05$). Thus, it is suggested that high level of PM10 may cause respiratory health problem among children in urban area. VOCs do not show any significant association with coughing among children.

Lung function test on FVC (Forced Vital Capacity) and FEV1 (Forced Expiratory Volume in One Second) were conducted to evaluate the presence of airways obstructive and restrictive diseases. FVC, FEV1, FVC % and FEV1 % shows that there were significant difference between urban and rural area ($p < 0.001$) while no significant difference between urban and rural area for FEV1/FVC.

There was significant difference for FVC and FEV1 for lung function abnormality between urban and rural area but no difference for FEV1/FVC. There are several factors that influenced the abnormality of the lung function which include various home's indoor air pollutant. However, analysis shows that there was no significant association between concentration level of PM10 and VOCs with indoor air sources such as mosquito repellants and smoking. Distance from the main road and from factory shows a significant association ($p < 0.001$). This is supported by a study done in Korea by Son et al. (2003) that the difference in outdoor VOC concentrations between metropolitan city and medium city may affect the indoor VOC concentrations and personal exposures.

Conclusion

The finding above indicate that the level of PM10 and VOCs is higher in urban areas than in rural areas and children in urban areas are at greater risk of getting abnormal lung function as well as increased respiratory symptoms. Further studies on the correlation between exposure to PM10 and VOCs with respiratory health problem among school children need to be carried out. Result and data obtained should be assessed with greater focus on how to improve the quality of indoor air especially in urban areas.

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Chapter 4
Environmental Geochemical Cycles of Persistent Toxic Substances and Emerging Chemicals of Concern

Ming-Hung Wong

Abstract The environmental geochemical cycles of some major toxic chemicals are briefly reviewed, with focus on their environmental and health impacts in the Pearl River Delta, the most developed region in China. The associations of higher concentrations of these toxic chemicals in food items and their body burdens in the general population, in general, and the residents of electronic waste recycling sites, in particular, called for better management of these toxic chemicals.

Highlights

- Controlling the sources and fates of emerging contaminants is difficult.
- Higher concentrations of some major toxic chemicals called for better management.
- Adverse health impacts were reflected by the higher morbidity of several diseases.

Introduction

The major aim of this article is to review the sources, fates and effects of persistent toxic substances (PTS) and emerging chemicals of concern (ECC), focusing on the Pearl River Delta, one of the most developed regions in China. Persistent toxic substances include various toxic chemicals such as heavy metals (notably mercury

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and lead) and persistent organic pollutants (POPs) such as chlorinated hydrocarbon pesticides (e.g. DDT) and dioxins/furans. In addition, a large amount of different chemicals has been commercialized for various medical or industrial applications. They were previously thought to be harmless to the environment and human health, but it has now been gradually found that they are not. The term "Emerging Chemicals of Concern" (ECC) is therefore a moving target, which is both time and location dependent (Wijbenga and Hutzinger 1984).

Environmental Pollutants

In terms of water pollution, pathogenic organisms causing various waterborne diseases were of much public concern in the early days (1950's). Water tested for indicator organisms was accompanied by fecal contamination with coliform group, the most common bacterial indicator (APHA 1995). Measuring different nutrients such as nitrogen and phosphorus were important in the 1970's to ensure that these plant growth nutrients would not give rise to algal bloom and red-tides (Middlebrooks et al. 1971); while chlorophyll-a was commonly employed for measuring phytoplankton biomass (Holm-Hansen and Riemann 1978). The problem of water pollution due to chemical pollutants came slightly later. During 1970's and 1980's, testing for heavy metals was regarded as being important to safeguard the water quality (Hutchinson and Meema 1987).

Persistent Toxic Substances and Emerging Chemicals of Concern

Efforts were made during the 1990's on detecting persistent organic pollutants (POPs), such as DDTs and PCBs, which shared these common properties: (1) very persistent; (2) bioaccumulative and lipophilic; (3) highly toxic to biota; and (4) able to travel long-distance through air and water (Whylie et al. 2003). From 2000 onwards, accompanied with the advancement of analytical techniques, more and more toxic chemicals have been detected in the environment. A study showed that new born babies contained over 200 chemicals including pesticides, PCBs and plastic additives (such as bisphenol A), in their umbilical cord blood (Goodman 2009).

Sources and Fates of Emerging Chemicals

The sources of these chemicals are from residential wastewater, agriculture and consumer products, including pharmaceuticals. Sewage treatment works were originally designed to treat domestic sewage but not these chemicals. In fact, most

of these chemicals could not be removed effectively during different treatment processes, and a substantial amount of these chemicals are concentrated in the sludge. The major concern is that these chemicals have been in the environment for as long as they have been on the market. In particular, they are of relatively recent origin and have not been included in regular monitoring programs, with no limits set for their safe levels of concentration in the environment.

Environmental and Health Effects of Emerging Chemicals

There are various pathways in which these emerging chemicals may enter into the food chains and exert adverse effects on different biota, which include changes in the sexuality of different aquatic organisms, e.g. hermaphroditism has been found in African clawed frogs exposed to atrazine (25 ppb) (Hayes et al. 2002). The effects of most of these compounds have not been tested on humans. However, it has been observed that they mimic natural hormones and interfere with human physiology, and affect semen quality (Olea and Fernandez 2007). In addition, the health risk of long-term chronic exposure to suites of trace contaminants in drinking water is largely unknown (Benott et al. 2009).

Current Situation in the Pearl River Delta (PRD)

Being the most developed region in China, PRD has suffered from severe environmental problems (Huang et al. 2012; Zhao et al. 2012; Zhang and Wong 2007). The area has in fact become the world's centre for producing electrical and electronic equipment, and also for uncontrolled recycling of electronic waste (e-waste). The mixture of toxic chemicals emitted during recovering precious metals (such as gold, silver and platinum) contained in the e-waste via using strong acids and opening burning resulted in extremely high concentrations of some of the toxic chemicals (such as flame retardants [PBDEs]) in different ecological compartments—food items available locally and in body tissues (placenta, milk and hair) of residents of e-waste sites. The subsequent adverse health impacts were reflected by the higher morbidity of several major diseases (e.g. cancer and heart diseases) recorded by a local hospital in Taizhou, a major e-waste recycling site (Chan et al. 2013; Leung et al. 2011; Wong et al. 2007).

Environmental geochemical cycles of some of these food contaminants have generated public concerns. A recent example is contamination of heavy metals (notably Hg) and emerging chemicals (e.g., DDTs, PBDEs) in freshwater and marine fish cultivated in the region (Cheung et al. 2008). A significant correlation was noted between POPs concentrations (especially DDTs and HCHs) found in human milk and the age of the donors especially those who consume a high proportion of locally reared fish in their diet, (Wong et al. 2002). Significant

correlations between POPs concentrations in adipose tissues in patients with uterine tumours were also observed, which were linked with their seafood diet (Qin et al. 2010). A subsequent study analysing the blood plasma supplied by the Red Cross indicated that HCH concentration was rather high, when compared with other countries (Qin et al. 2011).

International Conventions for Controlling Emerging Chemicals

Currently, there are three conventions: Basel Convention, Rotterdam Convention and Stockholm Convention, which were established to control the abuse and movement of problem chemicals. There is also a problem with the movement of electrical and electronic waste (WEEE) across boundaries, where primitive e-waste recycling methods (typically via open burning) release toxic chemicals into the environment, imposing serious environmental and human health concerns (Wong et al. 2007). The European Union has introduced regulations to control the recycling of electrical and electronic equipment (EEE) waste and to prohibit the use of certain toxic chemicals in manufacturing EEE.

Conclusion

Controlling the sources and fates of emerging contaminants is difficult but not entirely hopeless because some confidence can be drawn from previous experience with other chemicals such as DDTs and PCBs. The long-term exposure to low levels of mixtures of emerging chemicals should not be neglected.

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Chapter 5
Nitrogen Release Properties of Urea–Kaolinite Controlled Release Fertilizer with Chitosan Binder

Bita Roshanravan, Fariba Mahdavi and Suraya Abdul Rashid

Abstract To reduce environmental and economic concerns of feeding crops with traditional fertilizers, a new type of controlled release fertilizer was prepared. In this study, urea–kaolinite was mixed with chitosan as a binder and then was granulated. The granules were incubated in water at room temperature for 30 days and urea release was measured in 5-days intervals using UV/Vis technique and through diacetylmonoxime (DAM) calorimetric method. In this study, different binder concentration was investigated. The results of UV–Vis spectroscopy illustrated that by increasing the chitosan concentration, nitrogen release decreased from 41.23 to 25.25 % after 24 h and from 77.31 to 59.27 % after 30 days incubation in water. By doing this, the prepared controlled release fertilizer (CRF) behaved according to the standard for CRFs. Compressive stress at break was measured for granules with different size and various concentration of chitosan. Results show that the force required to crush the granules is a function of the granule diameter and binder concentration.

Keywords Chitosan binder · Urea · Kaolinite · Controlled release fertilizer · Nitrogen release · Compressive stress at break

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Highlights

- As the amount of chitosan increases, urea release percentage decreases.
- The binder concentration was effective on the release behavior of granules.
- Fertilizer with 6 % chitosan has highest resistant and require high force to break.

Introduction

One of the main sources of environmental pollution and NO_x emission is fertilization of soils with nitrogen containing chemicals. Urea contains 46 % nitrogen and is widely used as N fertilizer. Only a small portion of urea is consumed by plants after application to soil (Boli and Mingzhu 2009; Park and Komarneni 1997). Controlled release fertilizers (CRFs) can be a good way for eliminating the environmental concerns of conventional fertilizers (Boli and Mingzhu 2009; Lan and Mingzhu 2008; Tomaszewskaa and Jarosiewicz 2006). They can release the nutrients at a slower rate by controlling water solubility of material and slowing the hydrolysis of low soluble chemicals. By doing this, CRFs decrease the nutrient loss into the environment and have more efficiency (Trenkel 2010). According to the standard of European Standardization Committee, the nutrient released during a 24 h period should not be more than 15 % of the total amount of nutrients at 25 °C or it should be less than 75 % of total nutrients after 30 days (Trenkel 2010).

In addition to having controlled release properties, CRFs also need to be fairly robust during storage and handling to avoid the granules from breaking which will increase nitrogen release. Therefore the hardness of the fertilizer granules is also an important criteria.

Materials and Methods

Highest degree of intercalation which contains the highest urea content (20 %) was used to prepare nitrogen based controlled release fertilizer granules (NCRFs). To investigate the effect of weight percentage of chitosan on urea release behavior of granules, four different samples of granules (chitosan 3, 4.5, 6, and 7.5 %) were prepared in the same size. Prepared granules were dried at 50 °C overnight. To study the controlled release behavior of prepared granules, 1 g of every sample was kept in a beaker containing 200 ml water. The beaker was sealed and kept in room temperature (25 °C) for 30 days (Trenkel 2010). After 1, 5, 10, 15, 20, 25, and 30 days of incubation (Boli and Mingzhu 2009; Lan and Mingzhu 2008). The urea content of 0.1 ml of each sample was measured. Determination of released urea was carried out according to the diacetylmonoxim (DAM) colorimetric method using UV/Vis spectrometer. This method is based on reaction of urea with

DAM under acidic conditions and measuring the color absorbency of reaction product by UV/Vis spectrophotometer at maximum absorbance of 527 nm. The absorption related to the urea content of 0.10 ml of each sample was measured after preparing the calibration curve of absorption versus concentration (ppm) using UV/Vis spectrometer and then the concentration of urea was calculated through equation provided by calibration curve. Ultimately, the concentration was reported by the percentage based on the primary concentration of urea in each sample.

Results and Discussion

The results of urea release from conventional urea fertilizer and urea–intercalated kaolinite fertilizers prepared in various concentration of chitosan is shown in Fig. 5.1.

From the results it can be seen that increasing the chitosan amount from 3 to 7.5 % caused the decreasing in the urea release from granules. Percentage of release from fertilizers with chitosan 3, 4.5, 6 and 7.5 % after 24 h was 41.23, 37.62, 26.28, and 25.25 % and after 30 days were 77.31, 76.28, 60.82, and 59.27 % respectively. From the results it is clear that fertilizer with chitosan 6 and 7.5 % follow the standard of CRFs. The crush strength of granular fertilizer has been accurately determined using Universal Testing Machine. Figure 5.2 shows the correlation between force required to crush granules with different binder concentration and various granule diameter. The pressure required to crush each granule remained relatively constant.

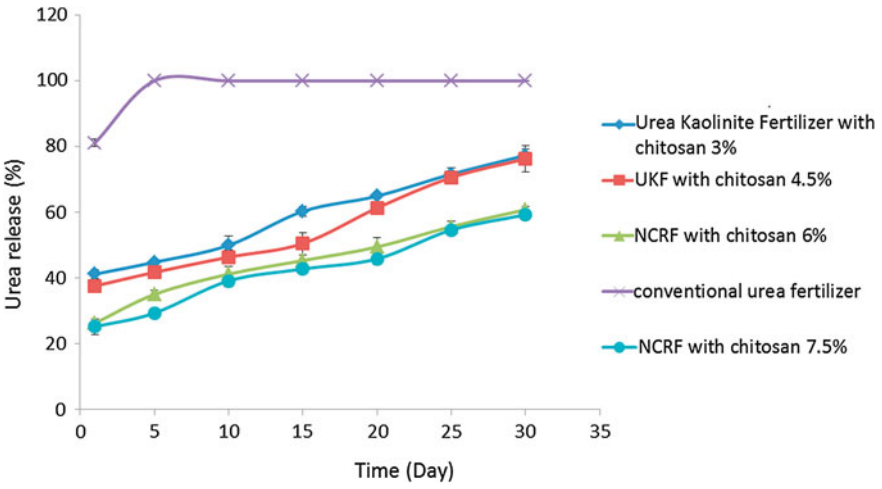

Fig. 5.1 Urea release behaviour of conventional urea fertilizer and fertilizer granules with different amount of chitosan

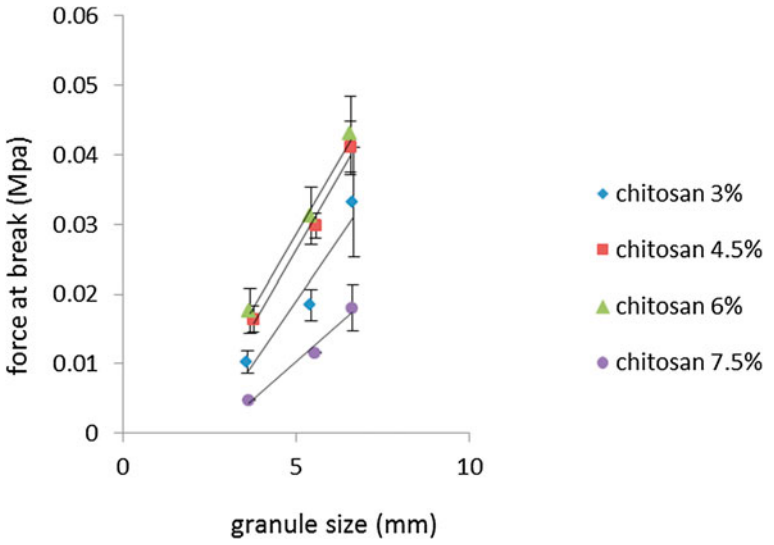

Fig. 5.2 Effect of granule size on force required to break fertilizer granules with various binder concentrations

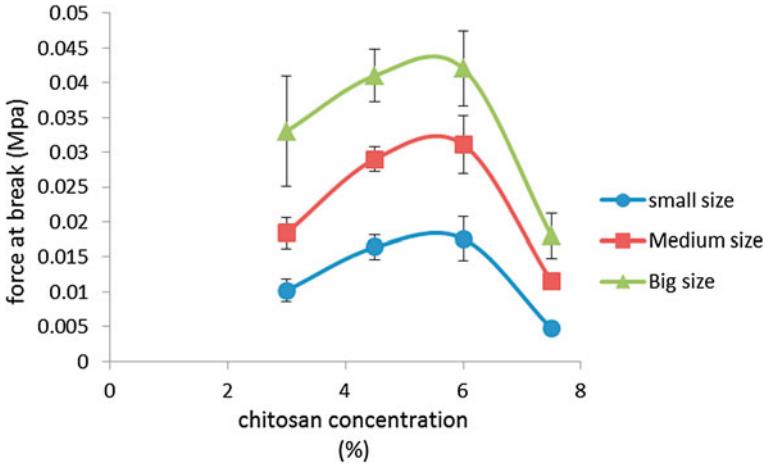

Fig. 5.3 Effect of different amount of chitosan on force required to crush for three different sizes of granules

The results confirm that direct relationship exists between granule size and compressive stress. Figure 5.3 illustrates the effect of different concentration of chitosan on compressive stress for granules with the same size.

As it can be seen in Fig. 5.3 by increasing the chitosan concentration, the force required to crush increases.

Conclusion

In this work urea–kaolinite was mixed with different concentration of chitosan as a binder and the effect of binder concentration on release behavior of NCRFs was investigated. The results revealed that by increasing the amount of chitosan, urea release percentage decreased. By doing this, the binder concentration was effective on release behavior of granules. Also the tensile strength of fertilizer increased with increasing the size and chitosan amount. In conclusion, fertilizer with chitosan 6 % has highest resistant and require high force to break. As the chitosan is biodegradable in soil, this fertilizer can be also environment friendly (Linden et al. 2000).

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Chapter 6
Stability Studies of Reactive Black 5 (RB5) Dye Standard Solution in Various Conditions Using UV–VIS Spectrophotometry

Nur Syamimi Zainudin, Mohamad Hadzri Yaacob and Noor Zuhartini Md Muslim

Abstract Studies of Reactive Black 5 (RB5) dye in various conditions based upon azo functional group using a UV–VIS Spectrophotometry are described as part of method development using voltammetric technique. 20 and 200 mg/L concentrations of RB5 dye standard solutions were multiple scanned at maximum wavelength (596 nm). The absorbance of RB5 dye exposed to the ambient weather for 7 h a day for three consecutively days in 1 month time was measured. The average absorbance for three consecutive days of 20 mg/L RB5 dye ranged from 0.3589 ± 0.0073 to 0.3640 ± 0.0024 whereas for 200 mg/L was in the range of 3.5199 ± 0.0342 to 3.5643 ± 0.0481. Within 1 month, the absorbance range for 20 and 200 mg/L were from 0.3721 ± 0.0032 to 0.3769 ± 0.0032 and 3.4215 ± 0.0074 to 3.5361 ± 0.0180, respectively. Using dye solutions unexposed to the ambient, the average range of 20 and 200 mg/L RB5 dye was from 0.3470 ± 0.0045 to 0.3640 ± 0.0024 and 3.4290 ± 0.0187 to 3.5630 ± 0.0536 for 3 days measurement, respectively. The absorbance range was from 0.3577 ± 0.0036 to 0.3668 ± 0.0050 and 3.4246 ± 0.0213 to 3.5513 ± 0.0059 for respective concentrations within one month. Another stability studies have been performed by considering the effect of heat. The solutions were boiled and cooled to room temperature before measurements were made. The average range of 20 and 200 mg/L for three consecutive day measurement was 0.4013 ± 0.0022 to 0.4178 ± 0.0027 and 3.6837 ± 0.0191 to 3.6882 ± 0.0344, respectively. Finally, the impact of acid (pH 2.5) and basic medium (pH 9.0) to the absorbance of RB5 dye was carried out within 3 days. For RB5 dye with concentrations of 20 and 200 mg/L at pH 2.5, the average range was from 0.3493 ± 0.0029 to

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0.3586 ± 0.0025 and 3.4904 ± 0.0225 to 3.5184 ± 0.0294 whereas for pH 9.0, the range was from 0.3515 ± 0.0043 to 0.3564 ± 0.0054 and 3.6007 ± 0.0296 to 3.6352 ± 0.0134, respectively. It was concluded that the RB5 dye standard solutions are stable in these four different conditions within 1 month time and the azo functional group of this dye which is electroanalytical active was not affected.

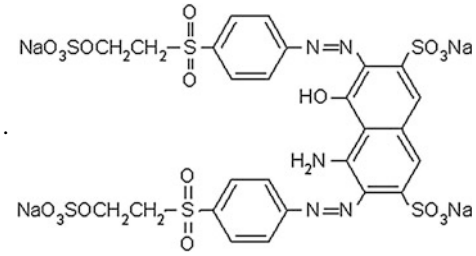
Keywords RB5 dye · Azo group · Stability · UV–VIS Spectrophotometry

Highlights

- RB5 dye standard solutions are stable in test conditions of 1 month time.
- The azo functional group is electroanalytical active and was not affected.
- Impact of acid and base medium on the absorbance of RB5 dye was assessed.

Introduction

Dyes are generally be defined as coloured substances with an affinity to the applied substrates (Paláez-Cid et al. 2008). Most of wastewater from dyeing activities is directly discharged into watercourses without any treatments. Azo and reactive dyes are the two mostly used organic dye. Azo dyes reduction will give off aromatic amines like aniline and 4-chloroaniline which have carcinogenic and genotoxic characteristic (Pinheiro et al. 2004). **2,7**-naphthalenedisulfonic acid, 4-amino-5- hydroxy-3,6-bis ((4-((2-(sulfooxy) ethyl) sulfonyl) phenyl) azo)-tetra-sodium salt] or Reactive Black 5 which its structure shown below is categorized in vinyl sulphonate azo dye due to the presence of –N = N– bonds combined with vinylsulphone as the reactive group (Tunc et al. 2009). The production of carcinogenic aromatic amines as the result of azo reduction has posed a significant risk of bioaccumulation in the environment. Reactive dyes are potentially reported to have a long half-life in environment too (Zanoni et al. 1997).



Dye wastewater from textile including RB5 is one of the most difficult to treat industrial wastewaters. It is usually treated by physical or chemical treatment processes including flocculation combined with flotation, membrane filtration, ion-exchange and precipitation. Srinivasan and Viraraghavan (2010) reviewed decolorization of dye wastewaters by various biosorbents such as fungi, bacteria, chitosan, algae and peat. They concluded that biosorbents have the potential to remove a wide variety of dyes and they found that chitosan, algae and fungal biomass have an excellent biosorption capacities.

Materials and Methods

The stability of 20 and 200 mg/L RB5 dye stock solution, prepared with deionized water were observed using UV–VIS Spectrophotometer. The deionized water was used as a blank. The solution has been exposed and unexposed to the ambient respectively. A 3 ml of these stock solutions was scanned starting from wavelength (λ) of 700–300 nm. The measurement was done every hour (7 h per day) for three consecutive days for 1 month. The 20 and 200 mg/L RB5 dye stock solution were adjusted to pH 2.5 and 9.0 with 0.1 M NaOH solution and 0.1 M HCl solution to represent acidic and basic medium, respectively and were exposed to ambient. The stability studies of this dye in two different mediums were monitored using the same λ range. The measurement was done every hour from 0 to 7th hour per day for three consecutive days. The 20 and 200 mg/L RB5 dye standard solution were heated to the boiling point and cooled to the room temperature before being scanned using the same procedures as previously mentioned.

Results and Discussion

The average of absorbance obtained for three consecutive days of 20 mg/L RB5 dye was from 0.3589 ± 0.0073 to 0.3640 ± 0.0024 whereas for 200 mg/L, it was from 3.5199 ± 0.0342 to 3.5643 ± 0.0481. In one month, the observed absorbance range for 20 and 200 mg/L were from 0.3721 ± 0.0032 to 0.3769 ± 0.0032 and 3.4215 ± 0.0074 to 3.5361 ± 0.0180, respectively. Results for the dye solutions that was not exposed to the ambient was from 0.3470 ± 0.0045 to 0.3640 ± 0.0024 and from 3.4290 ± 0.0187 to 3.5630 ± 0.0536 for 3 days measurement, for 20 and 200 mg/L RB5 dye respectively. The absorbance range was from 0.3577 ± 0.0036 to 0.3668 ± 0.0050 and 3.4246 ± 0.0213 to 3.5513 ± 0.0059 for respective concentrations within 1 month. Another stability studies were performed by considering the effect of heat. The solutions were boiled and cooled to room temperature before the measurements were made. The average measurement range of 20 and 200 mg/L for three consecutive days was 0.4013 ± 0.0022 to 0.4178 ± 0.0027 and 3.6837 ± 0.0191 to 3.6882 ± 0.0344,

respectively. Finally, the test on the effect of acid (pH 2.5) and basic medium (pH 9.0) on the absorbance of RB5 dye was carried out within 3 days. For RB5 dye with concentrations of 20 and 200 mg/L at pH 2.5, the average absorbance range was from 0.3493 ± 0.0029 to 0.3586 ± 0.0025 and from 3.4904 ± 0.0225 to 3.5184 ± 0.0294 respectively and for at pH 9.0, the range was from 0.3515 ± 0.0043 to 0.3564 ± 0.0054 and 3.6007 ± 0.0296 to 3.6352 ± 0.0134, respectively.

Conclusion

Our findings show that RB5 dye standard solutions are stable in these different conditions within one month period of time and the azo functional group of this dye which is electroanalytical active was not affected.

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Chapter 7
Cathodic Stripping Voltammetry (CSV) Analysis of Reactive Black 5 (RB5) Dye Using Hanging Mercury Electrode (HMDE) in Basic Medium

Mohamad Hadzri Yaacob, Nursyamimi Zainudin and Noor Zuhartini Md. Muslim

Abstract A CSV analysis of Reactive Black 5 Dye (RB5) in Britton-Robinson buffer (BRB) using a hanging mercury drop electrode (HMDE) is described. CSV was carried out by cathodic potential scan through a potential range of −100 to −1000 mV without any accumulation time. The effect of the pH of BRB solution on the peak height (I_p) and peak potential (E_p) of RB5 dye were studied. Results showed that in pH 8.0–12.0, three peaks at −417 to −564 mV, −661 to −772 mV and −774 to −879 mV respectively for the first, second and third reduction peak were observed. All potentials were referred against Ag/AgCl as reference electrode. The BRB solution at pH 9.0 was selected as the best condition for the detection of RB5 dye in basic medium which gave maximum I_p. Effects of the scan rate (v), accumulation time (t_{acc}), accumulation potential (E_{acc}), pulse amplitude and equilibrium time were also studied. Results showed that the optimum parameters for CSV analysis of RB5 dye in BRB solution at pH 9.0 were v: 15 mV/s, t_{acc}: 30 s, E_{acc}: −100 mV and pulse amplitude: 150 mV. By this optimization procedure, the I_p was increased from 13 to 173 nA for the second reduction peak which was considered as the well characteristic peak for analysis. Future works should validate this technique using those optimum parameters before being used for a routine analysis of RB5 dye in environmental samples.

Keywords RB5 dye · Britton-Robinson buffer · Cathodic stripping voltammetry analysis

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Highlights

- CSV has been developed for determination of RB5 dye using HMDE in basic medium.
- Effect of BRB solution on pH 8.0–12.0 was studied for representing basic medium.
- Voltammetric parameters were optimized to obtain the highest peak of RB5 dye.

Introduction

In Malaysia, wastewater from dyeing activities is commonly discharged directly into watercourses without any prior treatments. Azo and reactive dyes are the two mostly used organic dye. Reduction of Azo dyes was reported to give off aromatic amines like aniline and 4-chloroaniline which was observed to show carcinogenic and genotoxic characteristic (Pinheiro et al. 2004).

2,7-naphthalenedisulfonic acid, 4-amino-5-hydroxy-3,6-bis ((4-((2-(sulfooxy)ethyl)sulfonyl)phenyl)azo)-tetrasodium salt or Reactive Black 5 (Fig. 7.1) is categorized as vinyl sulphonate azo dye due to the presence of –N=N– bonds combined with vinylsulphone as a reactive group (Tunc et al. 2009). The production of carcinogenic aromatic amines as a result of azo reduction has been revealed to pose a significant risk of bioaccumulation in the environment. Reactive dyes are reported to have a long half-life in environment (Zanoni et al. 1997). Textile, printing and pharmaceutical industries are the major consumers of azo dye (Karipcin et al. 2009).

Analytical methods for determining dye compounds in aqueous and non-aqueous media include thin layer chromatography (TLC), high performance liquid chromatography (HPLC), pyrolysis gas chromatography (Py-GC) and capillary electrophoresis (CE). Ultra-violet (UV), mass spectrometry and electrochemical detection are the common detection techniques to determine dye compounds. GC, HPLC and CE involved costly instrumentation, expensive and hazardous chemicals, multiple requirements for sample preparation, low speed of analysis, high

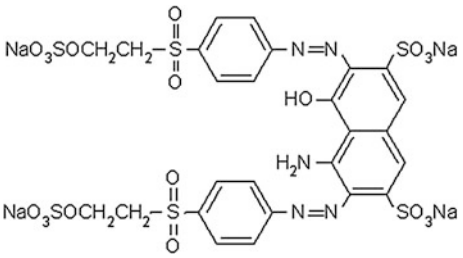

Fig. 7.1 Reactive black 5

maintenance, high skilled labour requirements and low analyte detection limit. On the other hand, UV will give moderate analyte detection limit, has no specific compound identification and moderate susceptibility to interferences (Pinheiro et al. 2004).

Materials and Methods

One mL of 20 mg/L RB5 dye standard solution was spiked using micropipette into the voltammetric cell containing 9 mL of BRB solution. The resulting concentration of standard solution in the cell was 2 mg/L. The solution was purged with purified nitrogen gas for 300 s to remove the oxygen. Initial pH for BRB solution was measured by scanning 2 mg/L of dye in BRB pH 2.0. The measurement was repeated for pH 3.0 until 12.0. Initial parameters applied before method optimisation were initial potential (−100 mV), final potential (−1000 mV), scan rate (15 mV/s), accumulation time (0 s), accumulation potential (0 mV), equilibrium time (0 s) and pulse amplitude (50 mV). Those parameters were optimized for method optimization where peak height and peak potential of RB5 were recorded for every parameter change. The value for scan rate was varied from 5 to 40 mV/s. A graph of peak current against scan rate was plotted and the optimum scan rate was then selected. Series of scan with increasing accumulation time from 0 to 60 s were carried out. Based on previously optimized parameters, accumulations potential ranging from 0 to −650 mV were applied for optimization. Finally, pulse amplitudes ranging from 25 to 175 were also applied for optimisation.

Results and Discussion

In basic medium, three cathodic peaks of RB5 dye were obtained including the second peak that was considered as a good and well characteristic peak. The peak potentials (E_p) are −417 to −564 mV, −661 to −772 mV and −774 to −879 mV for the first, second and third reduction peak respectively. In basic medium, small response to change of pH of BRB was observed except for the second peak. BRB solution at pH 9.0 was chosen as the optimum condition for RB5 dye determination in the basic medium as the highest peak current (I_p) has been obtained at this pH. The I_p was 12.73 nA and the E_p was −677 mV. Both scan rate (v) of 10 and 15 mV/s gave maximum response which was 18.37 nA. However, v of 15 mV/s was chosen as an optimum v for analysis since it offered faster scanning rate. For accumulation time (t_{acc}), the highest I_p obtained at 30 s where the I_p was 60 nA and E_p was −665 mV. The increasing I_p with t_{acc} (0–30 s) is contributed by the accumulation of RB5 dye at the electrode surface in larger amount since longer time has been given for the accumulation to occur. At higher t_{acc}, the I_p values were almost constant as the overall surface of mercury electrode is saturated with

RB5 dye (Chaiyo et al. 2013). A −100 mV was the optimum accumulation potential (E_{acc}) with I_p obtained was 66.27 nA at E_p of −665 mV. The highest I_p obtained was 173 nA with E_p of −570 mV at 150 mV pulse amplitude. For all optimization steps, no significant change on the peak potentials of RB5 dye was observed.

Conclusion

The CSV analysis of RB5 dye has been successfully developed. The optimised parameters were initial potential (−100 mV), final potential (−1000 mV), scan rate (15 mV/s), accumulation time (30 s), accumulation potential (−100 mV) and pulse amplitude (150 mV). Based on these optimised parameters, the I_p was increased from 13 to 173 nA. Future works will cover validation of the method before being used for analyzing real samples such as waste water from batik industry.

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Chapter 8
Biomonitoring of Trace Elements Using Epiphytic Lichens Collected in a Suburban Area of Selangor, Malaysia

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Abstract Lichen samples (*Dirinaria sp.* and *Parmotrema sp.*) were collected in a suburban area of Selangor. Their chemical compositions were determined using the instrumental neutron activation analysis (INAA) and 21 elements (Al, As, Ce, Co, Cr, Cs, Eu, Fe, Hf, Hg, K, La, Mn, Na, Rb, Sc, Se, Sm, Th, V and Zn) were reported. Most of the concentrations found in the lichens were similar to those of baseline data from unpolluted areas. Regression analysis found that the elements Al, As, Ce, Cr, Eu, Fe, Hf, La, Mn, Na, Sm, and Th showed statistically significant correlations ($p < 0.05$) with Sc, which suggests that they were associated with crustal materials. Other elements Co, Cs, Hg, K, Rb, Se, V and Zn showed weak correlations with Sc implied that they were possibly contributed by anthropogenic sources. The enrichment factors of the elements Hg and Se were found to be high signifying that they may be originated from long-range transport from sources. The elements V and Zn were slightly enriched in the lichen samples, which could be due to some anthropogenic inputs. From correlation with Sc and enrichment factors, some constrain on potential elemental pollutants namely Hg, Se, V and Zn that could be due to anthropogenic pollutants could be identified. The use of lichens as biomonitor for trace elements has been able to indicate possible natural and anthropogenic inputs, which could provide information on air pollution in the study area.

Keywords Biomonitoring · Trace elements · Epiphytic lichens · Selangor · Instrumental neutron activation analysis

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Highlights

- Lichens are good bioindicators of trace element for air pollution study.
- Concentrations found were similar to those of baseline data from unpolluted areas.
- Able to indicate possible natural and anthropogenic inputs.

Introduction

Lichens are symbiotic organisms of fungus and alga. Lichens are slow-growing and commonly found growing on tree trunks, rock surfaces, or walls. Lichen thalli have no root systems or cuticle and they depend on atmospheric inputs for minerals and moisture. Besides, there are perennial and found in many areas around the world. Lichens provide an alternative way of air monitoring apart from using the conventional air filters. Among the air pollutants monitored using lichens include heavy metals, sulphur compounds, ozones, fluorides, nitrogen compounds, polyaromatic hydrocarbons and radionuclides. The use of lichens as air pollution monitors has been conducted for many years and results were reviewed by Conti and Cecchetti (2001) and Garty (2001).

In Malaysia, the use of lichens as biomonitor is still very limited as compared to European countries. There is a great potential for lichens to be a good biomonitor for air pollutants in Malaysia as lichens are available throughout the country. In this study, the state of Selangor is selected because it is the most developed state in Malaysia and it consists of urban, suburban and industrial areas, which provides an attractive location to study the level of air pollution by analyzing trace elements accumulated in lichens. A recent study by Mokhtar et al. (2010) reported the results of trace elements (As, Cd, Cr, Cu, Mn, Pb, V, and Zn) in lichens collected at Universiti Kebangsaan Malaysia (UKM), Selangor, and forest of Maliau Basin, Sabah. They found that lichens from UKM contain higher concentrations of trace elements than those from Maliau Basin. Mokhtar et al. (2010) concluded that lichens from UKM were slightly polluted and these data are useful for comparison in future studies in Malaysia.

Determination of trace elements in lichens can be performed using various analytical techniques such as atomic absorption spectrometry and inductively coupled plasma mass spectrometry. In order to reduce potential contamination due to sample digestion, we adopted the instrumental neutron activation analysis (INAA). The INAA technique is particularly useful for quantification of trace elements and it is a well-established method with high sensitivities for many trace elements found in lichens. The high accuracy and precision of INAA have been demonstrated in many previous studies (e.g. Saiki et al. 1997; Bergamaschi et al. 2004), which is essential to obtain reliable data for meaningful discussions.

This study aims to determine minor and trace elements in lichens thalli using INAA and to identify potential elemental pollutants in a suburban area. The results were also compared to baseline data from unpolluted locations around the world (Bergamaschi et al. 2004).

Materials and Methods

Lichen samples (*Dirinaria sp.* and *Parmotrema sp.*) were collected at four sampling locations around the compound of the Malaysian Nuclear Agency, Bangi, Kajang, Selangor, which is located about 40 km south of Kuala Lumpur. Lichens grown on palm trees at a height of about 1–1.5 m were collected using clean knives and kept in plastic bags. At each location, about 5–10 lichen thalli were collected from several trees and considered as one sample. In the laboratory, lichen thalli were examined and cleaned to remove substrate remains. Lichens were not washed in order to prevent leaching of trace elements from thalli. The samples were then immersed in liquid nitrogen and subsequently ground in agate mortar to obtain homogenized lichen powder. For INAA, about 0.20 g of powdered lichen samples were sealed in acid-cleaned polyethylene vials and irradiated at the TRIGA Mark II reactor of the Malaysian Nuclear Agency. Details of irradiation procedures and gamma-ray measurements were described by Wee et al. (2006). Quality control was conducted by analyzing the reference material (IAEA 336 Lichen). Elemental concentrations in the lichen samples were calculated based on comparative method and reported as dry weight basis.

Results and Discussion

Trace elements (Al, As, Ce, Co, Cr, Cs, Eu, Fe, Hf, Hg, K, La, Na, Mn, Rb, Sc, Se, Sm, Th, V, Zn) could be determined reliably in lichen samples based on the current experimental settings. Comparison between our data and those of baseline data reveals that most of the trace elements in lichens are within the ranges of values reported for unpolluted areas (Bergamaschi et al. 2004). The concentrations of elements As, Cr, Cs, and Th were slightly high but still within the ranges of the baseline data when considering the uncertainties of the current data.

For the purpose of identifying clastic inputs to lichens, the elemental data are compared with Sc as geological referent to identify elements that are associated with crustal material (Ribeiro Guevara et al. 2004). By plotting the elemental data against Sc, a linear correlation could be an indication that the element is of crustal origin. Many elements (Al, As, Ce, Cr, Eu, Fe, Hf, La, Mn, Na, Sm, and Th) analyzed here showed good correlations with Sc because all lichens were collected from trees exposed to windblown dust, which is an important source of minerals to lichens. Elements that showed weak correlation ($r \leq 0.8$) are Co, Cs, Hg, K, Rb,

Se, V and Zn, which may be associated with lichen physiology (Backor and Loppi 2009) or inputs from anthropogenic sources.

The enrichment factors (EF) for trace elements in lichens are used to discriminate between anthropogenic and natural sources of trace elements in lichens. Results showed that most of the EFs reported in this study are similar to those reported for unpolluted areas (Bergamaschi et al. 2004). The element As showed EFs of 16.3–24.0, indicating that a fraction of the concentration is originated from other sources apart from soil. The element Zn showed slight enrichment with EFs between 8 and 19, which could be due to addition of anthropogenic sources or different accumulation mechanisms (Loppi et al. 1999). The elements Hg and Se showed elevated EFs compared to other trace elements analyzed in this study. The EFs of Se ranged from 95 to 339 were much higher than those of baseline data. The high EFs of Hg and Se could be associated with sources that released these volatile elements into the atmosphere.

From the above discussions, we are able to focus on a few elements namely Hg, Se, V and Zn, which are potential pollutants in this area. The presence of Hg in lichen is of concern because it is related to potential health hazard to humans due to its toxicity. In Hg contaminated area such as Bariloche City, the Hg contents in lichens were above 0.8 μg/g (Ribeiro Guevara et al. 2004). Thus, the Hg values found in lichens collected in Bangi were less affected by Hg contamination. The Se concentrations reported here are within the baseline data but weak correlation with Sc and high EFs suggest that there is possible contamination of Se. The volatility of Hg and Se may cause these elements to disperse from anthropogenic sources far from the sampling site. Burning of coal especially in coal-fired power plants and refuse incineration could contribute to Hg and Se contents in the atmosphere (Adriano 1986). The elements V and Zn showed higher concentrations than baseline data and less correlation with Sc, indicating that there were possible anthropogenic inputs related to burning of fossil fuels, coal combustion and automobile emissions (Adriano 1986).

Conclusion

Lichens collected in the suburban area Bangi were analyzed for their trace element contents using INAA. Two species of lichens were collected namely *Dirinaria sp.* and *Parmotrema sp.*, which were found to be suitable biomonitors for elemental pollutants. Comparison of our results to those of baseline data showed that most of the element concentrations were within the ranges except for Rb, V and Zn, which were slightly high. The applications of regression analysis and EFs were able to provide indications that Hg, Se, V and Zn could be the potential trace element pollutants in the study area. The presence of elements Hg and Se could be from long-range transport of atmospheric pollutants. The elements V and Zn could be associated with automobile emissions. The present study has provided information

on trace element pollutants found in lichens that could be used to assess the level of air pollution.

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Chapter 9
Seasonal Variation of Aliphatic Hydrocarbons in Atmospheric Environment of Kota Kinabalu, Sabah

Mahyar Sakari, Jupri Bin Mohd Bani, Zhi Yang Soon, Sohail Rafiq and Justin Sentian

Abstract Suspended particulate matters of atmospheric samples were collected and analyzed for aliphatic hydrocarbons from Kota Kinabalu, Sabah, on 2011. Samples were extracted using Soxhlet apparatus, run in two-step column chromatography and the final fraction was spiked into gas chromatography-mass spectrometry. An authentic n-alkane standard (10 mg/l) ranging from C_{10} to C_{40} was used as external standard for quantification and qualification of target compounds in the samples. The result showed that the dry season had the highest concentration of atmospheric n-alkane of around 151 ng/m^3/d comparing to a minimum of 89 ng/m^3/d in the wet season. The results indicate that the amount of high molecular weight n-alkane increases during dry season while wet season had the peak range of lower molecular weight. The carbon preference index value indicates an important contribution from petroleum and diesel materials in the study area. Presence of unresolved complex mixture in most of the samples reveals vehicular exhaust output involvement. Natural hydrocarbons as the minor contributor in the samples were observed during dry season due to the availability of plant material and dust in the atmosphere. It seems that frequent tropical rain clears the atmosphere from dust, burned particulate matters and plant residues during wet season while less rain in dry season provides availability of particulate matters in the atmosphere.

Keywords Wet and dry season · Atmospheric environment · Aliphatic hydrocarbon · Particulate matters

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Highlights

- High atmospheric hydrocarbons in dry season.
- High proportion of high molecular hydrocarbon.
- Insignificant seasonal influence on hydrocarbons structural change.
- C_{10} and C_{19} dominance during dry season.

Introduction

Sources of particulate matters in the atmosphere may come from anthropogenic and biogenic sources where biogenic sources usually happen during summer time due to wax plants and biomass burning of agricultural wastes (Schwarzenbach et al. 1993). The presence of anthropogenic and biogenic sources can be identified by the analysis of aliphatic hydrocarbons in the atmospheric environment (Andreou and Rapsomanikis 2009). In aliphatic fraction of the hydrocarbons, lower molecular weight hydrocarbons ($<C_{26}$) are mainly come from incomplete combustion of fossil fuels that provides lower carbon preference index (CPI) as indicated by Duan et al. (2010) and Mandalakis et al. (2002) while higher molecular weight hydrocarbons (HMW) with higher values of CPI delivers from plant waxes (Duan et al. 2010; Andreou and Rapsomanikis 2009; Oros and Simoneit 2001). In studies on hydrocarbons, usually specific hydrocarbons with higher concentration play an important and leading role of source identification and pollution orientations as known as C_{max} (Bendle et al. 2006). This study expects to experience a new pattern of seasonal changes of aliphatic hydrocarbon.

Materials and Methods

Sampling Description

The samples were supplied by the Malaysian Meteorological Department, using a high-volume air sampler (Andersen Sampler—RFPS-1287-063) located at 2 m height from the ground at meteorological stations near Kota Kinabalu International Airport, Sabah. Samples were selected from February and December to represent wet season and July as dry season of 2011. The average volume sampled air was around 1.13 m^3/min (1627.2 m^3/24 h).

Analytical Technique and Instrumentation

The analytical techniques followed previous research done by Bahry et al. (2009) except for instrumentation. Samples were analyzed in Gas Chromatography—Mass Spectrometry (GC–MS) using Agilent Technologies System (7890A) was equipped with Inert XL EI/CI 5975C mass selective detector. The instrument had 30 m fused capillary column, 0.25 mm and 0.25 μm film thickness. The helium was used as inert carrier gas. The injection port was maintained at 300 °C and the samples injected with split less mode followed by 1 min purge after the injection. The temperature of the column was maintained at 70 °C for 1 min then increased by 30 °C/min until 150 °C, immediately continued by 5 °C/min of increase until 310 °C and hold for 10 min. The temperature of the detector was maintained at 310 °C. A 10-ppm solution of n-alkane standard was injected along with eight samples in the day of instrumentation.

Results and Discussion

The seasonal changes of n-alkane concentration in the study area have shown the values where ranging from a minimum of 33.36 ng/m^3 at 10 February 2011 as wet season to the maximum of 158.31 ng/m^3 at 22 July 2011 as dry season. The average concentration of the month February as one of the wet season has reach 102.71 ng/m^3 while in dry season on July presented 151.21 ng/m^3 of concentration (Fig. 9.1). This value in the next wet season increase partially by an average of 88.89 ng/m^3 in the month of December. Kishida et al. (2009) reported on another class of hydrocarbons (PAHs) were found in the wet season were at higher concentration due to inversion factor and/or less photo oxidation effects and finally tendency of increasing car use during rainy days. Findings from this study is consistent with the study done by Omar et al. (2007) where they found almost similar trend in Kuala Lumpur (102 ng/m^3) during wet season, however,

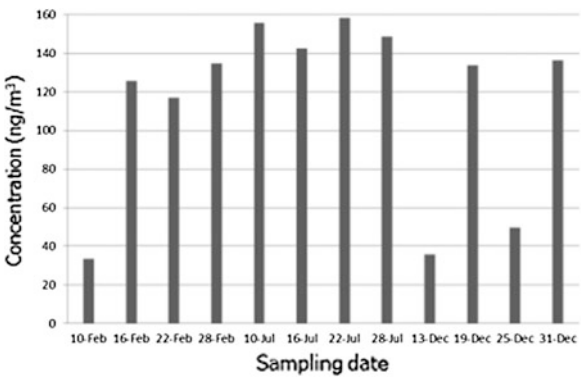

Fig. 9.1 Total n-alkane concentration in the study area

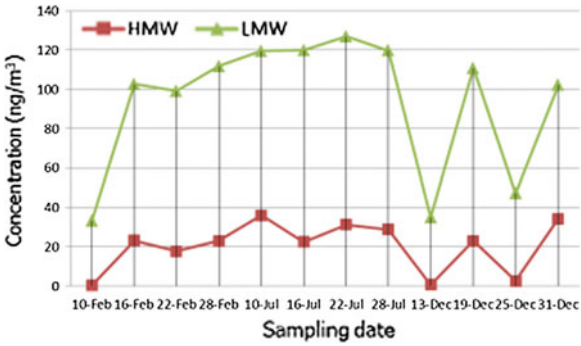

Fig. 9.2 Seasonal changes of LNW vs. HMW hydrocarbons in the study area

the concentration was slightly higher than Kota Kinabalu (85 ng/m^3). The concentration of high molecular weight hydrocarbons (HMW; C_{26}–C_{40}) was observed as low as 15.10 ng/m^3 in December, 16.04 ng/m^3 in February and 29.69 ng/m^3 in July as wet and dry seasons. The LMW hydrocarbon that has higher proportion than HMW ranged from a minimum of 33.07 ng/m3 to maximum of 119.89 ng/m3 in wet and dry season, respectively. The ratio of LMW over HMW (L/H) has shown that in dry season, the proportion of LMW compound to HMW has been decreasing compared to wet season (Fig. 9.2). Towards the wet season, there is higher proportion of LMW while in dry season the LMW/HMW was decreasing. The value of CPI, which is a ratio of odd over even number hydrocarbon, ranged widely (0.01–0.72). In general, the values were higher during dry season (0.65) comparing to wet season (0.35–0.50). Incomplete combustion of fossil fuels usually provides more lower molecular weight (LMW) alkanes ($<C_{23}$ or $<C_{26}$) through emission with CPI value close to one or lower (Duan et al. 2010; Mandalakis et al. 2002) while high molecular weight (HMW) are derived from higher plant waxes where CPI appears more than unity (Duan et al. 2010; Andreou and Rapsomanikis 2009; Oros and Simoneit 2001). The odd carbon number hydrocarbon has the highest concentration in average during dry season, reaching to 58.95 ng/m^3 comparing to wet season (27.33–37.15 ng/m^3). As shown earlier in CPI values as a result of odd over even numbered hydrocarbons ratio, the study area received higher anthropogenic hydrocarbons than natural since the CPI values are mostly below the unity (Fig. 9.3). This is consistent with reports by Kavouras et al. (1999) and Wang et al. (2006).

Petroleum pollution is known with the presence of certain hydrocarbons such as C_{16}, C_{18} and C_{20}. It was found that petroleum indexed hydrocarbons were elevated during dry season than the wet season (Alves et al. 2012; Andreou and Rapsomanikis 2009; Xie et al. 2009). They ranged from an average of 5.00 ng/m^3 during wet season (December) to 13.20 ng/m^3 during dry season (July). The study of this class of hydrocarbon (C_{16}, C_{18}, C_{20}) showed that during wet season the concentrations were lower. The percentage of the total aliphatic hydrocarbon during the wet season ranged from 4 to 6 % when compared to 9 % during dry season.

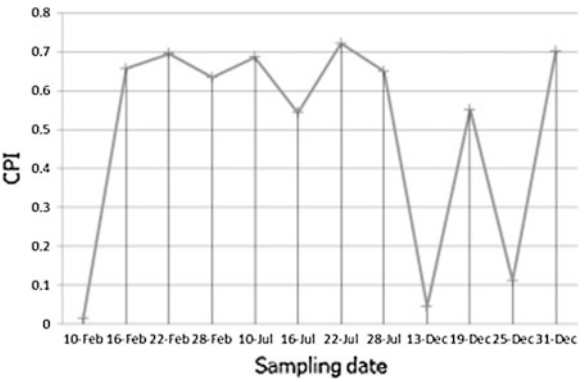

Fig. 9.3 Seasonal variations of CPI values in the study area

Conclusion

This study concluded that dry season contributed higher alkane concentration when compared to wet season. Due to biomass burning, the study area showed to include more biomass residual hydrocarbons in dry season. In addition, wet season eliminates particle availability due to the rain factor and wet deposition. The received hydrocarbons performed the freshness due to lower molecular patterns. Moreover, fossil fuels and vehicular output had significant input due to low and high molecular weight performances and the presence of certain hydrocarbons such as C_{16} to C_{20}. We have observed that the sources of n-alkane in both wet and dry seasons remain the same whereby the sources are from vehicular emission and fossil fuels.

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Chapter 10
Occurrence and Dietary Intake of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in Malaysia

Yin-Hui Leong, Pui-Nyuk Chiang, Hajjaj Juharullah Jaafar, Chee-Yuen Gan and Mohamed Isa Abdul Majid

Abstract A total of 126 food samples (seafood, meat and dairy products) from Malaysia were analyzed for polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs). The concentration of PCDD/Fs ranged from 0.13 to 0.23 pg WHO_{05}-TEQ g^{-1} fw (mean 0.137 pg WHO_{05}-TEQ g^{-1} fw) was found in these samples. According to the food consumption data from Global Environmental Monitoring System (GEMS)—Food Contamination Monitoring and Assessment Programme by World Health Organization, the dietary exposure to PCDD/F from seafood, meat and dairy products for general population in Malaysia was of 0.0364, 0.128 and 0.412 pg WHO_{05}-TEQ kg^{-1} bw d^{-1}, respectively. However, the exposure was higher in seafood (0.249 pg WHO_{05}-TEQ kg^{-1} bw d^{-1}) and meat (0.225 pg WHO_{05}-TEQ kg^{-1} bw d^{-1}) when the data was estimated using the Malaysian food consumption statistics. Lower exposure was observed in dairy products with the estimation of 0.241 pg WHO_{05}-TEQ kg^{-1} bw d^{-1}. Overall, these dietary exposure estimations were much lower than the tolerable daily intake (TDI) as recommended by World Health Organization. Thus, it is suggested that the dietary exposure to PCDD/F does not represent a risk for human health in Malaysia.

Keywords PCDDs · PCDFs · Exposure · Malaysia

Highlights

- The concentration of PCDD/Fs ranged from 0.13 to 0.23 pg WHO_{05}-TEQ g^{-1} fw.
- The daily intake of PCDD/Fs was below the relevant legislative limits.
- Based on the calculated WHO-TEQs, the food was safe for human consumption.

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Introduction

Polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) are highly toxic and persistent organic pollutants (POPs) that widely distributed in the environment and exhibiting adverse effects on human health. In the strategy to reduce human exposure to these contaminants, European Council (EC) has established the maximum levels for PCDDs and PCDFs in various food groups, for instances meat and meat products, fish and fishery products, raw milk and dairy products, via Council Regulation No. 1881/2006 (EC 2006). World Health Organization (WHO) has set a tolerable daily intake (TDI) range of 1–4 pg TEQ kg^{-1} body weight for dioxins (WHO 2000), analogous to the tolerable weekly intake (TWI) of 14 pg TEQ kg^{-1} body weight fixed by the European Union Scientific Committee on Food (EC SCF 2001). Recently, these maximum levels were reviewed by the Commission Regulation (EU) No 1259/2011 using the WHO_{05}-TEF (EC 2011). At this moment, PCDD and PCDF are not regulated in Malaysian Food Act and Regulations.

The main pathway of human exposure to these contaminants is via the food ingestion, estimated at over 95 % of the total intake for non-occupationally exposed persons (Parzefall 2002). Due to their highly lipophilicity and low biodegradability characteristics, these POPs tend to accumulate in the food chain, particularly in animal fat (Fernandes et al. 2004). Fish, seafood, meat or meat products, and dairy products are some of the major sources of exposure in adults and children (Bordajandi et al. 2004). In this study, levels of biologically active congeners of PCDD and PCDF in seafood, meat and dairy samples were investigated. The generated data will provide an overview of the occurrence and serve as the preliminary information to assess the potential health risks to the general population in Malaysia.

Materials and Methods

Food samples including seafood, meat and dairy products collected in 2011 from Malaysia were analyzed for PCDD/Fs. Samples were prepared by homogenizing the edible portion using a food blender and stored at −18 °C in polyethylene container prior to analysis.

Detection and quantification of 17 PCDD/Fs congeners were performed according to the procedure based on the principle laid by US EPA method 23, 1613 and 8290 using high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS). Extraction of PCDD/F from the food samples was carried out using Accelerated Solvent Extraction (ASE) method adopted from the US EPA Method 3545 while the clean-up process was conducted by Power-Prep Fluid Management System with a series of multi-layer silica, alumina and carbon columns.

In the calculation of dietary intake, the daily food consumption was multiplied by the corresponding concentration and divided by an average adult body weight of 60 kg.

Results and Discussion

The concentration of PCDD/Fs ranged from 0.13 to 0.23 pg WHO_{05}-TEQ g^{-1} fw (mean 0.137 pg WHO_{05}-TEQ g^{-1} fw). Average concentrations of the most toxic 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD congeners among the samples was 0.0214 and 0.0521 pg WHO_{05}-TEQ g^{-1} fw, with the maximum values of 0.05 and 0.1 pg WHO_{05}-TEQ g^{-1} fw, respectively. Both the 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD congeners were found in all the samples. Among the 17 congeners, 1,2,3,7,8-PeCDD was the most abundance congener and contributed around 35.7–72.8 % (average 38.1 %) to TEQ. Highest concentration of PCDD/F was detected in full cream milk powder (0.23 pg WHO_{05}-TEQ g^{-1} fw) followed by prawn (0.22 pg WHO_{05}-TEQ g^{-1} fw). Pork contained the highest PCDD/F (0.16 pg WHO_{05}-TEQ g^{-1} fw) compared to beef and other meat and their products. Dairy products contained relatively higher 2,3,7,8-TCDD congener than other food samples. In general, the congener profiles were rather similar among all the tested samples in this study, regardless the different food groups or type of processing. Mean percentage of contribution of each PCDD/F congeners to the WHO_{05}-TEQ in examined samples is represented in Fig. 10.1.

In the present study, the WHO_{05}-TEQs of PCDD/Fs for all the analyzed samples were below the permitted limits (4 pg WHO-TEQ g^{-1} fw for PCDD/Fs) according to Commission Regulation (EC) No 1881/2006 (EC 2006). On average,

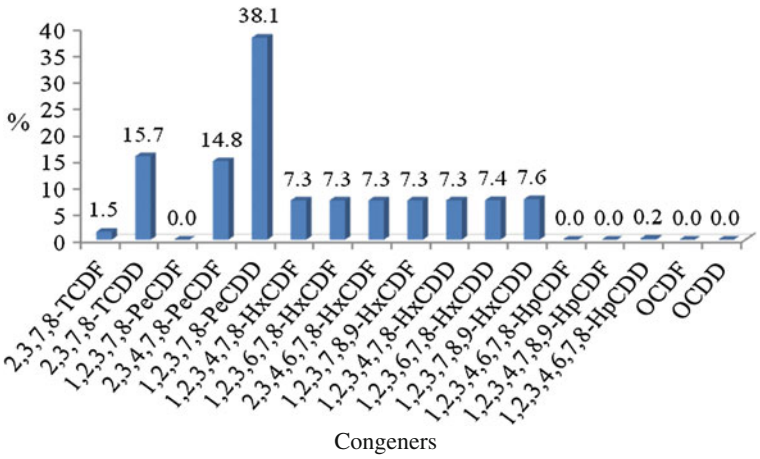

Fig. 10.1 Mean percentage contribution of each PCDD/F congeners to the WHO_{05}-TEQ in analyzed samples

our results for dairy products were lower compared to those reported by O'Donovan et al. (2011) and De Mul et al. (2008). In Spain, similar concentration range of PCDD/F for meat and meat products (mean 0.05 pg TEQ g^{-1} product for poultry and mean 0.18 pg TEQ g^{-1} product for beef) was found by Marin et al. (2011). For fish and seafood samples, the PCDD/F levels detected in this study were lower than most of the findings reported by other researches (Storelli et al. 2011; Godliauskienė et al. 2012; Zacs et al. 2013).

According to food consumption data from GEMS, the dietary exposure to PCDD/F from seafood, meat and dairy products for general population in Malaysia was 0.0364, 0.128 and 0.412 pg WHO_{05}-TEQ kg^{-1} bw d^{-1}, respectively. However, the exposure was higher in seafood (0.249 pg WHO_{05}-TEQ kg^{-1} bw d^{-1}) and meat (0.225 pg WHO_{05}-TEQ kg^{-1} bw d^{-1}) when the data was estimated using the Malaysian food consumption statistics. Lower exposure was observed in dairy products with the estimation of 0.241 pg WHO_{05}-TEQ kg^{-1} bw d^{-1}. The dietary exposure to PCDD/F of 0.238 pg WHO_{05}-TEQ kg^{-1} bw d^{-1} was estimated for the general population in Malaysia. This exposure was much lower than the tolerable daily intake (TDI) of 1–4 pg WHO-TEQ kg^{-1} bw as recommended by World Health Organization (WHO 2000). In addition, this exposure was also lower compared to dietary intake reported in Spain (1.17 pg WHO-TEQ kg^{-1} bw d^{-1}) (Marin et al. 2011) and in Germany (0.88 pg I-TEQ kg^{-1} bw d^{-1}) (Malisch 1998). Thus, it is suggested that the dietary exposure to PCDD/F does not represent a risk for human health in Malaysia.

Conclusion

This study is the first to report the contamination levels of PCDD/F three major food groups in Malaysia and their exposure in daily diet. The findings demonstrated that the levels of these contaminants in seafood, meat and dairy products in Malaysia were far below the relevant legislative limits and gave no indication of particular health risk associating with consumption of these food matrices.

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Chapter 11
Environmental Forensics on Appropriate-Technology-Enhanced Supply Chain of Rural Commodities

Corinthias Pamatang Morgana Sianipar, Gatot Yudoko and Kiyoshi Dowaki

Abstract Rural commodities have become important in any kind of rural development. Considering the common difficulties happen in rural areas, and by looking at common uneven distribution of profit margin in many long supply chains of rural commodities, rural governances have begun to apply Appropriate Technology (AT) to pull such distribution back to rural communities as the producers of rural commodities. Such applications become more interesting in term of environmental forensics. Due to the different characteristics between environmental forensics on supply chain and AT, this study aims to integrate such characteristics into a single map of forensics. Characteristics of each kind of forensics are completely taken to deliver a holistic framework. Previous approaches in each forensics are explored to discover the potential integration. Based on such exploration, the cross-sections between forensics are carefully explained to avoid inaccuracy of assessment. The result provides an integrated framework to assess environmental impacts imposed both through supply chain and AT. By looking at previous researches, this study significantly contributes to the common understanding of environmental forensics on supply chain. Then, this study will be expanded by including cost-based approach to evaluate the unit emission per unit-distributed value added throughout a supply chain due to AT application.

Keywords Environmental forensics · Appropriate technology · Supply chain · Rural commodities · Cleaner application · Cleaner production

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Highlights

- Map of forensics on AT-enhanced supply chain of rural commodities is provided.
- A new forensics is developed by taking the characteristics of supply chain and AT.
- This study contributes to the common understanding of forensics on supply chain.

Introduction

Rural development has been widely known as a critical facet of regional development in underdeveloped regions (Sianipar et al. 2013b). One of the biggest focuses in rural development is on the market of rural commodities. Among issues in such market, supply chain becomes a medium to bring rural commodities to wider market coverage. It has a critical position due to the difficult access of rural communities to outside area, meaning that they have to do more efforts to access higher market levels (Swinnen 2007). Besides, supply chain of rural commodities is usually applied through a long chain that consists of many connected parties from rural communities to end-users. Thus, some issues have risen for questioning the efficiency of related activities throughout such kind of supply chain.

One of important issues in a long supply chain is about environmental impacts imposed by any activities among supply chain parties (Jones 2002), meaning that even a small impact from a single activity would produce high impacts accumulated throughout a long chain. Furthermore, environmental impacts from a long chain would be considerably higher if the impacts are calculated by taking the characteristics of rural commodities into account. Difficult access of rural communities to better solutions in improving the quality of their commodities have forced other supply chain parties to do further processing activities (Swinnen 2007). The activities are applied to rural commodities before low-level buyers trade any commodity to higher-level buyers, meaning that they can get higher profit due to quality improvement. However, additional processing means that more impacts would be imposed to environment through the use of machines.

On the other hand, long chains of rural commodities have produced unequal profit distribution. Due to the low quality of rural commodities on producers' side (Sianipar and Widaretna 2012), profit margins have been pulled to higher supply chain parties who do more efforts than producers. In fact, higher market level means higher profit. Besides, additional profits would be gained by parties who are doing more processing activities (Marsden et al. 2000). Thus, local government attempts to pull profit distribution back to rural communities as the producers. One of their solutions is by doing quality improvement through post-harvest processing but due to local limitations it would be more difficult to do (Sianipar et al. 2013b).

Thus, a better technological solution with affordable price (Sianipar et al. 2013a) is needed, meaning that Appropriate Technology (AT) would be useful to achieve it.

However, a new technology implementation on producers' side has another consequence in term of environmental impacts. AT might have less ecological burden (Yanful 2009), yet assessing the impacts throughout supply chain must be proven. Therefore, a holistic forensics technique is required to analyze all imposed impacts on an AT-enhanced supply chain. The analysis has to consider the characteristics of both entities. Thus, this study needs to answer the following questions:

RQ1 What kind of characteristics that must be considered in the forensics?
RQ2 How to establish the forensics on an AT-enhanced supply chain?

The Basis of the Forensics

Environmental forensics on supply chain is conducted by focusing on energy conversion into imposed environmental impacts considered as negative ones, such as heat and emission (Fig. 11.1) in order to assess either impacts or green characteristics (Jones 2002). Throughout all possible activities in a supply chain, it is investigated to discover impacts both from each discrete activity and the whole supply chain, and then interpreted as required in the purpose of an investigation.

On the other hand, environmental forensics on AT has never been really interesting. It is usually focused on the basic characteristics of AT as an alternative to support environmental preservation in developing areas (Yanful 2009). However, later attention has started to investigate broader coverage by including better production method to achieve environmental appropriateness (Sianipar et al. 2013a).

Such effort aims to combine cleaner application (Sianipar et al. 2014a) and cleaner production (Kjaerheim 2005) approaches. The idea comes out to simultaneously investigate impacts imposed by both approaches in all life-cycle stages of AT (Sianipar et al. 2014b) since its construction until materials degradation

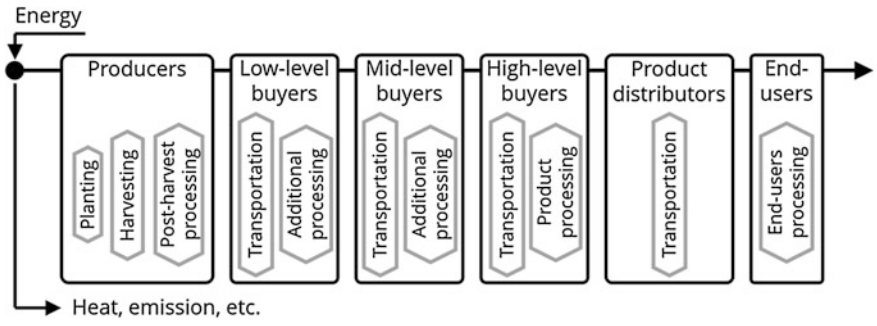

Fig. 11.1 Basic forensics on supply chain

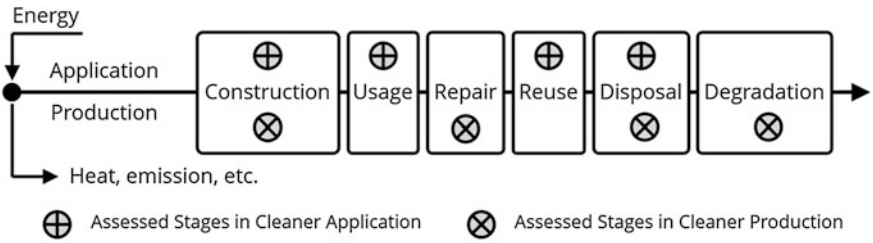

Fig. 11.2 Basic forensics on AT

(Fig. 11.2). Thus, it will result in an AT that can do environmental-friendly tasks and is produced through an environmental-friendly production process, so it will reach the ultimate condition an environmentally-appropriate AT.

Map of the Environmental Forensics

By looking at previous explanation, environmental forensics on supply chain and AT can be integrated. Due to the intention of technology implementation for improving quality of commodities on producers' side, the simplest way was conducted by applying AT in post-harvest processing activities. Thus, such positioning also becomes the cross-section between forensics on supply chain and AT. It is started by planning some possible investigations among all possible options (Fig. 11.3). Putting the cross-section also means that there are two possible scenarios: usage-based and reuse-based. The coverage on one or both scenarios is decided based on observed time coverage in an investigation. Broader time coverage would deliver holistic investigation result, yet the complexity of observation must be carefully considered. Usage-based is taken if an AT is predicted to have a single life-cycle, and reuse-based is taken for more than one cycle of usage term. In post-harvest processing, forensics on AT is more likely to overlap with forensics of supply chain, so an assessor must be careful for not double-counting imposed impacts in such activities. Besides, there is a juncture between scenarios to reproduce some components in repair activities, so there are only some complete production repetitions. On other objects, normal assessment can be conducted.

On other activities, there are some further assessments. In Planting, fertilizer will considerably impose impacts due to chemical reaction phenomena. Additional processing activities also impose impacts due to energy conversion. In Harvesting and Transportation, the assessment can be done through Tank-to-Wheel approach (Silva et al. 2006), with some extension on Well-to-Tank approach if required. Forensics on supply chain side must be planned to provide as wide as possible coverage without ignoring the main purpose of an investigation.

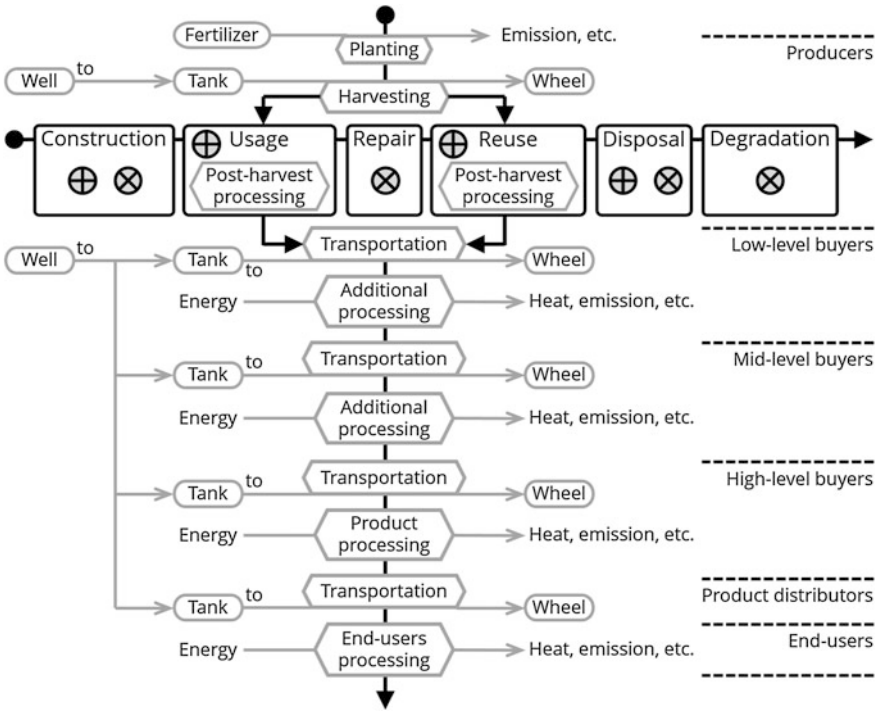

Fig. 11.3 Complete mapping of the forensics

Conclusion

The application of AT as a means for improving quality of rural commodities on producers' side has made environmental forensics on supply chain of such commodities to be more interesting. In this study, the forensics is developed based on both supply-chain-based and AT-based approaches, which significantly contribute to the understanding of common forensics on the supply chain. Future works of this study will include cost-based approach to evaluate the effect of AT application in term of unit emission per unit distributed value-added in a supply chain.

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Chapter 12
Hazardous Waste Management in Malaysia: The Needs of Environmental Forensic

Norhazni Mat Sari and Mazlin Bin Mokhtar

Abstract In the past years of economic development in Malaysia, focus has changed from agricultural to the industrial manufacturing and demand to support the sustainable development is always a challenge. The nation intends to become developed and fully industrialization by the year 2020. One of the consequences of such development is the increase in the generation of industrial waste and effluent containing toxic and hazardous industrial waste and sludge. Following such example from development in the 'top-peers' environmental agencies, among new approach of hazardous waste management is the integration of forensic enforcement and investigation, and the needs is anticipated to bring a great challenge to the current system of hazardous waste management in Malaysia. Under the hazardous waste management system, this paper discusses the environmental forensics in the field of the enforcement program to address the investigation of the peculiar hazardous waste issues, namely: (i) Hazardous waste generation and compliances to the legislation; (ii) Hazardous waste management facilities; (iii) Illegal dumping of hazardous waste; (iv) Importation and exportation of hazardous waste; and (v) Contaminated land.

Keywords Hazardous waste management · Scheduled waste · Environmental forensic enforcement

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Highlights

- The demand to adopt forensics approach for hazardous waste management is in need.
- Chemical fingerprinting (data bank) and waste generators need to be established.
- Five major issues on hazardous wastes need to be explored.

Introduction

Environmental forensics in Malaysia has progressively institutes initially under the roof of academic requirements where research pertaining the source identification of oil pollution in the Straits of Malacca, Malaysia (Zakaria et al. 2000; Zakaria and Takada 2007) and distribution of Polycyclic Aromatic Hydrocarbon (PAH) in rivers and estuaries in Malaysia being conducted (Zakaria et al. 2001; Sakari et al. 2008, 2010). However, the real environmental investigation with environmental forensics approach for environmental management purposes within the environmental authority obligations are not heard for. Thus, it is significant that a study be conducted among the environmental agencies in seeking the application of environmental forensics needs in the environmental enforcement and investigation. In this article, we will discuss hazardous waste management development in Malaysia with respect to forensics enforcement and investigation program needs of the Department of Environment, Malaysia (DOE).

Materials and Methods

A literature review and a pilot study were conducted in determining the issues and the potential agency to lead the environmental forensics for Malaysia. A review of the legislation, the Environmental Quality Act, 1974 and Scheduled Wastes Regulations especially the Scheduled Wastes Regulations 2005 specifically identifying the hazardous waste concern related to environmental forensics elements were carried out. A more in depth study focused largely on interviewing the officials from the Department of Environment; (30) the senior enforcement officials and the on-ground enforcements officers who conducted the enforcement program and hazardous wastes investigation.

Results and Discussion

Hazardous Waste Generation and Compliances to the Legislation

The guiding principle for hazardous waste management activities in Malaysia is clearly stated in the Environmental Quality Act 1974. Although the EQA was enforced since 1975, the regulation and order dealing with hazardous waste were only developed and came into force in 1 May 1989 with two Regulations and one Order. The demand to adopt forensics approach for hazardous waste management is in need looking at the trend increment of hazardous waste generation by industries in Malaysia jumped for more than seventh fold from the ninetieth and portrays no sign of reduction over the years (DOE 2000, 2010, 2011). Details of chemical fingerprinting (data bank) of each of the scheduled waste, waste generators (source) need to be established. Two items on the lists that are predominant for forensic investigation such as; liability for future clean-up cost and means of forensically compliance, i.e., means of doing the investigation, adequate sampling program and procedures (Mudge 2009a), representative data (Petrisor 2005) and analysis of data (Mudge 2009a, b) are not tabulated.

Hazardous Waste Management Facilities

The legal framework that governed the monitoring of the facilities is the Environmental Quality (Prescribed Premised) (Scheduled Wastes Treatment and Disposal Facilities) Order in 1989 (Amendment 2006). Currently, there are four hundred and twenty-two (422) recovery facilities for toxic and hazardous wastes in Malaysia, in comparison to only thirty-one facilities (31) in the year of 2000. Despite having good regulations and establishment of the scheduled waste management facilities, some illegal dumping of hazardous waste events also occurred in the country.

The procedures or the manner of operation to which these licensed premises should adhere to the stipulated Environmental Quality (Prescribed Premises) (Scheduled Wastes Treatment and Disposal Facilities) Regulations, 1989. The Regulation provides for the licensing application, renewal and ownership transfer, requirements for record keeping and license submissions to the DOE are specified. From the perspective of forensic investigation, these documents could be used as important information in identifying the source or origin of the hazardous waste and also presenting the way of the premise manage the hazardous waste.

Illegal Dumping of Hazardous Waste

Many incidents of illegal dumping of hazardous and toxic waste before the establishment of the integrated facility of scheduled waste has been documented. This trend continue after the establishment of Kualiti Alam Sdn Bhd, an integrated facility for scheduled waste collection, treatment and disposal at Bukit Nanas, Port Dickson, Negeri Sembilan (Rosnani 2006, 2007; Kualiti Alam 2006; Mat Sari et al. 2012). There are at least 90 cases of illegal dumping of scheduled wastes in the country from 2001 to 2005 (Lee 2006) and; 148 cases until 2010 (Mat Sari et al. 2012) but only 39 has been tracked, prosecuted and responded to the clean-up. The case of Sg. Gatom, Labis, Johor, residents had to be evacuated due to the release of ammoniacal gases from the illegal dumping site (DOE 2006, New Straits Times 2006; Kualiti Alam Sdn Bhd 2006).

Importation and Exportation of Hazardous Waste

To support the implementation of the Basel Convention in Malaysia, the following legislations were in place since August 1993; (i) Customs (Prohibition of Export) Order 1998 and later repealed by Custom (Prohibition of Export) Order 2006; (ii) Customs (Prohibition of Import) Order 1998 and repealed by Custom (Prohibition of Import) Order 2006 and (iii) Section 34B, Environmental Quality Act, 1974, prohibition against placing, deposit, etc., of scheduled waste.

According to DOE Malaysia (2010), there are 49 reported cases of illegally importation of hazardous waste. An apparent case was Syenviro Sdn Bhd, a company claimed to make brick, that conducted massive illegal importation of the metal hydroxide from Taiwan in 2004 (Department of Environment 2004; Mat Sari et al. 2012). Forensic investigation demands for the investigative team to establish case that the metal hydroxide originated from the wastewater treatment plant (the type of contaminant and source). More recent cases that require environmental forensic investigation are: electric and electronic wastes (E-waste); the new waste list, SW 110 under Scheduled Waste Regulation, 2005 as to more illegally importation of E-waste has been reported to DOE for investigation (Department of Environment 2010).

Contaminated Land

The legislation in governing soil contamination is stipulated in the Section 24, EQA, 1974. In 2010, the DOE has come up with the compilation of contaminated soil in Malaysia and establish soil pollution guidelines. For the land contamination

management, through the Guidelines a 'risk based approach' is adopted (Mat Sari et al. 2012). In other aspects, the DOE is looking at the assessment and clean-up of decommissioned petrol stations.

Conclusion

Some of components of environmental forensics might be absent in the current environmental investigation system, such as, establishing chemical fingerprinting; source signature, source age, and source apportionment. However the needs of environmental forensics; a scientific investigation of criminal and civil offences against the environment, as a new approach of conducting the enforcement and environmental investigation of hazardous waste management are essential.

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Chapter 13
Polychlorinated Biphenyl Contamination to the Canadian Arctic from Landfills and Sewage Treatment Outlets

Narayanan Kannan, Senthil Kumar Kuruthachalam, Monica Danon-Schaffer and Won Joon Shim

Abstract An investigation was undertaken in soil from the Canadian polar circle [Yellowknife (YELL), Iqaluit (IQA), and Cambridge Bay (CAM)]. Twenty four soil samples (YELL = 3, IQA = 15, CAM = 6) were collected with the depths of 0–20 cm below surface. Eighty major PCBs congeners were analyzed and twenty two PCBs were detected. Concentrations of PCBs in IQA were found to be the highest (0.11–1111 ng/g on dry weight basis), following in decreasing order: CAM (0.07–145 ng/g) and YELL (0.4–7.1 ng/g). Contamination profiles of PCB congeners were different between Iqaluit samples, while PCBs congener profiles were similar in Yellowknife and Cambridge Bay areas. The background sample sites were chosen to be representative of clean and undisturbed soils. The large difference in concentrations observed between dumpsites and background soil samples suggest PCB deposition into these dumpsites from materials discarded within. This is yet another evidence to show that previously pristine Polar Regions are increasingly getting contaminated through human activities. PCBs are excellent industrial markers in this forensic investigation.

Keywords PCBs · Arctic · Forensic

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Highlights

- PCBs are excellent industrial markers in forensic investigation.
- Previously pristine Polar Regions are increasingly contaminated.
- The spatial distribution of PCBs contamination can determine the sources and transport.

Introduction

Persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs) are lipophilic and semi-volatile and hence are found even in remote marine/terrestrial environments through atmospheric transport and biological processes (Kannan et al. 1989a, 1995, 1998). Exposure to dioxin-like PCBs (coplanar congeners) is of concern because of their toxicity, including endocrine disruption, hypothyroidism, carcinogenicity, neurotoxicity and reproductive effects in humans and wildlife (Kannan et al. 1988, 1989b; Van den Berg et al. 1998). Even at low dosage, PCBs can cause cancers, neurological and learning disabilities, hormonal (endocrine) disruption, and subtle changes to reproductive and immune systems in wildlife in pristine Arctic environment (Van den Berg et al. 1998).

The Canadian North is remote, containing polar region with a perennial frozen sea. The Arctic appears to have a greater capacity for storage of POPs as compared to other regions; therefore, once POPs enter the Arctic, they are readily incorporated within biological systems (Senthil Kumar et al. 2002). Hence, there is a growing burden of pollutants in Arctic air, water, animals, and humans (Danon-Schaffer et al. 2008). In Canada's far northern ecosystem, mass balances are needed to indicate the sources, transfers and accumulation of the various PCB congeners in air, water and soil. Studying the leachability of PCBs from electronic wastes (e-wastes) and examination of landfill sites to determine the fate and transport of PCBs are logical and important starting points (Danon-Schaffer 2009). The spatial distribution of PCBs contamination around landfill areas could assist in determining the sources and spread of PCBs. Consequently, in this study we examine profiles of PCBs in soil samples collected in impacted sites near three major communities in the Canadian arctic and in background locations. The sites selected were assessed to be impacted by landfill leachate (dumpsites) and wastewater effluents.

Materials and Methods

A sampling trip was made to three northern Canadian locations (Yellowknife "YELL", Iqaluit "IQA", and Cambridge Bay "CAM"). Twenty four soil samples (YELL = 3, IQA = 15, CAM = 6) were collected (with the depths of 0–20 cm

below surface). The detailed sampling locations are shown in Fig. 13.1. Multiple samples were collected at both the Iqaluit and Yellowknife landfills. A sample from a dumpsite in Cambridge Bay was also collected for comparison purposes. YELL and IQA samples were drawn from town locations, including close to wastewater effluent discharge areas. Most sites sampled contained sewage effluent or leachate discharged into the water body nearest each site. Hand trowels were used for soil collection. Samples were refrigerated at 4 °C until analysis.

A total of eighty major PCB congeners were analyzed in this study. The soil samples were extracted and the analysis is described elsewhere (Yim et al. 2005). Briefly, soil was extracted with dichloromethane using Soxhlet extractor for 16 h. The extract was cleaned using alumina-silica gel column chromatography. After concentration, the extract was cleaned again using size exclusion chromatography (Phenomenex Co., 100 Å column) to remove biogenic materials. PCBs were analyzed using gas chromatography with ^{63}Ni μ-electron capture detector (GC/μ ECD).

Quality assurance/quality control (QA/QC) procedures included analysis of duplicates, standard reference materials, and spiked internal standards. In the PCB analyses, internal standards were added at the beginning of the procedure and carried through the extraction, cleanup, and instrumental analysis steps to determine recovery. The following specific quality assurance steps were used to ensure measurement accuracy and precision: one procedural blank, one matrix spike, one duplicate spike and one standard reference material were run with each batch of not more than 20 samples.

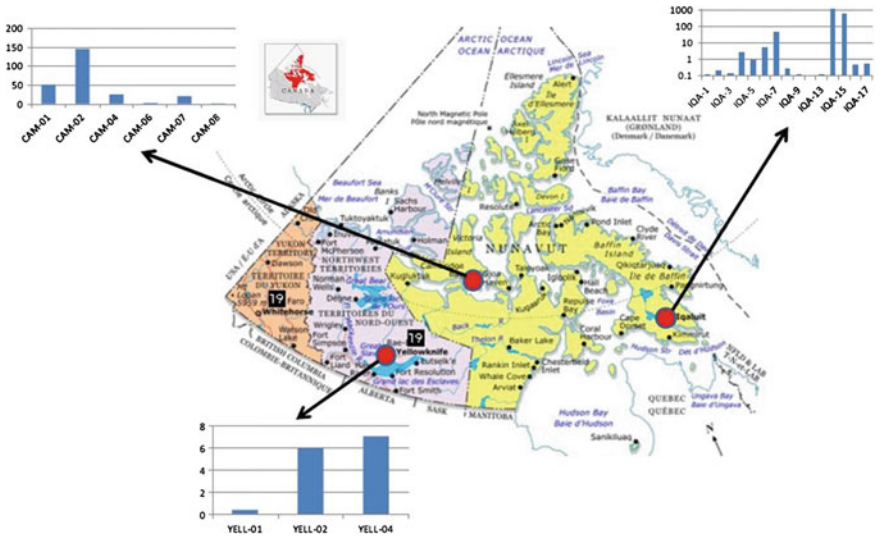

Fig. 13.1 Concentration of PCBs in the sampling locations

Results and Discussion

Concentrations of PCBs in IQA were found to be higher (0.11–1111 ng/g dry weight basis), in comparison to (in decreasing order of) CAM (0.07–145 ng/g dry weight) and YELL (0.4–7.1 ng/g dry weight) (Fig. 13.1). Contamination profiles of PCB congeners were different between Iqaluit samples, while PCB congener profiles were similar in Yellowknife and Cambridge Bay areas. The higher PCBs from IQA14 and IQA15 were significantly greater than what was measured in corresponding background locations IQA 1–9, 12–13 and 16–17. The background sample sites were chosen to be representative of clean and undisturbed soils. The large difference in concentrations observed between dumpsites and background soil samples suggest PCB deposition into these dumpsites from materials discarded within. The levels measured in background soil samples are assumed to reflect deposition from atmospheric transport. There were significant variations between the lowest and highest concentration measured in soil samples within each of the dumpsites that could be attributed to multiple factors including the historical movement of material within each site and the drainage characteristics of the site (Danon-Schaffer 2009).

PCBs-153, -170 and -180 were found to be an important congener measured in most of the dumpsite soil samples in IQA. PCB-52 was a major congener from YELL and lower chlorinated PCBs (e.g. PCB-8, -18, -28, -44 and -52) were the predominant contributors in CAM soils. Soil samples were collected from various locations within each of the three communities. These samples were gathered with the intent to characterize soils in areas close to known sources of contamination (i.e. landfills, dumps). Metal dumps are a common occurrence in Northern Canada. However, they are not typically located close to the municipal dumps and can be found inside of the town boundaries or haphazardly situated in remote areas, many times adjacent to a major body of water.

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Chapter 14
Exploring the Relationship Among Issues on Awareness in Practicing Waste Minimization (Malaysia)

Shadi Kafi Mallak, Mohd Bakri Ishak and Sabrina Abdullah

Abstract This study is carried out to identify the level of awareness associated with waste minimization practices and industrial solid waste. It focuses on the issues of 'lack of awareness and information' as preventive factors in waste minimization practices by industries in Malaysia. About 30 industries were randomly sampled from the industrial area using a structured questionnaire, and employs severity index and correlation analysis for data analysis. The correlation analysis is used to identify the relationship between issues in this research. Results revealed that the lack of accurate or sufficient knowledge of waste minimization practices is a serious barrier in waste minimization practices among the industries given the severity index value of 64 %. However, the results also show a statistical significant relationship on the lack of accurate or sufficient knowledge and untrained personnel ($r = 0.75$, $p < 0.01$), absence of experts ($r = 0.66$, $p < 0.01$) and limited technical information ($r = 0.61$, $p < 0.01$).

Keywords Waste minimization · Industrial waste · Barriers · Information and awareness

Highlights

- Waste as problem is a global challenge.
- Waste minimization is the most effective method for managing industrial wastes.

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- Waste minimization usually requires knowledge of the production process.
- Waste minimization is a practicable approach to prevent waste from being generated.

Introduction

Malaysia have been facing an increasing trend of waste generated from industrial activity. This increasing trend will continue due to the population growth and their demands for high standard of livings (Desa et al. 2011). The current system of solid waste management in Malaysia is poor and its responsibility is under the local government (Saeed et al. 2009). Lack of information and data hamper the effort of Malaysia government to implement an effective waste management system (Sakawi 2011). Research evidence reveals that, limited information and lack of basic data on industrial waste generation is one of the most fundamental barriers for planning suitable waste management (MHLG 2006). Attitudes regarding waste minimization practicing by industries play fundamental role in waste management (Teo and Loosemore 2001) as it is an effective waste management approach in reducing the pollution issues from manufacturing process (Vigneswaran et al. 1999).

Materials and Methods

This research is a case study of 30 industrial sectors in one of the biggest industrial zone in Malaysia. Almost 8 industrial types were selected as the respondents in this research. Frequency analysis and severity index (SI) were used to analyze the data using 0–4 point Likert scale structured questionnaire in order to assess the intensity of respondent's opinion regarding awareness in waste minimization practicing. The Spearman rank correlation was applied to measure the relationship between barriers regarding awareness.

Results and Discussion

The results from the analysis of frequency and SI calculation reveal that the absence of accurate knowledge about waste minimization is a serious issue as given by the sensitivity index range of $62.5 \leq SI < 87.5$ (Fig. 14.1). It was concluded that providing accurate knowledge of the relative agencies and information play effective role in enhancing waste minimization. To show the relationship between the lack of knowledge regarding waste minimization with other preventive factors, Spearman rank correlation was used to measure the relationship between lack of knowledge on waste minimization with other items. Results shows that there is correlation relationship among the variable at 0.01 significant level

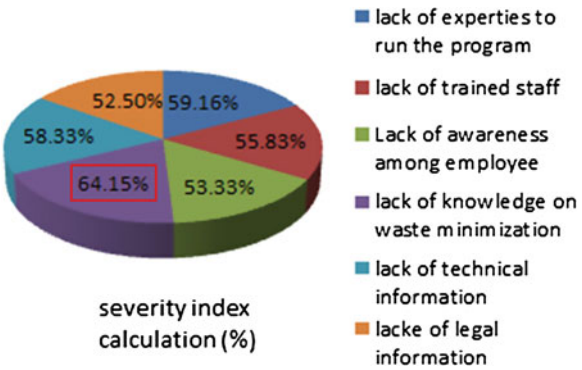

Fig. 14.1 SI of issues regarding awareness and information

Table 14.1 Spearman correlation between lack of knowledge on waste minimization and awareness factors

Variables	r	p
Lack of expertise to run the program	0.660**	0.000
Lack of trained staff	0.759**	0.000
Lack of technical information	0.611**	0.000

**Correlation is significant at 0.01 level (2-tailed)

(Table 14.1). The limited knowledge on waste minimization could affect the efficiency of waste minimization practise and its principles at the industrial sectors by absence of trained staffs and expertise to implement waste minimization methods, also the limited technical information can be affected by the weakness in general knowledge of waste minimization among employee and experts.

Conclusion

This study provides acceptable and helpful evidence regarding the awareness and information role in practicing waste minimization by industrial sectors. The result have shown that the lack of awareness and information is considered as a serious issue that prevents factories from effective waste minimization practices that is effective in the implementation of sustainable wastes management. It is apparent that improving the level of awareness and training personnel for better waste minimization practicing is necessary. Without understanding the concepts of waste management hierarchy, a successful industrial waste management and process efficiency cannot be achieved.

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Chapter 15
Potential Health Risk Assessment of Urban Soil on Heavy Metal Content in Seri Kembangan

Sarva Mangala Praveena, Nurul Syazwani Yuswir, Ahmad Zaharin Aris and Zailina Hashim

Abstract Rapid urban development has made environmental quality of urban soil to decline. To have a an understanding of heavy metal pollution in urban soil, in this study, concentrations of Pb, Cr, and Cd in urban surface soil of Seri Kembangan, Selangor (Malaysia) were analysed and investigated. Potential health risk assessment from these heavy metals was also assessed. Results showed that surface soil of Seri Kembangan has been polluted by heavy metals. A total of 16 sampling locations were sampled representing three major areas namely residential, industrial and playground in Seri Kembangan. The results showed that Pb and Cr concentrations are the highest at playground area. While Cd concentration is the highest concentration in residential area. Heavy metal concentrations were subsequently used to establish potential health risk assessment (non cancer risk) using Hazard Index. The order of hazard index of heavy metal in urban soil of Seri Kembangan was Pb > Cd > Cr. Hazard Quotient values exceeded 1 for Pb indicating potential non-cancer effect to human health via soil ingestion. Since health effects caused by Pb have long-term effects, especially on children, other pathways (inhalation and dermal) need to be considered. Other pathways are crucial to provide a bigger picture of potential health risk assessment of urban soil in Seri Kembangan.

Keywords Urban soil · Heavy metal · Ingestion · Hazard quotient

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Highlights

- Heavy metal concentrations (Pb, Cr and Cd) were detected in Seri Kembangan soil.
- Pb and Cr levels were highest at playground area while Cd in residential area
- Hazard Quotient for Pb (>1) indicated potential non-cancer effect to human health

Introduction

Heavy metal in urban soil is exposed to rapid industrial development (Karim and Qureshi 2013). According to Afroz et al. (2003), major sources of pollution in Malaysia are from motor vehicles, open burning and industrial emissions. Urban soil with high heavy metal concentrations poses significant human health risks. For heavy metal determination in soil, total heavy metal concentration is commonly measured (Praveena et al. 2010; Ščancar et al. 2000). Total heavy metal determination will overestimate pollution level and impacts of heavy l metals on soil and water (Lee et al. 2006). Total heavy metal concentration is insufficient for exposure and health risks assessment as well as inadequate for toxic effect determination. Using bioavailability of heavy metal concentration via in vitro digestion model provides more realistic—exposure and health risk assessment. High concentrations of heavy metal in urban soils have been recognized as an important source of human metal intake particularly in children who are more susceptible through soil ingestion than adults (Figueiredo et al. 2011).

Health Risk Assessment (HRA) process is described as hazard identification is the selection of key research studies that can provide accurate, timely information on the hazards posed to humans by a particular chemical. It is achieved by examining physical, chemical and biological properties of contaminants in terms of mobility as well as the point of exposure (Man et al. 2010). Even though, bioavailibility concentration using in vitro digestion model is capable of calculating cancer and non cancer risk to human, its application to urban soil is limited.

Seri Kembangan is a city located on the North–South Expressway Southern Route. The city is surrounded by land based (industries, agricultural) and anthropogenic activities. Seri Kembangan is rapidly developing there are many residential developments planned in this area. Therefore, it is important to study urban soil quality as well as its health risk. The study was aimed to determine heavy metal (Cd, Pb and Cr) in urban soil of Seri Kembangan. This study was also to assess non-cancer risk using the HRA through ingestion pathway.

Materials and Methods

A total of 16 surface soil samples were collected in Seri Kembangan, Selangor, based on its different soil activities, which are, industrial, residential and playground land. At each sampling site, surface soil samples were randomly collected using a stainless steel scoops and then placed in a polyethylene bag and transported to the laboratory. The surface soil samples were air-dried and homogenized using pestle and mortar. After the homogenization process, the samples were passed through 2 mm mesh screen and stored in polyethylene bags. In order to ensure the quality control, all the apparatus were acid washed overnight and rinsed with deionized water before used. In addition, all samples were run in triplicate samples.

Descriptive statistics was analysed using Statistical Package for Social Science (SPSS) ver.21. HRA using ingestion pathway based on the framework developed by United States Environmental Protection Agency was adopted. Exposure is expressed in terms of average daily dose (ADD) and is calculated for each heavy metal. The potential health risk (non-cancer risk) is determined using reference dose values.

Results and Discussion

The mean values of heavy metal concentrations (Cd, Pb and Cr) for each sampling location are given in Table 15.1. The heavy metal concentrations were in the following order, Pb, Cr and Cd. Pb and Cr concentration are the highest at SK16 (playground area) and SK14 (playground area), respectively. On the other hand, Cd is the highest in SK5 (residential area).

According to Karim and Qureshi (2013), increased of PB concentrations in urban soil are associated with anthropogenic activities. Alloway (1995) stated that soil located near roads usually contains high Pb concentration. This is supported by Mashal et al. (2009) which showed that Pb concentration in urban soil is four times higher than the rural soil in Scotland. Pb contamination was attributable to vehicular emissions despite the gradual shift from leaded to unleaded petrol, it still remains as a major pollutant for some urban areas (Lu et al. 2009). Cd was highest in the residential area from this study. Cd anthropogenic sources are related with atmospheric deposition which depends on the distance from emitting sources. Major sources of Cd atmospheric emissions are non-ferrous metal production as well as iron and steel production (Alloway 1995). Heavy metal concentrations in surface soil are insufficient to describe health risk arises from the exposure (Karim and Qureshi 2013). Therefore potential health risk assessment needs to be conducted.

HRA was calculated using the Chronic Daily Intake (CDI) and Hazard Quotient (HQ) via ingestion pathway. HQ values (non-cancer risk) for Cd, Pb and Cr are indicated in Table 15.2. From Table 15.2, HQ values for Pb exceeded 1 for

Table 15.1 Mean values of heavy metal concentrations (Cd, Pb and Cu) in surface soil of Seri Kembangan (mg/kg)

Sampling location	Land activity	Cd	Pb	Cr
SK1	Industrial land	65	77.5	78
SK2	Residential area	22	262	147
SK3	Residential area	51.75	744.75	28.35
SK4	Playground area	11.25	1082.25	59.4
SK5	Residential area	67.5	1785	66
SK6	Residential area	47.5	2212.5	52.5
SK7	Playground area	57.5	2382.5	78.75
SK8	Industrial land	32.5	2392.5	17.25
SK9	Industrial land	60	2945	48.75
SK10	Industrial land	50	3485	51
SK11	Residential area	35	4210	109.5
SK12	Residential area	60	5520	64.8
SK13	Residential area	66	4419	50.4
SK14	Playground area	30	3352	165
SK15	Residential area	52.5	4412.5	54
SK16	Playground area	51	5547	113.4

Table 15.2 HQ values (non-cancer risk) for each studied heavy metal using Seri Kembangan surface soil samples

Sampling location	Cd	Pb	Cr
SK1	0.1	0.0	0.0
SK2	0.0	0.1	0.1
SK3	0.1	0.3	0.0
SK4	0.0	0.5	0.0
SK5	0.1	0.8	0.0
SK6	0.1	1.0	0.0
SK7	0.1	1.0	0.0
SK8	0.0	1.0	0.0
SK9	0.1	1.3	0.0
SK10	0.1	1.5	0.0
SK11	0.1	1.8	0.1
SK12	0.1	2.4	0.0
SK13	0.1	1.9	0.0
SK14	0.0	1.5	0.1
SK15	0.1	1.9	0.0
SK16	0.1	2.4	0.1

locations SK6 to SK16 c(residential, industrial and playground areas). These values indicated that Pb contamination in Seri Kembangan urban surface soils may pose adverse effects to human health. From the HQ value, Pb is the main contaminant and non-cancer risk via soil ingestion. Children are more susceptible to Pb exposure than adults in due to its neurotoxin properties. Neurotoxin affects brain development and inhibits hemoglobin production (Karim and Qureshi 2013).

Conclusion

This study showed that heavy metal concentrations were in the following order, Pb, Cr and Cd. Pb concentration is the highest at SK16 (playground area) while Cr is the highest in SK14 (playground area). In addition, Cd is the highest in SK5 (residential area). The concentrations of Pb, Cr and Cd are associated with anthropogenic activities and vehicular emissions. The HQ values (non-cancer risk) for Pb exceeded 1 for samples located in SK6 to SK16, which consist of residential, industrial and playground areas. From the HQ value, Pb is the main contaminant for the non-cancer risk via soil ingestion. In conclusion, heavy metal exposure from soil ingestion can cause non-cancer risks especially in locations from SK6 to SK16. These findings are important for future research to calculate HI values via different pathways (inhalation and dermal). Inclusions of these pathways are crucial to provide a bigger picture of human health assessment.

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Chapter 16
Health Risk Assessment of Heavy Metal Exposure to Classroom Dust in Primary School, Serdang (Malaysia)

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Abstract Investigation of indoor dust is one of the major pathways in children exposure to heavy metal. High concentration of heavy metal in dust will have significant unequivocal ecological impacts and pose a potential health hazard. Dust samples were collected from seven randomly selected classrooms using a clean plastic brush and shovel. The dust samples were digested using aqua regia method and analyzed for Cd, Pb and Cu using Flame Atomic Absorption Spectrophotometer. Non-cancer effects due to heavy metal exposure from the classroom dust were also assessed. The heavy metal concentrates found on the floor, fan and windows were 0.17–6.14 μg/g for Cd, 0.34–454.86 μg/g for Pb and 12.63–185.82 μg/g for Cu, respectively. In comparison to other reported studies in the literature, the maximum levels of Cd, Pb and Cu were comparable or lower to those reported elsewhere. According to the calculation on Hazard Quotient (HQ) in the case of non-cancer effects, primary school children are experiencing no adverse effects since.

Keywords: Classroom · Dust · Heavy metal · Inhalation · Hazard quotient

Highlights

- Heavy metal concentrations (Pb, Cu, Cd) are highest in the windows of the classroom.
- Possible routes of dust were through open windows.
- Hazard Quotient (< 0.1) showed there is no any adverse health effect.

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Introduction

Urbanization process involves economic and industrial development which in turn leads to problems related to air pollution (Alahmr et al. 2012). Afroz et al. (2003) stated that major sources of air pollution in Malaysia are motor vehicles, open burning and industrial emissions. Rapid growth of these sources can contribute to increasing pollution levels in surrounding areas including heavy metal in dust. Therefore, heavy metal in dust is a significant sign of pollution in urban environments. Street dust in urban area is not only affecting human health but also a source of urban atmospheric pollution (Yap et al. 2011).

Street dust contaminated with heavy metal poses health risks to children and adults. Health risks are especially high for children because of their low tolerance to toxins as well as unintended ingestion of significant quantities of dust (Alahmr et al. 2012; Zheng et al. 2010). Yap et al. (2011) also stated that children are more susceptible to respirable dust inhaled from their surroundings, especially schools which are near man roads. Since schools in Serdang areas are situated near busy roads and industrial activities, dust from the surrounding area need to be investigated. In Malaysia, there are only few studies highlighted on heavy metal in dusts (Alahmr et al. 2012; Latif et al. 2009, 2011; Yap et al. 2011). Health risk assessment (HRA) process is described as hazard identification is the selection of key research studies that can provide accurate, timely information on the hazards posed to humans by a particular chemical. It is achieved by examined physical, chemical and biological properties of contaminant in terms of mobility as well as point of exposure (Man et al. 2010).

This study aimed to determine heavy metal concentrations (Cd, Pb and Cu) in classroom dust Sekolah Kebangsaan Sri Serdang).

Materials and Methods

Classroom dust was collected using a clean plastic brush and shovel. The methodology followed Radojevic and Bashkin (2006). A total 1.0 g classroom dust was digested using 15 mL of aqua regia at 120 °C about 30 min. Heavy metal concentrations (Cd, Pb and Cu) were determined using the Atomic Absorption Spectroscopy.

Descriptive statistics was carried out using Statistical Package for Social Science (SPSS) ver. 21. HRA using inhalation pathway developed by the United States Environmental Protection Agency was employed. Exposure is expressed in terms of average daily dose (ADD) and calculated for each heavy metal. With the ADD (inhalation) calculated, potential health risk (cancer-non-cancer risk) can be determined.

Results and Discussion

The minimum, maximum, mean and standard deviation values of heavy metal concentrations (Cd, Pb and Cu) in classroom dust (floor, fan and window) are given in Table 16.1. Heavy metal concentrations were in the following decreasing order, Pb, Cu and Cd. Cd concentrations were ranged between 1.73 to 7.5 μg/g. For Pb, the concentrations ranged between 59.81 μg/g and 101.87 μg/g. As for Cu concentration, the results ranged between 20.27 μg/g to 82.13 μg/g.

All classes have fans and are well ventilated with open windows and doors. According to Komarnicki (2005), possible routes of heavy metal to enter classroom are through open windows for cooling and ventilation. The movement of occupant's in and out from the building also contributed to heavy metal concentration in the building. Heavy metal finds their way into indoor building or in the classroom either as airborne dust or through items used or activities carried out within the school. In addition, activities carried out at surrounding areas also can contribute to indoor dust accumulation within comparison to other studies, Pb concentration is the highest in all studies (Table 16.2). This elevated level might due to classrooms location which was near—the main road. This will lead to more dust deposition in the classroom as well as minimal classroom cleaning. In addition, this school is located near the auto workshops bus stops. Anthropogenic sources of Pb in classroom dust are related to heavy road traffic during peak hour which can circulate in the classroom. Lu et al. (2009) reported that Pb contamination was attributable to vehicular emissions despite the gradual shift from leaded to unleaded petrol.

HRA was calculated using Chronic Daily Intake (CDI) and HQ. Based on the calculated CDI for every element, HQ values that are less than 0.1 (Table 16.3) indicated that there is no possibility of adverse health effect. The risk of exposure via inhalation to indoor dust is in the following order: Pb > Cu > Cd >.

Table 16.1 Descriptive statistics of heavy metal concentrations (Cd, Pb and Cu) in classroom dust (floor, fan and window)

Element	Minimum (μg/g)	Maximum (μg/g)	Mean (μg/g)	Standard deviation
Floor				
Cd	1.02	2.47	1.81	0.53
Pb	6.93	152	59.81	50.1
Cu	11.85	27	20.27	5.3
Fan				
Cd	0.40	2.65	1.73	0.75
Pb	0.17	408.25	94.17	142.86
Cu	6.44	86.47	57.41	27.28
Windows				
Cd	1.21	41.70	7.5	15.90
Pb	40.74	169	101.87	39.82
Cu	56.40	103.48	82.13	17.57

Table 16.2 Comparison between current study and other studies done in Malaysia

Author/Year	Heavy metal concentration (μg/g)		
	Pb	Cd	Cu
This study	89.05 ± 85.71	1.89 ± 0.76	53.27 ± 31.67
Muhammad-Darus et al. (2011)	31.24	–	–
Yap et al. (2011)	734 ± 140	442 ± 75	145 ± 2.03
Tahir et al. (2007)	92 ± 15	–	30.19 ± 6.25
Latif et al. (2011)	31.6 ± 0.98	–	–

Table 16.3 HQ for studied heavy metal

Element	HQ value
Pb	4.67×10^{-6}
Cd	9.93×10^{-8}
Cu	2.79×10^{-6}

Conclusion

The present study showed that heavy metal concentrations were in the following increasing order Pb, Cu and Cd. Cd concentrations ranged between 1.73 to 7.5 μg/g. For Pb, the concentrations ranged between 59.81 μg/g and 101.87 μg/g. As for Cu concentration, the results ranged between 20.27 μg/g to 82.13 μg/g. Dust from windows showed the highest heavy metal concentrations. HQ values were less than 0.1 indicated that there is no any an adverse health effects. Since health effects caused by heavy metal contained in dust may have long-term effects on the children, crucial actions, such as, a good housekeeping practice and maintenance of the ventilation system in classrooms should be taken into consideration.

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Chapter 17
Does Trade in Industrial Products have the Potential to Improve Distribution of Global Virtual Water?

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Abstract Virtual water refers to the amount of water used in the production of a product (a commodity, goods or services). This study examines the extent to which trade in industrial products (i.e. mining and manufacturing) between Malaysia and other countries will affect the distribution of water in water-abundant and water-scarce countries. Analyses of virtual water for 67 industrial sectors are conducted using the input–output model. This model has the ability to decompose virtual water content in the domestic demand and exports as well as virtual water import. This model also distinguishes virtual water flows (export and import) by trade destinations. Results show that resource based products are water intensive whereas electronics and electrical, machinery and equipment, and transport equipment are water non-intensive. Exports explain more than two-thirds of water consumption. Malaysia exports water non-intensive products and import water intensive products. The potential role of trade in industrial products as a policy instrument for global water distribution is limited. First, since the production of industrial products is essentially water non-intensive, thus exports of these products are not associated with large amount of water outflows. Second, trade in industrial products involves water flows among the water-abundant countries but not in water scarce countries.

Keywords Virtual water · International trade · Input–output model · Industrial products · Water flows

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Highlights

- Resource based industries are very water intensive.
- Electronics and electrical, machinery, and transport are water non-intensive.
- Malaysia exports water non-intensive products and imports water intensive products.
- Industrial export does not help to improve the distribution of global virtual water.

Introduction

The world population is projected to grow from 6.9 billion in 2010 to 8.3 billion in 2030 (UNDESA 2009) and this rapid growth of population increases the demand for water that sometimes create conflict between neighboring countries. When water is scarce there is a global responsibility to use water efficiently. Trade in 'virtual water' (also known as embedded water) is a possible policy strategy for global water saving. The term 'virtual water' was introduced by Allan (1996, 1998) who referred to the volume of water used in a product (a commodity, goods or services). Thus, when products are traded from one country to another country, the virtual water resources flows and are redistributed spatially. For example, exports of agricultural products from the United States of America (USA) to Japan and Mexico promote the global water savings by 11 % (Hoekstra and Mekonnen 2011). The quantification of virtual water are focused on agricultural products such as crops and livestock because it is related to food security and being the largest water consumption activities (Dietzenbacher and Velázquez 2007; Zhao et al. 2009). According to Chapagain and Hoekstra (2008), 16 % of the global water use is for export products and not for domestic consumption. The water use for production of agriculture products for export is 15 % while the industrial sectors consumed 34 %. It is important to note that the production of some industrial products, such as, paper and rubber processing use substantial amount of water. Due to increasing importance of industrial products as growth-drivers for some countries, the concept of virtual water flows should be extended to include industrial products and services (Zhao et al. 2009). This paper extends the analysis of virtual water by examining the extent to which trade in industrial products between Malaysia and other countries affect the global virtual water distribution. Malaysia is considered as a water-abundant country with the total rainfall in 2010 amount to 59,518 mm (Department of Statistics Malaysia 2011). Despite its abundance, Malaysia has trade advantage mostly in industrial products (essentially water non-intensive products) rather than agricultural products (essentially water-intensive products). In 2005, surplus in trade of industrial products amounted to 210 billion *Ringgit* compared to the deficit of 1 billion *Ringgit* in trade of

agricultural products (excluding forestry, logging and rubber products). This quantifies our choice on the analysis of water content in industrial products. The study addresses the two questions: (1) Does virtual water trade from Malaysia destined mostly to the water-scarce countries improve global water distribution? and (2) Is Malaysia a net exporter of virtual water?

Materials and Methods

The input–output analysis is an economic modeling technique that aims to understand the interactions among production sectors and consumers. The ability of input–output analysis to capture the whole production interdependencies leads to the wide application of the model for environmental and resources studies. Further readings on the application of virtual water analysis can be found in Duarte et al. (2002), Velázquez (2006), Dietzenbacher and Velázquez (2007), and Zhao et al. (2012). There are three main data sets used in this study: (1) The input–output table for 2005 that is published by the Department of Statistic Malaysia (2010). This input–output table consists of 120 sectors and was classified according to the Malaysia Standard Industrial Classification; (2) Water consumption by production sectors measured in cubic meters (m^3). Data for water consumption in 2005 are obtained from the Economic Census published by the Department of Statistics Malaysia (2006); and (3) Data for exports and imports classified by the Standard International Trade Classification (SITC) is used to disaggregate exports and imports by destinations of trade in the input–output table.

Results and Discussion

Analysis of virtual water for 67 industrial sectors indicates that rubber gloves; fertilizers; meat production; iron and steel products; and basic chemicals are the most water-intensive industries (Table. 17.1). For example, the coefficient for rubber gloves indicates 5.42 cubic meters of water directly consumed by the sector to produce 1,000 *Ringgit* of output. The resource based industries (such as a group of food production, wood products and rubber processing products) require more water per unit of output produced than the non-resource based industries (such as a group of electrical and electronic products, machinery and equipment and transport equipment).

In total, 79 % of the total virtual water consumed by industries is used for exports while only 21 % is required for domestic demand. In an extreme case, the motor vehicles industry used 92 % of total virtual water for domestic demand. Malaysia has surplus in virtual water trade; the surplus is mostly explained by the exports of water non-intensive products which constitutes 47 % to the total surplus

Table 17.1 Top five most water-intensive and top five least water-intensive industries in the virtual water content in the final demand and trade in 2005 (in thousand cubic meters)

	Water coefficient	Total water use	Virtual water content in		Virtual water import	Net virtual water trade	Share of export (%)
			Domestic demand	Exports			
	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Water-intensive							
Rubber gloves	5.42	27,587	1,105	26,481	3,007	23,474	2.09
Fertilizers	3.69	14,214	3,320	10,893	3,888	7,005	0.79
Meat and meat products	3.46	4,207	3,411	796	2,585	−1,789	0.01
Iron and steel products	3.32	66,983	14,140	52,842	56,481	−3,639	−0.00
Basic chemicals	2.94	70,987	6,907	64,080	25,843	38,237	4.71
Non water-intensive							
Measuring, checking and industrial process equipment	0.06	527	25	502	374	128	1.27
Petroleum refinery	0.13	9,829	3,015	6,814	23,522	−16,708	−0.19
Tobacco products	0.13	410	110	300	281	19	0.65
Other transport equipment	0.16	546	34	512	55	458	1.41
TV, Radio Receivers and Transmitters	0.16	10,739	1,531	9,208	7,846	1,362	3.78

in trade of goods. Virtual water outflows (imports) from other water-scarce countries—Mexico, Saudi Arabia, South Africa and Spain to Malaysia are larger than virtual water inflows (exports) from Malaysia (Table not shown). This trade pattern would not help to improve the water scarcity in the countries, in particular Saudi Arabia.

Conclusion

Malaysia is a net exporter of virtual water for industrial products. However, the potential role of trade in industrial products as a policy instrument for global water distribution is limited. Since production of industrial products requires less amount of water, exports of these products are not associated with large amount of water outflows. Trade in industrial products involves water flows among the water-abundant countries but not to some water-scarce countries. Hence, the current trade policy of exporting industrial products is not helping to improve global virtual water to countries like Mexico, Saudi Arabia, South Africa and Spain. However, the same practice is beneficial to other water scarce countries such as Australia, China and the Netherlands.

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Chapter 18
Spatial Variation and Source Distribution of Organic Contaminants in Langat River Basin, Malaysia Using Chemometric Techniques

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Abstract Monitoring organic contaminants is becoming an important feature in environmental forensic as they are potential chemical markers to pollution source identification. This study investigates the potential of using 13 selected organic contaminants (polycyclic aromatic hydrocarbons (PAHs), sterols, pesticides and phenol) to evaluate the spatial variation of 10 monitoring sites located along Langat River. Chemometric techniques namely, hierarchical agglomerative cluster analysis (HACA), discriminant analysis (DA), principal component analysis (PCA) and the factor analysis (FA) were used to assess the spatial variation of the selected organic contaminants and to relate them to their possible sources. HACA classified the sampling sites into three clusters, which can be correlated to the level of pollution. Forward and backward DA was able to discriminate two and seven organic contaminants variables, respectively, from the original 13 selected variables. PCA and FA (varimax functionality) were used to identify the possible sources of each organic contaminants based on inventory of local activities provided by the Department of Environment, Malaysia (DOE). Five principal components were obtained with 64.83 % of the total variation. Result from FA indicated that PAHs (pyrene, fluorene, acenaphthene, benzo[a]anthracene and benzo[a]pyrene) originated from industrial activity; while sterols (coprostanol, stigmastanol and β-sitosterol) were associated with domestic sewage and local socio-economic activities. The occurrence of phenol was correlated to industrial activities. This study shows that the application of chemometric techniques can reveal meaningful information on the spatial variability of a large and complex river water chemical data.

Keywords Hierarchical agglomerative cluster analysis · Discriminant analysis · Principal component analysis · Chemometric

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Highlights

- Chemometric techniques showed variations of organic contaminants along Langat River.
- Organic contaminants were associated with the local activities.
- Anthropogenic activities were the main sources of contaminants.

Introduction

Emerging contaminants has become one of the rising issues in the field of environmental research. The movement of organic contaminants into water takes place through disposal of waste, effluent discharges from industries and chemicals (Osman et al. 2012), thus deteriorate the quality of surface water. Surface water pollution is identified as the major problem affecting Langat River Basin, Malaysia. The expansion of developed areas within the river basin, will result in increasing pollution load in the Langat River (Juahir et al. 2011). Studies have shown that the quality of surface water is commonly determined by both natural and anthropogenic influences including catchment geology, atmospheric inputs, anthropogenic inputs and climatic conditions (Huang et al. 2010). Source distributions of organic contaminants also become particularly important for regulating the input of organic contaminants into the environment. In this study, 13 organic contaminants were selected which include polycyclic aromatic hydrocarbons, sterols, chlorpyrifos and phenol as they are potential marker to pollution sources. The data sets obtained were analysed using chemometric techniques to investigate the spatial variations and correlate these contaminants to the local activity. This approach may reveal the possible sources of organic contaminants along the Langat River Basin.

Experimental

Sampling

Ten sampling sites were selected from a list (24 sites) of monitoring sites of the Department of Environmental (DOE) Malaysia. Samplings were conducted along the Langat River Basin from February 2012 to January 2013. Organic contaminants such PAHs (acenaphthene, acenaphthalene, pyrene, fluorene, benzo[a]anthracene, and benzo[a]pyrene); sterols: (coprostanol, cholesterol, stigmasterol, stigmastanol and β-sitosterol); chlorpyrifos and phenol were selected in this study.

Extraction and Analysis of Organic Contaminants

Organic contaminants from water samples were extracted using tandem solid phase extraction approach (Osman et al. 2009). Two SPE cartridges (C_{18} and LiChrolut EN) were conditioned separately and arranged in tandem. After sample loading, the two cartridges were separated. PAHs, sterols and chlorpyrifos were eluted from C_{18} sorbent, while phenol eluted from LiChrolut EN sorbent. Gas chromatography with flame ionization detector (GC-FID) was used for separation and quantification of PAHs and sterols. Chlorpyrifos and phenol were analysed using gas chromatography with electron capture detector (GC-ECD) and chromatography with mass spectrometry detector (GC-MSD), respectively.

Chemometric Analysis

In this study, three chemometric techniques were used, namely, hierarchical agglomerative cluster analysis (HACA), discriminant analysis (DA) and principal component analysis (PCA) with the factor analysis (FA). The XLSTAT2013 was used for multivariate statistical analysis.

Results and Discussion

Spatial Similarity and Site Grouping

HACA was performed on the selected organic contaminants data set to evaluate spatial variation among the sampling sites. This analysis resulted in the grouping of sampling stations into three clusters. Cluster 1, (1L09 and 1L10) are classified as 'high pollution'. The stations are located near the city and industrial area. These sites are situated in a tributary of Batang Nilai, which flows through the industrial areas (Osman et al. 2012). Cluster 2 (1L01, 1L02, 1L03, 1L04 and 1L05) are 'moderate pollution'. Possible sources of contaminations are mainly domestic discharges and socio-economic activities. Cluster 3 (1L06, 1L07 and 1L08) are 'low pollution', these sites are located away from municipal discharges and industrial activities.

Spatial Variation of Organic Contaminants

Discriminant analysis (DA) was used to discriminate the organic contaminants in water samples. Based on the inventory of local activities provided by the Department of Environment, Malaysia (DOE), the sources of pollution can be

divided into three groups which consist of domestic sewage, industrial activities and socio-economic activities/urban discharges. The standard mode DA correctly discriminate the pollution source to 77.50 % using 13 discriminant variables. In the forward stepwise mode, 73.33 % was correctly classified using two discriminant variables (stigmastanol and stigmasterol), while the percent of cases correctly classified in backward stepwise mode was 75.00 % using seven discriminant variables (acenaphthene, fluorene, pyrene, stigmasterol, stigmastanol, β-sitosterol and phenol).

Identification Sources of Organic Contaminants

Principal component analysis (PCA) was performed to identify the possible sources of organic contaminants in Langat River Basin. In this study, five components or varifactors (VFs) were extracted and explained 64.83 % of the total variance. From the five VFs, VF1 explains 13.83 % from the total variance, showing strong positive loading of coprostanol and stigmastanol. These contaminants were detected from sampling sites associated with domestic sewage or urban discharge. This observation concurred with the study reported by Osman et al. (2010), whereby these contaminants were indicators for faecal contamination. VF2 explains 14.63 % of total variance which was dominated by pyrene, fluorene and benzo[a]pyrene, while VF3 with a total variance of 13.43 % was dominated by acenaphthene and benzo[a]anthracene. Inputs of the contaminants in VF2 and VF3 can be associated with urban activities along Langat River Basin. As reported by Li et al. (2012), the possible sources of pyrene and fluorene were from anthropogenic activities such as combustion. Benzo[a]pyrene was associated with incomplete burning activities (Osman et al. 2012) while acenaphthene and benzo[a]anthracene were associated with vehicle exhaust (Retnam et al. 2013). VF4 accounted for 11.62 % of the total variance, was predominated by β-sitosterol and phenol. The inputs of β-sitosterol and phenol may come from livestock farming and industrial activities along the Langat River Basin. β-sitosterol was found in water samples associated with bird species (Saim et al. 2009) and phenol associated with industrial activities (Jiang et al. 2003). VF5 contributed to 11.33 % of total variance with moderate loadings of acenaphthylene, cholesterol and chlorpyrifos.

Conclusion

In this study, the application of chemometric techniques provides valuable information in assessing the spatial variation of organic contaminants in Langat River Basin. The sources of specific organic contaminants can be explained by correlating the groupings obtained through chemometric approach with local activities.

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Chapter 19
Acute and Chronic Environmental Risk Assessment (ERA) for Pharmaceuticals in South East Asia

Eugenie Sin Sing Tan and Najat Al-Odaini

Abstract Pharmaceuticals are classified by the United States Environmental Protection Agency (US EPA) as emerging pollutants. Its ubiquitous nature and high persistency in the environment is alarming. As such, this study undertakes to determine possible acute and chronic environmental risk for pharmaceuticals in South East Asia (SEA). The calculated risk quotient (RQ_{max}) depicts worst-case-scenario. High risk of acute toxicity was demonstrated by diclofenac in Mekong River, Vietnam. Diclofenac in Langat River, Malaysia had shown high chronic risk; while two other pharmaceuticals showed medium chronic risk.

Keywords Pharmaceuticals · Environmental Risk Assessment (ERA) · Risk Quotient (RQ)

Highlights

- The first ERA for Pharmaceuticals in Malaysia and Vietnam.
- The first chronic ERA assessment in Thailand.
- High acute ERA risk for Mekong River and high chronic risk for Langat River.

Introduction

Pharmaceuticals are the emerging class of pollutants in the past decade due to its ubiquitous nature, toxicity and persistency in the environment. They are capable of eliciting biological responses in human and livestock. Pharmaceuticals are

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constantly discharged into the environment in large quantities. Their presence in the aquatic environment had shown to cause toxicities such as antibacterial resistance, growth inhibitions and retardations (Khetan and Collins 2007). Some pharmaceuticals are endocrine disrupting compounds (EDCs) capable of causing sexual underdevelopments, infertilities and disrupt sexual behaviors (Caliman and Gavrilescu 2009). As such, it is important to assess possible toxicities that may arise from occurrences of pharmaceuticals in the environment. Environmental risk assessment (ERA) is often used to speculate possible acute or chronic aquatic toxicities.

Materials and Methods

ERA is essential for PPCPs whose predicted environmental concentrations (PEC) were above 10 ng/L. In this study, measured environmental concentrations (MEC) was adopted as PEC. According to Grung et al. (2008), MEC is preferred than PEC.

Predicted no-effects concentrations (PNEC) for both acute ($PNEC_{acute}$) and chronic ($PNEC_{chronic}$) were adapted from previous literatures. If PNEC values were not available, they were calculated based on concentration at 50 % effect (EC_{50}), concentration at 50 % mortality (LC_{50}) and no-observed effect concentration (NOEC) published. PNEC was calculated by dividing ecotoxicology data with assessment factor (AF). $PNEC_{acute}$ was calculated by dividing EC_{50} or LC_{50} with AF of 1000. $PNEC_{chronic}$ was calculated by dividing NOEC with AF of 10, 50 or 100 depending on the availability of long term NOEC values for 3, 2 and 1 trophic levels respectively (EC 2003).

Risk quotient (RQ) was calculated by establishing ratio of MEC/PNEC. Risk quotient (RQ) was further classified as "no risk" for below 0.01, "low risk" for 0.01 to 0.1, "medium risk" for 0.1–1 and "high risk" for ratio more than one (Hernando et al. 2007). All RQs were calculated based on maximum MEC (MEC_{max}) establishing RQ_{max}.

Results and Discussion

The main obstacle in ERA is the lack of toxicity data for pharmaceuticals. Compilation of acute and chronic toxicity data from previous studies are shown in Tables 19.1 and 19.2, respectively. In order to identify possible acute and chronic toxicity in SEA, three studies on occurrences of pharmaceuticals in major rivers of SEA were reviewed. They were Langat River in Malaysia, Mekong River in Vietnam and Chao Phraya River in Thailand (Managaki et al. 2007; Najat et al. 2011; Tewari et al. 2013). Assessments of acute and chronic toxicities are shown in Tables 19.3 and 19.4 respectively. The calculated RQ_{max} depicts worst-case scenario.

Table 19.1 Compilation and calculation of $PNEC_{acute}$

Pharmaceuticals	Lowest EC_{50} (ng/L)	AF	$PNEC_{acute}$ (ng/L)
Acetaminophen	[a] 9.2×10^6	1000.0	9.2×10^3
Diclofenac	[a] 1.5×10^7	1000.0	1.5×10^4
Erythromycin	[b] 2.0×10^4	1000.0	2.0×10^3
Mefenamic acid	[c] 4.0×10^6	1000.0	4.0×10^3
Metoprolol	[a] 7.9×10^6	1000.0	7.9×10^3
Sulfamethazine	[b] 1.3×10^6	1000.0	1.3×10^3
Sulfamethoxazole	[a] 2.7×10^4	1000.0	2.7×10
Trimethoprim	[a] 1.6×10^7	1000.0	1.6×10^4

[a] Grung et al. (2008)
[b] Ji et al. (2010)
[c] Zhao et al.(2010)

Table 19.2 Compilation and calculation of $PNEC_{chronic}$

Pharmaceuticals	Lowest NOEL (ng/L)	AF	$PNEC_{chronic}$(ng/L)
Diclofenac	[a] 1.0×10^3	10.0	1.0×10^2
Erythromycin	[b] 2.0×10^3	10	2.0×10^2
Ibuprofen	[a] 1.0×10^3	50.0	2.0×10^4
Metoprolol	[a] 3.1×10^6	100.0	3.1×10^4
Naproxen	[c] 1.0×10^6	50	2.0×10^4
Salicylic acid	[c] 6.0×10^6	100.0	6.0×10^4
Sulfamethazine	[b] 1.6×10^6	10.0	1.6×10^5
Sulfamethoxazole	[a] 5.9×10^3	50.0	1.2×10^2

[a] Grung et al. (2008)
[b] Ji et al. (2010)
[c] Zhao et al. (2010)

Table 19.3 Acute ERA for pharmaceuticals in SEA

Pharmaceuticals	Langat river[a], Malaysia			Mekong river[b], Vietnam		
	MEC_{max} (ng/L)	RQ	ERA	MEC_{max} (ng/L)	RQ	ERA
Acetaminophen	346.3	3.8×10^{-2}	NO			
Diclofenac	280.9	1.9×10^{-2}	LOW			
Erythromycin				12.0	6.0×10^{-3}	NO
Mefenamic acid	82.7	2.1×10^{-2}	LOW			
Metoprolol	190.7	2.4×10^{-2}	LOW			
Sulfamethazine				28.0	2.2×10^{-2}	LOW
Sulfamethoxazole				33.0	1.2	HIGH
Trimethoprim				19.0	1.2×10^{-3}	NO

[a] Najat et al. (2011)
[b] Managaki et al. (2007)

Acute ERA for Chao Phraya River had been published previously (Tewari et al. 2013). All pharmaceuticals in Langat River and Mekong River demonstrated low

Table 19.4 Chronic environmental risk assessment (ERA) for South East Asia

Pharmaceuticals	Langat river[a], Malaysia			[b]Mekong river, Vietnam			[c]Chao Phraya river, Thailand		
	MEC_{max} (ng/L)	RQ	ERA	MEC_{max} (ng/L)	RQ	ERA	MEC_{max} (ng/L)	RQ	ERA
Diclofenac	280.9	2.8	HIGH				19.0	1.9×10^{-1}	MEDIUM
Erythromycin				12.0	6.0×10^{-2}	LOW			
Ibuprofen							49.0	2.5×10^{-3}	NO
Metoprolol	190.7	6.2×10^{-3}	NO						
Naproxen							41.0	2.1×10^{-3}	NO
Salicylic acid	131.2	2.2×10^{-3}	NO						
Sulfamethazine				28.0	1.8×10^{-4}	NO	5.0	3.1×10^{-5}	NO
Sulfamethoxazole				33.0	2.8×10^{-1}	MEDIUM	2.0	1.7×10^{-2}	LOW

[a] Najat et al. (2011)
[b] Managaki et al. (2007)
[c] Tewari et al. (2013)

or no risk except for sulfamethoxazole, which showed high acute risk. Environmental concentrations were unlikely to cause acute toxicity as they were detected in concentrations below lethal doses. However, their continuous discharge into the environment present risk to non-target organisms in a life-long cycle. Chronic toxicity is a more relevant measure of risk as it takes into account cumulative effects.

Chronic toxicities were more evident with high calculated risk for diclofenac in Langat River. Medium risks were calculated for diclofenac in Chao Phraya River and sulfamethoxazole in Mekong River. High risk quotient for diclofenac had been documented in Shijing River of China (Zhao et al. 2010). Hernando et al. (2007) predicted that diclofenac, ibuprofen and naproxen pose high risk to non-target organisms in surface water. In this risk assessment for SEA, it is only true for diclofenac while ibuprofen and naproxen had no calculated risk.

High risk of sulfamethoxazole had been linked to development of antibiotic resistance bacteria and growth inhibitions. Meanwhile, high risk of diclofenac had shown bioconcentration and adverse effect to the liver, kidney, gills and muscles (Khetan and Collins 2007).

Conclusion

ERA for pharmaceuticals in SEA showed high acute and chronic toxicities. Mixture effects of pharmaceuticals were not assessed in this study. Thus, this demands for more detailed assessments as well as mitigation and reduction measures.

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Chapter 20
Persistent Contaminants in Waste Oils: A Short Review on PCBs and PAHs as Main Contaminants

Fatemeh Abootalebi Jahromi, Narayanan Kannan, Mohamad Pauzi Zakaria and Ahmad Zaharin Aris

Abstract Persistent organic pollutants (POPs) include organochlorine compounds such as polychlorinated biphenyls (PCBs). Polycyclic aromatic hydrocarbons (PAHs) are considered as POP-like chemicals because of their similar characteristic. One source of entry of PCBs into the environment is from the improper handling and disposal of PCB-contaminated waste oil from old or discarded transformers. Polychlorinated hydrocarbons are natural constituents of transformer oils and are essential in prolonging transformer in-service lifetime. The existence of PCBs and PAHs in waste oils is reported in different studies. The aim of this review paper is to investigate the source and level of such pollutants like PCBs and PAHs in all kinds of oils with more attention to waste motor oil.

Keywords Waste oil · Transformer oil · PCBs · PAH

Highlights

- Improper handling of PCB-contaminated waste oil is a possible source of PCBs to the environment.
- PAHs are natural constituents of transformer oils.
- Waste motor and transformer oils are main sources of PCBs.

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Introduction

The occurrence of persistent organic pollutants (POPs) in environmental compartments has received great attention due to their persistence, biomagnification potential, long-range transport capacity and toxicity (Miglioranza et al. 2013; Kannan et al. 2012). POPs include organochlorine compounds such as polychlorinated biphenyls (PCBs), an industrial indicator, DDTs, an insecticide used in agricultural and health applications (Nozar et al. 2013). Polycyclic aromatic hydrocarbons (PAHs) are considered as POP-like chemicals because of their similar characteristic (Zhang et al. 2009). These components have 2–6 fused aromatic rings. PCBs are a group of chemicals, non-polar hydrocarbons that having one to ten chlorine atoms at biphenyl rings. These compounds have low solubility in water, but they tend to be soluble in organic solvents, fat, and oil (Erickson 1997). Therefore, PCBs are excellent chemicals for electrical applications. Among all 209 theoretically possible PCB congeners, no more than 130 congeners have been found in commercial products. These congeners are used in natural gas pipeline, voltage regulator, cable, heat transfer system, lubricating and cutting oils; as coolants and insulating fluids in capacitors and transformers, copping paper, adhesives, heat transfer fluids, and carbonless copy; as stabilizing agents in plastics and PVC coating of wires and electronic components; as additives in pesticides; as plasticizers in paints and cements, surgical implants, and vacuum pump fluids; and as fixatives in microscopy (Erickson 1997). PCBs are not naturally present in the environment; they are produced as complex mixtures and as by-products in numerous chemical processes, such as water chlorination and thermal degradation of chlorinated compounds (Erickson 1997). Due to the long service life of many PCB-containing items and the use of PCBs in some durable, relatively inert products, PCB-containing materials will continue to be disposed of and processed in waste and recycling operations. In some industrial processes, PCBs may be mixed with used oil and therefore some recycled oils currently in circulation may contain PCBs at concentrations generally '<50 ppm'. PCBs may also be present where used oil has been used for dust suppression/road oiling, weed control, and energy recovery. The aim of this review paper is to investigate the source and level of such pollutants like PCBs and PAHs in all kinds of oils with special attention to waste motor oil.

Source of Persistent Organic Pollutant

PCBs

A main source of PCBs in the environment is from improper handling and disposal of PCB-contaminated waste oil from old or discarded transformers (Ogata et al. 1980). Thirty-three transformer oils were analyzed by Shin and Kim (2006) as a

main source of PCBs emission into environment and collected by NIER in Republic of Korea (Shin and Kim 2006). Waste motor and transformer oils are considered as a main source of polychlorinated biphenyls (PCBs) emission into the environment. In another study the levels of total PCB in 26 randomly selected samples of waste motor and transformer oils from different regions of Poland were studied (Lulek 1998). Insulating oil has been also reported to contain PCBs.

PAHs

Mineral oils serve a variety of functions in maintaining healthy transformers including minimisation of heat losses, corrosion and conduction effects. These oils contain polycyclic aromatic hydrocarbons (PAHs) (Pillai et al. 2005). Crude and refined petroleum contains PAHs. They are introduced to aquatic environments through accidental oil spills, discharge from routine tanker operations, municipal and urban runoff, and so on (Zakaria et al. 2002). The combustion of fossil fuel (coal and petroleum) and biomass also produces PAHs, which are released into the environment in the form of exhaust and solid residues (Zakaria et al. 2002). Zakaria et al. (2002) analyzed four used crankcase oil samples taken from storage tanks in a gas station, an automotive workshop, garages, and a motorcycle workshop in Malaysia as a source of PAHs. The author found that the sediment samples taken from river sediments carried the signature of waste oil.

Level of Persistent Organic Pollutant

PCBs

Lulek (1998) reported that six from 13 waste motor oils and six from thirteen transformer oils were not contaminated with PCBs. The total PCBs concentration was determined by a visual pattern matching and summing selected peaks to obtain a total amount. The determined content of PCBs in motor oils was by one order of magnitude higher than in transformer oils, but in both types of analysed samples, except one sample, did not exceed 50 μg/g. Different PCBs mixtures were present in 50 % of the samples (Lulek 1998). In another study which was done in Korea, the concentrations of PCBs in transformer oils were between N.D. (not detected) and 48.33 mg kg^{-1}. PCBs concentrations did not exceed 50 mg kg^{-1} which is generally the accepted limit for the definition of waste in POPs Guideline of Basel Convention (Shin and Kim 2006).

PAHs

Zakaria et al. (2002) reported that the concentration of PAHs in used crankcase oil is 3 orders of magnitude higher than that in fresh crankcase oil (total PAHs: 518,000–1719,000 ng/g). PCB emissions in old diesel engines are 2 orders of magnitude greater than modern diesel engines (Laroo et al. 2012).

Conclusion

The existence of PCBs and PAHs are reported in waste and transformer oils in different countries. The source and level of the oils were investigated by different methods. The amount of these pollutants is significant in transformer and waste oils. Different congeners of PCBs in waste oils were investigated. Investigation on PCBs and PAHs in waste oils need urgent consideration since these contaminants are very resistant in the environment.

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Chapter 21
Factor Controlling the Total Exchangeable Cation of Estuaries and Coastal Sediment

Ley Juen Looi, Ahmad Zaharin Aris and Fatimah Md. Yusoff

Abstract A preliminary study on exchangeable cation of sediments was conducted at 56 sampling stations along the Straits of Malacca in order to examine the most significant factor that control the total exchangeable cations in estuaries and coastal sediments. Physico-chemical characteristics (pH, salinity, and electrical conductivity), and organic matter content were determined in the laboratory. Total exchangeable cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) of sediment samples were analysed using flame atomic absorption spectrophotometer. The pH (2.85–7.97), electrical conductivity (8.92–46.37 μS/cm), salinity (4.97–30.13 ppt), organic matter (2.34–14.76 %), exchangeable sodium (23.98–123.65 meq/100 g), exchangeable potassium (0.05–3.08 meq/100 g), exchangeable calcium (3.42–18.98 meq/100 g), and exchangeable magnesium (5.96–24.12 meq/100 g) of estuaries and coastal sediments showed variations. Principal component analysis employed in this study clearly shows that exchangeable Na^+ was controlled by salinity which is mainly contributed from halite minerals (NaCl) and electrical conductivity. Thus, halite does play an important role in influencing the total exchangeable cations in estuaries and coastal waters.

Keywords Coastal sediments · Exchangeable cations · Estuaries · Straits of Malacca

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Highlights

- Exchangeable Na^+ was strongly correlated ($r = 0.974$, $p < 0.01$) with CEC.
- CEC of estuaries sediment was influenced by salinity.
- Halite ions are the most exchangeable fraction in estuaries and coastal sediment.

Introduction

Cation exchange capacity (CEC) is the capacity of soils or sediments to adsorb and exchange cations. CEC also represents the total amount of negative charge ions available on the surface of clays and organic matters (Shafie et al. 2012). As such, particle size and organic matter content in soils or sediments do play important roles in the controlling CEC. Some researchers believe that CEC can be related to the migration of metals in soil (McLean and Bledsoe 1992) and thus it is regarded as an important factor that relates to the pollution magnitude of sediment. Unfortunately, there are limited studies on exchangeable cation status in estuaries and coastal sediments of Malaysia, especially, concerning the importance of organic matter and particle size towards CEC. Therefore, this study is crucial as it provides baseline understanding on exchangeable cation status of sediment along the Straits of Malacca. Furthermore, present study will generate better insight on the influential factors that control exchangeable cations and metals' mobility in the sediment. Thus, this study aims (i) to determine the physico-chemical characteristics of estuaries and coastal sediments and (ii) to investigate the influential factors that govern the amount of exchangeable cations in sediments of Straits of Malacca.

Materials and Methods

Site Description

A total of 56 sampling points were straddled along the coastal area and estuaries of the Straits of Malacca. The sampling locations were chosen in a way that it is accessible and could accurately represent current activity of exchangeable cation in estuaries and coastal sediment.

Sample Collection and Analytical Methods

Coastal and estuaries sediment samples were collected from 56 sampling points along the Straits of Malacca during February–May 2012. Surface sediment

(0–10 cm) samples were collected by using plastic scoops and homogenized into an acid-washed polyethylene zip-locked bag. Then, sediment samples were preserved in an icebox (<4 °C) and transported to laboratory for further analysis. In the laboratory, sediment samples were air-dried at room temperature until constant weight is achieved. Subsequently, air-dried sediment samples were meshed by using pestles and mortars before it is sieved through 2mm sieve for physico-chemical and exchangeable cation analyses. pH, electrical conductivity (EC) and Salinity (Sal) of the sediment samples were measured in triplicate by using WTW pH330i (WTW Wissenschaftlich-Technische, Germany) and YSI 63 (YSI Inc., Yellow Springs, Ohio) with sediment to Milli-Q® water ratio of 1:2. In addition, loss on ignition (LOI) method was employed in order to determine the organic matter in sediment samples. In order to determine total exchangeable cations in estuaries and coastal sediment samples, cations displacement method by using sodium chloride (NaCl) and ammonium chloride (NH_4Cl) (Appelo and Postma 2005; Shafie et al. 2012) were employed in present study. NaCl solution was used to determine potassium (K^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}) in sediment samples while NH_4Cl solution was used to displace sodium (Na^+) from sediment samples. This method is suitable for current study because it can effectively remove cations from saline and brackish pore water in sediment samples that contribute to falsified results. Finally, exchangeable cations were analysed by using the flame atomic absorption spectrophotometer (FAAS, Shimadzu).

Results and Discussion

Descriptive statistic for the analysed estuaries and coastal sediments are given in Table 21.1. The CEC for sediment of the Straits of Malacca ranged from 40.23 to 159.09 meq/100 g.

Pearson's correlation analysis revealed that exchangeable Na^+ was strongly correlated with CEC (Fig. 21.1). This relationship was further proven via principal

Table 21.1 Descriptive statistic for selected parameters for sediment of the Straits of Malacca (n = 56)

	Unit	Maximum	Minimum	Mean	SD	CV (%)
pH		7.97	2.85	6.24	1.63	26.14
EC	µS/cm	46.37	8.92	18.53	6.40	34.51
Sal	ppt	30.13	4.97	11.04	4.24	38.40
LOI	%	14.76	2.34	7.71	3.38	43.84
Na^+	meq/100 g	123.65	23.98	67.58	22.87	33.83
K^+	meq/100 g	3.08	0.05	1.74	0.58	33.64
Ca^{2+}	meq/100 g	18.98	3.42	8.06	3.69	45.76
Mg^{2+}	meq/100 g	24.12	5.96	13.74	4.77	34.74
CEC	meq/100 g	159.09	40.23	91.11	26.40	28.98

Notes SD Standard deviation; *CV* Coefficient of variation

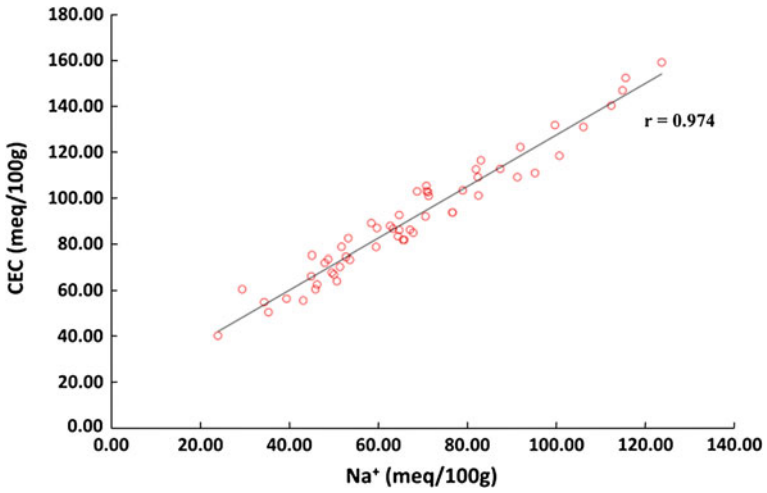

Fig. 21.1 The relationship between cation exchange capacity and exchangeable sodium of sediment along Straits of Malacca

component analysis (PCA) conducted in the overall datasets. From the output of PCA analysis, it was found that EC, salinity, Na^+ and CEC were in the same principle component that accounts for 36.57 % of total variance (Fig. 21.2). This explained CEC of estuaries and coastal sediments received significant influence from seawater. In the estuaries, halite (Na^+) become the dominant and readily exchanged with Ca^{2+} and Mg^{2+} on the surface of sediment colloid (Appelo and Postma 2005; Praveena et al. 2011; Aris et al. 2012).

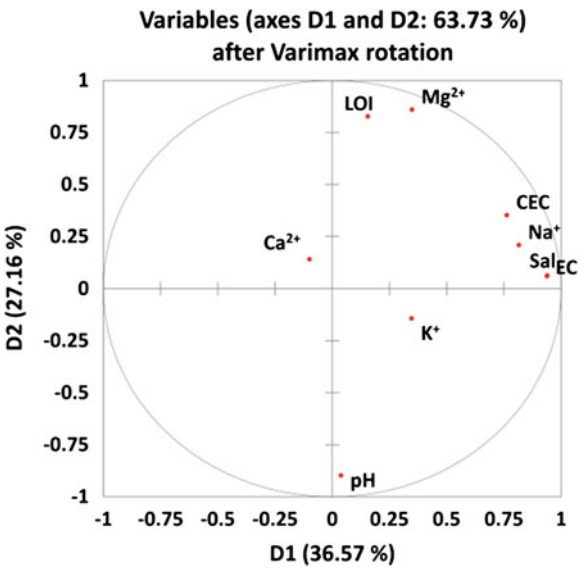

Fig. 21.2 Variance for principal component analysis after varimax rotation

Conclusion

This study revealed that Na^+, salinity and EC play significant role in controlling total exchangeable cations in estuaries and coastal sediment. Besides, other parameters such as LOI, K^+ and Mg^{2+} correspond significantly with CEC in estuaries sediment. Despite Ca^{2+} is the predominant component in soils, with the presence of halite ion, the most exchangeable fraction is dominated by Na^+. Present investigation via the application of geostatistical and geochemical approaches provide background data on exchangeable cation status for estuaries and coastal sediment of the Straits of Malacca. Due to limited data available for exchangeable cations in sediments, periodic monitoring and comprehensive study on CEC in future studies are warranted.

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Chapter 22
An Experimental Approach on the Removal of Cd (II) and Pb (II) Ions from Aqueous Solutions by Using Dead Calcareous Skeletons

Ai Phing Lim, Ahmad Zaharin Aris and Hafizan Juahir

Abstract Calcareous skeletons were studied to determine its ability in removing cadmium (Cd (II)) and lead ions (Pb (II)) from aqueous solutions. The factors affecting adsorption were evaluated with respect to adsorbent size, contact time, adsorbent dosage, pH, and initial concentration to determine the optimum conditions for Cd (II) and Pb (II) removal. The optimum dosage for removal of Cd (II) and Pb (II) were 20 and 10 g/L, respectively. The pH of both metal solutions had shifted from acidic to alkali condition after equilibrating with the adsorbent. The adsorption capacity of CS appeared to be higher when the initial metal concentrations increased above 1 mg/L. This investigation has proved that CS has a great potential for removing metal contamination in acidic water.

Keywords Calcareous skeletons · Cadmium · Lead · Removal efficiency · Adsorption capacity · Calcium carbonate

Highlights

- Calcareous skeletons have ability to remove Cd (II) and Pb (II) ions in aqueous solution.
- Small pore size did not determine the removal efficiency of absorbent.
- Calcium carbonate shifted the pH of Cd (II) and Pb (II) solutions to alkali condition.

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Introduction

In recent years, many alternative methods were studied to develop a cheaper approach for metal removal in water. Waste products were among the popular choice for adsorbing metals in water due to the abundance, availability and low cost. Agricultural and food wastes are famously used for biosorption, for examples, rice husk, palm shell, coconut husk, nut shells, fruit seed, baggase, and seashell (Bailey et al. 1999; Saifuddin et al. 2005; Demirbas 2008; Farinella et al. 2008; Olu-owolabi et al. 2012). The present study focuses on removing Cd (II) and Pb (II) from aqueous solution by using dead calcareous skeleton (CS). Dead calcareous skeleton mainly consists of $CaCO_3$ which have great metal-interaction for adsorption of toxic metals (Prieto et al. 2003). Previously, calcareous skeletons have shown great criteria as trace metal indicator (Matthews et al. 2006; Mokhtar et al. 2012). This paper has focused on the ability of calcareous skeleton in removing Cd (II) and Pb (II) ions. This involved the effect of contact time, adsorbent sizes, dosage concentration, pH and initial concentration.

Materials and Methods

Batch Experiment

For the effect of contact time, the Cd (II) and Pb (II) solutions were continuously agitated for 24 h and the aliquots were withdrawn at definite interval time. Various dosage of CS, at 5, 10, 15, 20, 30, 40, and 50 g/L were investigated for the influence of solid–liquid ratio. The pH of each solution was controlled at 3, 4, 5, 6, and 8, respectively, prior to the additional of CS into the metal solutions; while one solution was kept at its original state without adjusting pH. The solution's initial pH was not adjusted with any chemical to observe the effect of CS to the solution pH. The influence of initial concentration was investigated by varying Cd (II) and Pb (II) concentrations to 1, 5, 10, 50, and 100 mg/L.

Characterization of Adsorbent

The physical surface characteristic of the adsorbent, CS, comprising of specific area and pore size were determined by using Brunauer Emeett and Teller (BET) method analysis. The CS undergoes a degassing process at 300.0 °C for 21.8 h to eliminate surface impurities. Then, it was followed by an adsorption process where the CS were left to adsorb N_2 gas at 77 K. The surface area of CS was determined by BET equations.

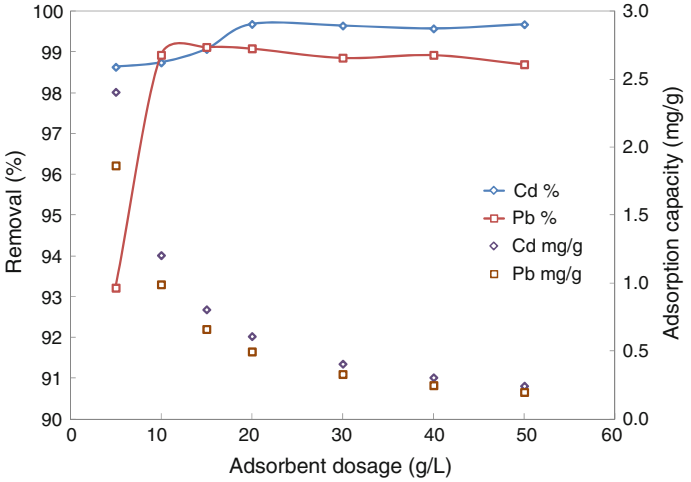

Fig. 22.1 Effect of different adsorbent dosage on the removal of Cd (II) and Pb (II)

Results and Discussion

The rapid removal of Cd (II) and Pb (II) by CS were observed at the beginning stage of first 60 min. For the following contact times, the removal efficiency trends for all sizes of CS were rather constant. The removal patterns for both metals were observed to remain at constant after the early stage of adsorption. As the dosage of CS increased, the removal of Cd (II) and Pb (II) also increased (Fig. 22.1). The initial pH (3, 4, 5, 6, 7, 8) of the both metal solutions were observed to shift from acidic to alkali condition (pH > 8) after equilibrating with CS for 12 h. The CS was also able to adsorb high metals concentration with increased of adsorption capacity.

CS has 0.2115 m^2/g of surface area, which is considered to be relatively smaller compared to the common adsorbents used in other studies. However, CS showed a high efficiency in removal of Cd (II) and Pb (II). This situation indicated that the surface area might not be an influential factor in the adsorption activities. The relationship between metal-sorption and BET surface in this study was inconsistent because the small surface area of CS did not restrict the adsorption of Cd (II) and Pb (II) from aqueous solution.

Conclusion

The present study showed that CS could remove >99 % of Cd (II) and Pb (II) without adjusting the initial pH. The BET surface area of CS was relatively small but the adsorption capacity was high, which indicates that the BET surface area

does not necessarily correlate with the adsorption efficiency. The output of this study provides a better understanding and cost-effective approach in metal removal application which will be beneficial to the water treatment plants.

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Chapter 23
Preliminary Physicochemical Assessment of Groundwater in Kg. Salang, Pulau Tioman, Pahang, Malaysia

Azrul Normi Idris, Ahmad Zaharin Aris, Saim Suratman and Ismail Tawnie

Abstract Fourteen groundwater samples were collected from Kg. Salang in the north-west of Pulau Tioman, Pahang and were analysed for their physicochemical characteristics. The physicochemical parameters were analysed to know the present groundwater quality as well as the possible source of ions in the groundwater. The groundwater in the study area is fresh and the dominant water type is Ca–Mg–HCO_3. The occurrence of these facies is identified to be natural due the calcite of corals and shells. The statistical analysis shows strong correlation between Ca–EC. Results concluded that the parameters which were taken for the study of water quality are below the pollution level for groundwater which satisfy the requirement for the use of various purposes like domestic, agricultural, and industrial.

Keywords Groundwater · Physicochemical · Ions · Facies · Corals

Highlights

- Physicochemical characteristics of groundwater were within the permissible limits.
- Water samples were classified mainly as Ca–Mg–HCO_3 water type.
- Calcium–EC showed significant relationship as an indication of mineralization process.

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Introduction

Islands are vulnerable to human activities and natural disaster in relation to their features as being small in size, insularity and remoteness as described (Briguglio 1995). Due to absence of surface water in dry season, Kg. Salang depends entirely on groundwater resources for domestic use. In some parts of the island, the current rate of groundwater extraction is depleting the resource faster than it is being recharged; this is because of seasonal monsoon in Malaysia. Islands have become renowned locations among tourists where an increasing number of visitors to the island caused an increase of freshwater demand (Aris et al. 2009a, b; Fleeger 1999).

The present work attempts to study the physicochemical properties in groundwater of Kg. Salang, Pulau Tioman, which is, situated 54 km from land area in Mersing, Johor or Kuala Rompin, Pahang. The results of the study will help in gathering significant data pertaining to the quality status of groundwater of Pulau Tioman. The aim of this study is to determine the physico-chemical characteristic of groundwater sample in and around Kg. Salang low lying area.

Materials and Methods

Kg. Salang encompasses area between 2°52.580′ to 2°52.582 N latitude and 104°09.291′ to 104°09.275′E longitude. Kg. Salang is one of the main tourist attraction areas in the west coast of Pulau Tioman. Water levels were measured from each well before pumping using deep meter. A total of fourteen groundwater samples were collected during the sampling campaign that was conducted in September 2012. Polyethylene bottles were used to collect and preserved the groundwater samples based on the method described by APHA (2005).

Measurement of pH and temperature were done on the field using HACH pH meter. The total dissolved solids (TDS) and electrical conductivity (EC) were also measured using the conductivity meter. Bicarbonate (HCO_3^-) concentrate was determined with HACH. Concentration of sodium and potassium were determined by using a flame photometer. Magnesium and calcium concentrations were determined by atomic absorption spectrometry. Chloride concentration was measured by silver nitrate titration. Sulphate and nitrate concentrations were measured by using colorimetric-spectrophotometer.

Results and Discussion

The relative abundance of cations in the groundwater is in the order $Ca^{2+} > Na^+ > Mg^{2+} > K^+$ and that of anions is $HCO_3^- > Cl^- > SO_4^{2-} > CO_3^-$. Ca^{2+} and HCO_3^- are the dominant cation and anion respectively.

Table 23.1 Summary of the physicochemical parameter

Variable	Minimum	Maximum	Mean	Standard deviation
pH	6.200	8.300	7.279	0.642
EC (μs/cm)	79.000	510.000	326.143	131.450
TDS	72.000	282.000	176.250	59.510
K	0.050	3.000	1.118	0.901
Mg	0.130	13.600	4.895	3.455
Na	4.800	79.000	14.786	18.928
Ca	4.700	94.000	55.186	29.081
HCO_3	33.000	365.000	219.714	112.763
Cl	8.000	31.000	12.000	6.263
SO_4	1.500	18.000	3.571	5.324
NO_3	0.020	52.000	4.506	13.727

Statistical Analysis

The summary of physical and chemical parameters obtained from the analysis of water samples are shown in Table 23.1. The correlation matrix in Table 23.2 displays the physicochemical parameters of the groundwater samples of 11 parameters. There is a good correlation exist between the Ca and EC, Bicarbonate. Identically a good correlation exists between TDS and EC.

EC–Ca correlation is the strong positive correlation with high EC and Ca. EC–HCO_3 and HCO_3–Ca correlation is moderate correlation with value *r* between 0.3 to 0.7 (Fig. 23.1). EC–Mg, Cl–Mg and EC–Na can be considered as no correlation with outliers data. EC–Na is negative correlation with high Na value associated with low EC value.

Hydrochemical Facies of Groundwater

The chemical composition of water samples from the study area is shown on the Piper diagram (Fig. 23.2). In the cation plot field, the samples plot mainly toward Ca^{2+} corner indicating calcium type water. In the anion plot field, the samples mostly plotted towards the $CO_3^{2-} + HCO^{3-}$ corner indicating carbonate or bicarbonate type water, but some of the samples plotted towards the middle triangle indicating no dominant anion type. Principally, the water samples plotted in the Ca–Mg–HCO_3 dominant of the diamond field.

Table 23.2 Correlation matrix for the water quality parameters

Variables	pH	EC	TDS	K^+	Mg^{+2}	Na^+	Ca	HCO_3^-	Cl^-	SO_4^{-2}	NO_3^-
pH	**1**										
EC (μs/cm)	0.527	**1**									
TDS	0.524	0.559	**1**								
K	0.197	0.215	0.563	**1**							
Mg	−0.052	0.118	0.114	0.176	**1**						
Na	0.479	−0.108	0.285	0.187	0.183	**1**					
Ca	0.429	0.952	0.420	0.011	−0.027	−0.129	**1**				
HCO_3^-	0.516	0.669	0.293	0.265	0.259	0.313	0.612	**1**			
Cl	−0.512	−0.047	−0.073	0.219	0.569	−0.029	−0.086	0.138	**1**		
SO_4^{-2}	−0.124	−0.043	0.200	−0.086	0.028	−0.078	−0.103	−0.191	0.097	**1**	
NO_3^-	0.181	0.436	0.506	0.301	0.153	0.012	0.328	0.261	0.256	0.552	**1**

Values in bold are different from 0 with a significance level alpha = 0.05

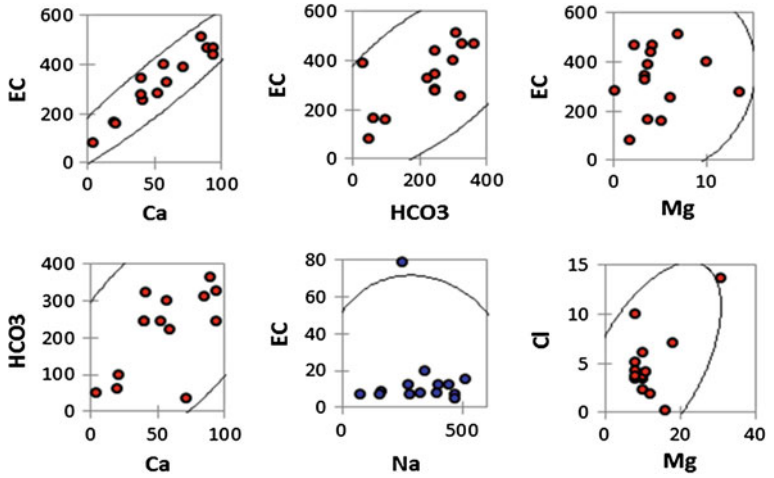

Fig. 23.1 Graph of confidents ellipse in different strength correlation

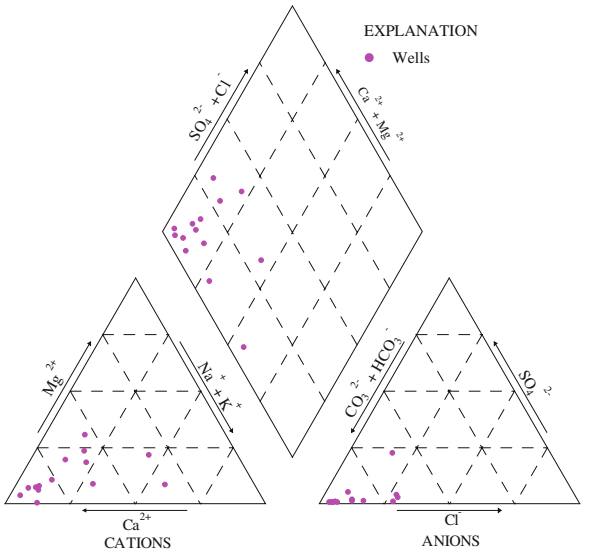

Fig. 23.2 Most of the wells in the study area have a good quality of water where shown in the *piper diagram*

Conclusion

The analysis of the water quality parameters of groundwater from fourteen different wells in Kg. Salang, Pulau Tioman of Pahang district shows that the pH, electrical conductivity, calcium, magnesium, chloride and bicarbonate are well within the permissible limits. The dominant cation in the water is calcium whereas the dominant anion being bicarbonate. Bicarbonate is high in the study area

indicating the biodegradation of the organic matter in the sub surface environment. The source of the ions could therefore be from the decay of organic matter and minerals concentrated in the soil zone.

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Chapter 24
Crude Oil Biodegradation Using Isolated Bacteria from Oil Polluted Soil

Pardis Karimi Alavijeh, Normala Halimoon, Mohamad Pauzi Zakaria, Wan Lutfi Wan Johari and Benyamin Karimi

Abstract Contamination due to the spillage of petroleum or petroleum-derived hydrocarbons on different ecosystems has become critical issues to environment and living things. The use of native bacteria as an environmental friendly treatment of hydrocarbons pollution is very promising. The objective of the study is to identify the native hydrocarbon-degraders isolated from oil refinery. Bacteria from crude oil were isolated and cultured in enrichment media. The isolated strains were then cultured in different oil concentration. The isolated bacterial strains were Gram-stained and further identified via 16S rRNA sequencing. The resultant sequences were then aligned with the available online database for identification of the bacteria. The isolated bacteria belonged to families of *Pseudomonadaceae* and *Moraxellaceae* (*Acinetobacter genus*). The bacteria show high degradation of hydrocarbon and can be used to remediate polluted soils in tropical environment.

Keywords Oil pollution · Bacterial Bioremediation · Hydrocarbon polluted soils

Highlights

- Native, tropical petroleum-degraders were isolated.
- Isolated bacteria can degrade up to 50 % (v/v) crude oil in media.
- Isolated bacteria belonged to families of *Pseudomonadaceae* and *Moraxellaceae*.

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Introduction

Hydrocarbon pollution nowadays has become a serious environmental threat in our modern world (Rahman et al. 2003). It poses serious damages to the biotic and abiotic factors of the earth, which subsequently effects human health through water, soil or air pollution and even causes economical problem (Wang et al. 2008). There are varieties of techniques which can be used to clean up hydrocarbons that have been extensively discussed in other literatures. Bacterial degradation of hydrocarbons is proven to be more effective than other techniques and is an environmental-friendly way of removing hydrocarbons from the environment. Most of organisms are able to remove organic and in some cases inorganic pollutants through their enzymatic actions and use those pollutants as their sources of energy (Thapa et al. 2012). In this study, bacteria capable of degrading crude oil were isolated, identified and characterized. In near future, these bacteria can be utilized for bioremediation of oil-polluted soil in the tropical regions, such as Malaysia, which is advancing towards an industrial era and will be dealing with such problems.

Materials and Methods

Soil samples were collected from oil-polluted soil in vicinity of an oil refinery in Port Dickson. For bacteria isolation, 1 g of soil sample was added into Tryptic Soy Broth (TSB) medium and incubated at 30 °C. After 24 h, 1 ml of each TSB medium was added to oil-containing basal mediums. The bacteria that have formed colonies and were able to grow in the presence of oil were then isolated. A single colony-forming unit of bacteria was cultured on 10, 20 and 50 % (v/v) of oil concentrations. The bacteria cultures which have been able to grow in 50 % oil concentration were selected for further identification. They were Gram-stained and growth curve was drawn at varying oil concentrations, pH and temperature to search for their optimum growth conditions. 500 bps of ribosomal RNA of selected bacterial strains were amplified, sequenced and aligned for identification of the bacteria.

Results and Discussion

Although the optimum temperature and pH for bacterial growth varied for different species of isolated bacteria, the results show that all selected bacteria are capable of efficiently degrading oil at 30 °C and pH 7.5, which are the normal conditions in the natural environment. Based on the high growth rate of bacteria in 50 % of oil concentration, three strains of bacteria were chosen and the sequencing results

showed that the strains are *Pseudomonas putida*, *Acinetobacter calcoaceticus* and *Acinetobacter johnsonii*. *P. putida* is capable of degrading naphthalene and compounds with naphthalene ring (Gomes et al. 2005) and *Acinetobacter* is more capable of removing alkanes such as *octadecane* (C18), *nonadecane* (C19), *eicosane* (C20), *docosane* (C22), *tricosane* (C23) and *tetracosane* (C24) (Lal and Khanna 1996). In the future, the study can be focused on identifying more species and strains of potential petroleum-degraders as well as determining the biochemical degradation pathways.

Conclusion

In conclusion, as many different studies have suggested, it is recommended to use native soil bacteria to remove the hydrocarbon pollutions such as oil spills. Here, three different strains of bacteria can be suggested to be used in tropical environments for bioremediation of crude oil spills. Other than that, they can be utilized to break down both aromatic hydrocarbons and medium-chain alkanes.

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Chapter 25
Cesium Removal from Waste Seawater by Nanocrystalline Mordenite

Keun-Young Lee, Minsung Park, Eil-Hee Lee, Kwang-Wook Kim, Dong-Yong Chung, Kyoung-Woong Kim and Jei-Kwon Moon

Abstract Up to the present, the process for the liquid waste with high salt content such as the waste seawater generated from the unexpected accident of nuclear power plant has not been studied extensively. In this study, the adsorption efficiencies of Cs in the seawater environment were investigated using mordenite, a type of zeolite, with different particle sizes. Commercial and synthesized mordenites were used for the treatment of the simulated liquid waste based on the seawater containing Cs, and the reaction kinetics and adsorption capacities of nano-sized mordenite were compared with those of bulk scale mordenites. The experimental results clearly showed that the nano scale adsorbent showed fast adsorption kinetics and high binding capacity for Cs. Also, the nano-sized mordenite are well-dispersed in the solution as a colloid, thus, it could be successfully applied to the static adsorption condition. Interestingly, the colloidal mordenite gradually flocculated in the seawater condition. Since self-flocculation occurred after the maximum adsorption of Cs, even in the static condition, it might be beneficial to separate the solid particles from the solution.

Keywords Radioactive waste · Cesium · Ion exchange · Zeolite · Seawater

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Highlights

- The nano-mordenite showed fast adsorption rate and high binding capacity for Cs.
- Self-flocculation of colloidal mordenite occurred with Cs removal in the seawater.
- The nano-mordenite can be successfully applied to the static adsorption condition.

Introduction

There are several conventional techniques for the treatment of radioactive liquid waste, such as precipitation, adsorption, ion exchange, evaporation, micro/ultra-filtration, solvent extraction, and electrochemical processes (Abdel Rahman et al. 2011; Fu and Wang 2011). The process for the liquid waste with high salt content such as waste seawater generated from unexpected nuclear power plant accident, has not been studied extensively (American Nuclear Society 2012). In this study, in order to develop the precipitation based treatment process preparing for the accident, the adsorption efficiency of Cs in the waste seawater with high salt content were investigated by using several types of mordenites with different particle sizes.

Materials and Methods

Commercial and synthesized mordenites were used for the treatment of the simulated liquid waste based on the seawater containing Cs, and the reaction kinetics and adsorption capacities were investigated. Table 25.1 shows the concentrations of major cations and anions in the simulated wastewater prepared by dissolving Cs, as the concentration of 100 mg/l, into the seawater collected from the Korean East Sea.

Four types of mordenites: nano- and micro-sized mordenites and pellet type mordenite and ground powder, were selected for the adsorption experiments. The mean particle size of the nano-sized mordenite (Alfa Aeser) was 203.5 nm. The micro-sized mordenite was prepared by the hydrothermal synthesis in alkaline condition (18.7 μm of mean particle size) (Kim and Ahn 1991; Aly et al. 2012).

Table 25.1 Concentrations (mg/l) of major ions in the simulated waste seawater

	Na^+	Mg^{2+}	K^+	Ca^{2+}	Cl^-	SO_4^{2-}	Br^-	Cs^+
mg/l	10,675	1,200	424	420	19,700	2,610	73	100

Also, AW300 (Aldrich) as the pellet type mordenite (more than 2 mm of particle size) and its ground powder (less than 200 μm of particle size) were compared.

The concentrations of Cs before and after the adsorption experiments were analyzed by Atomic Absorption Spectrometry (AAS-AAnalyst 900, PerkinElmer, USA). Also, the physicochemical and mineralogical properties of zeolites before and after the adsorption reactions were observed by Particle Size Analyzer (PSA-3500S, Microtrac, USA), Scanning Electron Microscopy (SEM-SNE 4500 M, SEC, Korea), Energy Dispersive Spectrometry (EDS-QUANTAX, Bruker, Germany) and X-ray Diffractometry (XRD-D/MAX 2500G, Rigaku, Japan), which made it possible to explain the Cs removal properties of mordenite. The dispersion properties of the nano-sized colloidal mordenite were evaluated by measuring turbidities with time (Turbiscan Lab, Formulaction, France).

Results and Discussion

The crystallinities of commercial nano-sized mordenite and synthesized micro-sized mordenite were confirmed by XRD analysis, and the main peaks representing crystalline mordenite were the same (Fig. 25.1). Although another type of mordenite, commercial AW300, contains a minor amount of impurity such as clay as a pelletizing material, the XRD peaks were the same as the peaks of pure mordenite (data not shown). Figure 25.2 showed the SEM images of nano- and micro-sized mordenites. Overall, the shapes of particles were not uniform, whereas the specific particle was an aggregated complex with nano-scale spherical mordenite (Fig. 25.2a). A particle of micro-sized mordenite was more than several μm, and it consisted of an aggregation of many plate-shape mordenite crystals (Fig. 25.2b). Although the crystal size and shape were different due to the difference of synthesis method, we could be sure that both materials were crystalline pure mordenite.

Figure 25.3a represents the adsorption yield of Cs after shaking for 2 h by each mordenite with different injection amounts. The Cs adsorption efficiencies of pure

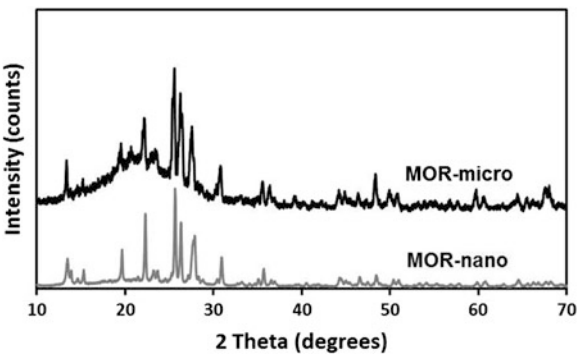

Fig. 25.1 XRD peaks of nano- and micro-sized mordenites

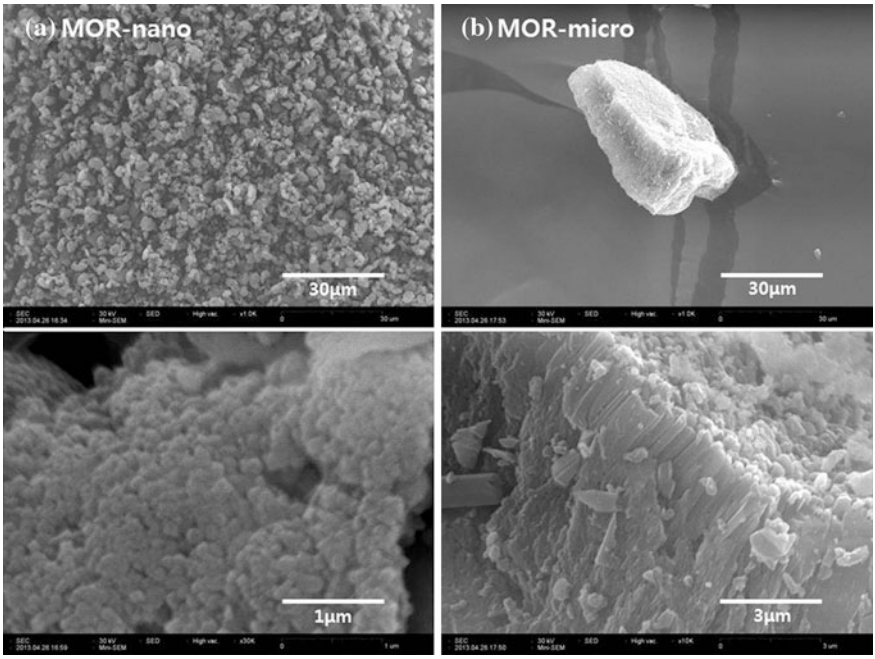

Fig. 25.2 SEM images of **a** nano- and **b** micro-sized mordenites

mordenite powders were higher than those of pellet-type mordenite and its ground powder in this experimental condition. Because the commercialized pellets consist of mordenite crystals and specific pelletizing reagents, the binding sites of Cs might be smaller than those in pure mordenites. Also, the diffusion and adsorption of Cs in the particle might be disturbed by the impurities, which could make the maximum Cs adsorption delayed. In order to confirm the difference of Cs adsorption rate between nano- and micro-sized mordenites, the normalized adsorption coefficients of Cs with time in a constant condition (shaking with 1 g/l of mordenite dose) were compared (Fig. 25.3b). The results clearly showed that the adsorption rate of nano-sized mordenite was significantly faster than that of micro-sized mordenite. In the emergency case, such as the accident of nuclear power plant, the rapid processing for the radioactive wastes must be one of the most important points for the prompt action to minimize the damages. The application of nano-scale adsorbents can satisfy the requirement in such a viewpoint.

Also, the adsorption yield of Cs in the static condition (without shaking) was evaluated with time. The nano-sized mordenite showed significantly higher efficiencies comparing to other bulk mordenites (data not shown). Therefore, the nano-sized colloidal zeolite should give a great advantage to treat the wastewater when the stirring process is not achievable. In this experiment, especially, it was observed that the colloidal mordenites have gradually coagulated and flocculated

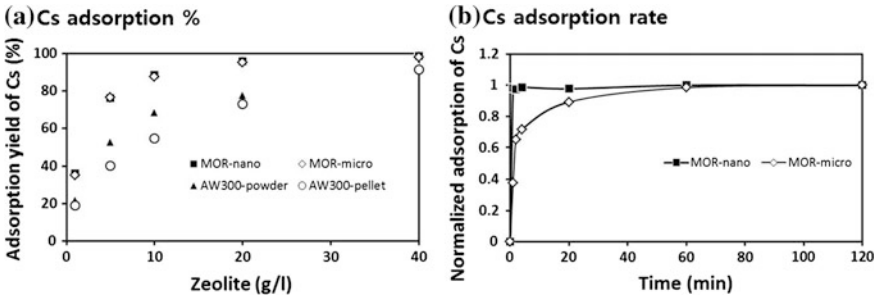

Fig. 25.3 **a** Adsorption yield (%) of Cs (shaking for 2 h with different mordenite dose) and **b** Normalized adsorption of Cs with time (shaking, 1 g/l zeolite dose)

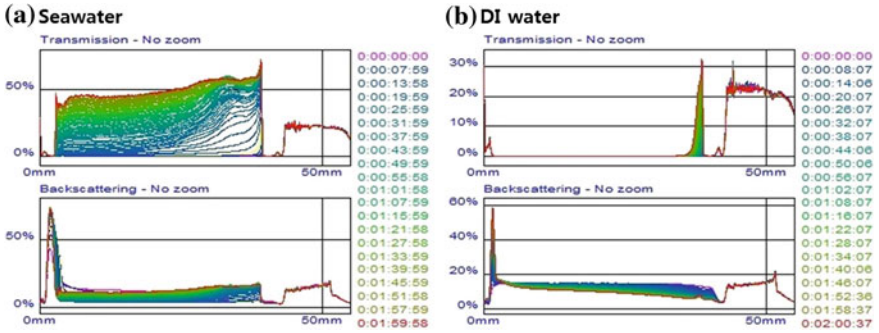

Fig. 25.4 Dispersion properties of nano-sized mordenite in **a** seawater and **b** DI water (static condition for 2 h)

in the waste seawater. Figure 25.4 showed that the dispersion properties of nano-sized mordenite in seawater and DI water with static condition for 2 h. Only in the seawater condition, the transmission rate significantly increased with the increase of backscattering rate at the bottom of vial. This result supports that the self-flocculation of nano-sized colloidal mordenite was caused by the change of surface properties in the solution of high salt content.

Conclusion

The experimental results strongly supported that the nanocrystalline mordenite showed fast adsorption kinetics and high binding capacity for the target contaminant. Because the nano-sized colloidal mordenite can be successfully applied to the static adsorption condition, an economical benefit might be expected when the stirring process is not achievable. In order to increase the feasibility of nano-scale

based adsorption process, the evaluations of the floc stability and solid/liquid separation efficiency after the self-flocculation in the seawater environment should be required.

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Chapter 26
Compound-Specific Isotope Analysis of Diesel Fuels in a Forensic Investigation

Syahidah Akmal Muhammad, Russell David Frew and Alan Ross Hayman

Abstract Compound-specific isotope analysis (CSIA) is fast becoming an indispensable tool to provide chemical evidence in a forensic investigation. Many attempts to trace environmental oil spill were successful where isotopic values were particularly distinct. However, difficulties arise when a large dataset is analysed and the isotopic differences between samples are subtle. In the present study, forensic discrimination of diesel oils involved in a diesel theft case was carried out to infer the relatedness of the samples to potential source samples. This discriminatory analysis used a suite of hydrocarbon diagnostic indices, alkanes, to generate isotopic data of the compositions of the compounds which were then processed using multivariate statistical analyses to infer the relatedness of the data set. The results from this analysis was put into context by comparing the data with the $\delta^{13}C$ and $\delta^{2}H$ of alkanes in commercial diesel samples obtained from various locations in the South Island of New Zealand. Based on the isotopic character of the alkanes, it is suggested that diesel fuels involved in the diesel theft case were distinguishable. This manuscript shows that CSIA when used in tandem with multivariate statistical methods can be a collection of tools for the source apportionment of hydrocarbons by demonstrating a straightforward approach thus eliminating lengthy analytical processes.

Keywords Diesel fuel · Alkane · Compound-specific isotope analysis (CSIA) · Principal component analysis (PCA) · Hierarchical clustering

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Highlights

- The isotopic signatures of hydrocarbon indices discriminate diesel fuels.
- CSIA is an indispensable tool to provide chemical evidence.
- CSIA with multivariate statistical analyses identify sources of diesel fuels.

Introduction

Traceability of diesel fuel is becoming increasingly important especially in a forensic context. From an environmental perspective, it is important to ascertain culpability for a diesel oil spill and likewise in a criminal investigation, such as, the theft of diesel fuel. In either situation, it is important to demonstrate any linkages, or relationships, between diesel samples. Compound-specific isotope analysis (CSIA) has been shown to distinguish petroleum-derived hydrocarbon samples of different origin and/or history based on the stable isotope signatures albeit the differences obtained are subtle (Smallwood et al. 2002; Philp et al. 2002). The objective of this study is to utilize CSIA in a forensic fingerprinting of diesel fuels using hydrocarbon such as alkanes, as diagnostic indices. The relationship between samples in the data set was then explored using multivariate statistical analyses to provide a defensible means of classification.

Materials and Methods

Sample Details and Preparation

The samples involved in the diesel theft case were labelled in two different categories: (1) RB Control (2 samples); (2) GKT ### (9 samples). The RB Control samples (source samples) were taken from the storage tanks located at a ski field resort where the diesel theft occurred and the GKT samples with different denominations were sub-sampled from containers found with the suspect. A few of the GKT samples have unique names (GKT 106 and GKT 108) but the rest of the GKT samples were labelled with the same denominations such as GKT 105 (1; 2 and 3), GKT 107 (1 and 2), and GKT 202 (1 and 2). To provide context for the analysis of the diesel fuel involved in the theft case, as many as 45 commercial diesel samples were obtained from different service stations located around the South Island of New Zealand coming from areas such as Dunedin City, North and South Otago, Twizel, Christchurch City and South Canterbury (Muhammad et al. 2013).

GC Analysis

Isotopic compositions of each *n*-alkane are expressed as δ values per mil (‰) deviation relative to isotopic standard reference materials:

$$\delta = [(\text{Rsample}/\text{Rstandard}) - 1]$$

where $R = {}^{13}C/{}^{12}C$ or ${}^{2}H/{}^{1}H$. The $\delta^{13}C$ were reported relative to the Vienna Pee Dee Belemnite (VPDB) scale, while $\delta^{2}H$ values were reported relative to the Vienna Standard Mean Ocean Water (VSMOW) standard.

Isotopic Composition of Alkanes in Diesel Fuel

Diesel fuel is a very complex mixture of thousands of individual compounds, most with carbon numbers between 9 and 23. This complexity can cause analytical problems as true compound-specific isotopic analysis requires baseline resolution and no co-eluting peaks. The measured stable isotope ratios across selected peaks may therefore include some underlying co-eluting material and are not entirely specific for individual compounds. However, the data remain forensically relevant as part of an "isotopic fingerprint pattern". The alkane compounds which were able to be reliably quantified and yielded reproducible isotopic values using a GC-IRMS system in this study started with $n\text{C}_{12}$ and ended with $n\text{C}_{23}$.

Results and Discussion

Stable isotope ratios of individual alkanes from the diesel theft case samples were subjected to principal component analysis (PCA) and hierarchical clustering analysis. The information obtained from the statistical analyses was used to associate and differentiate diesel samples based on its $\delta^{13}C$ and $\delta^{2}H$ values. The results from PCA were visualised on a 3 dimensional scores plot in Fig. 26.1. The scores plot shows two distinct clusters with RB Control, GKT 106, GKT 107, GKT 108 and GKT 202 in one group; GKT 105, Caltex and Mobil in another with BP sample as an outlier.

The stable isotope data of the samples from the diesel theft case were then combined with the data from the commercial diesel fuels and analysed using cluster analysis and presented in a dendrogram in Fig. 26.2. It shows that the diesel samples from the diesel theft case were clustered closely together. However, GKT 105 diesels were more closely correlated with the samples from Dunedin City

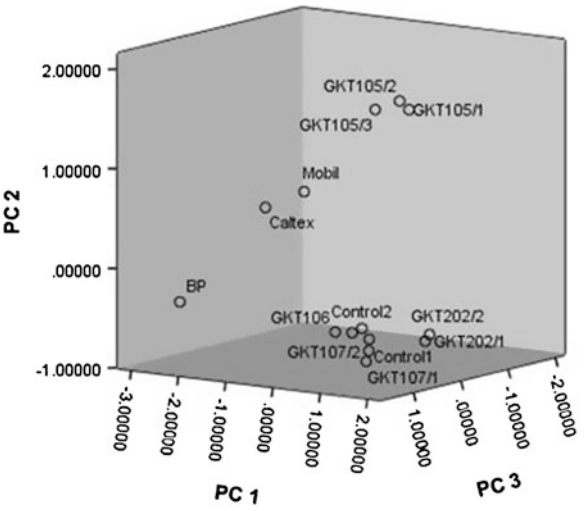

Fig. 26.1 Scores plot for principal components analysis. It holds the scores for each sample on PC1, PC2 and PC3, respectively

service stations than the samples from the diesel theft case, and this can be seen by the large jump of the linkage which indicates the clusters are far apart (read to the right of the dendrogram to see the clusters).

Conclusion

The forensic discrimination of diesel fuels involved in a theft case utilizing stable isotope fingerprint of hydrocarbon indices was achieved. There were variations in the stable isotopic compositions of alkanes within the diesel samples that can be used to differentiate them. Multivariate statistical analyses confirmed the findings that the RB Control diesel samples were strongly correlated with GKT 106 and moderately correlated with GKT 107, GKT 108 and GKT 202 samples although interestingly, GKT 105 samples were grouped separately from them. In our opinion, the relatedness of these diesel samples was due to the fact that the samples share a common history. To further strengthen this finding, these results were combined with the data set of commercial diesel fuels from 45 local service stations in the South Island of New Zealand. This was done to put the data into context as well as to rule out statistical coincidence. From a forensic perspective, when two samples are indistinguishable it does not prove they are related because there is no such thing as a match in this type of analysis and that term should never be used. Hence, when we measured a large number of individual samples and were able to differentiate all of them but were unable to differentiate the suspect's and the source samples, then that provide support for the notion that they are related.

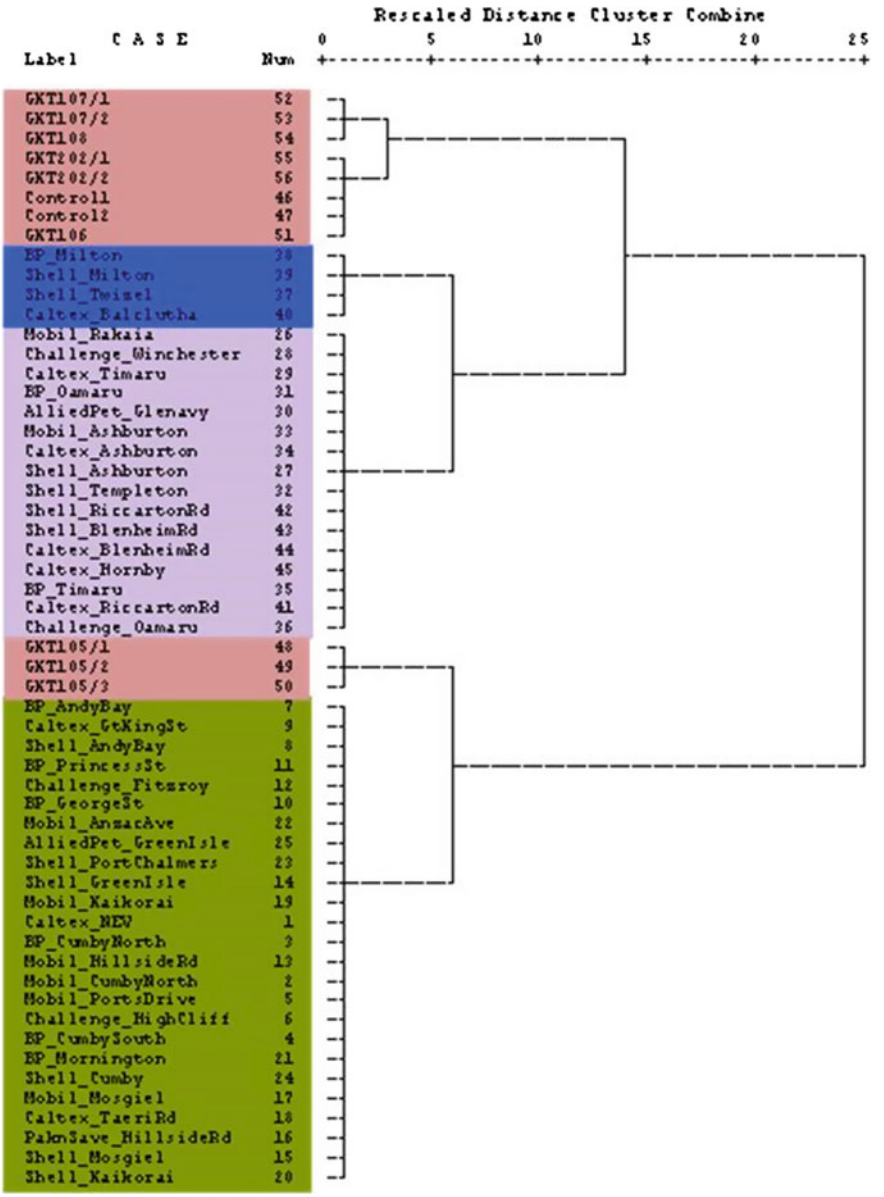

Fig. 26.2 Dendrogram using Ward's method showing cluster relationship between samples. Lengths of *vertical lines* represent statistical difference between multivariate components in each sample. Distinct clustering can be seen for samples from Dunedin City (*green square*), Canterbury and North Otago (*voilet square*), Twizel and South Otago (*blue square*), and stolen diesels (*pink square*)

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Chapter 27
Opportunities for Household Solid Waste Recycling and Policy Status in Malaysia

Yiing Chiee Moh, Latifah Abd Manaf and Hafizan Juahir

Abstract Malaysia provides ample opportunities for solid waste recycling due to their dependence on recyclable materials, which could be observed from the dominance of recyclables in the wastes disposed at the landfills. This paper attempts to develop an overview on the opportunities for solid waste recycling in Malaysia at the most basic level of a community or nation which is the household unit, besides reviewing on the Malaysian solid waste management and recycling policy status. Information on solid waste recycling is significantly underdeveloped, as most studies tend to focus more on general aspects of solid waste management in Malaysia. Substantial progress has been made by the government and related authorities in developing a more comprehensive solid waste management, recycling policies, awareness campaigns and relevant projects. Waste separation and recycling are part of the major changes in the current policy implementation. However the local participation has not been encouraging and the recycling rate falls back at merely 5 % that proves how uncommon recycling practice is. Households are not aware of proper waste recycling etiquette. Environmental considerations exist among households but space limitations and misconceptions hinder recycling practice. The role of monetary rewards seems to be overplayed and the influence of other reasons for recycling has been slightly underestimated when it comes to implementing recycling policy and programme strategies.

Keywords Recycling · Solid waste management · Policy implementation · Household · Malaysia

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Highlights

- Household solid waste is the highest among the solid waste sources.
- No distinct and formal policy to manage solid waste management in Malaysia.
- Wastes separation and recycling are in the current policy implementation.

Introduction

At present, solid waste management is one of the major environmental problems faced by municipalities globally (Omran et al. 2009) and the biggest environmental problem in Malaysia (Osman et al. 2009). Excessive landfill dumps are testament to the fact that solid waste problem is out of control and not going anywhere. Landfill dump is still a common method in managing solid waste in Malaysia (The Ingenieur 2009) since it is cost-effective and simple, unlike the other common disposal method using the incinerator which is costly and requires technological experts to operate it. Solid waste disposal via landfilling is becoming more difficult because most landfills are approaching its threshold or already exceeded its maximum capacity. At the same time, constructing new landfill is becoming even more difficult because of land scarcity and the increase of land prices and high demands due to the increase in population (Latifah et al. 2009). The concept of turning materials that would otherwise become waste into valuable resources of financial, environmental and social returns (US EPA 2012) has gained increasing attention as a means of protecting the environment. Recycling has been widely accepted as a sustainable solid waste management method because it offers one of the most sensible solutions both economically and ecologically for managing solid wastes (Omran et al. 2009)

Opportunities for Household Solid Waste Recycling

Compared to other developing countries, where recycling rate is about 30 to 47 %, Malaysia is falling back (Mahmud and Osman 2010). Malaysia targeted 22 % of total solid waste could be recycled by 2020 but the current rate is about 5 % (Agamuthu et al. 2011). Dominance of recyclables in the solid waste composition generally comprises of food waste, paper, plastic, glass, ferrous metal and aluminium (MHLG 2006). Overall waste composition in Malaysia is dominated by municipal solid waste (64 %), followed by industrial waste (25 %), commercial waste (8 %) and 3 % consists of construction waste. About 80 % of municipal solid wastes are recyclables, which are disposed at the landfills (MHLG 2006) and under the category of municipal solid wastes, the contribution of household waste

is the highest among sources consisting of recyclables at most 70 to 80 % of total solid waste composition as found placed in the landfills (Sumiani et al. 2009). However, these recyclables are not fully recovered and recycled due to the limited source separation and certain materials are not employed at large scale. Plastic, paper and glass are more identified as having the greatest potential for recycling compared to other recyclables (Zamali et al. 2009).

Recycling Status and Policy in Malaysia

As part of the Rio Declaration signed in 1992, Malaysia has made commitments which include a commitment to significantly improve the national's solid waste management services. The number of available information on solid waste management and recycling in Malaysia is limited with no systematic analysis and periodic documentation nationwide from local authorities, resulting in accurate and outdated databases (Nasir et al. 2000). There was no distinct and formal policy to manage solid waste management in Malaysia, what more when it comes to recycling policy strategies. The Action Plan for a Beautiful and Clean Malaysia (ABC Plan) was formulated in 1988 with the aim to produce a national uniform municipal solid waste system that is productive, environmentally sound and socially acceptable in Malaysia by 2020. However, this plan was neither officially endorsed nor implemented, even with the recycling programme were introduced such as the first recycling campaign in 1993 and the following in 2000. The first National Recycling Programme (NRP) showed lack of success as local authorities were not able to sustain the programme and it did not improve the existing waste management practice. This resulted in re-launched programme in 2000 with a more reformed objective which is to inculcate recycling in reducing usage of land for waste disposal, reduce expenditure on solid waste management and to reduce the importation of waste. November 11th was designated as National Recycling Day in 2001 to raise public awareness and since then it has become an annual event, besides a series of other public awareness campaigns. However, recycling practice is still not common among Malaysians.

The National Policy on Municipal Solid Waste Management or commonly known as the National Strategic Plan (NSP 2005) succeeded the ABC Plan when it was formulated in 2002 and later adopted in 2005. This strategic plan would be considered up to year 2020 with periodic review during the planning period to ensure its relevance with respect to the prevailing conditions within the time of review. Subsequently, the Waste Minimization Master Plan (WM-MP) was launched in 2006 to realize the minimization of the natural resources consumption and the maximum reduction of environmental load in the society, where waste minimization activities are systemized and sufficiently embedded in the behavior of government, private sector and public. With the adoption of WM-MP in preparing the Master Plan for 3Rs, the Ministry of Housing and Local Government (MHLG) formulated Solid Waste Management Act (SWM Act) 2007 which

includes the promotion of waste minimization through 3Rs activities, defining recycling as in collecting and separating solid waste for the purpose of producing products.

The Solid Waste and Public Cleansing Management (SWPCM) Act 2007 (Act 672) was approved by the Parliament of Malaysia on the July 17th, 2007 and is officially enforced starting from September 1st, 2011. With that, waste separation at source for every household is made mandatory starting from September 1st, 2012 as one of its effective strategies as stated in Clause 74 of SWPCM Act 2007. This Act standardizes solid waste management service with its enforcement conducted in stages and was expected to ensure proper household waste management with a promotion of waste separation and recycling. Still it presents a challenge to develop a solid waste management system with all elements particularly recycling.

Perspectives of Household Solid Waste Recycling

Effective measures and appropriate approaches to address current issues and challenges are very rigid with the lack of required knowledge and technical expertise. For decades until the end of 1987, there was no systematic analysis and periodic documentation nationwide from any local authorities to record waste generation rate, which has resulted in inaccurate and outdated databases (Nasir et al. 2000).

With no Federal or State legislations that comprehensively deals with all aspects of solid waste management, existing provisions of the Environmental Quality Act 1974, the Local Government Act 1976 and the Street, Drainage and Building Act 1974 are not specifically established to manage solid waste management issues including waste recovery and recycling. Waste generators, collection service providers, waste pickers, traders, recycling centre operators, NGOs and end-users have limited information and linkage with each other, resulting in loopholes which could be beyond magnitude to control at times.

From the perspectives of households, they are more aware of global warming and climate change compared to proper waste recycling etiquette. But they are not aware of the basics of recycling such as what materials can be recycled and what not. Environmental considerations do exist among households but space limitations and misconceptions hinder majority of households from recycling. Providing incentives or monetary rewards is necessary to encourage recycling practice among households but the role of monetary rewards seem to be overplayed and the influence of other reasons for recycling has been slightly underestimated when it comes to implementing recycling policy and programme strategies.

Conclusion

This paper attempts to develop an overview on the opportunities for household solid waste recycling in Malaysia, besides reviewing on the Malaysian solid waste management and recycling policy status. The contribution of household solid waste is considerably the highest among the solid waste sources in Malaysia. There are ample opportunities for solid waste recycling due to the dependence on recyclable materials, which could be observed from the dominance of recyclables in the waste disposed at the landfills. Plastic, paper and glass are among the recyclable materials which have the greatest potential for recycling as they are widely used but disposed indiscriminately to the landfills. The government is committed to significantly improve the national's solid waste management services. However there was no distinct and formal policy to manage solid waste management in Malaysia, what more when it comes to recycling policy strategies. Fortunately the emphasis on recycling as a sustainable waste management strategy has taken a shift in paradigm as wastes separation and recycling are part of the major changes in the current policy implementation.

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Chapter 28
Equivalent Noise Level Response to Number of Vehicles: A Comparison Between a High Traffic Flow and Low Traffic Flow Highway in Malaysia

Herni Halim and Ramdzani Abdullah

Abstract In this study, 5 days measurement of noise level during peak hour and off peak hour has been carried out at two types of highways; high traffic flow highway (Sungai Besi Expressway) and low traffic flow highway (Duke Highway). Findings indicated that heavy traffic flow highway recorded higher noise level compared to low traffic flow highway. It was due to the higher number of vehicles on the heavy traffic flow highway than low traffic flow highway. At certain i.e. above 500, noise level is stabilized.

Keywords Road traffic noise · Noise assessment · Noise stabilization

Highlights

- Number of vehicles on the highway influence the noise level.
- Heavy traffic flow highway recorded higher noise level compared to low traffic flow.
- Noise level stabilized at above 500 vehicles on the road.

Introduction

Noise pollution is by now recognized worldwide as a major problem for the quality of life in urban areas (Piccolo et al. 2005). The rapid industrialization, commercialisation and urbanization witnessed by many developing countries in recent

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years has given rise to the steady increase in the environmental noise climate. The environmental noise climate is influenced drastically by road traffic noise because that type of noise produces a continuous sound which fluctuates from hour to hour in irregular trend with the passage of individual vehicles. Thus, road traffic noise has become a fundamental issue of immediate concern to many authorities.

Materials and Methods

The present investigation on evaluation and analysis of the relationship between number of vehicles and noise level conducted in urban residential areas in the city of Klang Valley, Malaysia. Two sampling locations of highways in the Klang Valley city selected for noise pollution study were Sungai Besi Expressway and Duke Highway. The noise monitoring activities were carried out from 14 June 2011 until 17 June 2011.

Results and Discussion

A strong relationship between traffic volume and noise level has been reported in the study carried out by Ma et al. (2006) and Swain et al. (2012). As traffic volume increase noise level also increases. In our study, the correlation between the total number of vehicles for every 15 min and L_{eq} were tested. The analysis of noise level at two highways were carried out during peak and off peak hours. Figure 28.1 presents the noise level at Sungai Besi Expressway and Duke Highway from 0700 to 0900 representing peak hours and 2300 to 0100 representing off peak hours.

In Fig. 28.1, the noise level of heavy traffic flow highway which is Sungai Besi Expressway was higher compared to low traffic flow highway, Duke Highway. Other than that, the highest noise level was 74.9 dBA during peak hours and 73.4 dBA during off peak hours while the lowest L_{eq} was 73.8 dBA and 72.6 dBA respectively. All the values exceed outdoor noise limit by the World Health Organization (WHO 2000) as well as Malaysia guidelines (DOE 2000). As can be seen from the figure, noise level during peak hours was significantly higher compared to off peak noise level, which is consistent with results obtained in previous studies by Nadaraja et al. (2010). However, both graphs show the same fashion of noise level, which the noise level was high at the beginning and gradually decreased towards the end of the measurement. Similarly, the number of vehicles also declined steadily throughout the measurement period. This result may be explained by the fact that the number of vehicles on the road caused the noise level on the highway. This statement is in line with study carried out by Ozer et al. (2009) in Turkey. However, peak hour does not have that pattern as the noise

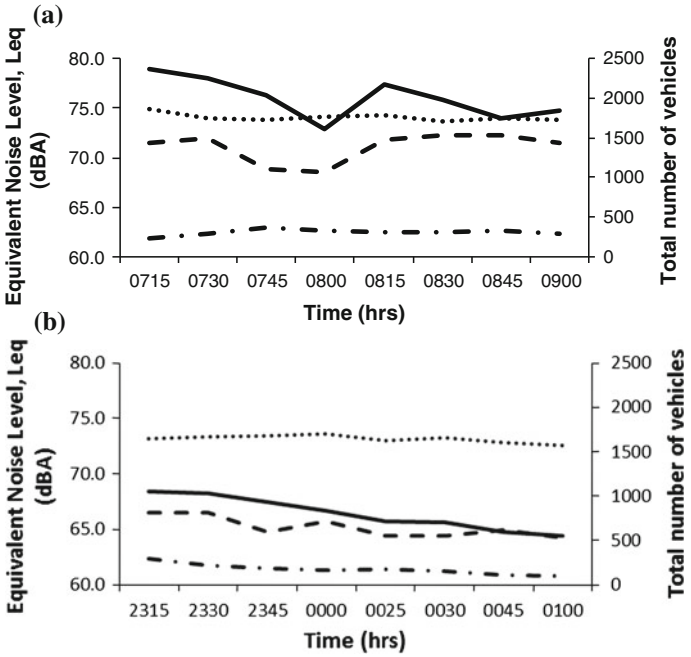

Fig. 28.1 Equivalent noise level (L_{eq}) between (**a**) peak hours and (**b**) off peak hour period at Sungai Besi expressway, Selangor and Duke highway, Kuala Lumpur

level drop drastically at 0745 to 0800 but starts increasing afterwards. This situation happens due to the decreasing number of heavy vehicles in that period of time which consequently reduce the noise level (Swain et al. 2012).

Conclusion

The results showed that heavy traffic flow highway recorded higher noise level compared to low traffic flow highway.

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Chapter 29
Retrofitting as an Environmental Hybrid Approach (EHA) in Conservation Works on Historical Buildings in Malaysia

Muhammad Khairi Kamarudin, Rosta Harun, Aini Jaapar and Zaharah Yahaya

Abstract Historical buildings bring out the symbols of history, memories, social and culture of a place as well as representing the economic standard of the local people. It can be seen from the architecture style of the building, size and material used. That is why it is very important for us to preserve and conserve it not only for county's heritage and legacy but also making them as tourist attractions. Therefore, this paper is aim to identify the potential of retrofitting mechanism as Environmental Hybrid Approach (EHA) in conservation works on the historical buildings as well as to investigate students perception on retrofitting mechanism. Triangulation methods were used for this research. Retrofitting means fitting in new mechanism that was not installed during first construction. It can be adapted as cross-integrated mechanism and can be use in architecture sector. By retrofitting, the vacant historical building can be reused back for new purpose such as an office or theater that can be use to generate income while maintaining the historical values of the original historical building. Practically, this method also brings positive impact to the environment. Retrofitting is consider as an Environmental Hybrid Approach (EHA) in conservation works of historical buildings due to the facts that it use less new materials for new construction by reuse and re-enhancement back original material from historical building, reduce the production of construction waste thus minimizing negative impact to the environment.

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Retrofitting mechanism also undergo shorten construction period, hence it use less energy, less construction workers on-site and able to reduce the total cost construction compare to conventional construction.

Keywords Retrofitting · Historical building · Preserve · Maintaining · Reused

Highlights

- Historical buildings are very important to the country economics.
- HEA combines all possible techniques to promote sustainable construction works.
- Retrofitting reduces construction waste, saves money and construction period.

Introduction

The identity of a people and nation is largely defined by their heritage. Heritage is something, which can be passed down from one generation to another. Malaysia heritage and history largely represented by its architecture, social, fabrics, language, foods and architecture fabric is apparently the most abide. An inventory study conducted in 1992 and 1993 by the Heritage Trust of Malaysia revealed that there are almost 39,000 historic buildings built between 1800 and 1948 throughout the country such as in Geoge Town, Ipoh, Malacca, Kuching and Kuala Lumpur which are worthy for preservation and conservation (Syed Zainol Abidin 1995). There are classified as 'pre-war buildings' since they had be build ranging from 1800 to 1948. Most historical building was demolished due to perception of high maintenance cost (Fels 2002). That is why some owner sold their building to property developer, while some allow the government and local authority to bring down their building especially shop houses because they could not afford or bear the cost of maintenance (Oldfield 2012).

Historical buildings are very important to the country economic in terms of revenue from tourism activities (Dressler and Roth 2011; Sarvarzadeh and Abidin 2012). Therefore, preservation of historical building not only plays an important role in preserving the history and culture but also for economic purpose (De Cesari 2010). According to Ahmad (2009), heritage conservation is important for historical evidence, architectural values, education, local pride and tourism. Tourism sector is the second most important sector for Malaysia's economy, with 22.5 million foreign tourists visiting Malaysia in 2008, bringing in RM 49.1 billion (USD 16.2 billion) in revenue and in 2011, 24 millions tourist was recorded

entering Malaysia bringing in RM 58.6 billion (USD 18.3 billion) an increment of 12 % compared to 2008 (Bharian 2012). According to Malaysia Economic Transformation Plan (ETP), RM 106.3 billion (USD 33.1 billion) is expected contributed by tourism sector from 36 millions tourist to national gross revenue (KDK) in 2020.

Retrofitting: A Hybrid Approach (HA) in Conservation Works

Retrofitting means 'fitting in' new spaces in the historical building incorporated with new constructions method and material not fitted during original construction (Oxford Dictionaries 2012). As result there will be enhancement to the original building majorly from its façade (exterior and interior) together with new mechanical and electrical system but still remaining some part of the original historical buildings (Boeri et al. 2011; Langston 2012). Therefore, retrofitting is consider as Hybrid Approach (HA) in conservation works due to its unique mechanisms which combines few methods in one conservation works and the positive impacts that it brings to the socio-economics as well as to environment (Plevoets and Van Cleempoel 2011). Retrofitting of existing buildings is one of the most environmentally friendly and efficient solutions to optimize the energy performance of building. As a matter of fact, when compared to new buildings construction, this kind of intervention reduces the consumption of land energy and could be applied to a large building stock (Boeri et al. 2011). Retrofit construction implemented new technology and new type of material into its construction process in order to strengthen up the original structure of the historical building, adding up spaces or enhancing the façade. Retrofitting not only restoring back the historical building but it also preserve, conserve and maintain the historical value, culture and legacy. Therefore it is very important for us to know the benefit of retrofitting in order to not only saves the historical building but also to indicate other significant impact that it brings to the environment aside from economic and social aspects.

Materials and Methods

Triangulation method was used for this research, which includes site visits to retrofitted historical building theater and conventional theater, case study of retrofitted historical buildings, interviews with architect, theater manager and set of questionnaires was handed over to undergraduate student from faculty of build environment. The student was chosen to represent youngster that one day will become the players in build environment industries.

Kuala Lumpur Performing Art Centre (KLPAC) was chose as case study for this research. KLPAC was originally owned by a Chinese's entrepreneur and was used as factory back in 1892. In 1941, the British used this building as warehouse for military weapons. Then in 1957, this building remained its usage as repairing warehouse for locomotives under Keretapi Tanah Melayu Berhad (KTMB). In 2004 YTL Corporation bough the surround land including this building and that was the end of life for this building as warehouse. May 2005, this building was officially opened to public with its new name, The Kuala Lumpur Performing Art Centre (KLPAC). This building was restored and refurbished to its new function as performance center by using retrofitting method and was under construction for 7 months with total cost of MYR 30 million. 40 % of the previous building remain the same especially the façade of brick walls and the new 60 % were mainly from new structure, including the new roof structures, additions of floors (from 2nd to 4th floor) and for new spaces such as 9 new studios, set construction workshop, recording studio, food and beverage outlet, proscenium theater (*Pentas 1*) with 504 seats and experimental theater (*Pentas 2*) with 200 seats.

Steel structure was used for the new part of the building as well as other raw material such as unpolished cement rendered for flooring and clay bricks for walls. This material was chosen based on the original building, which used the similar materials and it has been integrated with modern material such as long span steel structure and double coating glass panel. Other than that, new mechanical and electrical system was installed in order to achieve optimum comfort for the end users. The additional spaces above the actual floor which is the 2nd and 3rd floor has been using for art classes such as dance, music and acting as well as the location of the main theater that took one-third of the total space. The transformation of this building has brought some significant impact especially on social and economic.

Results and Discussion

The questionnaires survey shows that, 76 % of the respondents agreed with statement that retrofitting can increase the aesthetic and function of the historical building especially when the building has been restored, refurbished and maintained as well as having new function rather than left vacant without any maintenance. With retrofitting, the building will have new image as result from integration between modern and its original façade. New mechanical and electrical mechanism will also make the building more up to date, safer and comfortable interior for further usage. Retrofitting mechanism not only enhance the external and internal quality of the historical buildings, but also saves construction period and money as well as minimizing negative impacts to the environment by reducing waste from construction sites, reusing back suitable material from the original

buildings, reutilizing certain materials to be use as landscape features such as broken bricks from the original building for walkways. When constructions waste being reduces, chemical contamination from the waste material such as paints or chemical coatings, automatically will be reducing so does the constructions waste management process. Retrofitting is an Environmental Hybrid Approach (HEA), it combines all sort of technique possible to promote sustainable construction works especially conservation works on historical buildings, it also enhancing the value of the historical buildings as well as promoting green technology by cross-boundary technology from one specified sector to another relevant sector. It will then ameliorate new theories, new technology or new mechanism in order to cater the demands and to maximizing supply in an appropriate manner, without jeopardizing the environment and the future generations.

Conclusion

It is basically normal as building aged, it will be exposed to deterioration and other building defects since it is truism nowadays that there is no building without maintenance-free. Therefore for heritage and historical building, there must be efficient maintenance mechanism and management in order to extend the life span of the building as well as minimizing cost of repair works and avoiding damage on the building heritage value since some of the historical building was left vacant or has been demolished. Therefore it is very crucial for Malaysian to take extra initiatives on preserving the heritage and historical building by implementing more modern method such as retrofitting.

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Chapter 30
Awareness of Behaviours that Cause and Alleviate Global Warming and Intention to Perform the Behaviours Among Malaysian Educated Laypeople

Zamzul Rizal Zulkifli, Rosta Harun and Kuang Hock Lim

Abstract Reducing global warming is not simply the domain of government but should start at the individual level, by knowing the right behaviours for mitigating global warming. This study examines Malaysian educated layperson's knowledge about global warming and their awareness of behaviours that both cause or alleviate global warming. In this study, a total of 300 participants were asked to list their behaviours which cause global warming and their behaviours they might think reduce global warming. They were then asked to rate their intention regarding these behaviours. Results showed that the respondents were well aware on the effects of air-conditioning and automobiles on global warming but underrated eating meat and using washing machines as causes of global warming, while also misjudging the impact of littering as a cause of global warming. Respondents did well in rating recycling and driving less as a relative impact in reducing global warming but underrated the impact of reducing meat consumption and reduce air travelling as a global warming mitigation. Even though knowledge about behaviours that reduce global warming was not strongly linked to intention to perform the behaviour, the belief in effectiveness that an action that reduces global warming, whether the behaviour is accurate or not, was strongly linked to intention to perform the behaviour.

Keywords Global warming · Effectiveness knowledge · Effectiveness belief

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Highlights

- Sample population was unsure on behaviors that reduce or do not reduce global warming.
- Females are more aware about behaviours that reduce global warming.
- Females are more willing to perform them than male.
- Effectiveness belief was moderately linked to intention to perform behav-iors.
- Effectiveness behaviour was very weakly linked to intention.

Introduction

This study is a partial replication done by Truelove and Parks (2012); Reynolds et al. (2010) and Read et al. (1994) on determining the level of knowledge on global warming of the public, focusing on the Malaysian educated laypeople. Educated laypeople are those who have gone through tertiary education, where they have picked up a specific knowledge. These people may be opinion leaders in their communities and are likely to take activist and leadership roles. Moreover, the technical beliefs held by educated laypeople will probably constitute "upper boundary" sophistication, and is likely that the error will be less common than the less educated sample (Read et al. 1994). In addition, this study also investigates the relationship of effectiveness knowledge and effectiveness behaviour of the lay-people with intention to perform behaviours that reduce GW. Here, this study can identify the misperceptions of the educated laypeople on GW and where to stress on in changing their perceptions and educated them on GW. This would make it easier for the decision-makers to carry out their awareness campaign to enlighten the public on which behaviours that cause and reduce GW, thus increasing their belief in performing pro-environmental behaviours.

Materials and Methods

The questionnaire was adapted from Truelove and Parks (2012), which was also an extended survey and partial replication of Read et al. (1994) and Reynolds et al. (2010) studies. The survey consists of two open-ended questions and three close-ended questions. The content of the survey is on behaviours that cause global warming; reduce global warming and level of willingness to perform behaviours that reduce global warming. There were four behaviours that do not reduce and cause global warming, which serve to identify misperceptions of the Malaysian educated laypeople. A total of 300 respondents participated in this study.

Results and Discussion

Results revealed that the respondents were aware of the effects of air-conditioning and driving on global warming but underrated eating meat and using washing machine as a cause of global warming, while overestimated littering as a cause of global warming. Respondents rated high on recycling and driving less as an effective global warming mitigator but underestimated the impact of reducing meat consumption and reduce air travelling as a global warming mitigator. Even though effectiveness knowledge on behaviours that reduce global warming was weakly linked to intention to perform the behaviour, the effectiveness belief that an action reduces global warming was moderately linked to intention to perform the behaviour. This shows that the Malaysian educated laypeople know only the obvious behaviours that cause and reduce global warming. They could not relate behaviours such as meat consumption, air travel and having many children with global warming and were not keen on performing behaviours that reduce global warming related to the behaviours they were not familiar with Tables 30.1, 30.2 and 30.3.

Table 30.1 Mean impact ratings of behaviours that contribute to global warming in close ended questions

Behaviour	Mean	Standard deviation
Cooling your house	7.01	1.55
Driving your car	7.00	1.49
Using aerosol spray cans	6.79	1.91
Throwing away recyclable materials	6.22	2.00
Lighting your house	5.85	1.86
Travelling by airplane	5.82	2.17
Using water heater to take a shower	5.76	1.97
Littering[a]	5.71	2.27
Using electronic devices	5.58	1.89
Using paper products	5.15	2.23
Using the washing machine	4.87	2.04
Not turning off the tap while brushingteeth[a]	4.57	2.36
Using black panels for solar power energy[a]	4.10	2.29
Purchasing items that are tested on animals[a]	3.85	2.28
Eating meat	3.52	2.32
Having many children	3.33	2.39

Note Rating scale for impact was 1 (No Impact) to 9 (Extremely High Impact)
N = 300
[a] Behaviours that do not have a distinct impact to global warming

Table 30.2 Top 3 and Bottom 3 mean effectiveness ratings on actions that reduce global warming and intention to carry out the behaviours

Top 3

Behaviour	Effectiveness ratings		Behavioural intention	
	Mean	Standard deviation	Mean	Standard deviation
Recycling	7.64	1.65	5.97	1.01
Reduce driving	7.59	1.43	5.18	1.46
Buy a fuel efficient car	7.47	1.55	5.92	1.17

Bottom 3

Behaviour	Effectiveness ratings		Behavioural intention	
	Mean	Standard deviation	Mean	Standard deviation
Buy locally grown and locally produced foods	5.48	2.39	5.15	1.38
Avoid buying products that are tested on animals[c]	5.16[b]	2.38	5.2	1.55
Reduce meat consumption	4.79[a]	2.23	4.55	1.66

N = 300

[a] women scored higher than men at $p < 0.5$

[b] women scored higher than men at $p < 0.001$

[c] Behaviours that do not distinctly reduce global warming

Table 30.3 Correlations between effectiveness knowledge and effectiveness belief *with* intention to perform possible behaviours *in reducing* global warming

Behaviour	Effectiveness knowledge—intention, r	Effectiveness belief—intention, r
Only run your washing machine when there's a full load	0.163[b]	0.467[b]
Reduce the number of kilometres you fly in airplanes	0.244[b]	0.460[b]
Reduce your meat consumption	0.111	0.446[b]
Avoid buying products that are tested on animals[c]	N/A	0.430[b]
Make sure your tire pressure is correct	0.347[b]	0.426[b]
Reduce usage of water heater when taking a shower	0.228[b]	0.349[b]
Turn off the tap while brushing teeth[c]	N/A	0.330[b]
Use environmentally-friendly cleaning products[c]	N/A	0.327[b]
Maintain your air-conditioner to 25 °C	0.232[b]	0.325[b]
When it is time for a new car, choose a more fuel efficient car	0.127[a]	0.272[b]
Throw away garbage in a trash can instead of littering[c]	N/A	0.254[b]
Reduce the number of kilometres you drive by walking, biking, cycling, carpooling or taking public transportation	0.157[b]	0.230[b]

[a] $p < 0.5$, N = 300

[b] $p < 0.01$

[c] Behaviour that do not distinctly reduce global warming

Conclusion

Essentially, the sample population was still unsure about recognizing their behaviours that cause global warming and was unsure which behaviours really reduce global warming, confusing them with behaviours that do not distinctly reduce global warming. The gender comparison showed that females are more aware about behaviours that reduce global warming and also are more willing to perform them. Even though effectiveness knowledge on behaviours that reduce global warming was not strongly linked to intention to perform the behaviour, but the effectiveness belief that an action that reduces global warming, whether the behaviour is accurate or not in reducing global warming, was moderately linked to intention to perform the behaviour on some of the behaviours.

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Chapter 31
Soil Carbon Dioxide Efflux and Atmospheric Impact in a 10 Years *Dipterocarpus* Recovering Lowland Tropical Forest, Peninsular Malaysia

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Abstract Recovering logged-over forest ecosystem increases CO_2 efflux into the atmospheric carbon pool in response of environmental factors to change in soil temperature and moisture. These CO_2 outbursts can have a marked influence on the ecosystem carbon balance and thereby affect the atmospheric carbon pool. The study was conducted in a 10 years logged-over forest of Sungai Menyala forest, Port Dickson, Negeri Sembilan, Malaysia. The measurements of soil CO_2 effluxes were conducted using a continuous open flow chambers technique connected to a multi gas-handling unit and infrared CO_2/H_2O gas analyser. The aim of this study is to determine the percentage of CO_2 contributed into the atmosphere from a recovering 10 year logged-over lowland forest. One-way analysis of variance (ANOVA) was used to test the significance correlation between soil CO_2 efflux and environmental variables. Post-hoc comparisons were made using Tukey test ($p < 0.05$), and multiple linear regressions were used to determine the impact of environmental factors on soil CO_2 efflux. Soil CO_2 efflux range from 345.6 to 600.4 $mg/m^{-2}/h^{-1}$ with the highest efflux in the afternoon attributed to increase in soil temperature and moisture. Higher soil temperature and moisture recorded signify the influential factor. Furthermore, the predictor environmental variables;

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Soil Organic Carbon (SOC), Total Organic Carbon (TOC), Soil Moisture Content (SMC), Bulk Density, Below Ground Carbon Stock, Total Aboveground Carbon Biomass (TAGB), soil pH, Nitrogen to Carbon ratio account for the spatial and temporal variation in soil CO_2 efflux. These factors attributed to increase in CO_2 efflux into the atmosphere.

Keywords Soil CO_2 efflux · Carbon pool · Biomass · Forest ecosystem and carbon sink

Highlights

- Age of trees and canopy density are key factors for carbon input.
- Soil properties and carbon stock are the determinants factors for soil CO_2 efflux.
- The tropical rainforest deforestation increases soil temperature and moisture.
- High rate of soil CO_2 efflux increases forest and atmospheric carbon pool.

Introduction

Increase in the greenhouse gas from oceanic, terrestrial and atmosphere carbon pool has been considered as a major contributor to global warming as well as climatic change (Conant et al. 2011). However, recovering forest of the terrestrial ecosystems are consider among the deforested areas to emit high efflux of soil carbon dioxide (CO_2) to the atmosphere (Brito et al. 2013). Soil CO_2 has been estimated to comprise of about 50–80 % of the terrestrial ecosystem respiration (Davidson et al. 2000a; Giardina and Ryan 2002), with a total of 60–80 Pg carbon annual (Raich and Potter 1995).

Recovering forest resulted from deforestation are found to have great implication on the atmospheric carbon pool, by contributing much percentage of CO_2 compared to undisturbed forest ecosystem (Ewel et al. 1981; Toland and Zak 1994). This action will resulted to unexpected change in physiological activity, microbial activity, litter fall input and root density, thereby increases efflux of soil CO_2 into the atmosphere as result of change in temperature and decay of fine roots (Hanson et al. 2000). In spite many researches on CO_2 efflux, little has been documented on the impact of recovering *Dipterocarpus* lowland tropical forest of peninsular Malaysia. This study will examine the rate and percentage of soil CO_2 efflux in the recovering 10 years forest and its contribution to the atmospheric carbon pool.

Materials and Methods

Site Description

Field experiment was conducted over a period of 6 months, January to June 2013, in the 10-year recovering logged-over *Dipterocarp* forest of Sungai Menyala, Port Dickson, Negeri Sembilan, Malaysia. The reserve forest is an extension forest for Seremban forest reserve. The study area is approximately 55 km from Kuala Lumpur. The reserve forest experiences equatorial climatic conditions with a temperature of 23.7 °C and relative humidity of 59–96 %, with an average of 83 %. Three experimental plot of 50 × 50 m, 70 × 70 m and 100 × 100 m with replicate were designed.

Soil CO_2 Efflux and Environmental Variables Measurement

Soil CO_2 efflux was measured each day from 0800 to 1700 h for 6 month, using two continuous open flow chambers connected to a multi gas-handler, which provides a channel to regulate the flow of CO_2 from various chambers to a flow meter connected to a CO_2/H_2O gas analyser. Soil temperature, soil moisture and soil water potential were measured at a depth of 5 cm at intervals of 5 min concurrently with each soil CO_2 chambers.

Litter trap net was placed 1 m above the forest floor of ten each in a plot for the collection of leaves at 14 days interval to ascertain Carbon to Nitrogen ratio. Total aboveground biomass and leaves area index (LAI) were determined both measuring a total 630 trees in each plot. Soil samples were taken randomly at three sampling points of each plot from a depth of 0–100 cm. Standard method was used to analysed for SOC, SMC, bulk density and pH while Walkley–Black method was used to determine TOC (Sollins et al. 1999), and below ground carbon stock was based on Eleanor 2008 method. To establish the attribution of the environmental variables to soil CO_2 efflux, and recovering 10 years forest, a statistical correlation and multiple linear regression models was employed. Also principal component analysis (PCA) was used to reduce large dataset (Yongming et al. 2006).

Results and Discussion

Based on the hourly and daily soil temperature and moisture changes, it was observed that soil CO_2 efflux significantly varies. Efflux ranged between 345.6 to 600.4 $mg/m^{-2}/h^{-1}$ across the 10 years logged-over *Dipterocarp* forest from 0800 to 1700 h with the low efflux occurring in the morning hours of 0800 to 1100 h and an instantaneous high efflux rates at 1300–1500 h. Higher values were

recorded in the month of January to March and lower efflux was experienced between April to June. The corresponding values for soil temperature, moisture and water potential in 5 cm soil depth fluctuate across the months from 23 to 25 °C, 18–38 % and 96.6–97.6 %, respectively. Soil bulk density increased with depth with a corresponding high value of top 10 cm soil containing TOC and SOC of 1.9 % and 5.55 %, respectively. Soil moisture content occurred at 20.0 with a corrective factor 1.2. The soil pH of the study area was slightly acidic in nature (5.55). In addition, carbon and nitrogen input from litter fall contributed about 42.92 % and 1.16 %, respectively with soil total carbon in top 100 cm was 75.2 Mg C/m^2.

The total amount of soil CO_2 contributed in the logged forest to the atmospheric carbon pool was calculated based on the flow rate and soil area sampled. The result indicated lower soil CO_2 efflux of 345.6 mg/m^{-2}/h^{-1} in the morning, with the highest peak of 600.4 mg/m^{-2}/h^{-1} in the afternoon and with an efflux declining in the evening. This coincided with the daily soil temperatures variation across the day. However, there were significant differences in total daily efflux between the early months and mid months of the year.

The multiple linear regression models indicated a strong correlation between soil CO_2 and environmental variables ($r = 0.85$, $p < 0.001$), explaining the impact of soil temperature and moisture on soil CO_2 efflux and the overall CO_2 efflux into the atmosphere due to deforestation. Results also indicated soil CO_2 efflux rate was in respond to the increase in TOC, SOC, soil moisture content and the acidic. Bulk density increases with depth, indicating the role of pore spaces played in water movement, capacity exchange catio, electric conductivity and microbial activity. The carbon to nitrogen ratio was attributed to canopy stand density based on the age of the forest, serving as a nitrate for microbial activities (lignin and cellulose). This explains the variation in soil respiration of different forest age stand. Therefore, the environmental factors were found to have much significantly relationship with soil CO_2 efflux across the 10 year logged-over *Dipterocarp* lowland forest.

Conclusion

The total amount of soil CO_2 efflux from the 10 years logged-over forest as was computed in the derived equation, showed that the recovering forest ecosystem displayed high rate of CO_2 efflux of 600.4 mg/m^{-2}/h^{-1}. This shows that the interaction among the environmental factor influences soil CO_2 efflux, therefore resulting to high percentage of soil CO_2 efflux from the 10 year logged-over *Dipterocarp* forest into the atmosphere. This situation is created as a result of deforestation as the forest is recovering, having less canopy stand density to capture CO_2 for photosynthesis and also to serve as a carbon sink. Therefore the

negative impact resulted from this scenario, is the increase in CO_2 efflux into the atmospheric carbon pool. This result will also help to determine the rate and the percentage of soil CO_2 efflux into the atmospheric carbon pool due to deforestation in Peninsular Malaysia.

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Chapter 32
Application of Geochemical and Geostatistical Analyses in Observing the Controlling Factors of Groundwater Compositions

Noorain Mohd Isa and Ahmad Zaharin Aris

Abstract The groundwater hydrogeochemistry assessment has been carried out based on physic–chemical parameters (which are *in situ* and major ions) to observe the hydrochemical mechanism that might occur and control the groundwater chemistry changes. A total of 216 groundwater samples from Kapas Island were collected bimonthly during two different monsoon seasons which were South–West Monsoon known as pre-monsoon (August–October 2010) and North–East Monsoon known as post-monsoon (February–April 2011). Geochemical data on dissolved major constituents in groundwater samples from the Kapas Island revealed the main processes responsible for their hydrogeochemical evolution. The abundance of major ions revealed $Ca > Na > Mg > K$ and $HCO_3 > Cl > SO_4$ dominations. Principal Component Analysis (PCA) extracts four (pre-monsoon) and three (post-monsoon) effective components which explained the origin of groundwater sources which have 81.6 and 78.9 % of total variances respectively. Comprised of variables TDS, EC, Salinity, Eh, pH, Cl, and Na in component 1, pre-monsoon experienced slightly saline process while component 1 in post-monsoon consist of Mg, TDS, EC, Salinity, Ca, Na, pH, Eh and HCO_3 described the mineralization process of the geological matrix have taken place. Saturation indices of carbonate minerals were calculated using PHREEQC for window software; calcite, dolomite and aragonite solubility showed strong and positive correlationship value ($p < 0.01$) with Ca constituent respectively, also indicating mineralization processes.

Keywords PCA · Saturation index · Small island · Hydrochemistry

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Highlights

- The seasonal changes affect the groundwater quantity and quality.
- Variation of major ions concentration in the hydrochemical processes.
- PCA reveals the main controlling factors of groundwater composition.
- PHREEQC calculation indicates mineralization processes.

Introduction

Small tropical islands became substantial issues regarding freshwater resources as its insularity character may expose to too many sources of defilement. The quality of fresh groundwater in small islands usually depends on the surrounding activities while, the presence of freshwater are based on its quantity, its surface storage and subsurface recharge (Aris et al. 2010). Groundwater pollution has been documented worldwide as results from anthropogenic disturbances into natural systems (Rosenthal et al. 1992). One of the most acute water resources problems in small tropical islands is the continuous salinization of groundwater. Seasonal changes have become vital contribution to groundwater hydrochemistry either in saline or freshening status. Therefore, a temporal distribution of seasons which are pre-monsoon (South–West Monsoon; dry season) and post-monsoon (North–East Monsoon; particularly wet season) were taken into consideration in present study (Desa and Niemczynowicz 1996; Wong et al. 2009). The objective of this paper is to determine the controlling factors affecting the groundwater hydrochemistry especially in different season.

Materials and Methods

Kapas Island is located at 5° 13.140′ N, 103° 15.894′ E with an area about 2 km^2 (Abdullah 1981; Shuib 2003). The climate is typically tropical climate with annual rainfall between 451 and 1102 mm. Kapas Island experiences constant mean temperature at 29.88 °C and has average daily relative humidity around 70–80 %.

The sampling design for this study was based on spatial and temporal scales. A total of 216 groundwater samples with replicates were collected bimonthly from six constructed boreholes during pre-monsoon (August–October 2010) and post monsoon (February–April 2011) at Kapas Island.

Results and Discussion

The cation concentrations order were Ca > Na > Mg > K while for anions were HCO_3 > Cl > SO_4. As different monsoons were concern, two types of groundwater

were found during pre-monsoon which are Ca–HCO_3 and Na–HCO_3 while post-monsoon is having only Ca–HCO_3 type.

Principal component analysis (PCA) was used in this study to reduce large of dataset by explaining the correlation among variables (Stetzenbach et al. 1999; Yongming et al. 2006). Pre and post-monsoon extract four and three components with 81.6 and 78.9 % of total variances respectively. Pre-monsoon shows salinization processes while having components TDS, EC, Salinity, Eh, pH, Cl, and Na. On the contrary, variables components viz. Mg, TDS, EC, Salinity, Ca, Na, pH, Eh and HCO_3 during post-monsoon described the mineralization process. Figure 32.1 shows the distribution of components in different monsoons.

Saturation indices (SI) indicate the behavior of carbonate minerals in groundwater. Most of groundwater samples during pre-monsoon are in dissolution state with 76 %. Meanwhile, the limitation of CO_2 during post-monsoon explained the super-saturation of carbonate minerals and only 30 % of dolomite mineral were found in dissolution state.

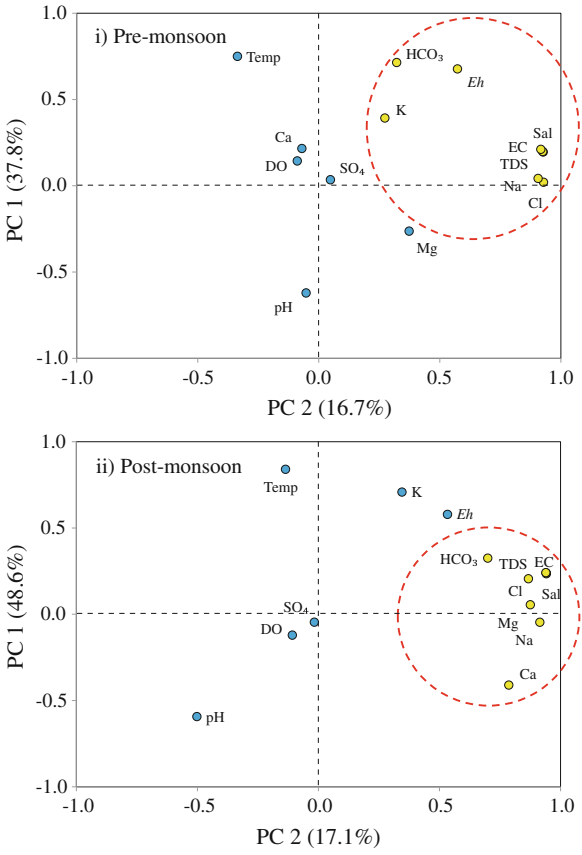

Fig. 32.1 Insert (i) and (ii) explained the variables of principal component in different monsoons

Conclusion

Present study indicated that the geostatistical tool of PCA and geochemical technique of SI rendered an important data reduction to identify the factor controlling groundwater hydrochemistry especially in seasonal variation. Comprise of two different groundwater types; Ca–HCO_3 (pre-monsoon) and Na–HCO_3 (post-monsoon), these analyses revealed the most significant factors responsible to groundwater evolution which are salinization and mineralization processes.

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Chapter 33
Green Biotechnological Approach as an Alternative to Chemical Processes: The Case of Bioflocculant Production through Solid-State Fermentation of Soybean Wastes

Zufarzaana Zulkeflee and Antoni Sánchez

Abstract Solid-state fermentation (SSF) from organic wastes can be considered as a novel biotechnological alternative for the development of new processes that may substitute the current chemical-dependence approaches. In this framework, the production of a bioflocculant through SSF using soybean fiber wastes as the sole substrate with the inoculation of *Bacillus subtilis* UPMB13 at different fermentation stages were carried out in a pilot scale near-to-adiabatic reactors of 4.5 L volume for 10 days. Samples collected at 2, 4, 7 and 10 days were checked for flocculating activity through kaolin assays and the crude bioflocculant was extracted through ethanol precipitation. The highest activities were measured at the 2nd day of fermentation and maintained until the 4th day with an average value of 88.1–92.0 and 92.4–92.7 % of bioflocculant activity for reactors inoculated at the beginning of SSF and after the thermophilic stage, respectively. The bioflocculant activities decreased around 30–40 % by the 7th day. About 30 mg of crude bioflocculant can be obtained from 20 g of sampled fermented substrate at the maximum flocculating activity measured. This SSF process can be considered as a new green alternative to produce bioflocculant from wastes under easily scalable conditions. Further studies may contribute to the industrial production of bioflocculants from wastes as an alternative to the commonly harmful commercial marketed flocculants.

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Keywords *Bacillus subtilis* UPMB13 · Extracellular polymeric substance · Soybean fibers · Pilot scale

Highlights

- Positive production of bioflocculant from soybean wastes.
- SSF may substitute SmF for bioflocculant production.
- Bioflocculant production proven feasible in scalable pilot scale.

Introduction

The emerging interest of finding and developing environmentally sound approaches in addressing environmental issues as alternatives to the conventional chemically-centered sector has brought the opportunity of exploring the vast possibilities of wastes use as raw materials sources. In that sense, solid state fermentation (SSF) as a promising green biotechnological process that utilizes wastes as substrates for the production of interesting materials, contributes not only to the production of these compounds, but also focuses on the minimization of wastes disposal. SSF is a fermentation process of humid solid substrate in the absence or near absence of free water (Navarro et al. 2011). In this case, soybean fibers residues were used as the sole substrate for the production of extracellular polymeric substances (EPS) with flocculating capabilities; known as bioflocculants, through SSF with additional inoculation of *Bacillus subtilis* UPMB13. Bioflocculants are EPS produced naturally from organisms that assist in the process of water clarification that are biodegradable in nature and environmentally safe (Deng et al. 2003). Most reported literature discussed the production of EPS; including bioflocculants, from submerged fermentations (SmF), which are reported to be comparably higher in cost due to the large amount of substrate needed to achieve maximum yield. In comparison, the implementation of SSF seek to overcome this issue by utilizing readily usable substrate that are of no use for other purposes and are available in large amounts (Zhao et al. 2012). This research aimed to determine the possibilities of producing the bioflocculants through SSF by utilizing soybean wastes with added inoculation at a scalable level as a projection for future prospect in a full scale industrial level.

Materials and Methods

Soybean fibers leftover from the production of tofu were selected as the sole substrate for the solid state fermentation. Addition of wood chips at the ratio of 1:2 to the soya fibers acted as bulking agent which promotes porosity and aeration to the substrate system. The substrate mixture with an initial moisture content of around 60–65 % was then inserted into 4.5 L pilot scale near-to-adiabatic bioreactors at a total mass of around 1,200 g of substrate in each reactor. Continuous oxygen supply was provided all throughout the fermentation at a rate of 0.1 nL/min. *Bacillus subtilis* UPMB13 strain; primarily researched to be able to produced bioflocculant via submerged fermentations (SmF), was used as the added inoculum at a level of 5 % (v/w) to the system. Two treatments were used, namely, inoculation at initial time (Bioreactor A) and after the thermophilic phase (Bioreactor B). Around 20 g of samples were collected at 2, 4, 7 and 10th day of fermentation for bioflocculant extraction and measurement of flocculating activities. The flocculating activities were measured according to the method described by Zulkeflee et al. (2012) using kaolin as the suspended particles. The bioflocculants were obtained from the fermented substrate at the point of maximum flocculating activity measured, by suspending the sample in 10 volumes of ultra-pure water, shaken on an orbital shaker for 1 h and gone through multiple steps of centrifugation and filtration to separate the residual visible substrate. The resulting filtrate was added to two volumes of ice cold ethanol to precipitate the bioflocculants. Crude solid bioflocculants were obtained through lyophilization.

Results and Discussion

The flocculating measurement reflects the bioflocculant production during fermentation. The results from the kaolin assay are depicted in Fig. 33.1.

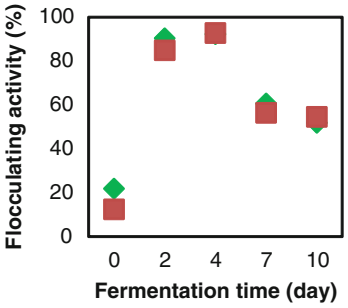

Fig. 33.1 Flocculating activity measured from the 20 g of fermented substrate sampled at the specific fermentation time. The symbol ■ denotes Bioreactor A, where inoculation of *Bacillus subtilis* UPMB13 was done at initial time while the symbol ◆ denotes Bioreactor B, inoculated after the thermophilic phase of the fermentation

At the initial point of fermentation, it is observed that a slight flocculating activity was measured in both treatments, noted to be considerably low, may be due to the charge destabilization by the ionic components presence in the substrate mixture when tested with the kaolin suspension. As the fermentation continues, the flocculating activities in both reactors increased steeply by the 2nd day and reached a maximum value of around 92 % by the 4th day of fermentation suggesting that the production of bioflocculant occurred in parallel with the strain growth. A decrement of about 30–40 % of flocculating activities can be seen at the 7th day of fermentation until the 10th day, suggesting that the declination of production of the bioflocculant and the loss of the available bioflocculant in the system as a result of prolonged cultivation, could have led to nutrients scarcity and, in consequence, the excreted bioflocculants could be consumed by the microbes as substitute for food (Xia et al. 2008). It is noted that the similar performance and production trend can be seen in both reactors suggesting the presence of indigenous microbial community in the substrate system that are capable of producing the bioflocculant and denoting that there were no direct effects of inoculation by the strain *Bacillus subtilis* UPMB13.

About 30 mg of crude bioflocculant can be obtained from the 20 g of fermented substrate sampled at the 4th day of fermentation. The value may be an underestimation caused by the potential loss throughout the extraction process.

Conclusion

The study showed promising results on the utilization of soybean fiber residues for the production of bioflocculant at an easily scalable pilot level. Although the effect of inoculation had not yet been proven, the possibilities of further production enhancement by the strain *Bacillus subtilis* UPMB13 to these SSF setup might be crucial to be explored as it had been observed in another study by the authors that the strain UPMB13 can produce high performing bioflocculant through SmF by using a soy based liquid substrate. Further research should address the optimization setup for the bioflocculant production with or without the strain by identifying key influencing factors highlighting both feasibility and efficiency for possible future projection to be implemented at an industrial scale level.

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Chapter 34
Determination of Veterinary Pharmaceuticals Residue in Soil and Biological Materials: A Review of Current Analytical Methods

Yu Bin Ho, Mohamad Pauzi Zakaria, Puziah Abdul Latif and Nazamid Saari

Abstract Veterinary pharmaceuticals have been extensively used in animal husbandry for control of disease and growth promoters. These compounds are excreted from animals via urine and faeces, end up in the environment through untreated animal waste disposal. Veterinary pharmaceuticals often exist in the complex solid environmental samples such as manure, slurry, and soil which require extensive extraction, clean-up and analysis method. This review highlights the current analytical methods for the analysis of veterinary pharmaceuticals in complex solid environmental matrices, including soil, animal manures and sediment. The aim of this review is to compare and summarize the performance of each method in terms of recovery, method detection limit (MDL) and method quantification limit (MQL).

Keywords Review · Veterinary pharmaceuticals · Soil · Manure · Analytical methods

Highlights

- Pharmaceutical analysis in solid samples requires complex extraction method.
- MeOH:EDTA:McIlvaince buffer is frequently reported as extraction solvent for solids.

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- MeOH:ACN:0.1 M EDTA:McIlvaine extraction buffer is proposed to improve recovery.
- LC–MS/MS allows multi-residue, sensitive and selective pharmaceuticals analysis.
- HPLC–UV and HPLC-FLD are still being used due to its lower operating cost.

Introduction

All the while, the trends for analysis of pharmaceuticals in environment are focused in aqueous samples especially on human pharmaceuticals. Unlike human pharmaceuticals, veterinary pharmaceuticals often exist in the complex solid environmental samples such as manure, slurry, and soil. Very few studies have been devoted to pharmaceuticals in solid environmental samples due to pharmaceuticals being a large group of pollutants from different chemical classes with different physico–chemical properties (polar, semi polar, non polar, acidic, basic, neutral, strongly, moderately and weakly sorbed). In this review, we summarized the current available methods for determination of veterinary pharmaceuticals in soil and biological materials; the performance of each method is presented in Table 34.1.

Materials and Methods

Sample Preparation and Extraction

Ultrasonic extraction is known as a popular technique which is rapid and does not require large volumes of solvent or expensive instrumentation. This method has been successfully applied to pharmaceuticals extraction in solid environmental samples (Blackwell et al. 2004; Kim and Carlson 2007; Carballo et al. 2007; Aust et al. 2008; Karcı and Balcıoğlu 2009). MeOH: EDTA: McIlvaince buffer was frequently reported as extraction solvent for ultrasonication to extract antibiotics from soil and biosolids (Blackwell et al. 2004; Aust et al. 2008; Karcı and Balcıoğlu 2009). However, this extraction buffer limits to extract only high polarity compounds such as antibiotics whereas low polarity compounds such as hormones are often difficult to extract due to the strong partitioning affinity to soil and organic matter (Ho et al. 2012). Therefore, MeOH:ACN:0.1 M EDTA: McIlvaine buffer was proposed by Ho et al. (2012) to improve the recovery of low polarity analytes.

Table 34.1 Methods to determine veterinary pharmaceuticals in different sample matrices

Antibiotic/hormone	Matrices analyzed	Extraction	Clean-up	Separation	Detection	Recovery (%)	MDL (μg/kg)	MQL (μg/kg)	References
Trimethoprim	Soil,	Ultrasonication with ACN: MeOH: EDTA-McIlvaine buffer (pH 6)	Oasis HLB 3 cc/ 60 mg	HPLC	MS/MS	72–103 (S)	0.5–3 (S) 1–5 (M)	2–10 (S) 3–16 (M) 5–15 (C)	Ho et al. (2012)
Tilmicosin	Chicken manure,			Waters Xtera C18, 10.0 cm, 2.1 mm, 3.5 μm	ESI (+)	63–113 (M)	2–5 (C)		
Tylosin									
Erythromycin						63–119 (C)			
Enrofloxacin									
Flumequine	Compost								
Norfloxacin									
Sulfadiazine									
Doxycycline									
Progesterone									
Oxytetracycline	Poultry manure, cattle manure, soil	Ultrasonication with MeOH: EDTA-McIlvaine buffer (pH 6)	SAX 6 cc/ 500 mg,	HPLC	FLD	60–86 (S)	NR	NR	Karcı and Balcıoğlu (2009)
Chlortetracycline				50 × 4.0 mm, 3 μm, YMC-Pack ODS-AQ column	(360 nm)	62–77 (M)	NR	NR	
Suldiazine			Oasis HLB 6 cc/ 200 mg		FLD	69–101 (S)	NR	NR	
Sulfathiazole					(270 nm)				
Sulfamethoxazole						14–82 (M)			
Sullfachloropyridazine									
Ciprofolxacin					FLD	46–55 (S)	NR	NR	
Enrofloxacin					(280/ 450 nm)	24–42 (M)			

(continued)

Table 34.1 (continued)

Antibiotic/hormone	Matrices analyzed	Extraction	Clean-up	Separation	Detection	Recovery (%)	MDL (μg/kg)	MQL (μg/kg)	References
Sulfamethazine	Cattle manure, soil	Ultrasonication with MeOH: EDTA-McIlvaine buffer (pH 6)	SAX	HPLC	MS/MS	38–73 (S)	NR	5 (S/M)	Aust et al. (2008)
Chlortetracycline			6 cc/ 500 mg, Oasis HLB	Nucleosil 125 × 3.0 mm, 100–5 mm reversed-phase column	ESI(+)		NR	5 (S/M)	
Tylosin			6 cc/ 200 mg				NR	3 (S/M)	
Tetracycline	Pig slurry, chicken manure, turkeys manure, soil	Ultrasonication with EDTA McIlvaine	SPE Isolute C_{18}	HPLC	MS/MS	71–94 (M)	NR	1.2–22 (M)	Carballo et al. (2007)
Chlorteteracycline				Luna C_8 (150 × 2 mm, 5 μm)	ESI(+)	61–89 (S)		0.49–25 (S)	
Oxytetracycline									
Trimethoprim									
Sulfadimidine		Buffer (pH 4)							
Sulfadiazine									
Sulfathiazole									
Sulfamethozazole									
Sulfadoxine									
Ciprofloxacin					MS				
Enrofloxacin					ESI (+)				

(continued)

Table 34.1 (continued)

Antibiotic/hormone	Matrices analyzed	Extraction	Clean-up	Separation	Detection	Recovery (%)	MDL (μg/kg)	MQL (μg/kg)	References
Tetracycline Chlortetracycline Oxytetracycline Minocycline Demeclocycline Meclocycline Doxycycline Sulfathiazole Sulfamerazine Sulfamethazine Sulfachlorpyridazine Sulfamethoxazole Sulfadimethoxine Erythromycin Roxythromycin Tylosin Monensin Narasin Salinomycin	Sediment	Ultrasonication with McIlvaine Buffer with 5 % EDTA	Oasis HLB 3 cc/60 mg	HPLC 2.1 mm × 50 mm, 2.5 μm	MS/MS ESI (+)	12.6–113.2	0.3–3.6	NR	Kim and Carlson (2007)
Tylosin	Soil, pig slurry	Ultrasonication with MeOH: EDTA-McIlvaine buffer (soil)	SAX 6 cc/500 mg, Oasis HLB	HPLC GENESIS C_{18} 150 mm × 4.6 mm, 4 μm	FLD (285 nm)	86 ± 4 (S)	40 (S)	NR	Blackwell et al. (2004)
Oxytetracycline					FLD (355 nm)	102 ± 5 (M) 75 ± 3 (S)	18 (S) 70 (M)	NR	
Sulfachloropyridazine		Ultrasonication with EDTA McIlvaine Buffer (pig slurry)	6 cc/200 mg		FLD (285 nm)	89 ± 2 (M) 85 ± 4 (S)	18 (S) 140 (M)	NR	

ESI (+) electrospray ionization positive mode, *NR* not reported in the study, *S* soil, *M* manure, *C* compost

Instrumental Analysis

Liquid chromatography is widely used as a complementary technique to gas chromatography in residue analysis because of its applicability to the determination of polar, water soluble and non-volatile compounds without derivatization. UV detection (Blackwell et al. 2004; Hu et al. 2008; Karcı and Balcıoğlu 2009), and to a lesser extent mass spectrometry (Haller et al. 2002), and fluorescence detection (Blackwell et al. 2004; Karcı and Balcıoğlu 2009), have been used in the detection techniques in coupled to HPLC, for the analysis of pharmaceuticals in solid environmental samples.

Conclusion

The current available methods for determination of veterinary pharmaceuticals in soil and biological material are reviewed and summarized. In general, most of the extraction methods for veterinary pharmaceuticals in soil and biological materials require ultrasonic extraction with the aid of appropriate extraction buffer and subsequently analyzed by HPLC-FLD or LC–MS/MS.

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Chapter 35
Mercury Distribution in Port Klang Mangrove and Estuarine Sediment

Hazzeman Haris and Ahmad Zaharin Aris

Abstract Mangrove and estuarine areas are important to the ecosystem and can act as a sink of pollutants, especially metal ions. However, the accumulation of metals in sediment can cause negative impacts on plant growth, microbial activity and soil fertility. The severity and nature of the impact is highly influenced by the type of metal found in the sediment. One of the metals that have adverse effects on the environment is mercury. Therefore, the objectives of this study are to determine the mercury concentration and its distribution in the study area. Sediment samples were collected from 30 sampling points that cover Langat River and Klang River estuaries, Lumut Straits, Pulau Klang and Pulau Indah in Selangor, Malaysia. The extractable mercury in sediment samples was determined at the laboratory using inductively coupled plasma mass spectrometry (ICP-MS). In this study, mercury was found to be concentrated along Lumut Strait especially in the mixing zone near the confluence of Langat River.

Keywords Mercury · Mangrove sediment · Estuarine sediment · Mercury distribution

Highlights

- Mercury distribution is concentrated within Lumut Strait.
- Two stations exceeded the Canadian interim mercury guidelines.
- Stations opposite Northport also have high mercury concentration.

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Introduction

Mercury can be found naturally in the environment. However, activities such as the production and improper disposal of mercury containing products can also contribute to mercury enrichment in the environment.

The toxicity and accumulative properties of mercury (Hg) is a serious threat to the mangrove and estuarine ecosystem. Mercury has been reported to have an effect on plant mineral uptake (Cho and Park 2000), photosynthetic integrity (Israr et al. 2006), transpiration (Godbold and Hüttermann 1988) and membrane structural integrity (Ma 1998). In humans and animals, mercury can affect the brain and nervous system (Rahman et al. 1997; UNEP 2002).

The Port Klang mangrove and estuary area were chosen for this study due to the various natural and anthropogenic factors within or near the area that may influence the mercury concentration in the sediment. The possible effect or threat posed by mercury on fisheries and recreational activities occurring in Port Klang was also a consideration when choosing it as the study area. Thus, this study was conducted with the aims to determine the concentration and distribution of mercury and to evaluate if there is any enrichment of mercury that occurs in Port Klang mangrove sediment.

Materials and Methods

Site Description

Port Klang (3°0′0″N, 101°24′0″E) is located 38 km southwest of Kuala Lumpur, Malaysia. It comprises of Northport, Westport and Southport. Port Klang as a whole is the busiest container port in Malaysia. The Port Klang area also receives inputs from Klang and Langat River, which flows through urban, industrial, commercial and agricultural area.

Sample Collection and Analytical Procedure

The top 0–5 cm surface sediment samples were collected in December 2011 from 30 sampling stations. These stations cover the estuary of Langat River, Klang River, Lumut Straits, Pulau Klang and Pulau Indah. Ultrasound assisted extraction methods as proposed by Collasiol et al. (2004) was applied to extract mercury from air-dried sediment that had been sieved through 63 μm pore size sieve.

Results and Discussion

Station PK 24 (149.97 ± 2.44 μg/kg) recorded the highest mercury concentration followed by PK 5 (143.50 ± 1.97 μg/kg) and PK 1 (138.60 ± 1.00 μg/kg) (Fig. 35.1). The lowest concentration was recorded at PK 30 (0.20 ± 0.10 μg/kg). Based on this result, PK 24 and PK 5 had exceeded the Canadian interim mercury guidelines for river and marine sediment where the threshold limit is 140 μg/kg (Gaudet et al. 1995).

Mercury concentration was found to be highest within Lumut Strait where the mixing of water and suspended particles from Langat River, Klang River and seawater occurs. PK 15 and PK 14 at Klang Island, which was located directly in front of Northport and the confluence where Lumut Strait meets South Klang Strait also recorded higher concentration compared to other stations. The accumulation of mercury within Lumut Strait and at PK 15 and PK 14 can be due to the sedimentation of mercury contaminated suspended solids or particles from Langat and Klang River. The weak water current in these areas, which was below the sinking velocity, encourages the sedimentation process (McDonnell and Buesseler 2010) of suspended particles carried downstream by Klang and Langat River.

It can be seen that areas receiving less flow from Klang and Langat River, have a lower mercury concentration. This suggested that Klang and Langat River may have been the source and main pathway for mercury to enter the Port Klang area. Activities such as releasing of untreated sewage and effluent by residential and industries (e.g. pulp and paper mills, metal smelting, and chlor-alkali plants) (Förstner and Wittmann 1979; Huber 1997; Wang et al. 2004; Eriksson and Donner 2009) and leachate from municipal waste landfill within the catchment areas of these rivers could have contributed to the mercury concentration in the water of Klang and Langat River (Haris and Aris 2012).

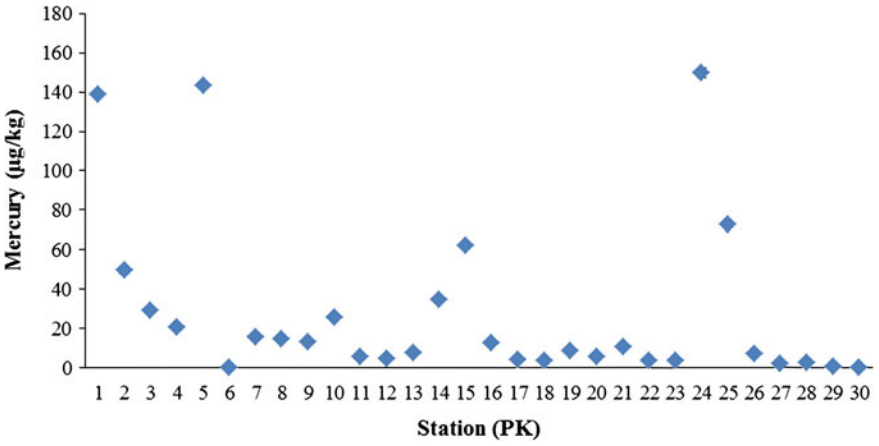

Fig. 35.1 Extractable mercury concentration in Port Klang mangrove and estuarine sediment

Conclusion

The results obtained from this study shows the concentration of mercury in mangrove sediment in the Port Klang area were concentrated along Lumut Strait and the area directly in front of Northport and the confluence where Lumut Strait merge with South Klang Strait. The result obtained indicated that the Klang River could have been one of the pathways transporting mercury to Port Klang.

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Chapter 36
Exposure to $PM_{2.5}$, Ultrafine Particle and Lung Function Among Photocopy Workers in Selangor

Nur Ayuni Bahruddin, Juliana Jalaludin and Sarva Mangala Praveena

Abstract This study investigates the relationship between exposure to $PM_{2.5}$ and ultrafine particle (UFP) with respiratory health among photocopy workers in Selangor. This cross-sectional comparative study involved 60 workers where 30 photocopy workers as exposed group and 30 administrative staff as comparative group. Questionnaire adapted from American Thoracic Society (ATS) was used to assess respiratory symptoms. Lung function test was conducted for each respondent to assess lung function status. Measurements of $PM_{2.5}$ and ultrafine particle were performed to obtain exposure level of the respondents. The mean personal exposure to $PM_{2.5}$ (62.30 $\mu g/m^3$) was five times higher and UFP (14567.10 pt/cc) was four times higher in exposed group. Reported respiratory symptoms of cough (26.7 %), phlegm (16.7 %), chest tightness (3.3 %) and wheezing (6.7 %) were higher in exposed group compared to the comparative group. There was a significant association between exposure to $PM_{2.5}$ with lung function of FVC % predicted ($r = -0.404$, $p = 0.027$) and UFP with lung function of FEV_1 % predicted ($r = 0.377$, $p = 0.040$). Continuous exposure to $PM_{2.5}$ and UFP among photocopy workers can cause lung function impairment as this study showed that respiratory symptoms was higher among exposed group compared to the comparative group. There was a significant association between personal exposures to $PM_{2.5}$ and UFP with lung function among exposed group. Emission and exposure to $PM_{2.5}$ and UFP can be reduced by regular service or maintenance. Good ventilation also will ensure improved indoor air environment.

Keywords Photocopiers · Ultrafine particle (UFP) · $PM_{2.5}$ · Lung function

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Highlights

- Pollutants emitted during photocopying affect indoor air quality.
- Printing worker exposed to ultrafine particle are at risk of reduced lung function.
- Lung function abnormality was associated with high concentrations of $PM_{2.5}$ and UFP.

Introduction

Indoor air pollutant consist of particulate matters that are classified as coarse particles, (particles with aerodynamic diameter greater than 2.5 μm and less than 10 μm), fine particles ($PM_{2.5}$) (particles with aerodynamic diameter less than 2.5 μm and greater than 0.1 μm) and ultrafine particles (particles with aerodynamic diameter less than 0.1 μm) (Morawska et al. 2004). Due to the nature of the job, photocopiers were exposed directly to particles emitted from the photocopy machine (Wensing et al. 2002). Pollutants emitted during photocopying would affect indoor air quality and potentially have adverse health effects on the employees as well as the residents of photocopy centers (Lee et al. 2007). They are at risk getting respiratory and lung disease.

Materials and Methods

This comparative study was conducted among 30 photocopiers and 30 administrative staff. Purposive sampling method was used to select the respondents. Study population was chosen from those who meet the inclusive criteria which were female photocopy workers, ages between 20 and 45 years old, non-smokers and with no history of respiratory disease. Questionnaires adapted from American Thoracic Society were used to obtain background information data and respiratory symptoms of the respondents. Personal Exposure Measurements ($PM_{2.5}$ and UFP) were sampled using Personal Aerosol Monitor of Model TSI AM510 (SidePak^{TM}) and P-Trak Ultrafine Particle Counter Model 8525, respectively. For each respondent, exposures of $PM_{2.5}$ and UFP were measured for 4 h simultaneously with logging time 60 s as outcarried by Massey et al. (2011). Lung function test was performed using Spirometer Model Spirolab II.

Results and Discussion

Basically, no significant differences were observed between photocopy workers and comparative group in terms of age and height. The mean value of work duration for exposed group and comparative group were 1.63 years (range 0.08–5.00 years) and 5.72 years (range 1.00–20.00 years), respectively. All exposed group (100 %) and most of the comparative group (93.3 %) are Malays.

One of the major finding of this study was the significant difference in personal exposure to $PM_{2.5}$ ($z = -6.398$, $p < 0.001$) and UFP ($z = -6.653$, $p < 0.001$) between photocopy workers and comparative group as mean exposure to $PM_{2.5}$ and UFP were higher in the exposed group. A study conducted by Lee et al. (2007) on measurement of fine and ultrafine particles formation in photocopy center in Taiwan found that particle number concentration in background air and during photocopying were higher than outdoors. Lee et al. (2007) has suggested that there were sources of UFP in photocopy center and UFP concentration would remain high when ventilation was inadequate, such as during close hours.

High respiratory symptoms among exposed group were observed in this study. This study conforms to Yang (2008) who studied on respiratory symptoms among 74 photocopy workers in Taiwan. Symptoms of chronic cough, phlegm, wheezing, chronic bronchitis and dyspnea were observed and there was no significant differences in the prevalence of chronic respiratory symptoms in the two groups. Similarly, findings of the study conducted by Penttinen et al. (2001) on respiratory health among 54 adult asthmatic in Helsinki, Finland, due to exposure to UFP in urban air has reported no association were observed with respiratory symptoms or medication use with exposure to UFP. According to Sharifah et al. (2013), among 430 healthy school children that were selected, there was a significant association between $PM_{2.5}$ and PM_{10} with IL-6.

All parameters of lung function except for FEV_1 (liter) showed significant reduction among exposed group compared to comparative group. This study also showed that lung function abnormality (FVC % predicted, FEV_1 % predicted) among exposed group was significantly higher ($p = 0.001$). A study conducted by James et al. (2002) on association between air pollution and lung function growth in three cohorts of Southern California children, a significant association ($p < 0.05$) was observed between lung function growth and $PM_{2.5}$. Although previous study was not conducted among photocopy those findings were similar to this study which shows exposure to $PM_{2.5}$ and UFP among photocopiers workers was significantly associated with reduction of lung function.

There was a significant association between fine particles exposure and lung function (FVC, FVC % predicted) among exposed group. This present study was consistent with findings of a study conducted by Jones et al. (2008) on respiratory health of 33 road-side vendors and 31 shopkeepers in a large industrialized city of Mongkok, Hong Kong, who found that FVC (liter) of shopkeepers (FVC = 2.79) and road-side vendors (FVC = 2.84) vendors was significantly lower ($p < 0.0005$) than the university cohort (FVC = 3.27). This study showed a significant

association between exposure to UFP and lung function (FEV_1 % predicted) which was supported by Kavita et al. (2011) who suggested that bus driver exposed to the particulates matter (PM_{10}, $PM_{2.5}$ and UFP) were at higher risk of getting respiratory illnesses and lung disease. Particulate matters were significantly associated with decrease in FVC and FEV_1 (James et al. 2000).

Conclusion

Photocopy workers are at higher risk of getting lung function impairment as the findings from this study successfully showed that personal exposure to $PM_{2.5}$ and UFP were significantly higher ($p < 0.001$) among photocopy workers compared to the administrative staff. Reported respiratory symptoms (cough, phlegm, chest tightness and wheezing) were higher among photocopy workers compared to comparative group. Photocopy workers t exposed to high concentration of $PM_{2.5}$ and UFP showed a significant reduction of FVC, FVC % predicted, FEV_1 % predicted and FEV_1/FVC % compared to comparative group. Personal exposures to $PM_{2.5}$ and UFP among photocopy workers were significantly associated with lung function.

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Chapter 37
Heavy Metals in Lichens and Mosses of a Tea Plantation in Cameron Highlands, Malaysia

Ahmad Saat, Zaini Hamzah, Ab Khalik Wood, Mahira Talib and Nurulsyuhada Harun

Abstract Lichen species *Platismatia glauca* and moss species *Meiothecium microcarpum* were used as bio-indicator for heavy metals pollutants of anthropogenic origins. These species are found to grow extensively and abundantly on the stems and branches of tea plant in the study area. The elemental analyses of heavy metals were carried out using Energy Dispersive X-rays Fluorescence Technique (EDXRF). Results showed that the mean concentration of the metals can be arranged in decreasing order as Zn > Cu > Pb > Cr > Cd > As > Ni for lichen and Zn > Cu > Pb > Ni > Cr > Cd > As for moss. Analysis of pollution based on anthropogenic factor (AF) indicated that only Cd shows slightly polluted, and Zn potentially polluted. However, the mean pollution impact based on pollution index (PI) shows a value of 0.38 and 0.29 for lichen and moss respectively, indicating the impact is still low. The sources of the two important metals, Cd and Zn can be traced to solid waste disposal, fossil fuel burning and application of phosphate fertilizers, which are the peculiar anthropogenic activities of the area.

Keywords Bio-monitoring · Heavy metals · Pollutants distribution

Highlights

- Lichen and moss can be used as bio-indicators for environmental pollutants.
- PCA identifies spatial distribution of heavy metals.
- Heavy metals concentration is attributed to anthropogenic activities.

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Introduction

Cameron Highlands sits on the Main Range of Peninsular Malaysia at an altitude reaching about 2000 m above sea level at the highest peak. Intensive and uncontrolled clearance of forest to make way for plantations and agricultural lands has contributed not only to "visual pollution" but environmental pollution as well through transport of soil particles by surface water during rainy season or wind-blown dust particles during dry season. Increment in the number of motor vehicles and non-resident visitors to the area also contributed to deterioration of the environment. This issue has raised alarm and concerned due to its negative impacts on human health. The pollutants of natural origin or anthropogenic sources contained heavy metals and trace elements (Barandovski et al. 2008) such as Cr, Cu, Zn, Ni, Cd, As and Pb that could be toxic and cause health risks at high concentration (Hamzah et al. 2011). One way of assessing the deposition levels of atmospheric pollutants is by applying bio-monitoring technique using lower plants such as lichens and mosses that are found widespread in the area. The technique to assess the impact of heavy metals pollutants is popular in many countries like Serbia (Dragovic and Mihailovic 2009), Turkey (Ugur et al. 2003), Romania (Lucaciu et al. 2004), and more recently applied in Malaysia around oil refinery area (Abdullah et al. 2011, 2012) and a coal-fired power station (Abu Bakar et al. 2013). The present study aims to assess the levels of ambient heavy metals pollutants in the study area by using lichen species *Platismatia glauca* and moss species *Meiothecium microcarpum* that are found to grow extensively and abundantly on the stems and branches of tea plant in the area.

Materials and Methods

Moss (*Meiothecium microcarpum*) and lichen (*Platismatia glauca*) samples were collected from the stem and branches of tea plants at about 1 m from ground level at fifteen sampling locations within a tea plantation that has been established for more than 50 years at Cameron Highlands, Malaysia. Within the sampling area there are networks of graveled service roads for the plantation. The geographic positions of the sampling locations were determined by GPS. Samples were prepared for EDXRF spectrometry technique based on the procedure described by Abdullah et al. (2011). The spectrometer was optimized earlier, giving the recoveries of between 83.7 and 102.5 % depending on elements being analyzed (Abdullah et al. 2011).

Results and Discussion

The mean concentration of seven elements studied in the fifteen lichen and fifteen moss samples are summarized in Fig. 37.1 and can be arranged in decreasing order

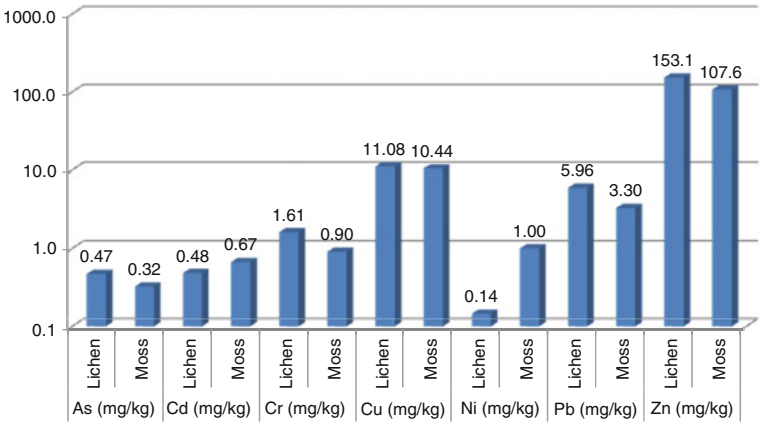

Fig. 37. 1 Mean heavy metals concentration in lichen and moss samples

as Zn > Cu > Pb > Cr > Cd > As > Ni for lichen and Zn > Cu > Pb > Ni > Cr > Cd > As for moss. Except for Ni and Cd, the mean concentrations of heavy metals in lichen are higher than in moss that might be attributed to the difference in uptake mechanism efficiency between lichen and moss for different types of heavy metals.

Analysis on the Anthropogenic Factor (AF) for each element based on the mean concentration relative to the background concentration was also carried out (Adamu and Nganje 2010; Deng et al. 2012). Except for Cd and Zn, all AF values are less than 1 either for lichen or moss. Cd in lichen shows slightly polluted (AF = 2.40) and in mosses polluted (AF = 3.34) respectively. For Zn in lichen slightly polluted (AF = 2.19) is observed while in moss potential pollution (AF = 1.94) is concluded. Enrichment of Cd and Zn could be traced to anthropogenic inputs. The presence of Cd in air can be traced to incineration of solid waste, fossil fuel burning and application of phosphate fertilizer (Dragovic and Mihailovic 2009; Bajpai et al. 2011). Being quite close to the main road and interlinked by service roads within the area the enrichment of Zn can be attributed to ware of tires and incomplete fossil fuel burning (Bajpai et al. 2011). Based on AF, the degree of anthropogenic pollution by the elements in lichen and in moss follows identical decreasing order of Cd > Zn > Pb > As > Cu > Cr > Ni. This shows that Cd and Zn are most enriched in both lichen and moss. The average pollution impact based on five elements Cd, Zn, Pb, As and Cu using Pollution Index (PI) as suggested Adamu and Nganje (2010) for lichen and moss are 0.38 and 0.29 respectively. The PI was calculated relative to the maximum tolerable concentration of the elements by plants. Thus, although lichen and moss were found to be enriched by Cd and Zn, on average the pollution impact by the five heavy metals is still low.

Table 37. 1 PCA variance and factor loadings of heavy metals in lichen

Component	Eigen-values	% of variance	Element	Factor loading		
				1	2	3
1	1.359	53.7	As	0.435	−0.031	0.060
2	0.673	26.6	Cd	0.434	−0.072	0.084
3	0.234	9.2	Cr	0.171	0.972	0.127
4	0.127	5.0	Cu	0.426	0.029	−0.876
5	0.065	2.6	Ni	0.463	−0.105	0.364
6	0.042	1.6	Pb	0.445	−0.191	0.270
7	0.004	0.1	Zn	−0.013	0.001	0.013

The relationship among the metals studied was investigated using Pearson Correlation Coefficient as well as Principal Component Analysis (PCA). Cd and Ni show strong positive correlation ($r = 0.615$) to one another, while As and Pb ($r = 0.385$) and Ni and Pb ($r = 0.360$) show moderate correlation in lichen. With ($r = 0.505$) Cd also shows strong correlation with Ni, in moss. The same strong correlation is also observable between Zn and Cr ($r = 0.431$). However Ni shows relatively moderate correlation with Pb ($r = 0.363$) and Zn ($r = 0.397$).

The PCA results are shown in Tables 37.1 and 37.2 for lichen and moss. The top three highest eigen-values of the principle components (PC) were retained. The total variance explained by the three PC was 89.5 % for lichen and 86.9 % for moss. For lichen, the first factor is loaded with As, Cd, Cu, Ni and Pb, while Cr in the second factor. No obvious association of heavy metals was observed in the third factor. Although the first factor elements could be associated to human activities, however the less enrichment (low AF) showed by As, Cu, Ni and Pb indicated that they are mainly represent the windblown dust contribution from soil of the study area (Dragovic and Mihailovic 2009). The Cr in lichen exhibit airborne transfer from diesel combustion from diesel-fueled vehicles (Bajpai et al. 2011), that are the most common form of transportation for agricultural products in the area.

The first two PCs for moss do not indicate any association between metals however the third factor is loaded with Cd and Ni (Table 37.2). This observation is

Table 37. 2 PCA variance and factor loadings of heavy metals in moss

Component	Eigen-value	% of variance	Element	Factor loading		
				1	2	3
1	1.190	59.1	As	−0.364	0.146	−0.213
2	0.292	14.5	Cd	−0.453	0.224	0.573
3	0.267	13.3	Cr	−0.275	−0.952	0.097
4	0.129	6.4	Cu	−0.522	0.064	−0.642
5	0.090	4.5	Ni	−0.367	0.099	0.443
6	0.042	2.1	Pb	−0.423	0.089	−0.084
7	0.004	0.2	Zn	0.023	0.004	0.015

consistent with the correlational study described earlier. Based on the anthropogenic factor (AF), Cd was enriched, not Ni. As mentioned earlier Cd originated from solid waste incineration and phosphate fertilizers known for having strong affinity to organic matter, especially at the moss exchange sites (Dragovic and Mihailovic 2009). Ni in moss originated from the same source as those found on lichen.

Conclusion

Finally, the study has shown the applicability of using local moss and lichen species for bio-monitoring of heavy metal pollutants. Of the seven metals investigated only Ni and Cd indicated the occurrence of anthropogenic enrichment.

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Chapter 38
Source Discrimination of PAHs in Industrial Soil of the Persian Gulf Coast

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Abstract The purpose of this study is to use environmental fingerprinting technique and to identify oil spills and their relationship with the oil derived from known oil fields. This is the first comprehensive study on PAHs distribution as oil spill markers in the Persian Gulf to investigate petroleum contamination in soil. Soil samples (0–10 cm) were collected from industrial zone. The results indicated that total PAHs range from 460 to 1730.4 $ng.g^{-1}$ for industrial soil. Polycyclic aromatic hydrocarbons in industrial area showed high concentration and it is associated with petrogenic input as these sites are located near gas and oil fields. Analysis of the results and application of biomarker ratios such as MP/P ratio showed that the main source of PAHs input is petrogenic sources. Analysis of all samples showed that contamination in the study area is derived from direct inputs of petroleum products and crude oil.

Keywords PAHs · Industrial soil · Molecular markers · Persian Gulf

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Highlights

- PAHs contamination level in industrial zone soil was moderate to high.
- Most of stations exhibited the presence of 3 rings PAHs.
- PAHs are derived from petrogenic sources.
- Petrogenic signature of PAH showed weathering impact of alkylated low molecular PAH.

Introduction

The Persian Gulf, located in southwestern Asia, is a vast expansion of the Indian Ocean situated between Iran and the Arabian Peninsula. The Persian Gulf and its coastal areas are the world's largest reservoir of crude oil. Industries in the region are highly correlated with oil and gas activities. The region is recognized as major economic income for the Gulf countries. The region is plagued by petroleum pollution as a result of oil spills. There is a severe lack of data on the study of oil pollution in the northern coast of Persian Gulf. Therefore, this study focus on qualitative and quantitative aspects of the oil pollution especially the investigation of compound-specific PAHs. More noticeably, they are generated normally from nature and anthropogenic sources. PAHs in the environment were originated principally from two different anthropogenic sources (combusted/pyrolyzed fossil fuel versus spilled petroleum, or pyrogenic versus petrogenic (Giger and Blumer 1974; Lee et al. 1977). Petrogenic PAHs are normally abundant in lower molecular weight compounds. Lower molecular weight PAHs can easily undergo weathering as compared to higher molecular weight PAHs.

In order to realize the fate and behavior of spilled oil in the environment, to differentiate spilled oils and to link the molecular markers to the original sources of spilled oils on the environment, this research has been conducted to carry out within the northern coasts of Persian Gulf. This study focused on the polycyclic aromatic hydrocarbons contamination, in the northern coasts of Persian Gulf in order to study petroleum pollution in industrial soils in Bushehr province.

Materials and Methods

Study area

This province with the area around 27653 km^2 is situated in the northern part of Persian Gulf and has 725 km border with the Persian Gulf, so it is economically and ecologically one of the most important provinces of the country. This province has 62.5 % of gas reservoirs, 8 % of oil reservoirs of Iran.

Sampling Location

Industrial samples of soil were collected from Bushehr province.. Samples were selected from 5 industrial samples. Relative location of each sampling site was investigated first, using aerial and satellite images. Soils were taken from 10 cm of top soil using quadrate which is thrown thrice randomly. The samples were stored in the ice box and darkness during transportation to the laboratory of Persian Gulf Research and Studies Center (PGRSC) and kept frozen (−20 °C) till being analyzed.

Analytical Procedure

The soil samples were dried with sodium sulphate anhydrous, spiked with 100 μL of 10 $\mu g.g^{-1}$ deuterated surrogates (naphthalene-d_8, anthracene-d_{10}, benzo(a)anthracene-d_{12} and perylene-d_{12}) and 100 μL of a 10 $\mu g.g^{-1}$ internal injection standard (p-terphenyl-d_{14}) (Zakaria et al. 2002). The samples were then subjected to soxhlet extraction with 350 ml dichloromethane for 8 h (Anyakora et al. 2005; Culotta et al. 2006; Nikolaou et al. 2009). Extracted samples were purified and fractionated into an aliphatic and an aromatic fraction through two-step silica gel column chromatography (Zakaria et al. 2001; Yim et al. 2005; Boonyatumanond et al. 2006). The hydrocarbon fraction was subsequently injected into the GC–MS using the Selected Ion Monitoring (SIM) mode. The recovery of surrogates generally ranged from 50 to 114 % of the spiked concentration. Samples with recoveries below 50 % were re-analyzed.

Result and Discussion

The values of total PAHs (Σ-PAHs) ranged from 459.9 to 1730.4 $ng.g^{-1}$. The highest concentrations of Σ-PAHs in sediments was found at site S9 in phase 1 of the Southern Pars gas field (1730.4 $ng.g^{-1}$) followed by S6 (1429 $ng.g^{-1}$), S8 in (1126.17 $ng.g^{-1}$), S7 in phase 2,3 of Southern Pars gas field (820.06 $ng.g^{-1}$), S6 in phase 9,10,17,18 of Southern Pars gas field (715.81 $ng.g^{-1}$). It can be seen that the highest concentrations was in S9 followed by S6 which are related to phase1 of gas refinery and petro Chemistry Company respectively. The single most striking observation to emerge from the data comparison was that data from aklylated phenanthrene was higher than the others, specifically within 3,2 methylphenanthrene. The highest concentrations were found in S6 with the concentration of 391.6 and 274.74 $ng.g^{-1}$, respectively. The alkyl PAHs often tend to be more persistent, have higher Kows, be less volatile, be less soluble, be less mobile, bioaccumulate more, have different chemical/physical characteristics, be equally or more toxic, be equally phototoxic, and be equally or more carcinogenic than the

parent compound PAH. Studies conclude that the toxicity of oil appears to be a function of its di-aromatic and tri-aromatic hydrocarbons, which includes three-ring hydrocarbons such as phenanthrene (Zakaria et al. 2002). As a result it indicates a distinguished difference among S6, S7, S8, S9 and S10 which is located in the petrochemical site and other samples as that site produces more petroleum products.

Applying molecular markers of PAHs lead to identify source of them according to their distribution in the environment. The contribution of petrogenic PAHs in these stations was noticeable. The ratio of Flu/Flu + Pyr ratios calculated for 3 samples (S6, S7, S8) were less than 0.4 (from 0.3 to 0.33). Although, this ration was more than 0.4 for the stations S9 and S10 (from 0.58 to 0.68) suggesting pyrogenic inputs at these two stations. The ratio Flu/Flu + Pyr revealed multiple PAHs sources (petrogenic and pyrogenic). A ratio of Pyr/Flu indicates the differentiation between petrogenic and pyrogenic source. The value >1 implies on petrogenic and <1 pyrogenic inputs. Based on this ratio the stations (S6, S7, S8) were more than unity hence, it confirms previous findings. However, in stations S9 and S10 the amounts were less than unity (0.74, 0.48) and it emphasizes partially on the pyrolytic inputs as fuel combustion simultaneously with the large inputs of unburned fuels and petroleum products. The ratio of methylphenanthrene/phenanthrene (MP/P) has been applied by other researcher groups (Takada et al. 1990; Zakaria et al. 2002). (MP/P) ratio which is used for discrimination between petrogenic and pyrogenic sources of PAHs was highly greater than 1 while it should be <1 in combustion mixture and between 2–6 in unburned fossil fuels (Youngblood and Blumer 1975; Garrigues et al. 1995). In other word, it confirms the petrogenic inputs of the PAHs. LMW/HMW PAHs ratio gives supportive evidence correlating with the low MP/P ratio for all stations, suggesting that the origin of PAHs is from petrogenic sources.

Conclusion

This research found that industrial soil were contaminated by fossil fuels and petroleum products. The result also indicated the existence of both pyrogenic and petrogenic sources.

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Chapter 39
Passive Treatment of Acid Mine Drainage with Limestone, Calcareous Rock and Serpentinite

Norinsafrina Mustaffa Kamal and Shamsul Kamal Sulaiman

Abstract Experiments of acid mine drainage (AMD) passive treatment were conducted to evaluate the performance of alkaline materials in increasing pH level and reducing heavy metals concentrations in AMD samples from effluent of an abandoned copper mine in Mamut, Sabah. The tests were performed using 40 L container filled with the alkaline materials and the mine water samples at various retention times. Results of the experiments showed that all materials were capable in achieving pH targets required for neutralisation of the AMD, Fe, Al and Cu were almost removed completely whilst Mn has shown a poor reduction.

Keywords Passive treatment · Acid mine drainage · Limestone · Calcareous rock · Serpentinite

Highlights

- Limestone has the best performance in raising pH level into neutral region.
- Calcareous rock has the best overall performance in removing heavy metals.
- Raise in pH level most probably related to dissolution of carbonate content.
- Consistency in pH level increment reflects the stability of metal hydroxides.
- pH is an important factor in removing heavy metals contents from the mine water.

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Introduction

An abandoned copper mine which is located in Mamut, Sabah has a serious acid mine drainage (AMD) issue. Sulphide minerals from the wastes oxidised when left exposed to air and water. Thus release heavy metal ions such as Fe^{2+}, Fe^{3+}, Al^{2+}, Mn^{+} and Cu^{2+}. AMD can pollute surface and ground water, harming the health of aquatic flora and fauna, causing heavy metal accumulation in living organisms (Sprynskyy et al. 2006). Active treatment and passive treatment are two common types of treatments for AMD. Active treatment involves addition of neutralising agent to the source of the AMD while passive treatment covers methods for pH increment and heavy metals removals via a constructed treatment such as wetland (Fripp et al. 2000). This study aims to examine the effectiveness of alkaline materials such as limestone, calcareous rock and serpentinite in terms of raising pH level and reducing concentrations of heavy metals in the AMD passive treatment.

Materials and Methods

Alkaline materials of limestone, calcareous rock and serpentinite with 30–50 mm in diameter were filled into the 40 L container until 2/3 of its height (Fig. 39.1). The mine water sample from the pit lake of Ex-Mamut copper mine was filled into the container until 10 cm freeboard. The retention time were fixed to 1−6 h with time interval of 1, 6−24 h with interval time of 3 h and the final 36 h. Sample of effluent was collected at each interval and were analysed for pH, alkalinity and, Fe, Al, Mn and Cu concentrations.

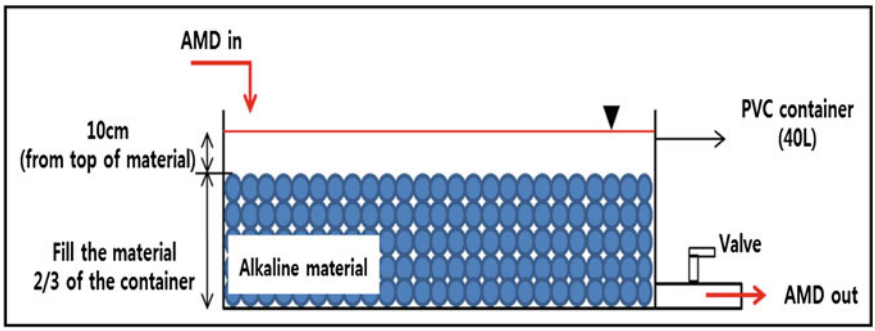

Fig. 39.1 Passive treatment experimental setup

Results and Discussion

Changes in pH

Limestone has the best performance followed by calcareous rock and serpentinite (Fig. 39.2). It took the minimum retention time of 1 h for the limestone to reach the neutral pH. The calcareous rock affected pH condition intensely for the first 6 h and reached pH 7 after 12 h of treatment and remained unchanged until the final hour. Changes in pH by treatment with the serpentinite started progressively and achieved pH 7 after 12 h of retention period. Subsequently, the pH maintained in the mild alkaline region until the end of the experiment. Increments in pH levels were probably related to dissolution of carbonate contents which in turns influencing alkalinity of the water sample (Wilson 2011). Table 39.1 presents treated

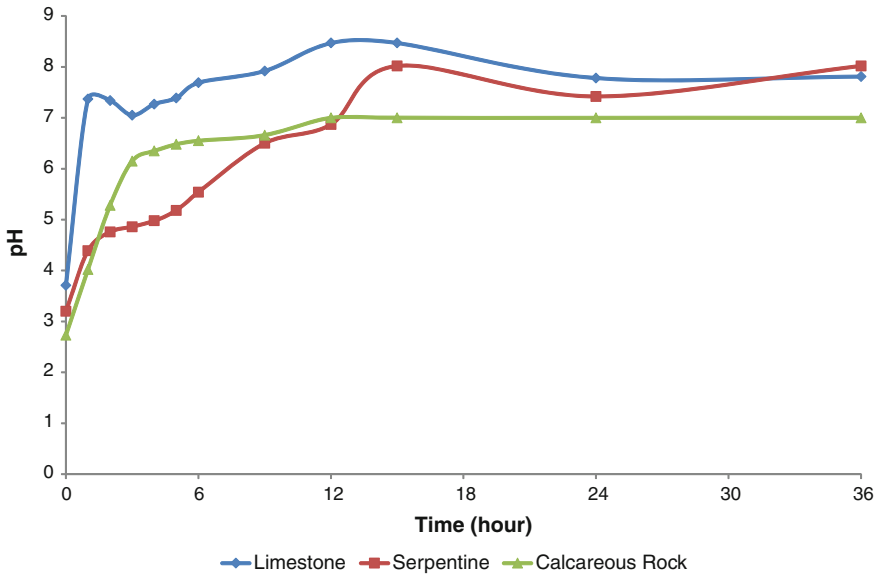

Fig. 39.2 Changes in pH by the Treatment with Limestone, Serpentinite and Calcareous Rock

Table 39.1 Range of water samples Alkalinity by treatment with the Alkaline materials

Alkaline material	Range of Alkalinity (mg/l as $CaCO_3$)
Limestone	440–1400
Calcareous Rock	240–1280
Serpentinite	40–960

water sample with high alkalinity were recorded after reactions with the limestone followed by the calcareous rock and the serpentinite. Thus, it could be suggested the limestone may have the highest carbonate content among all materials.

Removals of Heavy Metals

Graphs in Figs. 39.3–39.5 shows the calcareous rock outweighed limestone and serpentinite in terms of removing heavy metals from the water samples. Most heavy metals were almost removed completely ($\sim$100 %) after 3 h of retention time. Limestone took about 9 h to remove all metals except for Mn from the solution and serpentinite required about 12 h of retention period. This is most probably due to consistency in pH level increment by the calcareous rock which reflects the stability of metal hydroxide precipitation (Hendricks 2005). Overall, Fe is the quickest to be removed due to the fact that Fe starts to precipitate at pH $>$ 3.5 and forms iron (III) hydroxides (Balintova and Petrilakova 2011). On the other hand, Mn was the slowest to be removed because it only precipitates out at pH $>$ 8.5 (Silva 2012). The graphs show removals of the metal ions is in the order of Fe $>$ Al $>$ Cu $>$ Mn. All heavy metals were probably being removed by precipitation as Fe starts precipitates at pH $>$ 3.5, Al precipitates at pH $>$ 5, Cu precipitates at pH $>$ 4 to 6 and Mn precipitates at pH $>$ 8.5 (Armenante 1997). Clearly, pH is an important factor in the removal of the heavy metals.

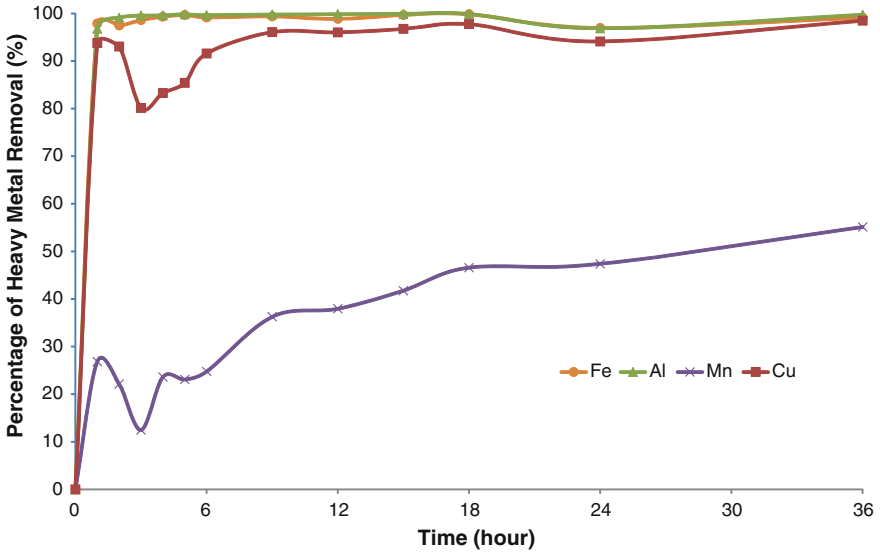

Fig. 39.3 Percentage of heavy metal removal by the treatment with Limestone

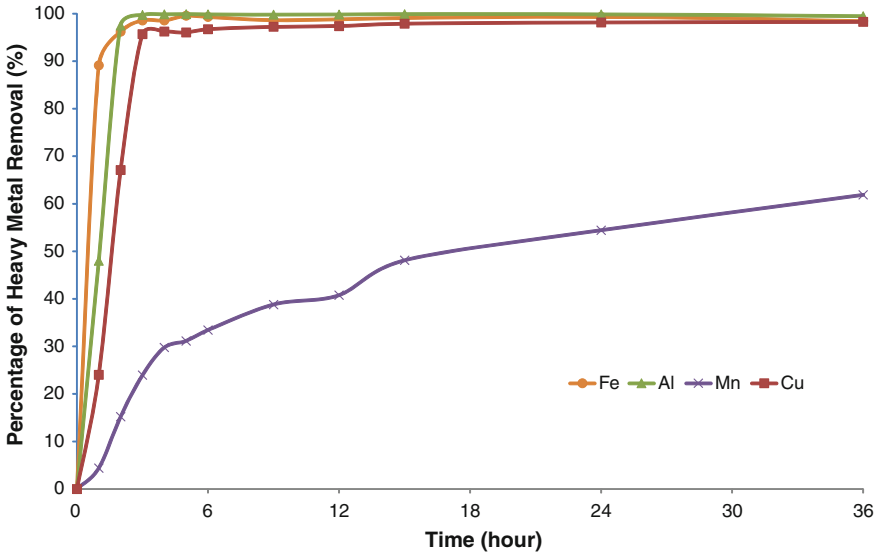

Fig. 39.4 Percentage of heavy metal removal by the treatment with Calcareous Rock

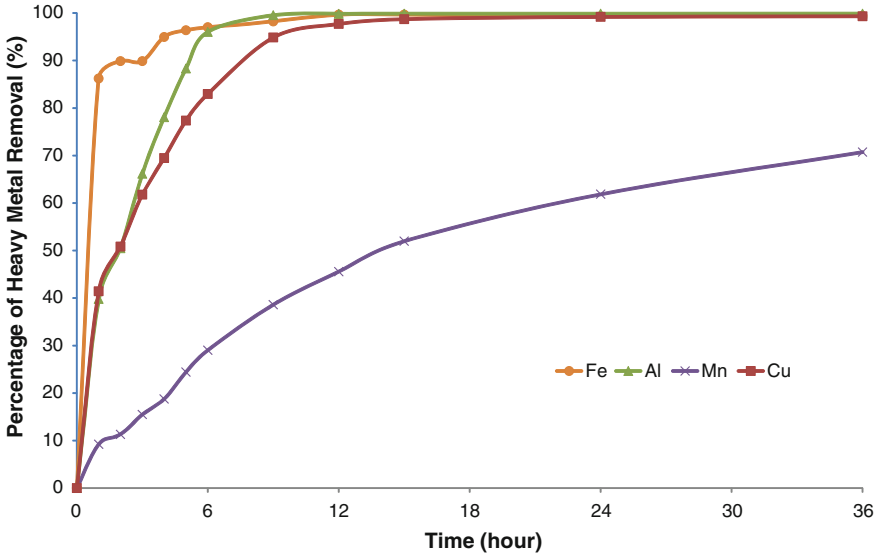

Fig. 39.5 Percentage of heavy metal removal by the treatment with Serpentinite

Conclusion

Limestone has the best performance in raising pH level into neutral region and calcareous rock has the best overall performance in removing heavy metals concentrations from the Ex-Mamut copper mine water sample. Serpentinite only has an average performance for increasing pH and removing heavy metals contents. This study has shown that the limestone only took 1 h to reach neutral pH and the calcareous rock needed at least 3 h for heavy metals removals to be completed (except for Mn). pH is an important factor in the removal of the heavy metals. Nevertheless, cost effective materials and sustainable resources have to take into consideration to determine the worthiness of the alkaline materials to be used in the passive treatment system of AMD.

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Chapter 40
Biosorption of Lead (Pb) by Three Bacillus species (*Bacillus cereus, Bacillus pumilus* and *Bacillus subtilis*) Isolated from *Scirpus grossus*

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Abstract Phytoremediation technology recently becomes a potential solution to address heavy metal pollution in aquatic environment. In this technology, the bacteria that grow in root zone of plants have an important role beside plant species itself. Study on lead biosorption using three rhizobacteria species isolated from *Scirpus grossus* namely *Bacillus cereus, Bacillus pumilus* and *Bacillus subtilis* was conducted to determine their ability to adsorb Pb from different concentrations of lead. Results would enhance the performance of phytoremediation process in future studies.

Keywords *Bacillus cereus* · *Bacillus pumilus* · *Bacillus subtilis* · Lead exposure · Bacteria growth

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Highlights

- Bacteria that grow in root zone of plants have an important role in phytoremediation.
- Lead has affected *B. cereus*, *B. pumilus* and *B. subtilis* growth on the medium of TSB.
- Although Pb had affected growth, *S. grossus* showed tolerance towards the heavy metals.

Introduction

Heavy metals pollution on aquatic environment is one of the global problems. Several methods have already been used, but most of them are costly and could not reach their optimum performance (Tangahu et al. 2011b). Recently, phytoremediation technology has been identified as an effective and affordable technological solution for contaminated soil and water by extraction or removal of inactive metals and metal pollutants using plant (Tangahu et al. 2013a, b). The advantages of this technology compared to others are aesthetically pleasing, the effectiveness in contaminant reduction, low cost, applicable for wide range of contaminants, environmental friendly method and less disruptive than current techniques (Tangahu et al. 2011b). However, there are several limitations to this technology which includes the knowledge on the root depth, soil chemistry, level of contamination, the amount of biomass produced, the age of plant, the contaminant concentration, the impacts of contaminated vegetation, climatic condition and the time-consumed for these methods (Tangahu et al. 2011b).

This study was conducted to assess the capability of *S. grossus* in phytoremediation of lead from wastewater and to increase the effectiveness of phytoremediation process by the plant. The growth performance of *B. subtilis* in medium containing Pb and its capability to adsorb lead (Pb) with regards to phytoremediation process will also be examined.

Materials and Methods

The species of *B. cereus, B. pumilus* and *B. subtilis* were isolated from rhizosphere of *S. grossus*. Concentration of Pb for exposure were 0 (control), 200 and 600 mg/L respectively. Observations on the growth of bacteria within the medium of TSB containing 0 (control), 200 and 300 mg/L Pb were made. Biosorption test was conducted for 150 mg/L Pb.

Results and Discussion

The growth profile of *B. cereus*, *B. pumilus* and *B. subtilis* on TSB medium is shown in Fig. 40.1.

The growth on TSB medium containing 0, 200 and 600 mg/L Pb was conducted to compare the effect of Pb on bacterial growth. The results are shown in Fig. 40.2, 40.3 and 40.4.

Biosorption by bacteria cell reached 8.01, 28.68 and 49.2 mg/g dry weight of *B. cereus, B. pumilus* and *B. subtilis* respectively (Fig. 40.5, 40.6, 40.7).

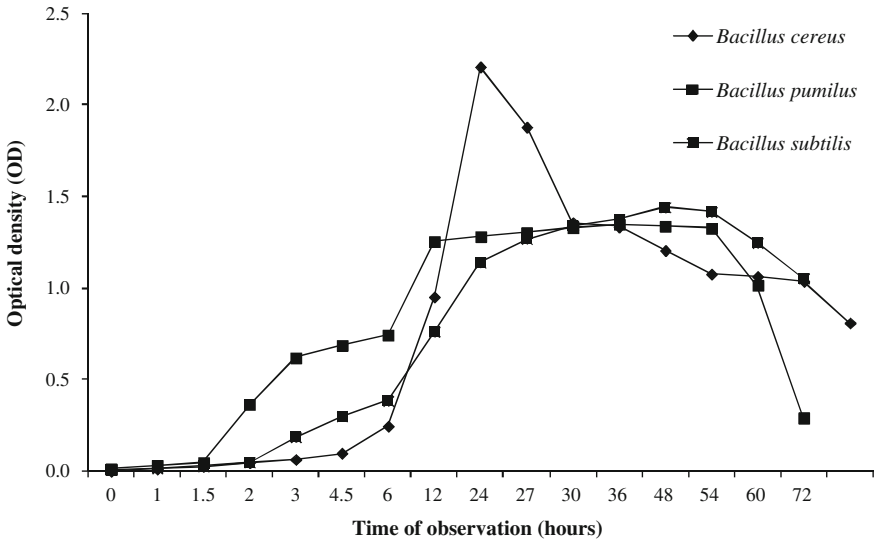

Fig. 40.1 Growth profile of *Bacillus cereus*, *Bacillus pumilus* and *Bacillus subtilis* on TSB medium

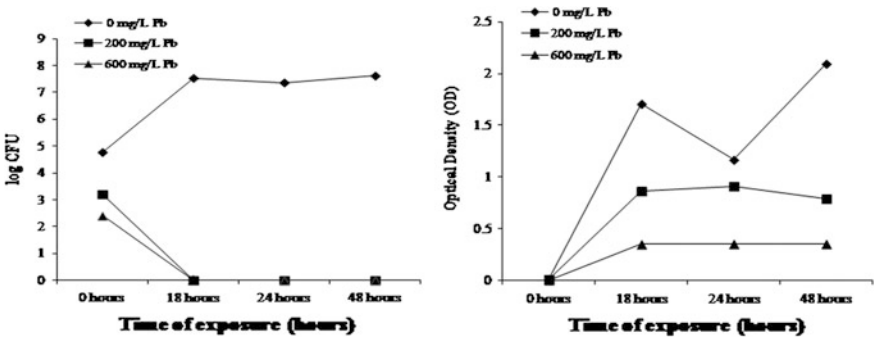

Fig. 40.2 The growth of *Bacillus cereus* on 0, 200 and 600 mg/L Pb

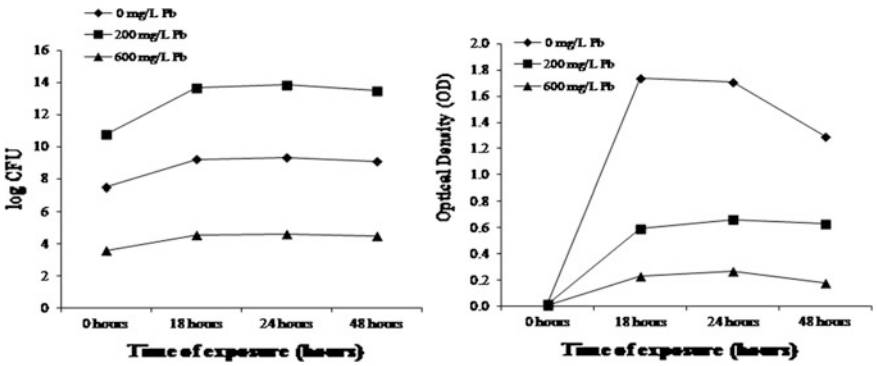

Fig. 40.3 The growth of *Bacillus pumilus* on 0, 200 and 600 mg/L Pb

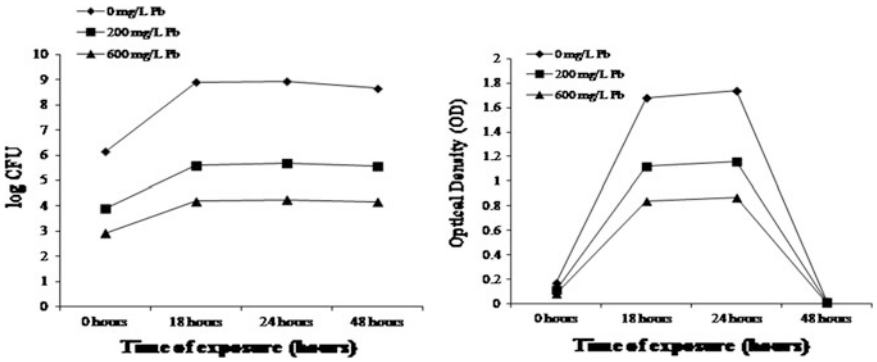

Fig. 40.4 The growth of *Bacillus subtilis* on 0, 200 and 600 mg/L Pb

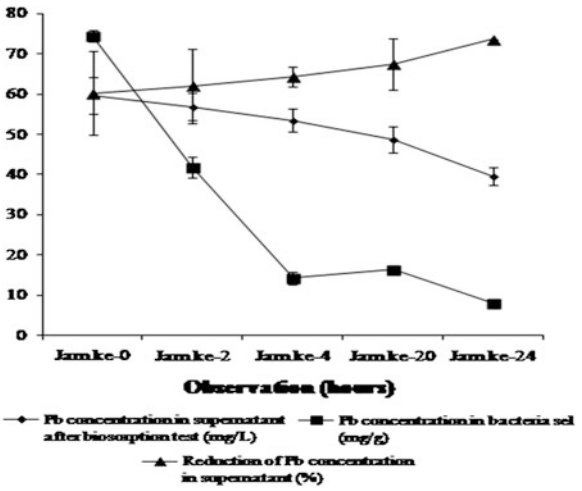

Fig. 40.5 *Bacillus cereus* performance on biosorption test

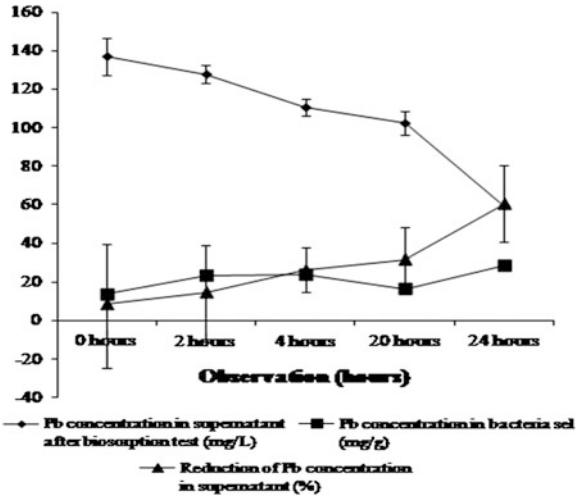

Fig. 40.6 *Bacillus pumilus* performance on biosorption test

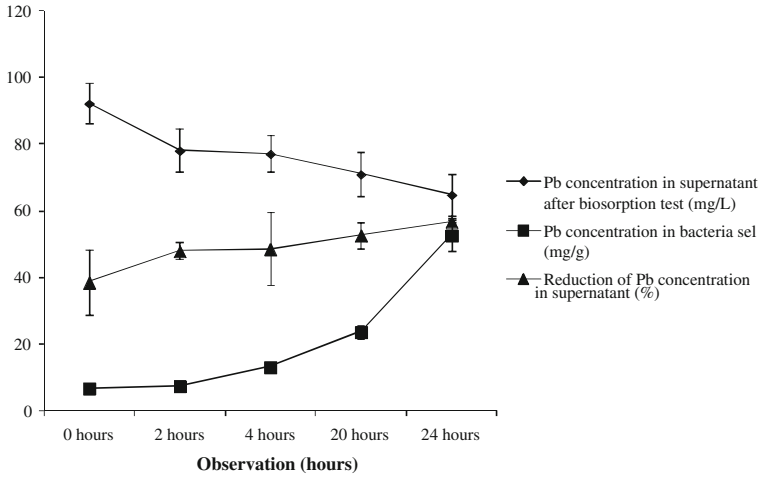

Fig. 40.7 *Bacillus subtilis* performance on biosorption test

Conclusion

The reduction of CFU for *B. cereus* reaches 100 % for both 200 and 600 mg/L Pb, whereas the OD reduction reaches 36.0 and 73.0 % respectively for 200 and 600 mg/L Pb. The CFU for *B. pumilus* increased 47 % and decrease 51 % respectively for 200 and 600 mg/L Pb, whereas the OD was reduce to 47.0 and

81.0 % for each concentration. For *B. subtilis* the CFU and OD measurement showed reduction of 36.5 and 33.3 % respectively for medium with 200 mg/L Pb and for medium with 600 mg/L Pb, the reduction were 52.4 and 50.0 % respectively.

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Chapter 41
Surfactant-Alcohol Experiments for Dense Non-Aqueous Phase Liquid Removal: A Review

Nor Asni Azizan, Samira Albati Kamaruddin, Shreeshivadasan Chelliapan, Norazli Othman and Wan Nor Azmin Wan Sulaiman

Abstract The aim of this paper is to review and to summarize the existing laboratory experiment studies from other researchers regarding surfactant alcohol experiment for dense non-aqueous phase liquid (DNAPL) removal, their approach, method of measurement, factor consideration and their findings together with result discussion. This review includes the selection of surfactant-alcohol, their important characteristics in the remediation of DNAPL, the laboratory experimental setup using 2-D laboratory model and enhanced remediation of DNAPL from recent laboratory studies. It has been shown in the laboratory experiment studies that solubilization is the dominant removal process of DNAPL. After surfactant concentration reached the critical micelle concentration, interfacial tension between DNAPL, water and soil decreased. This has resulted in increasing of solubility and removal rate of DNAPL. Mobilization also takes place in the removal process. However, most of the laboratory experiments did not consider other factor such as soil permeability, soil texture, and interfacial tension between soil and DNAPL. Further studies of surfactant-alcohol flushing shall be considered in the near future.

Keywords Non-aqueous phase liquid · Groundwater · Remediation · Laboratory model · Solubilization

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Highlights

- Surfactant increase the removal rate of DNAPL.
- Surfactant remediates DNAPL with solubilization and mobilization mechanism.
- The 2-D laboratory models physically stimulate the DNAPL migration.

Introduction

Dense non-aqueous phase liquid (DNAPL) is a group of liquid in soil and groundwater that has been exposed to hydrocarbon liquid spills or leaks. The DNAPL is denser than water, tends to sink below groundwater table and will stop when reached impermeable layer. The liquid is toxic and hazardous to human, animals and natural habitats (ATSDR 2002).

Surfactant flushing is one of the remediation treatment used to remediate DNAPL such as trichloroethylene (TCE). Trichloroethylene is the most frequent groundwater contaminant detected at hazardous waste sites (National Research Council 2005). It has been identified as a cost-effective treatment system. During the treatment, solubility of organic contaminants can be increased and helped in removing the DNAPL.

Materials and Methods

Selection of Surfactant-Alcohol

Surfactant has been widely used in remediation of DNAPL. Solubilization and mobilization are the two main mechanism involved in the remediation. Surfactant has polar and non-polar ends which help in forming micelles in certain condition. When the micelle starts to form, the surfactant concentration reached critical micelle concentration (CMC). Solubility of DNAPL increases due to hydrophobic compound in micelles above the CMC. Solubilization is a dominant removal process and little mobilization occur when viscous pressure of the DNAPL is less than capillary pressure of porous medium (Jeong and Corapcioglu 2005).

The selection of the surfactant-alcohol should consider some particular effects and properties to ensure the effectiveness of DNAPL remediation. The surfactant-alcohol commonly depends on the ethylene oxide content. The greater the ethylene oxide content, the greater the solubilization effect of surfactant. The moles of ethylene oxide function should be more than 12 mol as the solubilization properties. The hydrophilic-lipophilic balances are more precise measure for surfactant-alcohol with more than 15 mol of ethylene oxide. The surfactant should maintain the temperature limit under the cloud point. The cloud point is the

Table 41.1 Existing Laboratory Studies of DNAPL

Type of model	DNAPL source	Surfactant	Porous media	Reference
Micro model 0.013 × 6.4 × 4[1] 0.013 × 5.9 × 4.2[1]	Trichloroethylene	Sodium C14-16 olefin sulfonate	Homogeneous	(Jeong et al. 2000), (Jeong and Corapcioglu 2005)
Soil column 4.8 i.d[2]	Polyoxyethylene (20) sorbitan monooleate	14C-labelled dodecane	Homogeneous	(Abriola et al. 1993)
Soil column50 long × 2.42 i.d[2]	Automatic transmission fluid	Alcohol ethoxylate	Homogeneous	(Ang and Abdul 1991)
Soil column 91.44 long × 5.08 i.d[2]	2,3-dimethyl pentane 2,2,4-trimethylpentane 2,2,5-trimethyhexane	Hexadecyl (C16) diphenyl oxide disulfonate	Heterogeneous	(Sabatini et al. 1997)
Soil column 4.8 i.d[2]	Tetrachloroethylene	Polyoxyethylene Sodium, diamyl, dioctyl, dihexylsulfosuccinate	Homogeneous	(Pennell et al. 1994)
Soil column 15.4 × 5.0 o.d[3]	1,2,4-trichlorobenze	Sodium diphenyl oxide disulfonate	Homogeneous	(Lee et al. 2002)
Soil column15.0 height	Dichlorobiphenyl	Polyoxyethylene (23) lauryl ether, Polyoxyethylene (20) sorbitanmonooleate, Sodium dodecyl sulfate	Heterogeneous	(Chu and Kwan 2003)
4 mL glass tube	Tetrachloroethylene,	Pure-hydrophobe primary alcoholethoxylates, Witconol SN-120 primaryalcoholethoxylate,	Heterogeneous	(Cowell et al. 2000)
	Trichloroethylene, Chlorobenzene, 1,2-dichlorobenzene 1,1,2-trichloroethane	Tergitol 15-S series secondary alcohol, Tagatseriesethoxylatedglyceryl, Myrj and Tweenseriesethoxylated, Fatty acid estersethoxylatedsorbitan		
61 × 91	Tetrachloroethylene, Trichloroethylene	Polyoxyethylene (20) sorbitanmonooleate	Homogeneous	(Saenton et al. 2002)
50 mL glass tube	Hydrophobic dye, DO-11	Polyoxyethylene (20) sorbitanmonooleate, Polyoxyethylene (23) laurlether	Heterogeneous	(Chu 2002)

[1] Height × width × length
[2] Inner diameter
[3] Outer diameter

temperature at which a surfactant drops out of solution causing the solution to be turbid. The common use of surfactant-alcohol which have the solubilization properties is the nonionic surfactant-alcohol such as ethoxylated octyl phenols (Cowell et al. 2000).

Laboratory Experimental Setup

The built of 2-D laboratory models should have an adequate height and surface dimension to physically simulate the DNAPL migration in different zones of subsurface systems using the photographic method. The 2-D model was selected from the reviews given by previous researchers (Bob et al. 2008; McNeil et al. 2006; Oostrom et al. 2007; Schincariol 1993). Table 41.1 shows the existing laboratory studies of DNAPL remediation using different laboratory models, the DNAPL sources, the selected surfactant to remediate the DNAPL and the porous media used in the laboratory model.

Results and Discussion

Enhanced Remediation

Recent laboratory studies have contributed a major affect in remediation of DNAPL on field site. From the laboratory studies, researchers can study and investigate how the surfactant act and react to remediate DNAPL and factors contribute in reducing the dangerous DNAPL from the environment.

Most of the researchers have considered the solubilization, mobilization, displacement and physical forces analysis of surfactant in porous media to visualize the DNAPL removal (Abriola et al. 1993; Jeong and Corapcioglu 2005; Jeong et al. 2000). Surfactant partitioning which involved surfactant mixture polydispersity, surfactant hydrophobicity and interfacial tension also have been discussed previously (Cowell et al. 2000). This followed by the investigation of effect of heterogeneity of soil to identify the effectiveness of surfactant remediation technique (Lee et al. 2002; Saenton et al. 2002), as well as micelles in contributing removal of hydrocarbon (Chu 2002; Chu and Kwan 2003).

Conclusion

It has been shown in the laboratory experiment studies that solubilization is the dominant removal process of dense non-aqueous phase liquid. After surfactant concentration reached the CMC, the interfacial tension between DNAPL, water

and soil decreases. This has resulted in increasing of solubility and making the removal rate of DNAPL increases. Mobilization also takes place in the removal process. However, most of the laboratory experiment studies did not consider other factor such as soil permeability, soil texture, interfacial tension between soil and DNAPL, etc. More potential factor in surfactant-alcohol flushing must be taken into consideration in the future study.

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Chapter 42
Evaluation of Various Water Quality Indices for Water Quality Assessment of Sg. Sarawak

Nurzawani Md Sofwan and Sim Siong Fong

Abstract Water quality is a term used to describe the chemical, physical and biological characteristics of water in respect to its suitability for a particular purpose and related with a set of standards. The knowledge of water quality and its content are essential to track any influx of water pollutants that are detrimental to human and ecosystem. The study aimed to examine the water quality status of Sg. Sarawak particularly in Waterfront and Satok Bridge based on three water quality monitoring approaches namely Water Quality Index (WQI), average NWQS and the extended NWQS (eNWQS). The eNWQS was designed based on Partial Least Square (PLS) regression where multivariate water quality data is correlated to training samples created according to the guideline of NWQS. Generally, the average NWQS and eNWQS corresponded well with the WQI in determining the river water quality status. The river water quality for both sampling points was categorized as slightly polluted with the index ranged from 62 to 68. In terms of sensitivity, the average NWQS approach was less sensitive because only discrete classes of I, II, III, IV and V were considered. The eNWQS shows better sensitivity but further study is required to verify the sensitivity level between eNWQS and WQI. This study emphasizes that the eNWQS may be useful and practical.

Keywords Water quality · Water quality assessment · Water quality index · Extended National Water Quality Standards (eNWQS)

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Highlights

- The WQI serves as a basis for water quality assessment.
- The average NWQS and extended NWQS was positively correlated with WQI.
- The eNWQS is feasible as an alternative tool for water quality monitoring.

Introduction

Water component which is known as hydrosphere serves as a link between all other environmental components namely the atmosphere, lithosphere and biosphere. As a result, water acts as a trapping pool to all forms of pollutants in the environment (Lau 2011). With respect to this, water quality assessment is vital to monitor the water bodies in relation to pollution load categorization and to evaluate the suitability of water for certain uses.

In Malaysia, water quality monitoring programme is started since 1978 by a governing body, Department of Environment (DOE). It is called Water Quality Index (WQI) that is used to evaluate the status of river water quality by ranking it into five classes according to its appropriate usage. WQI is a well-established and effective method for determining river water quality in Malaysia. The National Water Quality Standards (NWQS) for Malaysia was developed serving as a benchmark to provide recommended water quality criteria according to parameters. The NWQS offers detail classification of the water quality according to parameters. Mathematically, there is no correlation between both NWQS and WQI in the way water quality is expressed.

Despite the advantages of WQI, there are some limitations of WQI. A large amount of data that is generated over time making the task of evaluating the water quality more complex and challenging because requires the integration of numerous parameters. Moreover, the methods used to calculate WQI are not based on the parameter themselves, but rather on their sub-indices whose values are obtained from the best-fit equations of rating curves (Gazaaz et al. 2012). Some parameters in the index equations can influence the final score without valid justification due to limited parameters involved (Ocampo-Duque et al. 2006).

For the past few decades, many advanced statistical approaches have been established integrating advances in computing allowing complicated calculations involving high dimensional data and advanced modeling. A water quality index has been designed internally based on the guideline of NWQS where Partial Least Squares (PLS) regression is adopted for prediction. This model is more flexible where the number of parameters involved can be expanded or restricted as necessary depending on the availability of the data. It is referred to as the extended National Water Quality Standard (eNWQS) where multivariate water quality data is correlated to the classes according to NWQS.

The research aims to apply the newly developed eNWQS to assess the water quality of Sg. Sarawak and compare the results with the traditional WQI and

average NWQS. The sensitivity of these indices in evaluating overall water quality status is also examined.

Materials and Methods

Description of the Study Area

Sg. Sarawak catchment is huge and has two main tributaries namely Sg. Sarawak Kiri and Sg. Sarawak Kanan that converge into Sg. Sarawak. The study was conducted in two locations in Sg. Sarawak near to Waterfront and Satok Bridge with many types of land uses such as recreational, residential and commercial that consumed large quantity of clean water, resulted in large quantity of treated and untreated wastewater discharge.

Water Quality Analysis

In this study, six parameters required for WQI calculation namely pH, dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solid (TSS) and ammoniacal-nitrogen (NH_3-N) were measured. Average NWQS and the eNWQS also employed the same parameters for statistical comparison. The analysis involved in situ measurement using designated instrument as well as laboratory analysis. All analyses were carried out according to the USEPA approved method for water quality.

Calculation of Water Quality Index (WQI)

The WQI calculation applied the formula established by the Department of Environment, Malaysia. The WQI was developed in three steps. The first step involved parameter selection and weight assignation on each parameter by the panel of experts (Gazzaz et al. 2012). The second step is determination of quality function by calculating sub-index for each variable to generate its own rating curve on a scale of improving water quality from 0 to 100 (Kaurish and Younos 2007; Liou et al. 2004). Consequently, the resultant sub-indices (SI) were combined to give an overall WQI value according to the following formula;

$$\begin{aligned}\mathrm{WQI} = {} & (0.22 * \mathrm{SI_{DO}}) + (0.19 * \mathrm{SI_{BOD}}) + (0.16 * \mathrm{SI_{COD}}) + (0.15 * \mathrm{SI_{AN}}) \\ & + (0.16 * \mathrm{SI_{SS}}) + \left(0.12 * \mathrm{SI_{pH}}\right)\end{aligned}$$

Calculation of Average NWQS

The class for each parameter examined was averaged to represent the overall water quality of the river. For instance, if the class for DO is II, class for BOD is I, class for COD is III, class for pH is I, class for NH_3-N is II and class for TSS is I, the average NWQS will be 1.83. The value ranges between 0 and 5 with 0 corresponding to the worst level and 5 to the ideal level. This approach is not considered the exact value of the parameter, but only the class where the value fell within it.

Extended National Water Quality Standards (eNWQS) Model

The extended NWQS has been programmed and written in MATLAB 6.5 for routine water quality monitoring. The water quality data acquired from the study became the input in the system for automated calculation where the parameters used to establish the model were predefined. All the parameters were directly measured based on the class stipulated from the NWQS for Malaysia without transformed it into sub-index. The training sets adopted in this model was 1000, which means 1000 datasets for each parameter were created for all classes of NWQS. This index calculates the water quality as a continuous variable taking any value between 0 and 5 and beyond where the value closer to 0 exhibits least polluted water quality.

Results and Discussion

The river water quality for both sampling points was categorized as slightly polluted and within Class III of WQI. The highest WQI value of 68 was detected in Waterfront, whilst the lowest value of 62 was observed in both sampling points. The slightly polluted status was mainly attributed to numerous land use activities in the vicinity of the area such as residential, tourism and commercial. The comparison between three water quality indices is shown in Fig. 42.1.

The findings revealed that all three indices were fairly presented the water quality status. Overall, average NWQS and the eNWQS corresponded quite well with the well-established WQI. The WQI was compared to the other two water quality monitoring approaches as it served as a benchmark for water quality assessment in Malaysia. The results suggested that the average NWQS was less sensitive because it resulted in identical index for the same classes of variables in the water samples without considering the exact value. Thus, it did not give clear indication on the water quality changes.

The eNWQS model interpreted the water quality discreetly based on the parameter itself which gave sensitive identification of the health status of the river.

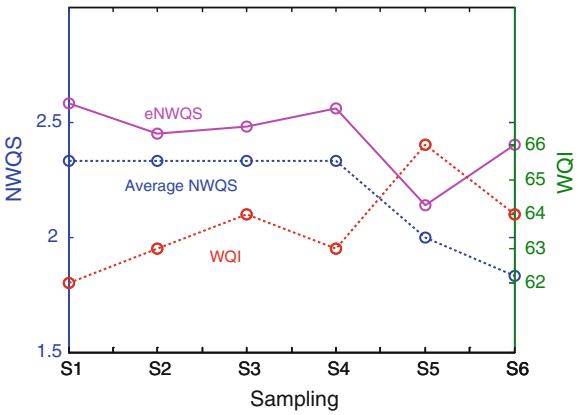

Fig. 42.1 Comparison between three water quality indices

In addition, the model simplifies computation of the WQI and saves substantial time and efforts. As for WQI, the methods used to calculate WQI was highly dependent on the sub-indices derivation which might influence the final computation.

Conclusion

The eNWQS and WQI were equally effective in determining river water quality status. Both approaches have their own sensitivity, however further study is desired to verify their sensitivity level. This study emphasizes that the eNWQS seems to be reliable and feasible to be used as an alternative for water quality monitoring.

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Chapter 43
Nauplii of Brine Shrimp (*Artemia salina*) as a Potential Toxicity Testing Organism for Heavy Metals Contamination

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Abstract This study was conducted using the 24 h cultured nauplii of brine shrimp (*Artemia salina*) as toxicity testing organism exposed to five selected trace elements (Cu, Zn, Cd, Ni, Fe). The objective was to determine the suitability of *A. salina* for heavy metals acute toxicity test. The tests were performed after 24 h *A. salina* cysts hatched. The screening tests and definitive tests were conducted in static non-renewal testing solution. Nauplii of *A. salina* were exposed to different concentration of single-metal solutions and landfill leachates. Mortality of nauplii was used as the end point of the toxicity test. The predicted median lethal concentration (LC_{50}) for each metal was determined by probit analysis. The LC_{50} values for single-metal exposure were approximately 0.28 ppm Cu, 2.47 ppm Cd, 2.72 ppm Zn and 10.23 ppm Ni, respectively. The order of the toxicity level of selected metals to *A. salina* is Cu > Cd > Zn > Ni. However, the LC_{50} values for landfill leachates exposure were approximately 0.08 ppm Cu, 0.01 ppm Cd, 0.11 ppm Zn and 0.10 ppm Ni, respectively. The order of the toxicity level of selected metals to *A. salina* is Cd > Cu > Ni > Zn. Lower LC_{50} values for all metals of landfill leachates proposed there could other factors that potentially induced the decreasing of tolerance level of *A. salina* nauplii towards these pollutants. Thus, this study proposes nauplii of *A. salina* as a sensitive bioindicator for heavy metals contamination.

Keywords *Artemia salina* · Nauphlii · Heavy metals · Toxicity test · Landfill leachates

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Highlights

- *Artemia salina* nauplii are sensitive to heavy metals in environment.
- Toxicity level of selected metals to nauplii of *A. salina* is Cu > Cd > Zn > Ni.
- Nauplii stage of *A. salina* is suitable to be used as toxicity testing organism.

Introduction

Various kinds of organisms have been used to predict the ecological effects of heavy metals (Sow et al. 2013). Among them, fishes are widely considered as suitable bioassay. However, these days there are tendency for substituting the use of laboratory animals for toxicity test due to high cost and the suffering of animal cause by these tests (Kanwar 2007). A lot of studies reveal that invertebrate larvae are usually more sensitive to heavy metal contamination. The brine shrimp (*Artemia salina*) is a suggested organism for bioassay because it functioning like others zooplankton that accumulate the trace elements and subsequently transfer them to higher level. Besides that, this organism is one of the important test organisms for toxicity test and researches in developed country because of its characteristic such as easy culturing (hatching from eggs gives organisms of similar age, genotype and physiological condition), short life cycle, and resistance to manipulation, wide geographic distribution, simplicity and cost-effectiveness of performed tests (Barahona and Sánchez 1999; Nunes et al. 2006).

Materials and Methods

This test is to aim the lowest concentration of toxicant that induced 100 % mortality. Ten individuals of *A. salina* nauplii were transferred with a Pasteur pipette into each petri dish. Minimal volume of seawater carried over with the nauplii. Each dish was filled with the 50 ml of the respective concentration of a metal (static non-renewal testing solution). Inorganic metal salts were used ($CuSO_4$, $ZnSO_4$, $CdSO_4$, $NiSO_4$, $FeSO_4$). The pH and salinity level in all testing solutions were maintained between 7.5 to 8.4 and 28 to 30 ppt, respectively. Number of dead larvae in each petri dish was counted after 24 h. Within 10 s, if the appendages of nauplii show have no movement, it will considered dead. The preliminary test will be carried out with 3 replicates. An additional dish with 10 nauplii in 50 ml artificial seawater will be included as control. Ten nauplii of brine shrimp were placed into each petri dish. The petri dish was placed in control temperature 25 °C for 24 h. Next is definitive test, this test aim the determination of the LC - 24 h on the basis of critical range obtained in preliminary test as suggested (Vanhaecke

et al. 1981).The data obtained was statistically analyzed using one way ANOVA. This is followed by Turkey's post host test when the ANOVA produced significant result. The test was performed using GraphPad Software ver 5.01 (GraphPad Software Inc., San Diego, CA). Differences are considered significant when $p < 0.05$. Besides we used StatPlus 2009 Professional for run the Probit Analysis.

Results and Discussion

First, morphological observations on *A. salina* nauplii were conducted after the 24 h toxicity test completed (Fig. 43.1). Results revealed nauplii *A. salina* in control concentration showed a normal development. Dead nauplii after exposure to certain concentration of metals showed persistent darker colour, deviation of longitunal body axis, failure in development of first pair appendages (antennae with sensory function) and the third appendages (mandible with food capturing function). These are similar to the criteria of abnormality of nauplii growth proposed by Bustos-Obregon and Vargas (2010).

Next, the degree of mortality in relation to heavy metals concentration of was measured. Preliminary test gave the concentration range for the definitive assay to determine the LC_{50} after 24 h exposing to the heavy metals. Table 43.1 showed LC_{50} data obtained after the nauplii exposed to pollutants. Three possible LC_{50} values for each pollutant were projected, including experimental LC_{50}, probit analysis LC_{50} and line regression LC_{50}. In general, the LC_{50} values from the experimental were not diverged different to the predicted LC_{50} obtained from the

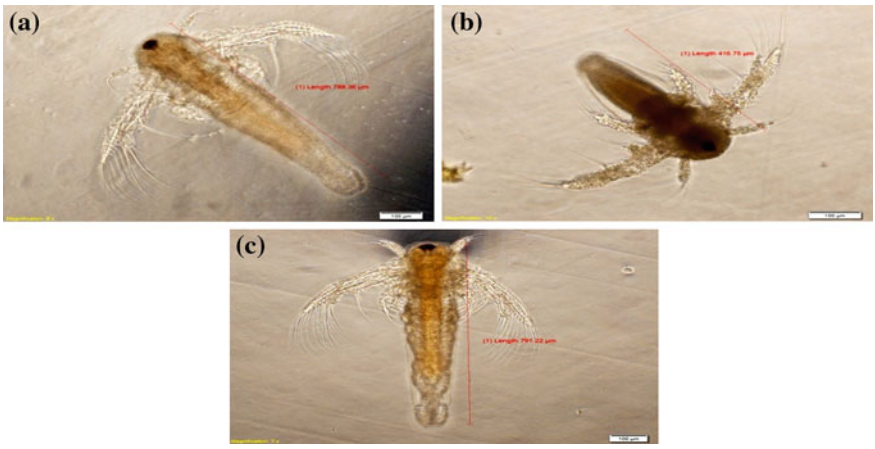

Fig. 43.1 Morphological comparison of A. salina nauplii after 24 h exposure **a** normal nauplii in control solution, **b** deformed dead nauplii during toxicity test, **c** deformed alive nauplii during toxicity test

Table 43.1 Comparison of predicted and experimental LC_{50} concentration for single metal testing solution

Metals	Experimental LC_{50} (ppm)	Predicted LC_{50} by probit analysis (ppm)	Predicted LC_{50} by line regression (ppm)
Cu	0.20	0.28	0.30
Ni	10.00	10.23	9.00
Zn	2.00	2.72	2.50
Cd	2.00	2.47	3.50
Fe	0.70	0.73	0.70

Probit Analysis and Line regression. However, the value of LC_{50} from the Probit Analysis was more precise to the experimental value compare to the line regression. Therefore, probit analysis are more significant to represents the LC_{50} data for determine the relative toxicity of chemicals to living organisms. The actual reading of LC_{50} for Cu is 0.2 ppm meanwhile the expected from the probit analysis is 0.28 ppm. For Zn and Cd the actual value of LC_{50} is 2.0 ppm, while the expected for Zn is 2.72 ppm and for Cd is 2.47 ppm. Then, for Fe the predicted LC_{50} from probit analysis is 0.73 ppm not much different to the experimental value that is 0.70 ppm. Moreover, highest value of LC_{50} for this bioassay is Ni, with the expected value is 10.23 ppm, while the actual value is 10.0 ppm. The lower value of LC_{50} for the organisms' survival in a particular solution meant it's a most toxic. Established order of toxicity of common trace element based on (GMP/UNESCO 1977) with respect to the most sensitive life stages is as follows, Cu > Zn > Ni > Cd > Fe. However, in the present research the level of toxicity of the metals to *A. salina* is Cu > Fe > Zn > Cd > Ni. The obvious difference was found between Ni and Cu. Ni was reported less toxic, meanwhile the copper being the most toxic. We categorized Ni is the least toxic to *A. salina* because of the survival of nauplii in high concentration of Ni compare to others heavy metals. Cu is the most toxic according to the reported and present study. The hazardous of Cu shown by the critical lethal concentration is only 0.2 ppm. Cu was reported highly toxic to most aquatic species because of rapid binding of copper to the gill membranes, which causes damage and interferes with osmoregulatory processes. High amount of cupric ion in the aquatic environment may cause toxicity to aquatic animals through gill damage (United States Environmental Protection Agency 2005).

This research also tested the acute toxicity test of landfill leachate using *A. salina*. The LC_{50} of leachate for *A. salina* determined by the probit analysis was around 84.24 ppm or 80 % from the pure leachate. Therefore we assumed that 80 % concentrations of each heavy metal from the pure leachate were contributed to the mortality of nauplii. Therefore, *A. salina* show a positive criteria in acute toxicity of leachate because it sensitive to the changes of concentration in pollutants. The mortality of *A. salina* is directly proportional to the increasing of leachate concentration.

Conclusion

In conclusion, the order of the toxicity level of selected metals to *A. salina* nauplii is Cu > Cd > Zn > Ni. Nauplii of *A. salina* can be used to detect the toxicity of pollutants in landfill leachate, subject to further studies on other chemicals. High tolerance level and sensitivity to metals make nauplii of *A. salina* suitable to be used as a toxicity testing organism testing.

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Chapter 44
Health Risk from Cu and Zn Contamination Through Consumption of Paddy Eel, *Monopterus albus*

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Abstract The main objective in this study is to determine Cu and Zn concentration in edible tissues (skin and muscle) of paddy eels, *Monopterus albus*. The collection of *M. albus* samples was based on four paddy seasons (plowing, seedling, growing and harvesting). A total of 163 individuals of *M. albus* were collected. Edible tissues were dissected, digested and analyzed using an atomic absorption spectrometer (AAS) for metal concentration. Results showed bioaccumulation of Cu and Zn in skin was higher than in muscle tissues. Comparison with the Malaysian Food Regulation showed Cu and Zn concentrations in muscle and skin tissues were within the permissible limits. The estimation of chemical doses was calculated in order to evaluate the health risk of Malaysian population via the consumption of *M. albus*. Result showed Cu and Zn levels were low in muscle and skin tissues, thus suggesting edible tissues of *M. albus* are safe for consumption.

Keywords Heavy metals · *Monopterus albus* · Paddy seasons · Risk assessment · Daily intakes

Highlights

- Concentrations of Cu and Zn are higher in skin than in muscle tissues of *M. albus.*
- Daily estimated intake demonstrate *M. albus* are safe for human consumption.
- Intakes of Cu and Zn in muscle tissues of *M. albus* were lower than the guidelines.

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Introduction

Fish is widely used as one of the potential bio-monitoring agents of contamination in aquatic environments (Khodadoust et al. 2013). Also, it is an important protein source that should be obtained by human's body. Therefore, fish is reported as the major part of the human diet. Paddy eel or *Monopterus albus*, is widely known as 'belut' and is considered to be likely consumed by major population of Malaysian in different ages of year.

Present, environments especially aquatic environments are likely subjected to pollutions due to human anthropogenic activities which can cause severe environmental problems (Zulkifli et al. 2010). Paddy cultivation area is one of the aquatic environments that received many pollutants from the application of agrochemical pesticides and fertilizers. In order to make sure the better growth of rice paddy, the rice farmers are likely to use intensive of agrochemical fertilizers and pesticides. In addition, the present of large scale of pest organisms such as golden apple snails and paddy rats in the paddy fields might cause a serious threat to the rice farmers (Sow et al. 2012). Also, it could cause the rice farmers loss their source of incomes due to the low-scale of rice paddy production. The deposition of heavy metals from the application of agrochemicals pesticides and fertilizers into the water and paddy soil is higher for the longer periods of times, which in turn accumulates up to toxic levels and cause an ecological damage (Güven et al. 1999; Jefferies and Freestone 1984). Since human is the top receiver in the food chain, the tendency to accumulate more heavy metals are high in their body tissues. Furthermore, an elevation of heavy metals in the body system can cause severe health problems which are cancers as stated by Nabawi et al. (1987).

Materials and Methods

Paddy eels were collected from paddy cultivation areas based on four paddy seasons namely as plowing, seedling, growing and harvesting season. The sampling location is situated at Kelantan, Peninsular Malaysia with the coordinate of N06°08.454′ E102°8.430′. Since the agricultural activity is the main source of income to the nearby villagers, thus, the major possibilities of contaminations might from the anthropogenic inputs which are agrochemical fertilizers and pesticides applied into the paddy cultivation areas. The dried selected organs were digested by using acid-digestion methods (Ismail and Ramli 1997) and metal determination was done by using an air-acetylene flame atomic absorption spectrometer AAS Perkin-Elmer Model AAnalyst 800.

Table 44.1 Mean metal concentration (μg/g d.w.) and standard deviation of Cu and Zn in the tissues of *M. albus* and comparison of different seasons for 2 years completed paddy cycle

Year	Season	Cu		Zn	
		Skin	Muscle	Skin	Muscle
2011	Plowing	1.262 ± 0.99^{b}	0.78 ± 0.57^{b}	83.61 ± 28.55^{a}	51.18 ± 19.06^{a}
	Seedling	1.281 ± 0.2^{ab}	0.90 ± 0.08^{ab}	63.29 ± 13.67^{ab}	47.37 ± 9.41^{a}
	Growing	4.73 ± 5.57^{a}	2.60 ± 2.41^{a}	52.77 ± 9.04^{b}	40.15 ± 3.21^{a}
	Harvesting	1.971 ± 0.93^{ab}	1.38 ± 0.57^{ab}	53.67 ± 6.97^{b}	47.33 ± 5.02^{a}
	Mean	2.31	1.03	63.34	46.51
2012	Plowing	2.729 ± 1.95^{a}	1.38 ± 0.59^{a}	62.48 ± 7.90^{a}	51.38 ± 6.95^{a}
	Seedling	1.87 ± 0.78^{a}	1.21 ± 0.36^{a}	66.88 ± 12.7^{a}	49.11 ± 11.21^{a}
	Growing	2.07 ± 1.27^{a}	1.22 ± 0.66^{a}	61.25 ± 8.94^{ab}	47.57 ± 3.45^{a}
	Harvesting	1.69 ± 0.35^{a}	0.99 ± 0.28^{a}	53.94 ± 6.61^{b}	44.02 ± 2.68^{a}
	Mean	2.09	1.2	61.14	48.02

^{a}, ^{b} : Post-hoc: Mean metal concentrations of different parts of tissues sharing a common letter for a particular metal are not significantly different, $p > 0.05$.

Results and Discussion

Data on Cu and Zn concentrations in tissues of *M. albus* collected in different seasons of a paddy cycle for two years are shown in Table 44.1. In year 2011 and 2012, muscle tissues accumulated low Zn concentrations among the paddy seasons with the ranges of 40.15 to 51.38 μg/g dw. Data showed muscle tissues accumulate lower Zn concentration than skin tissues, thus suggesting a poor bioaccumulation of heavy metals. Higher accumulation of Cu and Zn in skin tissues could be due to the present of thick mucus layer on its body and hard to remove completely during the analysis. According to Kemubu Agricultural Development Authority (2011), Zn is one of the elements that are used in producing agrochemical fertilizers. Several factors were reported contribute to the differences of Zn concentrations in muscle tissues such as locality (natural or an-thropogenic sources), the physiological condition of the fish (age and size), and seasonal variations (Le et al. 2009). According to the Malaysian Food Regulation (1985), the permissible Zn limit allowed is 100 μg/g. Based on this limit, this study suggests that muscle tissues are safe for human consumptions as food source. Yet, Cu metal is one of the elements that could be found in the compound fertilizers (Sow et al. 2012, 2013). Additionally, the essential metals particularly Cu, Zn and Fe must be taken up through three pathways which are food, water and sediment (Canli and Atli 2003). However, the effectiveness uptake of heavy metals might differ in aspect of ecological needs and metabolism of animals, contaminants gradients of water, food and sediment, and environmental parameters such as pH, salinity, temperature, and interacting agents (Heath 1987; Langston 1990; Roesijadi and Robinson 1994). Based on daily estimated intake, the intakes of Cu and Zn in muscle tissues of *M. albus* were lower than the guidelines as showed in Table 44.2. This reflected that, the consumption of muscle of paddy eel is safe during 4 paddy seasons.

Table 44.2 Daily intake of heavy metals (μ/kg/day) in paddy eel muscle for a person (50 kg) in Malaysia

Year	Season	n	Zn	Cu
2011	Plowing	38	7.32	0.49
	Seedling	9	29.94	0.569
	Growing	24	25.37	1.64
	Harvesting	11	29.92	0.876
2012	Plowing	32	32.47	0.87
	Seedling	8	31.04	0.766
	Growing	21	30.07	0.769
	Harvesting	10	27.82	0.629
	Reference Doses (RfDo) in μ/kg/day unit		300	40

Conclusion

The application of agrochemical fertilizers and pesticides are not increase the Cu and Zn metal in the paddy cultivation areas. Thus, suggested that, paddy eel of Kelantan are safe to be eaten by major population in Malaysia.

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Chapter 45
Geochronology of ^{210}Pb in Sediments of Sepang Besar River, Malaysia

Siti Aishah Ramsie, Syaizwan Zahmir Zulkifli, Ferdaus Mohamat-Yusuf, Ahmad Ismail and Che Abd Rahim Mohamed

Abstract Geochronological studies to determine pattern and rate of sediment deposition is still lacking in Malaysia. The aim of this study is to investigate geochronological pattern of ^{210}Pb in core sediments of the Sepang Besar River. Sediment cores were collected from rivermouth, middle course and upper course of the river. Sediment cores were cut at 2 cm interval for each layer, treated with established method and analyzed by beta spectrometry. Results showed the activities of ^{210}Pb along Sepang Besar River varied at a wide range. Significantly lower ^{210}Pb activity was found at the rivermouth as compared to middle and upper courses of Sepang Besar River. This could be due to the geology of the watershed and chemical weathering conditions around the area.

Keywords Geochronology · ^{210}Pb · Core sediment · Beta spectrometry · Sepang Besar River

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Highlights

- Activities of ^{210}Pb along Sepang Besar River are widely varied.
- Lower ^{210}Pb activities at rivermouth; higher at inner course of Sepang Besar River.
- Watershed's geology and chemical weathering conditions affect the ^{210}Pb activities.

Introduction

The radionuclides dating using ^{210}Pb have been used for more than two decades to provide geochoronology of annually deposited sediment and to construct pollution histories (Benoit and Rozan 2001). Zulkifli et al. (2010a, b) has reported worlwide scientists concern on resuspension of bottom sediments (polluted layer) in recent years due to sediments dredging and coastal reclamations. The isotopes ^{210}Pb (T1/2 = 22.3 yrs) is a decay product of ^{222}Rn which escapes from the earth crust to the atmosphere. ^{210}Pb short residence on atmosphere, falls into lake or river and tends to bury and permanently fixed on sediment particles as solid fallout (Althammer et al. 2010). ^{210}Pb has been widely used as marine tracers of particles/water transport and particulate scavenging (Benoit and Rozan 2001). The usage of tracer such as ^{210}Pb allows tracing the history and sources of pollution on studied area (Gelen et al. 2003).

The area around Sepang Besar River has been fully utilized for agriculture, animal farming, residential, aquaculture, ecotourism and power plant activities. The pollutants from anthropogenic activities could be accumulated in the sediments (Zulkifli et al. 2010a, b). Ismail and Ramli (1997) reported this river received high anthropogenic input of heavy metals in 1990s originated from massive pig farming activities. However, the outbreak of Japanese encephalitis (JE) in 1998 has caused pig farming activities to be closed. In order to understand the heavy metals enrichment in the sediments, geochronology of sediment should be studied. Thus, the aim of this study to investigate geochronological pattern of ^{210}Pb in core sediments of the Sepang Besar River.

Materials and Methods

The Sepang Besar River is located at the state boundary of Selangor and Negeri Sembilan, Malaysia. The core sediments were collected from three locations along Sepang Besar River as shown in Fig. 45.1. The sediment core samples were collected by using the 1 m hand corer (6 cm inner diameter). The corer was hand-pushed into the bottom sediment, capped and retrieved. The core samples were

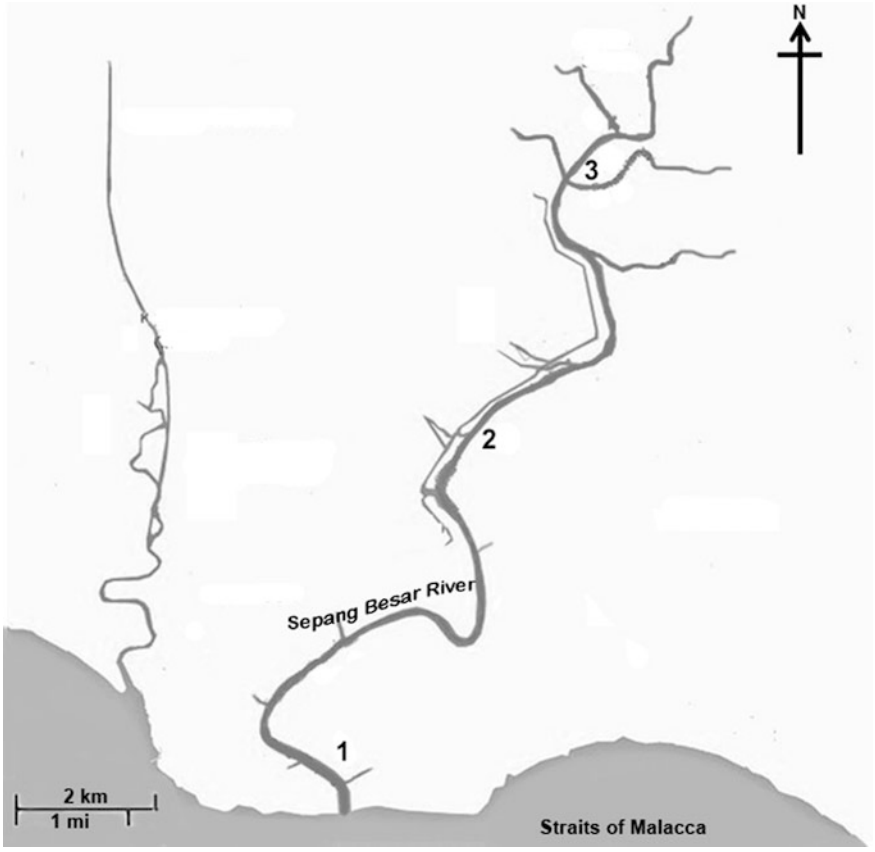

Fig. 45.1 Map of sampling locations along the Sepang Besar River, Malaysia

directly brought back to laboratory and stored in a freezer at −20 °C to prevent any chemical or biological reactions prior further analyses. Laboratory analysis started by thawing the core sediments. Each core was sliced into 2 cm intervals from surface to bottom of the core. All core sections were dried in an air-circulating oven at 60 °C to a constant weight and homogenized through a 250 μm mesh size sieve for analysis ^{210}Pb radionuclide dating. The digestion of sediment for radionuclide purposes was modified from Theng and Mohamed (2005). In general, about 5 g of homogenized core sediment sample was taken and spiked with 1.0 mL of $PbNO_3$ (20 mg/mL) and 1.0 mL of $FeCl_3$ (19.8 mg/mL). In the laboratory, samples were digested with a hot plate for 3 h. Then, the samples were filtered through membrane filter paper (0.45 μm pore size, 47 mm diameter) with a flow rate less than 10 mL.min^{-1}. The filtreate was acidified with 65 % concentrated HNO_3 till pH < 2 and spiked with iron carrier solution. The samples were centrifuge for 3 min at 4000 rpm. After that, the solution pH was increased to pH 10. The precipitate was filtered and redissolved in 1.0 M HNO_3. The ^{210}Pb was deposited on a platinum

bucket and redissolved with concentrated H_2SO_4 before filter with 0.45 μm filter paper. The precipitation of ^{210}Pb effluence was counted with beta (β) spectrometry to determine the activity of ^{210}Pb.

Results and Discussion

Three sampling locations have been selected, representing the behavior of the sediment. The activities of dissolved and particulate ^{210}Pb from three stations of Sepang Besar River were measured and corrected for the recovery. The sampling location, sample intervals and ^{210}Pb activity concentration are shown in Table 45.1. Based on the data shown in Table 45.1, the activities of ^{210}Pb in Sepang Besar River estuary showed a wide variation and this was probably due to the geology of the watershed and chemical weathering conditions. In Station 1, the ^{210}Pb activity concentration was varied between 6.16 ± 1.68 Bq/kg and 24.52 ± 7.64 Bq/kg. In Station 2, the ^{210}Pb activity concentration was varied between 171.14 ± 111.90 Bq/kg to 595.19 ± 159.75 Bq/kg, whereas the ^{210}Pb activity in Station 3 was between 185.56 ± 49.01 Bq/kg to 883.15 ± 303.55 Bq/kg. The activity of ^{210}Pb was lower in Station 1 as it faces the river mouth of the river. The ^{210}Pb activity in Station 1 was influenced by strong tides activities that occur daily as compared to ^{210}Pb activity concentration in Station 2 and Station 3.

In Station 1, the ^{210}Pb activites were higher on the surface layer (0–2 and 2–4 cm depth) of the core sediment. Based on personal observation, the sediment in this area was free from sheltered mangrove forest as compared to sediment collected from Station 2 and Station 3. The core sediment in Station1 received the highest amount was probably due to supply of deposition at atmospheric ^{210}Pb

Table 45.1 Activities of ^{210}Pb (Bq/kg) in the sediment cores of Sepang Besar River

Depth (cm)	Station 1	Station 2	Station 3
0–2	24.49 ± 6.82	179.89 ± 47.87	271.10 ± 71.03
2–4	24.52 ± 7.64	426.74 ± 111.90	303.39 ± 79.49
4–6	15.30 ± 4.62	171.14 ± 44.78	187.91 ± 50.68
6–8	15.59 ± 4.46	2541.12 ± 696.35	864.06 ± 236.29
8–10	18.81 ± 5.57	545.35 ± 144.94	185.56 ± 49.01
10–12	9.67 ± 2.61	541.85 ± 142.42	187.08 ± 49.79
12–14	14.41 ± 4.33	195.75 ± 51.90	813.25 ± 231.18
14–16	6.70 ± 1.81	553.04 ± 146.39	566.12 ± 152.09
16–18	6.16 ± 1.68	288.39 ± 76.77	524.15 ± 137.72
18–20	9.38 ± 2.64	551.08 ± 145.63	531.81 ± 165.65
20–22	8.09 ± 2.27	482.62 ± 131.41	479.95 ± 143.08
22–24	13.07 ± 3.84	515.85 ± 137.51	883.15 ± 303.55
24–26	n.a.	595.19 ± 159.75	563.59 ± 170.31
26–28	n.a.	528.04 ± 143.25	n.a.
28–30	n.a.	523.46 ± 145.80	n.a.

Remark: n.a. refers to not available

originated from the decay of ^{222}Rn (Yang and Lin 1992). Flying ashes from combustion of coals at the nearby power plant could potentially deposited into the sediment. The ^{210}Pb activities in both surface layer (0–2 and 2–4 cm depth) of Station 2 and Station 3 were higher than in Station 1 but based on ^{210}Pb count activities, it shows that ^{210}Pb activities were lowest among the same station. The core sediment collected in this area was covered with sheltered mangrove plants, so the tendency of ^{210}Pb particulate escape to the atmosphere to sink on sediment was low. The high ^{210}Pb activities reported in this study was probably due to supply of ^{210}Pb as these stations were in vicinity to the agricultural lands. The main agricultural activity that occurs in this area was oil palm plantation. Besides that, this area also received both domestic and industrial waste from nearby residential areas as the wastes released into this river. The ^{210}Pb activities reported in this study was same as a study reported by Theng and Mohamed (2005) in Kuala Selangor estuarine.

Conclusion

Inner course of Sepang Besar River has higher ^{210}Pb activities than rivermouth due to tidal actions. Further investigations are needed in order to related with deposition of pollutants.

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Chapter 46
Optimization of Arsenic Phytoremediation by *Ludwigia octovalvis* in Pilot Reed Bed System using Response Surface Methodology

Harmin Sulistiyaning Titah, Siti Rozaimah Sheikh Abdullah, Idris Mushrifah, Nurina Anuar, Hassan Basri and Muhammad Mukhlisin

Abstract The optimization of Arsenic (As) phytoremediation by *L. octovalvis* was conducted in reed bed system. Factors for optimization were As loading (5, 22 and 39 mg/kg), retention time (14, 28 and 42 day) and flow of aeration (0, 1 and 2 L/min). Performance evaluation was based upon six observations; As in *L. octovalvis*, TF, percentages of translocation, As uptake effectiveness by *L. octovalvis*, bioavailable As and total extractable As removal in As-spiked sand. Based on the response surface methodology using Box-Behnken design, the optimization condition for As phytoremediation occurred at As concentration of 39 mg/kg on Day 42 with 0.22 L/min flow of aeration. The optimum condition model gives the removal of bioavailable and total extractable As at 94.8 and 72.6 % respectively. The other responses were As in *L. octovalvis* (1157.87 mg/kg), TF (1.62), percentages of translocation (46 %) and effectiveness of uptake As by *L. octovalvis* (17.1 %). By comparing the model with a validation run, the optimization

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condition error for all responses was below 10 %. Factor such as As loading, retention time and flow of aeration could affect the performance of As phytoremediation by *L. octovalvis*.

Keywords Arsenic · Phytoremediation · Optimization · RSM · Box-behnken

Highlights

- Phytoremediation of arsenic by *Ludwigia octovalvis* in reed bed system was tested.
- Optimization factors were arsenic loading, retention time and flow of aeration.
- Six dependent variables were selected to determine the optimization.
- The optimization condition at concentration As of 39 mg/kg on Day 42 with 0.22 L/min.

Introduction

The main causes of arsenic (As) contamination are natural minerals of As and human activities. Examples of human activities that can cause As contamination in soil are the production and use of pesticides such as herbicides and insecticides (Gongaza et al. 2006). Industrial processes that use As containing materials such as paper and cement industriesù material smelting and burning of gasoline can cause As contamination in soil, water and air.

Phytoremediation is a green technology that uses plants and microorganisms to degrade or stimulate pollutants in soil and groundwater to be non-toxic (Sao et al. 2007). The phytoremediation is also referred as botanical bioremediation. Phytoremediation using *Ludwigia octovalvis* plant could be a strategy to remove As from contaminated area. *L. octovalvis* was chosen for this study since it was one of the plants that could survive contaminated site in Malaysia (Mushrifah 2011). According to Titah et al. (2013) *L. octovalvis* could uptake and accumulate As in their tissue.

Materials and Methods

The reed beds of As phytoremediation by *L. octovalvis* were constructed using fiberglass tanks. The walls were 0.5 cm in thickness and black in color with a dimension of 92 × 92 × 60 cm. A layer of medium gravel (ϕ in 2 cm) was placed at the bottom of the reed bed with another layer of fine gravel (ϕ in 1 cm) placed

on top. The thicknesses of both medium and fine gravel layers were 10 cm respectively. The As spiked sand was placed into the reed bed at a depth of 10 cm. The aeration was supplied by air compressor model HP2 (Orimas Malaysia) and air flow rate was measured using flow meter (Cole-Parmer, USA). The aeration system was placed on medium-sized gravel layer and run continuously throughout the experiment.

The optimization study was carried out using a response surface methodology (RSM). Box-Behnken design was chosen since this design has a smaller number of runs than others. The factors were As loading (5, 22 and 39 mg/kg), retention time (14, 28 and 42 day) and flow of aeration (0, 1 and 2 L/min).The dependent variable as response selected for the study were As in *L. octovalvis*, translocation factor (TF), percentages of translocation, effectiveness of uptake As by *L. octovalvis*, bioavailable As and total extractable As removal in As-spiked sand. Each experiment was replicated thrice. The predictive model was verified using the same factor in optimization conditions.

Results and Discussion

The results were analyzed using ANOVA to determine the accuracy of fit (Mojiri et al. 2013). Based on results, all responses showed a significant model due to the probability values were less than 0.05. R^2 value for all responses showed acceptable modification. The adequate precision for all responses were greater than 4, indicating an adequate signal for the models to be used to navigate the design space.

Three-dimensional surfaces plots are graphical representation of regression equation for the optimization of reaction conditions and are the most useful approach in revealing the conditions of the reaction system (Zhang et al. 2010). The results of the interactions between three independent variables and dependent variable are shown in Figs. 46.1a–f.

The optimization results show that optimized conditions under specified goals were obtained to a level of desirability of 0.725 at 39 mg/kg As on Day 42 with 0.22 L/min for flow aeration. At these optimized conditions, As concentration in *L. octovalvis* is 1157.87 mg/kg, TF is 1.62, percentages of translocation is 46.0, effectiveness of uptake As by *L. octovalvis* is 17.1 %, removal of bioavailable As is 94.8 % and removal of total extractable As is 72.6 %.

In order to validate the obtained optimum conditions, a validation experiment was executed. In the confirmatory run, As concentration in *L. octovalvis*, TF, percentages of translocation, effectiveness of uptake As by *L. octovalvis*, removal of bioavailable As and total extractable As were realized at 1103.71 mg/kg, 1.59, 44.0, 17.5, 86 and 70.6 %, respectively giving errors for all the parameter at below 10 %. In conclusion, factor such as As loading, retention time and flow of aeration could affect the performance of As phytoremediation by *L. octovalvis*.

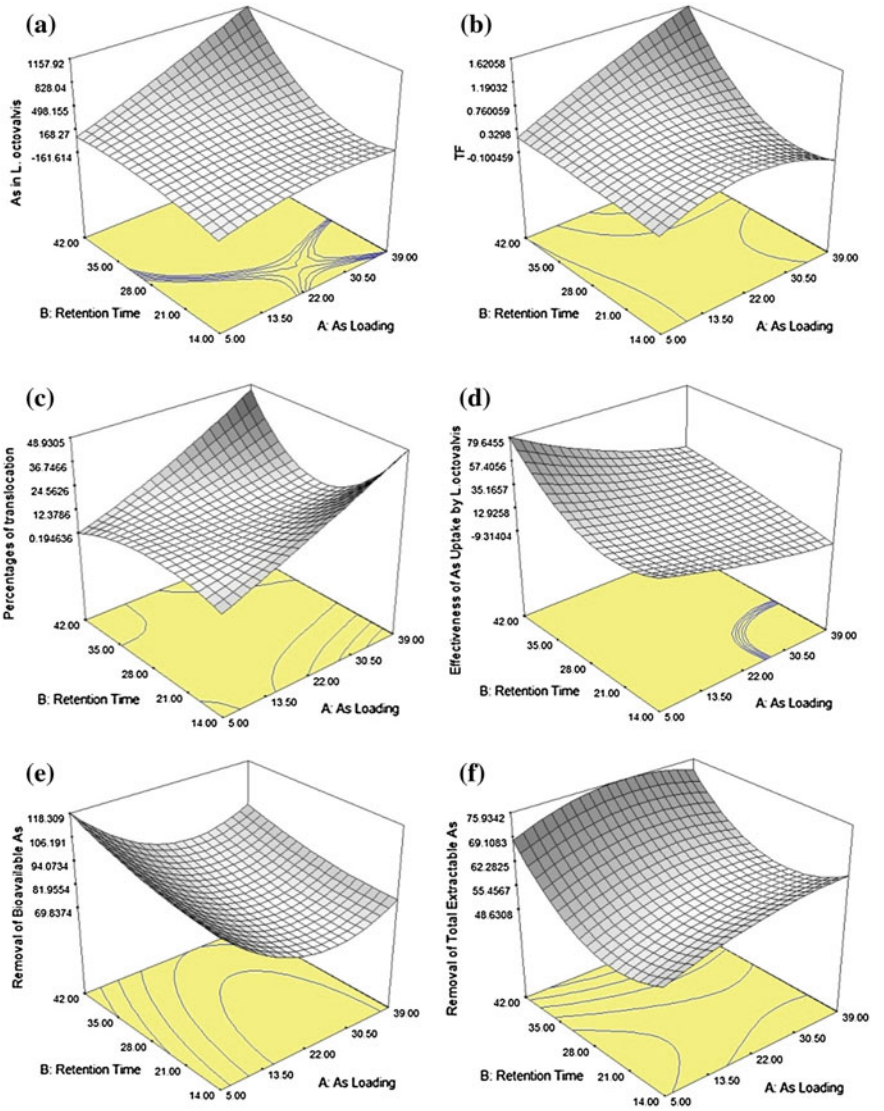

Fig. 46.1 **a** RSM for As concentration in *L. octovalvis,* **b** RSM for TF, **c** RSM for percentages of translocation, **d** RSM for effectiveness of As uptake by *L. octovalvis*, **e** RSM for removal of bioavailable As, **f** RSM for removal of total extractable As

Conclusion

At the optimum conditions of As concentration (39 mg/kg) on 42 days with 0.22 L/min for aeration, the removal of bioavailable and total extractable As on model verification were 86 and 70.6 % respectively. Results indicated that *L. octovalvis* is an accumulator plant for As phytoremediation due to the As uptake and accumulation in its tissue. The As concentration in *L. octovalvis* was 1103.71 mg/kg, TF was 1.59 and percentages of translocation was 44 %. In conclusion, factor such as As loading, retention time and flow of aeration could affect the performance of As phytoremediation by *L. octovalvis*.

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Chapter 47
GIS-Based Site Selection for Hazardous Waste Disposal Facilities in Penang and Kedah

Badriyah Zakaria, Ramdzani Abdullah, Mohammad Firuz Ramli and Puziah Abdul Latif

Abstract The GIS with an integration of multicriteria decision analysis (MCDA) has been widely applied in many areas to assist in siting facilities. The application of both has been demonstrated to produce sound decisions. This study is focused on site selection process to determine the location for hazardous waste disposal facility, with a case study on Penang and Kedah. A model was developed that incorporated criteria to be used for exclusionary areas and factor map. AHP method was used to assign weight for evaluation criteria which will be used as input in GIS analysis. There are ten constraint criteria: surface water (SW), environmentally sensitive lands (ESL), environmentally protected areas (EPA), areas with high groundwater pollution risk (HGPR), prohibitive geological conditions (PGC), topography (TOPO), land uses (LU), road networks and transportation (RNT), infrastructures and utilities (IU), and population and public places (PPP). The four factor maps were population and public places (PPP), topography (TOPO), road network and transportation (RNT), and geology (GEO). The model of site selection involved three phases: (1) generation of final constraint map, (2) generation of final factor map, and lastly (3) generation of final suitability map. The final suitability map has been classified into five discrete categories: (0) not suitable, (1) least suitable, (2) suitable, (3) moderately suitable, and (4) highly suitable. The model has generated about 95 % of study area to be excluded as potential sites. The remaining 5 % of land that was suitable for siting was further evaluated to identify their location. Those sites were in Putat, Padang Perahu, Jeram, Padang Lalang, Tebengau, Kangkong, Dulang, Singkir, Sok, Baling, Padang Meha, Bagan Sena, Sedim, Mahang, Sungai Batu, Kuala Selama, Karangan

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and Terap. The integration of GIS and MCDA has absolutely improved the site selection process, thus enhance decision making.

Keywords Geographic information system · Site selection · Multicriteria decision analysis · Hazardous waste disposal facilities · Suitability index

Highlights

- Integration of GIS with MCDA improves decision making in siting facility.
- AHP method produced weightage for criteria under evaluation.
- Index overlay method produce final suitability map.

Introduction

The evaluation procedure for locating unfavourable facilities is complicated because all facilities in particular hazardous waste disposal facilities may expose communities to potential risks or hazards (Hamer 2003). The government's proposals on siting of waste disposal facilities have always been negatively perceived by communities' interests that have resulted in significant resistance and opposition towards the siting. Geographical Information System (GIS) has emerged as a very important tool for land suitability analysis (Malczewski 2010) and it has been applied widely for site selection in many fields. The purpose of GIS was to perform an initial screening process to eliminate unsuitable land followed by utilization of a multicriteria decision analysis (MCDA) in identifying the most suitable sites. Malczewski (1999) defined MCDA as a set of procedures for analyzing complex decision problems involving non-commensurable, conflicting criteria on the basis of which alternative decisions are evaluated. The integration of both GIS and MCDA techniques has enhanced the decision making because it provides the scenarios for transformation and combination of geographical data and stakeholders' choice of preferences (Jankowski 2006). This study will identify the potential sites for siting of hazardous waste disposal facilities.

Materials and Methods

The study area is in Penang and Kedah, which is located in northern region of Peninsular Malaysia. The justification is that, these two states were considered as strategically and geographically located between four other states in the northern

region of Peninsular Malaysia namely Perlis, Kedah, Penang and Perak, which makes them easier for haulage transportation from waste generators. In recent years, Penang and Kedah have experienced rapid growth of industrial activities, thus resulting in more quantity of hazardous waste that goes into the waste lines. Based on statistics obtained in 2011, Penang has generated 194, 279.45 metric tonnes of hazardous wastes which formed the highest quantity amongst those four states, followed by Kedah generating 117,056.57 metric tonnes (DOE 2012). The quantities generated from these two states were exceedingly high, thus locating an integrated hazardous waste disposal facilities in either Penang or Kedah will justify the siting in the northern region of Peninsular Malaysia. Moreover, the location would be able to minimize risk associated with haulage distances.

The site selection model involves three steps, namely, the preliminary analysis, multicriteria evaluation, and identification of the most suitable site. The preliminary analysis stage involves creating a study area map to input the rasterized data layers, then creating constraint maps and factor maps as the available spatial data. Constraint maps indicate areas which are suitable represented by '1's, and unsuitable represented by '0's for siting of the hazardous waste disposal facilities. There are ten criteria selected for exclusionary areas, namely, surface water (SW), environmentally sensitive lands (ESL), environmentally protected areas (EPA), areas with high groundwater pollution risk (HGPR), prohibitive geological conditions (PGC), topography (TOPO), land uses (LU), road networks and transportation (RNT), infrastructures and utilities (IU), and population and public places (PPP). The constraint criteria under evaluation were assigned weight obtained through the Analytical Hierarchy Process (AHP) application. The Pairwise Comparison Matrices (PCM) synthesis, in due course produced the priority values at local and global scales to be used as input for the GIS analysis. The second step involves performing multi-criteria analysis, which is conducted by aggregating the factor maps based on grading values from '1' to '10'. There were four factor maps, namely, population and public places (PPP), topography (TOPO), road network and transportation (RNT), and geology (GEO). Finally, both final constraint map and final factor maps were eventually combined to produce a suitability map. The suitability map was further reclassified into five suitability classes, and the final step was to identify the suitable sites that can be considered as potential sites for siting.

Results and Discussion

There are three critical phases incorporated in this model of site selection for hazardous waste disposal facilities: (1) generation of final constraint map, (2) generation of final factor map, and lastly (3) generation of final suitability map. For each phase, models were developed and maps were displayed for each model run in the GIS analysis. The final step in the site selection was the overlay of the final constraint map and the factor map using the index overlay method. This operation resulted in the final suitability map which has the suitability index from 0 to 10.

Further analysis was performed to reclassify this suitability index into five discrete categories (0) not suitable, (1) least suitable, (2) suitable, (3) moderately suitable, and (4) highly suitable.

The finding showed that almost 95 % of land in the states of Penang and Kedah were not suitable at all for siting hazardous waste disposal facilities. The remaining 5 % was considered to be suitable for such siting. Further analysis was performed to identify those sites which have the suitability classes of suitable, moderately suitable and highly suitable. There were eighteen sites which can be considered as potential sites and these sites were located in the State of Kedah namely: Putat, Padang Perahu, Jeram, Padang Lalang, Tebengau, Kangkong, Dulang, Singkir, Sok, Baling, Padang Meha, Bagan Sena, Sedim, Mahang, Sungai Batu, Kuala Selama, Karangan and Terap.

Conclusion

Although GIS offers techniques and procedures for processing the geographic data to obtain information for decision making, MCDA provides an extended methodology for guiding decision makers through the critical process of evaluating criteria, and of defining values that are relevant to the decision making situation. The integration of GIS and MCDA has absolutely improved the site selection process for hazardous waste disposal facility, thus produced sounder decision making in hazardous waste management in Malaysia.

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Chapter 48
Organochlorine Pesticides (OCPs) in Aquatic Environment of Cameron Highlands, Malaysia

Md Pauzi Abdullah, Naghmeh Saadati and Zuriati Zakaria

Abstract This study aimed to investigate the status and the environmental fate of 18 organochlorine pesticides (OCPs) in aquatic environment of an intensive agriculture area as well as popular tourism destination of Cameron Highlands, Malaysia. In the study area, eight stations were selected along two main rivers, namely, Bertam and Telom Rivers. Water and sediment samples were collected seven times from each station throughout 2011. The descriptive data analysis showed that lindane (γ–HCH) and endosulfan were predominant components. The total OCPs values were between <DL (detection limit) and 67.41 (mean of 7.55 $\pm$ 11.46) ng/L in the water samples. They were between 0.41 and 82.16 (mean of 21.33 $\pm$ 18.54) ng/g of dry weight in the sediment samples. Variations on the types of OCPs and the levels detected were noted with regards to spatial (land use) and seasons i.e. wet and dry seasons. Despite the low levels of the OCPs detected, detail analysis of HCH isomers and endosulfan metabolites indicate the possible reintroduction of the banned pesticides into the study environment.

Keywords OCPs · Cameron Highlands · Seasonal variations

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Highlights

- Most of the OCP components in water and sediments were detected at low levels.
- Evidence of reintroduction of banned pesticides.
- Wet and dry seasons have major impact on the variation of OCPs.

Introduction

The Cameron Highlands river system, consists of three main rivers, Telom, Bertam and Lemoi, is an important source of water supply, irrigation for highland farming, recreation and hydroelectric power. Over the last decade, the rivers of Cameron Highlands were polluted, and many environmental problems emerged (Eisakhani and Malakahmad 2009). Therefore, improving the quality of water in rivers in Cameron Highlands is necessary to prevent further deterioration, thus enabling this area to continue as the main source of vegetable/flower production for Malaysia. This is very crucial since most developed area in Cameron Highlands was upstream area of the river. Since pesticides were intensively used by the highland farmers, it is imperative that the status of these compounds particularly the banned OCPs in the aquatic environment is studied.

Materials and Methods

Eight sampling sites along the Bertam and Telom Rivers were selected and a total of 112 sediment and water samples were collected. The sediment samples were collected with a Peterson grab sampler to depth of about 5 cm. Water samples were collected as grab samples straight from the rivers. Mixed organochlorine pesticide standards consisted of 18 OCPs was obtained from Supelco (Belle-Fonte, USA). Fresh working standard solutions containing a mixture of the mixed OCPs, surrogates (2, 4, 5, 6-tetrachloro-m-xylene & decachlorobiphenyl) and the internal standard component (pentachloronitrobenzene) were prepared by stepwise dilution of the stock solution with the range 1.95, 3.91, 7.81, 15.63, 31.25 and 62.5 μg/L.

Organic free water was prepared according to standard method (American Public Health Association 2005; USEPA 1995).All solvents used were pesticide grade. The anhydrous sodium sulfate was purified by heating it to 400 °C for 4 h. Florisil (PR Grade) was used for cleanup in an activated form (USEPA 2007). Disposable 6 mL SPE cartridges with 0.5 g sorbent-octadecyl bonded, end-capped silica UCT, ENVIROCLEAN were used to extract water samples. GC/MS analyses were performed with an Agilent 7890A gas chromatograph (GC) directly

coupled to the mass spectrometer system (MS) of an Agilent 5975C inert MSD with a triple-axis detector to confirm the order of components. Quantitative analysis of samples was also carried out using Varian chromopack CP-3800 Gas Chromatograph. The instrument was equipped with a ^{63}Ni electron capture detector and a 30 m × 0.32 mm i.d. (0.25 μm film thickness) HP-5 ms fused silica capillary column. The concentrations of the OCPs were not modified by the recovery ratios of the surrogates.

The sediment water content was determined by oven drying for 12 h at 105 °C. A series of mesh sieves ranging from 0.0125 to 64 mm were applied to determine the particle size of the sediment samples. 10.00 g of an air-dried grounded homogenized sediment sample mixed with 10.00 g of anhydrous sodium sulfate and spiked with 1 mL of 0.160 ppm surrogate solutions was extracted with 300 mL of n-hexane/acetone 50:50 for 6 h in a Soxhlet extractor. The extracted volume was reduced using a Rotovap evaporator to about 5 mL and then clean-up using Florisil column. The column was eluted three times with 65 mL of n-hexane, 45 mL of 70:30 n-hexane/dichloromethane and 55 mL of dichloromethane. The cleaned solution was concentrated using a Rotovapor-R-3000 evaporator. This solution was further concentrated to 2 mL with a stream of high purity nitrogen. 1 μL of the concentrated solution was spiked with exactly 1 μL at 100 ppm of internal standard before injection into the GC-ECD.

Results and Discussion

Spatial and Temporal Distribution of OCPs

The OCPs in water and sediment samples have a slightly different geographic property of being scattered over the area. The Bertam River has higher levels of OCPs, particularly in nearby rural areas, vegetable plantations, and tourist destinations, such as Taman Sedia, FAMA Office, and Parit Fall. In BOH Tea Plantation station, DDTs, HCHs, and endosulfans were also detected in water samples. Sediment samples from Blue Valley exhibited the highest values, followed by those collected from Taman Sedia, FAMA Office, Parit Fall, and BOH Tea Plantation stations. The spatial distribution of OCPs in water seems not to follow the expected pattern i.e. lower concentration at downstream station due to dilution. Many tributaries in the area, which flow into the main rivers, affect the level of OCPs in addition to the effect of rain or run-off from agriculture areas in the study area.

Figure 48.1 shows a box plot of the distribution of OCPs during the wet and dry seasons in 2011. Water and sediment samples from Bertam and Telom Rivers had higher values during the wet season in line with those of Zhou et al. (2006). Zhou et al. (2006) also stated that OCPs in Zhejiang Province (East China) were released from wet deposits or from soil being eroded into water because of heavy rains. In Cameron Highlands, the months of February, June, and July were considered as

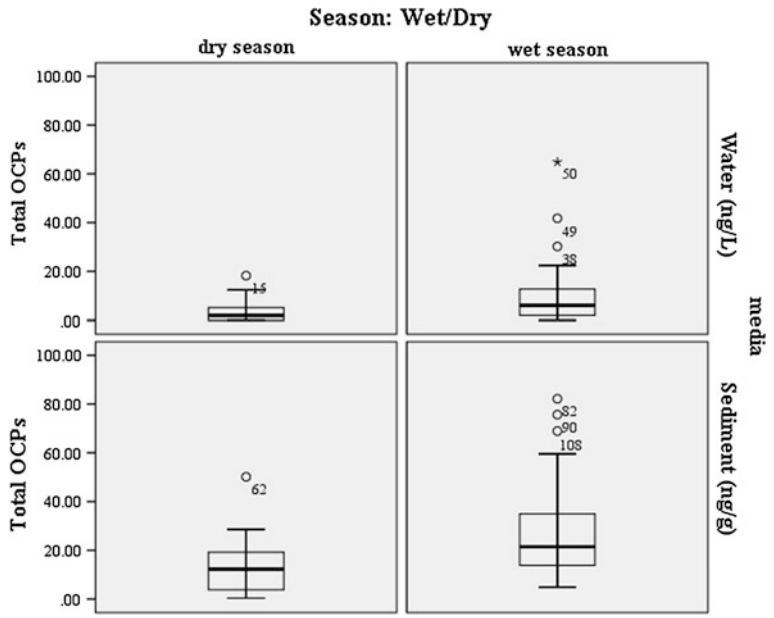

Fig. 48.1 A box plot of the distribution of OCPs during the wet and dry seasons in 2011 indicating higher values in wet season in the two media

dry season (monthly average rainfall of 50–150 mm). The months of April, May, August, and November were considered as wet season (monthly average rainfall of 300–400 mm).

The release of OCPs can be associated with surface runoff from tea and vegetable plantations and with the exposure of soil to pesticides. Pesticide usage increased during the wet season because the pesticides were wash off more quickly. Mazlan and Mumford (2005) also pointed out that an increase in pest infestation during the wet season results in using higher amounts of pesticides. The relationships among rainfall, soil erosion, and released OCPs can be determined by comparing OCP grouped values (Fig. 48.2). The highest amounts of HCHs, DDTs, endosulfans, endrins, and heptachlors were detected during the wet season. These components appear to come from vegetable farms and rural pollution sources near the stations. Pesticides were also able to be transported easily during the wet season because the slope area. Rainfall pattern changes lead to changes in the effects of various contamination sources. The study area did not experience any month without rainfall. Thus, the effect of rainfall could not be ignored completely even during the dry season.

γ–HCH in water samples showed slight difference between two seasons, thus indicating the possibility of sediments as pollution sources because β-HCH comes from impurities of γ–HCH products. The OCPs in sediment samples showed no difference during the wet and dry seasons except for γ–HCH ($p = 0.015$),

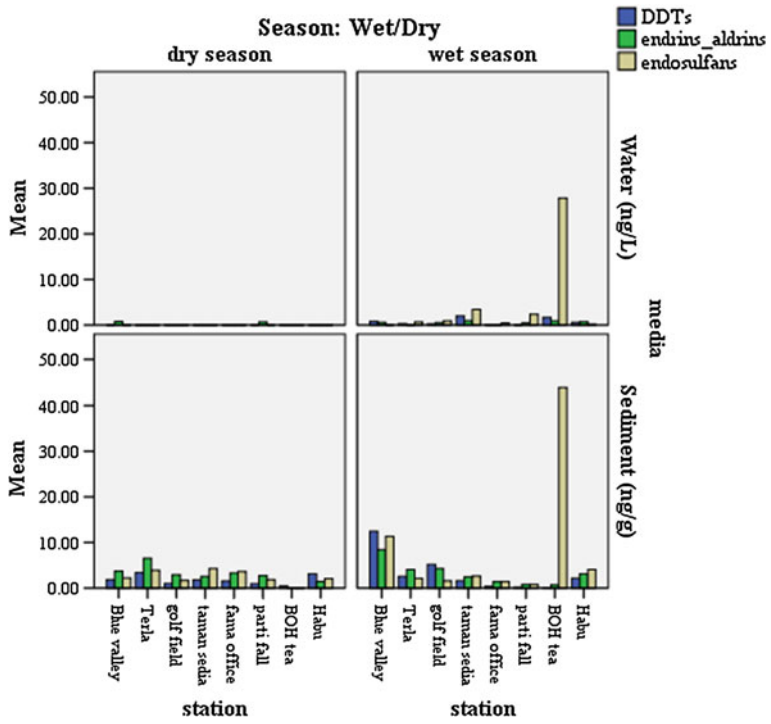

Fig. 48.2 The grouping OCP values including DDTs, HCHs, endosulfans and endrins distribution in wet and dry seasons in 2011 in water and sediment

endosulfan I ($p = 0.045$), and endosulfan II ($p = 0.014$). Differences found for γ–HCH and endosulfans indicate the possibility of new inputs to sediments during the wet season. This data analysis result supports the outcome of the HCH isomer ratio, which shows the possibility of new inputs of lindane (γ–HCH).

Conclusion

The OCPs in water and sediment samples have a slightly different geographic property of being scattered over the area. The Bertam River higher levels of OCPs, particularly in nearby rural areas, vegetable plantations, and tourist destinations. In BOH Tea station, DDTs, HCHs, and endosulfans were detected in water samples. Sediment samples from Blue Valley exhibited the highest values, followed by those collected from Taman Sedia, Fama Office, Parit Fall, and BOH Tea stations. An independent-sample t test was conducted to compare OCPs for wet and dry seasons. Significant differences were noted in water samples than in sediment samples, which is higher in wet season than dry season. Spatial distribution of

OCPs in the water did not follow the expected pattern since many tributaries in the area draining into the rivers.

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Chapter 49
Receptor Modeling Prediction for Potential Sources of PM_{10} at an Urban Location in Klang Valley, Malaysia

Md Firoz Khan, Mohd Talib Latif, Norhaniza Amil, Noorlin Mohamad and Negar Banan

Abstract This study aims to investigate the characterization and source apportionment of PM_{10} at an urban site in Peninsular Malaysia. Principle component analysis (PCA) coupled with absolute principle component score (APCS) and multiple linear regression analysis (MLRA) were employed as a hybrid receptor model to perform the apportionment of PM_{10} sources. An hourly real time in situ data set of gases (e.g. CO, O_3, SO_2, NOx, NO, and NO_2) and meteorological variables (e.g., ambient temperature, relative humidity and wind speed) measured at Petaling Jaya site of Selangor for a span of one year from January till December 2009 were used. The most sporadic variability of concentration of PM_{10} was noticed during south westerly and north easterly monsoon.

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PCA-APCS-MLRA predicted two predominant factors: (a) traffic emission and (b) meteorological factors-O_3 source by which contributed 25 and 8 %, respectively, to PM_{10} concentration.

Keywords PM_{10} · Gases · Meteorology · Source apportionment

Highlights

- Seasonal variability was remarkably observed in PM_{10} concentration.
- PCA-APCS-MLRA successfully apportioned pollutant sources.
- Traffic emission and meteorological factors were pronounced to PM_{10}.

Introduction

Particulate matter (aerodynamically $\leq$10 μm; PM_{10}) has been recognized as one of the signatures to urban air quality (Gupta et al. 2007). Some of the compositions of particulate matter contribute to modify the Earth radiation budget and cloud albedo and by means of these processes aerosol particles directly and or indirectly play key role in changing global climate. However, it is an utmost to know the source information of PM_{10} in the management plan of urban air quality. As a robust and state-of-the-art source apportionment tool, principal component analysis (PCA) coupled with absolute principal component score (APCS) and multiple linear regression analysis (MLRA) are widely applied and accepted methods to apportion the sources of PM_{10} (Thurston and Spengler 1985; Khan et al. 2010). Therefore, this study aims to investigate the prediction of PM_{10} sources with regard to surrounding meteorological factors by employing PCA-APCS-MLRA procedures.

Materials and Methods

Sampling Site

Secondary data was obtained from the Department of Environment Malaysia (DOE) which was captured at Petaling Jaya in Selangor. Petaling Jaya is an urban-industrial area. During the months of January and February, ambient temperature shows relatively lower at about 25 °C compared to other period of the year. However, relative humidity (RH %) is shown about steady all-round the year at

about 75 %. Wind speed triggered in the middle of the year at (4.2–4.9 km/hr) and nearly calm wind speed was observed in January and February with the largest variability.

Measurement and Analysis of PM_{10}, Gases and Meteorological Variables

PM_{10} (aerodynamic diameter $\leq$10 μm) was measured continuously with the Met-One Beta Attenuation (BAM 1020) aerosol mass monitor. The O_3 concentration was measured using the Teledyne O_3 Analyzer (Model 400A, UV absorption). The analyzers, Teledyne API M100A and Teledyne API M200A were used for the measurement of SO_2 and NOx, respectively. The CO analyzer (API M300) used is based on a non-dispersive, infrared absorption method. In parallel, meteorological parameters (e.g., wind speed, wind direction, ambient temperature and relative humidity) were also monitored at this site. PCA-APCS-MLRA, a multivariate receptor model, was employed to investigate the apportionment of PM_{10} sources in this study.

Results and Discussion

Arithmatic Mean and the Variability of Seasonal Concentrations

The summary of hourly measured PM_{10}, gases (e.g., CO, O_3, SO_2, NOx, NO, and NO_2) and meteorological parameters (e.g., ambient temperature, relative humidity and wind speed) are shown in Table 49.1. The yearly arithmetic mean ± standard deviation (SD) of PM_{10} was estimated as 46.0 ± 26.0 μg m^{-3} with 41 and 95 μg m^{-3} measured as 50 and 95 percentile concentration, respectively. This yearly mean value of PM_{10} maintains little lower line of the yearly Malaysian Air Quality Guidelines (MAQG) and the USEPA for National Ambient Air Quality (NAAQS) at 50 μg m^{-3} However, the above recorded yearly mean concentration of PM_{10} exceeded the yearly World Health Organization (WHO) recommendation at 20 μg m^{-3} and the European Union (EU) Air Quality Standard at 40 μg m^{-3}.

The monthly variability of PM_{10}, gases and meteorological parameters are demonstrated in Box-Whiskers plots (Fig. 49.1). The largest increase of PM_{10} was observed in June and second largest in July while the small variability of mean CO concentration was found in whole year. However, the extreme concentration of CO as outliers was noticed mostly in January, February and July. O_3 sporadically increased in June and December. An evenly distributed pattern was seen in SO_2 the whole year with a little variability in January. A similar pattern was shown for the

Table 49.1 Summary of hourly measured PM_{10}, gases and meteorological variables in 2009

	Mean ± SD	Min	Max	Percentile		
				5	50	95
PM_{10} (μg m^{-3})	46.0 ± 26.0	5.0	255.0	15	41	95
CO (ppbv)	1214.8 ± 677.8	10.0	5800.0	320	1,100	2,510
O_3 (ppbv)	16.0 ± 18.4	1.0	125.0	1	8	54
SO_2 (ppbv)	3.7 ± 2.6	1.0	60.0	1	3	8
NOx (ppbv)	59.8 ± 35.9	1.0	351.0	16	53	126
NO (ppbv)	33.5 ± 30.2	1.0	315.0	3	25	92
NO_2 (ppbv)	26.6 ± 13.5	1.0	115.0	8	25	52
Temp (°C)	28.4 ± 4.5	20.0	39.4	21.1	27.8	36.1
RH (%)	73.9 ± 12.6	36.0	94.0	51	77	90
WS (km/hr)	3.7 ± 2.5	0.9	16.9	1	3.1	8.6

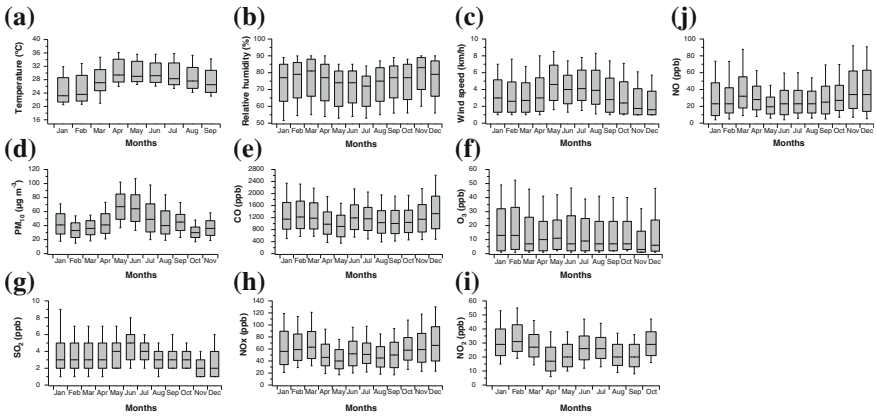

Fig. 49.1 Monthly Box-Whiskers plot

oxides of nitrogen (NOx, NO, NO_2) with higher concentration in January and February but relatively lower in June and July 2009. The seasonal trends of PM_{10} and gaseous variables suggest that the south westerly and north easterly monsoon believed to have contribution in changing the PM_{10} aerosol and gases concentration which were also observed by (Juneng et al. 2009).

Apportionment of PM_{10} Sources

Source apportionment of PM_{10} has been conducted using hourly monitoring data of gases and meteorology for the period of January till December 2009. PCA-APCS-MLRA procedures were taken into consideration in the apportionment of PM_{10} sources. This is a modified hybrid receptor model and provides robust and state-of-the-art apportionment results. A step wise detailed procedures were explained in other studies (Thurston and Spengler 1985; Khan et al. 2010).

Prior to run the PCA analysis, missing value of each variable was replaced with half of method detection limit (MDL) or lowest detection limits (LDL). A covariance matrix was used to obtain a consistent factor profiles with the largest percentage of explained total variance at 62 %. This model predicted two significant sources identified as group-1 and group-2 as shown in Fig. 49.2a. Group-1 is contributed by the oxides of nitrogen and carbon monoxide. These tracers mainly released from motor vehicle combustion source (Mohd Tahir et al. 2013) and this group has been classified as traffic emission source. However, group-2 predominated by meteorological parameters and O_3. Meteorological parameters are key factors in changing concentration of PM_{10}. Therefore, group-2 might be identified as meteorological factors-O_3 source.

PCA-APCS-MLRA predicted PM_{10} concentration by various sources as shown in Fig. 49.2b. Nonetheless, there was about 15 % overestimation or uncertainty resulted in this calculation. PC1 as traffic emission source contributed 13.0 μg m^{-3} or 25 % to PM_{10} concentration. At the same time, PC2 as meteorological factors-O_3 source accounted for 4.1 μg m^{-3} or 8 % to PM_{10}. Moreover, this method left 34.9 μg m^{-3} or 67 % of PM_{10} concentration undefined or undetermined. The percentage of various sources was made based on the predicted PM_{10} concentration.

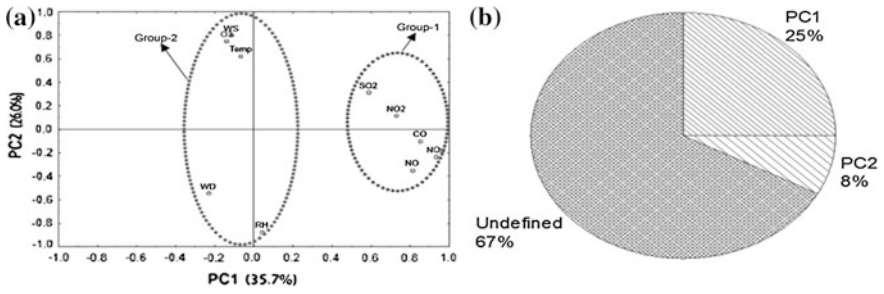

Fig. 49.2 **a** Quadruple plot of PCA factors and **b** contribution of sources

Conclusion

The most sporadic variability of the concentration of PM_{10} was noticed due to the south westerly and north easterly monsoon. PCA-APCS-MLRA predicted two predominant factors: (a) traffic emission and (b) meteorological factors-O_3 source by which contributed 25 and 8 %, respectively, to PM_{10} concentration.

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Chapter 50
Assessment of the Potential Contamination Risk of Nitrate in Groundwater Using Indicator Kriging (in Amol–Babol Plain, Iran)

Tahoora Sheikhy Narany, Mohammad Firuz Ramli, Ahmad Zaharin Aris, Wan Nor Azmin Sulaiman and Kazem Fakharian

Abstract In arid and semi-arid regions such as Amol–Babol Plain in north Iran, groundwater is a major source of drinking water. Excessive usage of fertilizers in agricultural land, domestic sewage and industrial wastewater may result in nitrate contamination. The main objective of this study is to assess the potential contamination risk of nitrate pollution. The groundwater samples were collected from 100 agriculture wells during wet and dry seasons in 2009 and analyzed for nitrate concentration. Indicator kriging (IK) method is applied to create maps indicating the predicted probability of nitrate concentrations in groundwater exceeding the WHO drinking water standard of 10 mg/L-N. Based on the risk probability maps, some areas on the southern side of Babol City and the north and north-western side of Amol City showed a high probability of nitrate contamination. Seasonal maps indicated that the probability of nitrate contamination increased in the wet season, compared to the dry season in the study area, due to increase runoff from irrigated lands. Indicator kriging with local indicator thresholds is shown to be a reliable method to assess uncertainty in the estimation.

Keywords Nitrate · Indicator kriging · Groundwater · Uncertainty · Amol–Babol · Iran

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Highlights

- Some areas showed a high probability of nitrate contamination.
- Indicator kriging characterized uncertainty of spatial prediction.
- Estimation errors were lowest in the central side of plain.

Introduction

Nitrate is recognized as one of the most important parameter of water quality. The anthropogenic sources, such as artificial fertilizers, waste disposal especially from animal farms, and septic tanks, are the main causes of the excessive amount of nitrate in groundwater (Haycock 1990). About 80 % of the Amol–Babol Plain is covered by irrigated land with groundwater as a main source of water supply. The irrigated agriculture practice utilizes a huge amount of fertilizer, which may lead to groundwater contamination (Ghaderi et al. 2012). The geostatistical technique predicts possible values based on the relationship between the sampling points and can also estimate the uncertainty of that prediction (standard error). The evaluation of nitrate contamination and the potential health risk have been assessed for groundwater using the IK method in various studies (Hu et al. 2007; Lee et al. 2007). Hu et al. (2007) assessed the risk of high nitrate concentration in the Quzhou groundwater in China. They showed that Ordinary Kriging (OK) was not suitable for datasets showing a trend of outliers; therefore, IK was applied as a reliable method to assess the risk of NO_3 pollution in the study. The results showed that the geostatistical technique is a reliable method for predicting geochemical contamination patterns. The main objective of this study is to assess the potential contamination risk of nitrate in drinking water in Amol–Babol Plain. The results of the study would be useful for the government to develop strategies for groundwater quality protection in the polluted areas and for optimizing the groundwater monitoring network based on the uncertainty of the estimated results for the further investigation in the study area.

Materials and Methods

Study Area

Amol–Babol Plain is located in the Mazandaran province in Iran. It is located in the southern side of Caspian Sea, and northern side of Alborz Mountain. The weather is influenced by moderate, semitropical climate with an average temperature of 25 °C in summer and about 6 °C in winter. The annual rainfall is

870 mm, with maximum quantity around 400 mm in October, November and December. The main activities carried out in this area are agriculture (rice field) activities, which cover near 80 % of land uses.

Geostatistical Technique

Interpolation maps could be created by using geostatistical technique when the measured points at different locations are given. These techniques produce a set of statistical tools for prediction surface, error and uncertainty of surface. As the first step, after normalization of data, semivariogram should be used between measured points to describe the variability of data with respect to spatial distribution. Uyan and Cay (2010) noted that spherical, exponential and Gaussian are the most widely used variogram models. The suitable model for fitness on experimental variogram is chosen by cross validation. Based on cross validation, the best model is determined by Root Mean Square Standardized (RMSS). The closest RMSS value to one will be chosen. Moreover, the nugget-sill ratio is utilized in the classification of the spatial dependency of groundwater quality parameters. Kriging is considered as an optimal geostatistical approach for interpolation at un-sampled location where sample points close to each other is more alike than that are far from each other. Indicator kriging (IK) is applied as a non-parametric geostatistical method to approximate the conditional cumulative distribution function at a un-sampled point based on the correlation structure of indicator transformed data points.

Results and Discussion

Indicator kriging was applied to create probability maps of nitrate concentration in groundwater for the dry and wet seasons in the study area. The exponential and spherical semivariogram models were the best-fitting models in both seasons. The classification of groundwater spatial dependency may be undertaken using the nugget-sill ratio. A ratio of less than 25 % has a low spatial dependency, a ratio between 25 and 75 % shows a moderate spatial dependency, and a ratio greater than 75 % represents weak spatial dependency. The nitrate concentration in the groundwater showed a ratio of around 48.9 % in the dry season and 41.1 % in the wet season, which indicates moderate spatial dependency.

The probability range is classified from very weak (0.0–0.2) to very strong (0.8–1.0) (Table 50.1). The probability map of NO_3 mg/l-N by indicator kriging showed that high concentrations of nitrate are located in the north, northwest and southeast of Amol and to the south of Babol during the wet season (Fig. 50.1). This pattern is very alarming. Domestic sewage and industrial wastewater coupled with an excessive use of fertilizers are possible sources of nitrate contamination to the

Table 50.1 Probability ranges of area exceeding groundwater nitrate threshold by indicator kriging

Probability range	Description	Wet season		Dry season	
		Area (km^2)	Area (%)	Area (km^2)	Area (%)
0.0–0.2	Very weak	1081.8	59.37	1002.1	55
0.2–0.4	Weak	450.3	24.71	750.1	41.16
0.4–0.6	Moderate	116.3	6.38	69.8	4.66
0.6–0.8	Strong	98.8	5.4	–	–
0.8–1.0	Very strong	74.8	4.1	–	–

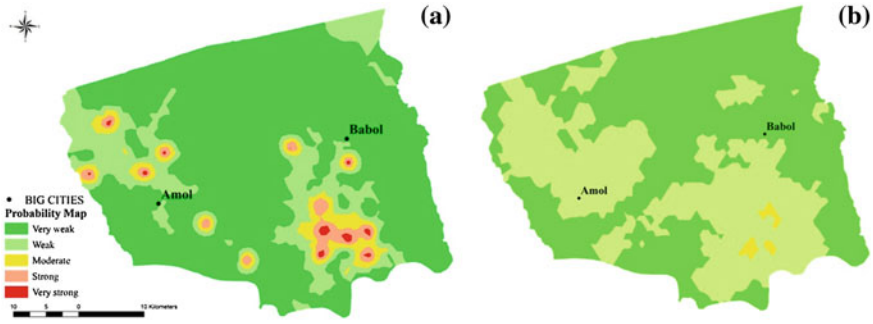

Fig. 50.1 Probability maps of nitrate concentration based on indicator kriging in the study area, **a** wet season, and **b** dry season

groundwater in these parts of the plain. In dry season, the strong and very strong probability of nitrate contamination was not found in the study area (Fig. 50.1).

The indicator kriging technique is commonly used to characterize local uncertainty of spatial prediction and design efficient sampling strategies. The indicator standard error will be small if the errors are small and where the errors are large, it tends to be large.

It is clear that the estimation error near the sampling points was minimal, and that it increased with the distance from the sampling location (Fig. 50.2). The standard error maps showed that the estimation errors were lowest at the central side of the plain and increased toward the boundaries. This may be due to the boundary effect. The accuracy of estimation will decrease when the sampling point's distance increases. However, the error values are lower than the standard deviation of probability levels, therefore, the overall reliability of the maps is appropriate for the current study. The boundary areas showed that the high errors are assumed to indicate the region with the low density of sample data.

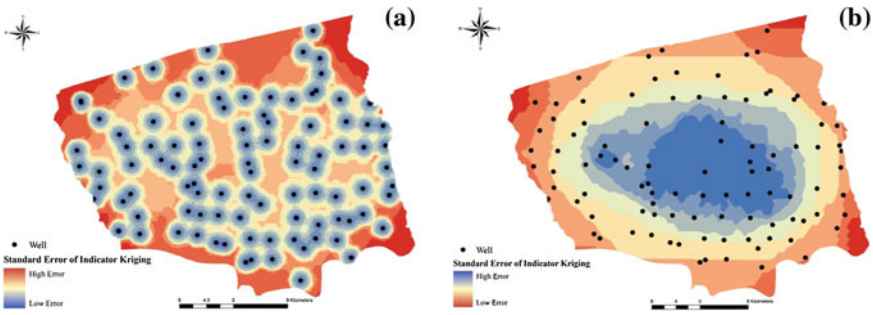

Fig. 50.2 Standard error maps of nitrate concentration in groundwater based on indicator kriging **a** wet season, and **b** dry season

Conclusion

This study intended to predict the spatial distribution and uncertainty of groundwater nitrate concentration using the indicator kriging method based on the limited sampling wells in the Amol–Babol Plain. It can be concluded that the indicator kriging method, correctly reflects the potential risk of nitrate pollution exceeding the maximum allowable value for drinking water, and is a suitable tool for the assessment of uncertainty in local estimation. Based on the results, the standard error maps portrayed the suitable reliability of the prediction maps during the wet and dry seasons, although extra sampling points are suggested for monitoring, especially near the boundaries to reduce the estimation error in a non-sampled region.

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Chapter 51
Current Practices of Clinical Waste Management in Private Clinics, Selangor, Malaysia

Golyasamin Khanehzaei and Mohd Bakri Ishak

Abstract Clinical waste comes from different sources, including hospitals, clinics, medical and dental surgeries, etc. Clinical waste is potentially dangerous therefore it is important to practice special caution in the handling and management of clinical waste in order to minimize its potential danger to public health or pollution to the environment. Management of clinical waste continues to be a major challenge in most healthcare facilities of the developing world. The definition of clinical waste has historically been used to describe waste produced from healthcare and similar activities that pose a risk of infection or that may prove hazardous. Lack of appropriate legislation, lack of specialized clinical staff and lack of awareness and effective control are the main reasons of the mismanagement of clinical waste in most of the cases. The aim of this study is to determine the clinical waste composition and its management system in private clinics of Selangor, Malaysia. A number of private clinics in Selangor was selected using simple random sampling method for this study. An appropriately designed questionnaire and semi-structured interview used for the purpose of data collection. The quantity of CW generated from most of the private clinic is less than 1 kg/day which would increase the possibility of disposing CW as general waste and at the same time the monitoring of CWM in private clinic is insufficient. The results of this study give a comprehensive understanding of current clinical waste composition and its management system in Selangor and therefore there are rooms for improvement.

Keywords Clinical waste · Management · Private clinics · Selangor

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Highlights

- The volume of clinical waste produced in Selangor is 806 MT/year.
- Management practice of clinical wastes in private clinics is not well documented.
- Waste generation depends on size, type, waste segregation and number of patients.

Introduction

It is important to practice special caution in the handling and management of clinical waste in order to minimize its potential danger to public health or pollution to the environment. Infectious situations at health care centers have to be a primary concern. Clinical waste refers to any waste which consists wholly or partly of human tissues, blood or other body fluids, excretions, drugs or other pharmaceutical products, etc. Management of clinical waste continues to be a major challenge, particularly, in most healthcare facilities of the developing world. Clinics and medical health centers in Selangor Malaysia are continually expanding. Thus, clinical waste management systems must be operated correctly.

Significant steps were taken on matters related to safe handling and disposal of the clinical waste, but improper management practice is witnessed from the point of collection to the final disposal. In most cases, the main reasons behind mismanagement of clinical waste are the lack of appropriate legislation, lack of specialized clinical staffs, lack of awareness and effective control. Most of the health care centers of the developing world have faced financial difficulties and therefore looking for cost effective disposal methods of clinical waste. In the last few decades, human activities and changes associated with lifestyles and consumption patterns have resulted in the generation of huge volumes of different types of wastes (Oweis et al. 2005). It is well known that inappropriate clinical waste management is pressing both health hazards and environmental pollution, facing many healthcare centers of this developing world (Bdour et al. 2007; Coker et al. 2009). Diseases like cholera, dysentery, skin infection, infectious hepatitis can spread epidemic way due to the mismanagement of clinical solid waste (Coker et al. 2009). Therefore determining appropriate methods for the safe management of clinical waste is an urgent need. Poor management of clinical waste is a significant problem in most developing countries. However, many researchers in developing countries have investigated the existing clinical waste management practices in selected healthcare centers within their countries (Bdour et al. 2007; Coker et al. 2009; Hassan et al. 2008; Marincovic et al. 2008). They argued that the successful clinical waste management represents a challenge in their countries due to insufficient financial investment, lack of awareness and effective control, lack of trained clinical staffs in the waste management framework. The principle source of clinical waste generation are hospitals and clinics, particularly those providing acute services such

as Operating Theaters, Accident and Emergency, Maternity ward, Mortuary, Intensive Care, Isolation Wards, Pathology Laboratories, Pharmacy and other research facilities (Bendjoudi et al. 2009; Blenkharn 1995; Da Silva et al. 2005; Marincovic et al. 2008). Other of clinical waste are ambulance services, public health laboratories, blood donation centers and blood banks, practice center of doctors, dentists, veterinary surgeons, immunization/vaccination clinics and hospitals, clinics and nursing homes providing community care, care of the elderly and services related to mental health and learning disabilities (Hagen et al. 2001; Marincovic et al. 2008). Generally, quantities of the waste generation rate in healthcare centers depends on type of healthcare facility, availability of instrumentation, general condition of Healthcare facilities area, ratio of disposable item in use and number of patient care (Alagoz and Kocasoy 2008; Bdour et al. 2007). Also, the economic, social and cultural status of the patients might change the amount of waste generation (Askarian et al. 2004; Hassan et al. 2008).

Materials and Methods

This research was a cross-sectional descriptive study using survey and documentary research. The survey research was used to examine and evaluate the clinical waste management process and to identify the factors that affect CWM. It also examined the problems that make clinical waste management operate inefficiently by using questionnaire as a tool for collecting information, opinions, and recommendations from the participants. In order to determine the current status of waste management of private clinics the set of questionnaires was provided. Base on number of society the amount of sample was defined. The raw data were collected from the questionnaire, interview and observation. In this study the data on clinical waste management are based on collection process, transportation, treatment, storage and disposal.

Study Area

Selangor state is located in the west coast of Peninsular Malaysia which covers 8000 square kilometers. In this study, a total of 30 private medical and dental clinics were randomly selected in order to identify the current status of clinical waste management practices in Selangor, Malaysia.

Data Collection

The first step in collecting data is to determine the informants. The concessionaire agreements for clinical waste management in health care facilities was signed

between ministry of health and three concession companies in October 1996 whereby all clinical waste generated in all government hospitals or clinics are managed by three concession companies which are Faber Medi-Serve Sdn Bhd for states of Perlis, Kedah, Penang, Perak, Sabah and Sarawak; Radicare (M) Sdn Bhd for Wilayah Persekutuan Kuala Lumpur and Putrajaya, Selangor, Pahang, Kelantan and Terengganu, and Pantai Medivest Sdn Bhd for Negeri Sembilan, Melaka and Johor. The informants were then interviewed. The purpose of the interview with the waste management officer at Concessions Company was to collect the primary data and background information about the waste management practices at the clinics. The data and information collected formed the basis for this study. An interview protocol was initially developed to cover qualitative data collection that included interview technique, sampling, ethical issues and data analysis. The interview was used to collect data on following variables: waste collection and on site transport, storage, off-site transport and final disposal. Informants were also asked about their knowledge about the existence of policies and regulations on health care waste, their accessibility and availability.

Results and Discussion

The results of this study are based on the interview with the relevant concessions companies and questionnaire survey among the selected private clinics in the study area. Estimated clinical waste generation rate from private clinics varies from 0.3 to 0.8 kg per day. For the state level generation rate based on data from Concession Company (Medivest) clinical waste collected by this company from Selangor was 806 MT/year. The quantity of CW generated from most of the private clinic is less than 1 kg/day which would increase the possibility of disposing CW as general waste as long as the monitoring of CWM in private clinic is not sufficient. During the survey, the practices of clinical waste management in the private clinics were observed. The amount of clinical waste generated in clinics depends upon factors such as: Size of clinic, Types of health services provided, Available waste segregation options, Number of patients, General condition of the area where the clinics are situated. Generally services provided by clinics are: General out-patient care, Drugs prescriptions, and Simple procedures (Minor Operations, Circumcision, and Incision), Specialist services and Laboratory services (Blood and Urine Examination). Clinical waste generated in the clinics came from various activities performed in the clinic. Common clinical waste composition in private clinics is: 5 % Pathological, 3 % PVC, 30 % Plastic other than PVC, 32 % Paper including wax Paper, 10 % Hospital dressing, 10 % Miscellany-flowers, rags etc., 10 % Non-combustible-glass, sharps, metal. The interview with concessions companies revealed that monitoring of CWM in private clinics from relevant authorities is poor.

Conclusion

In the study area the volume of clinical waste generated from private clinics is not properly documented and even the current status of waste management and planning system for private clinics is not well defined, therefore the impacts of the current system of management and planning on the health and environment is not clear. The main problem in clinical waste management in Malaysia is due to economic issue. The importance of management and disposal of clinical waste was ignored due to budget constraint and lack of awareness the community and personnel is the other problem issues.

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Chapter 52
Heavy Metals Analysis of Batik Industry Wastewater, Plant and Soil Samples: A Comparison Study of FAAS and HACH Colorimeter Analytical Capabilities

Noor Syuhadah Subki, Rohasliney Hashim and Noor Zuhartini Md Muslim

Abstract Zinc (Zn), iron (Fe) and copper (Cu) were chosen as representative of heavy metals for this study. The aim of this study was to analyze these heavy metals concentration in batik factories effluent. Samples from soil and plant nearby the factories were collected and analysed using flame atomic absorption spectrophotometer (FAAS) and HACH colorimeter. Results showed differences among the concentration of Fe, Cu and Zn from samples measured by both instruments.

Keywords Heavy metals · Atomic absorption spectrophotometer (AAS) · HACH colorimeter

Highlights

- Heavy metals concentrations in water, soil and plant samples were analysed.
- Differences among Fe, Cu and Zn concentration were detected.
- HACH colorimeter is more suitable for water samples.

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Introduction

The increasing level of heavy metals either plays an important role as nutrients or as toxic elements in the biosphere (Montero Alvarez et al. 2007). In textile industries especially batik making, effluents containing dyes and toxic heavy metals are discharged into the environment without any prior treatment (Department of Environment Kelantan 2009; Intan 2010). Accumulation of heavy metals can achieve toxic levels based on the environment condition (Güven et al. 1999). Zinc (Zn), iron (Fe) and copper (Cu) were chosen as representative heavy metals whose levels in the environment represent a reliable index of environment pollution. These metals play an important role in biological system of the environment. Many difference methods have been used for heavy metals analysis in water such as atomic absorption spectrophotometer (AAS) (Montero Alvarez et al. 2009; Ahmad Khan et al. 2004; Tüzen 2003; Narin et al. 2000) inductive coupled plasma emission spectroscopy (ICP-AES), total X-ray fluorescent (TXRF) (Montero Alvarez et al. 2007) and anodic stripping voltammeter (ASV) (Montero Alvarez et al. 2007). The purpose of this study was to analyse and compare the heavy metals concentration in the batik wastewater and in soil and plant samples around the batik factory near Kota Bharu using flame atomic absorption spectrophotometer (FAAS) and HACH colorimeter.

Materials and Methods

Sampling

Samples of batik effluents, plant and soil used in this study were collected from two batik factories in Kota Bharu, Kelantan in 2011. The factories were labeled as site A (N06°08.693' E102°14.361') and site B (N06°06.300' E102°13.889') in this article. Five samples of each effluents, plant and soil were collected from each site. Water effluent were stored in polyethylene bottles while plant and soil samples were dried and grounded pass through 2 mm sieve and kept in polyethylene zip lock bag for further analysis.

Wastewater, Plant and Soil Digestion

About 100 mL of samples was transferred to a conical flask where 5 mL concentrated HNO_3 and a few boiling chips were added. The digestion was conducted in a slow boil and concentrated HNO_3 was added until digestion is complete (shown by a light-colored, clear solution). Sample must not dry during digestion. Later, the flask walls were washed down with water and the digestate filtered.

Filtrate was transferred into 100 mL volumetric flask with two 5 mL portions of water. The filtrate was cooled and diluted to mark. Portions of this solution were taken for heavy metal determinations.

Portions of ground plant material in a 30–50 mL porcelain crucible were weighed to 1 gram. After that, porcelain crucibles were placed in a furnace where temperature was increased gradually to 550 °C. Ashing was continued for 5 h after attaining a temperature of 550 °C. The furnace was shut off and the door was opened cautiously for rapid cooling. After cooling, the porcelain crucibles were taken out carefully. The cooled ash was dissolved in 5 mL portions 1 N hydrochloric acid (HCl). After 20 min, the volume was filled up to 100 mL using DI water.

About 5 mL of concentrated HNO_3 was added into 1.0 gram sample and refluxed for 30 min. This procedure was repeated until digestate was entirely evaporated to 5 mL, and was left to cool. Digestion was continued by adding 2 mL water and 3 mL 30 % H_2O_2. Later, 1 mL aliquot of H_2O_2 was added until bubbling subsides. The volume was reduced to 5 mL where 10 mL of concentrated HCl was added to the digest from previous step and refluxed for 15 min. Finally, the digestate was filtered and made to volume (100 mL).

Instrumentation and Analysis

Flame atomic absorption spectrometry (FAAS) is a simple and well available technique for the determinations of heavy metals in the natural water samples. A Perkin–Elmer flame atomic absorption spectrometer (FAAS) and HACH DR890 colorimeter was used in this study. Atomic absorption measurements were carried out using air: acetylene flame while HACH colorimeter measurement used test kits provided. The operating parameters for working elements were set of a recommended by the manufacturer.

Results and Discussion

Results from the two instruments used for the samples from site A (Table 52.1) and site B (Table 52.2) were compared. Different results of heavy metals concentrations were found from the two instruments used. The Fe and Zn concentrations of site A detected by FAAS was 30 to 80 % higher compared to results from HACH colorimeter. However, the Cu concentrations for water, soil and plant samples were detected higher by HACH colorimeter. The Cu concentration in soil samples 1, 2, 4 and 5 were not detected in site A suggesting the low concentration of Cu in the soil samples was beyond FAAS detection limit (4 per million).

As for site B, HACH colorimeter was able to detect the concentration of Fe (50 to 90 %) and Zn (40 to 90 %) higher than FAAS for all water, soil, plants

Table 52.1 Heavy metals concentration in site A

Samples	Fe (mg/L)		Zn (mg/L)		Cu (mg/L)	
	FAAS	HACH colorimeter	FAAS	HACH colorimeter	FAAS	HACH colorimeter
Water 1	4.901	0.710	0.136	0.020	0.168	0.160
Water 2	5.189	2.000	0.101	0.060	0.206	0.330
Water 3	4.988	1.980	0.121	0.080	0.179	0.210
Water 4	4.935	0.670	0.111	0.040	0.210	0.190
Water 5	5.136	2.000	0.136	0.030	0.198	0.300
Soil 1	61.830	2.670	1.450	0.020	*	0.710
Soil 2	42.710	2.730	0.674	0.060	*	0.140
Soil 3	58.280	2.030	1.106	0.020	0.007	0.320
Soil 4	33.770	3.300	0.441	0.000	*	0.180
Soil 5	32.970	2.590	0.386	0.750	*	0.710
Plant 1	5.317	2.250	0.838	1.600	0.031	0.110
Plant 2	3.320	2.440	1.210	1.500	0.014	0.120
Plant 3	3.107	0.170	0.331	12.50	0.007	0.330
Plant 4	3.980	1.770	0.998	1.980	0.009	0.380
Plant 5	4.010	2.010	1.010	2.370	0.018	0.290

*Not detected

Table 52.2 Heavy metals concentration in site B

Samples	Fe (mg/L)		Zn (mg/L)		Cu (mg/L)	
	FAAS	HACH colorimeter	FAAS	HACH colorimeter	FAAS	HACH colorimeter
Water 1	3.078	0.330	0.952	18.75	0.379	0.500
Water 2	2.897	1.280	0.243	1.000	0.405	0.330
Water 3	2.900	1.010	0.290	1.438	0.387	0.455
Water 4	2.991	0.700	0.780	1.780	0.412	0.370
Water 5	2.850	1.230	0.950	1.340	0.400	0.400
Soil 1	115.1	2.140	3.400	68.750	0.171	0.170
Soil 2	137.1	1.530	12.300	75.000	0.382	0.780
Soil 3	190.6	2.930	9.000	25.000	0.095	0.230
Soil 4	160.8	0.500	7.000	78.130	0.034	0.270
Soil 5	206.6	1.800	56.700	125.000	2.119	0.720
Plant 1	2.888	2.330	0.698	31.250	0.115	0.350
Plant 2	16.090	0.720	1.200	91.880	0.151	0.770
Plant 3	37.090	1.120	3.007	88.120	0.169	0.300
Plant 4	21.780	1.560	1.490	67.130	0.180	0.880
Plant 5	25.210	1.990	1.980	80.330	0.177	0.700

samples, respectively. However, FAAS can only detect about 1 to 2 % of Cu concentration in water and soil samples. HACH colorimeter, on the other hand, managed to detect 58 % of Cu concentration in soil samples. Results showed that the differences between concentrations of heavy metals detected by FAAS and HACH colorimeter were about 10 to 90 % for both sites.

Conclusion

Flame atomic absorption spectrophotometer (FAAS) and HACH colorimeter were used to detect concentrations of heavy metals in water, soil and plant samples. However, HACH colorimeter showed better optimal functionality towards water compared to soil and plant sample.

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Chapter 53
A Novel Simple Pretreatment Approach for Fast Determination of Multi-residue Pesticides in Aqueous Samples

Chuen-Mei Chao, Yi-Ju Chen and Ying-Ming Weng

Abstract In this study, a simple and efficient pretreatment method to extract multi-class, multi-residue pesticides in water is developed. Based on high sensitivity and selectivity analytical instruments have been developed, large scale water sample is no longer to be needed for pretreatment and the solvent for extraction can be reduced. The method in the study combines two steps: A modified LLE process for less polar pesticides and solid supported liquid extraction (SLE) for more polar ones. The result shows that the mean recovery of each pesticide in three or four replicates of quality control and matrix spike samples is mostly good range from 70 to 140 % with relative standard deviations ranging from 2 to 25 %. It is worth to note that the venting during extraction process is important due to the high vapor pressure of DCM; poor venting will cause the sample spurt and lower analytes recovery and raise the deviation between samples. The method established in the study conjugates a simple pretreatment procedure and high sensitivity and selectivity detection system. It is adapted to quantify and qualify the trace pesticides in water, and also provided as a monitoring tool for the distribution and environmental fate of pesticides.

Keywords Pesticides · LLE · SLE

Highlights

- A modified and improved extraction method has been developed.
- A simple cartridge SLE possesses advantage of LLE, but no drawbacks of LLE.
- Modified LLE and SLE can extract less/more polar pesticides in water simultaneously.

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Introduction

In recent years, more different groups of pesticides were combined to prevent and control harmful organisms in agriculture. It has been estimated that around one-third of crops would be lost if pesticides were not applied against pests. Besides agriculture, the pesticides have also been used in many sectors, including wood preservation, disinfection or household uses. Most pesticides can be toxic to humans, animals and aquatic organisms. Their continuous and massive application can cause serious environmental problems, especially water pollution. Since the detection limits for most of the pesticides are in the low levels of parts per billion and in some cases parts per trillion, the trace pesticides in water must be extracted and pre-concentrated to a detectable quantity for analytical instrument. Conventionally, most pesticides in water are extracted by classic liquid/liquid extraction (LLE), and detected by gas chromatography (GC) or high performance liquid chromatography (HPLC) with appropriate detectors according to the physical and chemical properties of pesticides. Therefore, screening of multi-residue pesticides in water simultaneously demands both GC and HPLC analyses. The tedious and labor-consuming sample pretreatment and instrument requirement debase the application and performance efficiency. Nowadays, with the ultra-sensitive and selective analytical instruments, the requirement of the water sample volume for pretreatment can be reduced. The research has developed a simple, fast and more environmental friendly method than classic LLE to extract multi-class, multi-residue pesticides in water (Logan and Stafford 1989). In this study, an improved LLE method with low extraction solvent is presented, which combines solid-supported LLE that has successfully extracted 91 pesticides in water which were analyzed by LC/MS/MS. Most recoveries and relative standard deviations (RSDs) of the 91 pesticides are good.

Materials and Methods

Standards and Reagents

Ninety-one pesticides standards were obtained and certified from their respective manufacturers, which include 53 insecticides, 27 herbicides, 8 fungicides, 1 acaricide and 1 nematocides. The purity ranges from 94.5–99.9 %. The standard stock solutions of individual compounds were prepared by weighing about 10 mg of each analyte and dissolved in 10 mL methanol. Some analytes must be first dissolved in other solvent just like acetonitrile, acetone, hexane etc., and diluted with methanol to 10 mL. The working standard solutions were prepared by mixing appropriate amount of standard stock solutions and dilution in methanol. An 8-point calibration curve was established, with a range from 5 ppb to 1,000 ppb, were prepared by matrix and method match procedures. There are four quality

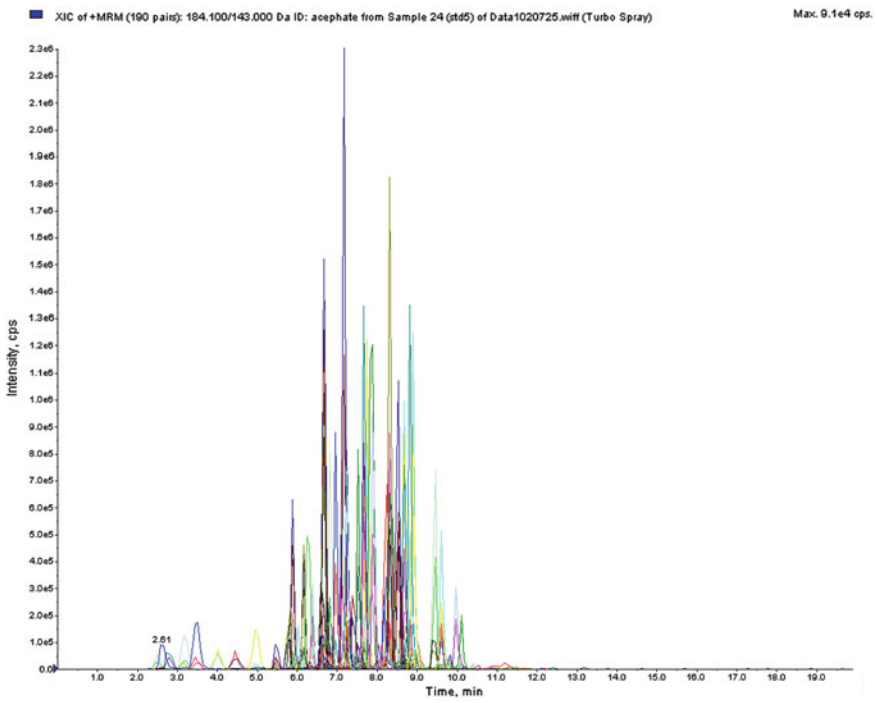

Fig. 53.1 The extract ion chromatograph of 82 pesticides (+) mode

control (QC) samples, three fresh water (FW) spike samples and four raw water (RW) spike samples. The spike concentration at final stage is 50 ppb, Calibration curves are all linear and 1/x weighting with a correlation coefficient (r) of ≧0.99.

Sample Preparation

The extraction is based on LLE and SLE methods and modified as follows: The first step—take 20 mL pH 4.5 water samples into 50 mL centrifuge bottle. 5 mL dichloromethane and 1 mL ethanol is added to each sample. Be careful to slowly upside down the tube and vent several times. Screw the lid on tightly and vortex agitation for 1 min. Vent and stand for 2–3 min. Draw the DCM layer into the K-D tube with glass Pasteur pipette. This step is mainly for less polar analytes. The second step-add about 2.5 g ammonium sulfate anhydrous into water layer in bottle. Be careful to slowly upside down the tube and vent several times. Vortex until the salt dissolved in water entirely. Pour the water sample to the SLE

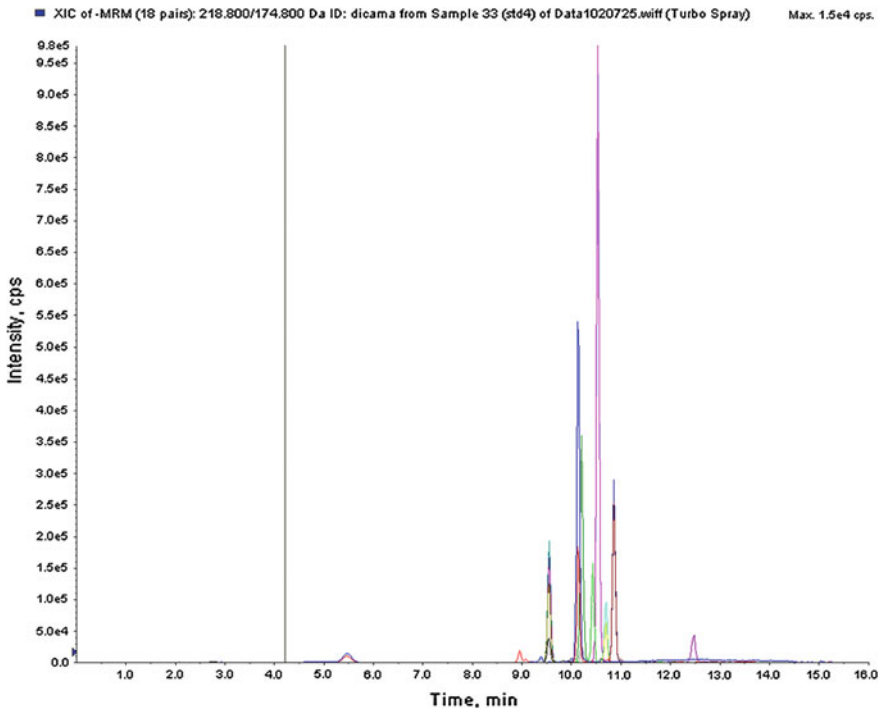

Fig. 53.2 The extract ion chromatograph of 9 pesticides (−) mode

cartridge and stand for 10–15 min. Apply 20 mL ethyl acetate to the SLE cartridge and stand for 2–3 min. Subsequently, elute the analytes with one drop per second by gravity flow. When the elution solvent merge into the upper frit in cartridge, apply 30 mL ethyl acetate with 10 % isopropanol to SLE cartridge and the elution step as mentioned above. The step is mainly for more polar analytes. Collect extract of the two steps and concentrate the extract with vacuum centrifugal concentrator and nitrogen blowing concentrator to 200 μL, substitute the residual solvent with 1 mL methanol/water with 0.1 % ammonium acetate and formic acid (40/60, v/v). The final volume is 1 mL. After filtrating with 0.22 μm PTFE filter, the extract is analyzed by liquid chromatography-tandem mass spectrometry (LC/MS/MS), 82 pesticides with positive ionization mode and 9 pesticides with negative mode. The mobile phases are water with 0.1 % ammonium acetate and methanol with 0.1 % formic acid. The analytical column is phenomenex Aqua C18 3 μm 150 × 2.1 mm. The LC mobile phase and analytical column in the two modes are the same (Klein and Alder 2003).

Results and Discussion

Figures 53.1, 53.2 show the extract ion chromatography of 82 pesticides with positive mode and 9 pesticides with negative mode, respectively. The mean recoveries (70–140 %) and RSDs (2–25 %) of 91 pesticides are mostly good. Some of the pesticides have poor recovery and deviations between the samples are due to the poor venting during pretreatment that has caused sample spurt and some analytes loss.

Conclusion

A modified and improved extraction method has been developed with high recovery rates to analyze multi-class, multi-residue pesticides in aqueous samples simultaneously. Analyses are relative fast and have a reasonable cost. New extraction schemes coupled to LC/ESI–MS/MS led to a high sensitivity and selectivity method. This method can be classified as a confirmatory method for the analysis of the 91 pesticides according to the directive 2002/657/EC. The technique provides a valuable tool to quantify and qualify the trace multi-class, multi-residue pesticides in water and evaluates the distribution and environmental fate of pesticides. Additional supplemental material for data can be requested from corresponding author.

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Chapter 54
Spatial Assessment of Water Quality Affected by the Land-Use Changes Along Kuantan River Basin

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Abstract This study addresses the effects of development on water quality in the Kuantan River Basin from 2003 to 2008. Chemometrics analysis namely MLR, HACA, DA and PCA was utilised as part of the methods for this study. From the result, MLR was irrefutably proven as an efficient predicting method for missing data. HACA classified seven stations as Low Polluted Stations (LPS), six stations as Moderate Polluted Stations (MPS) and two stations as High Polluted Stations (HPS). DA result depicted the accuracy rate for all reclassified data was 83.61 % respectively, while the constituting parameters namely Dissolved Oxygen (DO), *Escherichia coli* (*E. coli*), pH, Phosphate (PO_4), Chemical Oxygen Demand (COD), and Chloride (Cl), gave the biggest impacts towards water quality by means of forward and backward stepwise methods. The PCA result after varimax rotation indicated that five varimax factors have presented strong parameter coefficient exceeding 0.7 by *E. coli*, coliform, Dissolved Solids (DS), Total Solids (TS), Chlorine (Cl), Ammonical Nitrogen (NH_3NL), nitrate and pH. The relationship between land use and water quality denoted that after applying Spearman correlation based on 90 % interval population distribution, aspects influencing the rate of DO was successfully identified.

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Keywords Cluster analysis · Discriminant analysis · Principal component analysis · Multiple linear regression · Spearman correlation

Highlights

- Multiple Linear Regression produces a good prediction of missing data.
- HACA classifies region based on homogeneity characteristic.
- Discriminant Analysis produces significant results in discriminating river region.
- PCA was used to analyse loading factor contributing to the water pollution.

Introduction

The area Kuantan has been facing urbanization and drastic development, which adversely affect the water quality of Kuantan river basin (Rizwan 2008). Unsustainable development generates destruction to hydrological stability in the location. The sources are related to human activities, which have caused abundant changes to the assemblages and biodiversity of the river fauna (Hellawell 1986; Metcalfe 1989; Wright et al. 1993; Pinel-Alloul et al. 1996; Nedeau et al. 2003). The application of chemometric (known as multivariate analysis) in water quality analysis is easy and uncomplicated while simultaneously able to produce significant results (Mazlum et al. 1999). Chemometric techniques are capable of classifying the level of water quality based on region, and are helpful in decision making and problem solving with regards to the local environmental issues (Juahir et al. 2010).

Materials and Methods

Kuantan river basin is located in the north-eastern of Pahang, spreading across the capital city of Pahang (Ishak et al. 2008). The basin is located at coordinates N3°12'27.66" and E103°07'39.99", covering the water supply for the town with a population of 607,778. The length of the basin is about 86 km and the total area is 1638 sq. km. Secondary data used in this study was supplied by the Department of Environment, Malaysia (DOE). Hydrological data obtained from the Department of Environment (DOE) from 2003 to 2008, while the data on land use retrieved from Kuantan Municipal Council, and Technical Report of Kuantan Town Planning from 2003 to 2015. Chemometric techniques namely MLR, HACA, DA and PCA were used for this study to identify the sources of pollution in the river and the water quality criteria.

Results and Discussion

MLR is an efficient technique in predicting missing data, so that any collected data remain significant for further analysis. Parameters of land-use data includes the distribution of population, population alternatives stretch, industrial area, number of workers in the industry, the ratio between industrial areas and the number of workers, farming and livestock areas.

Based on the Water Quality Index (based on Interim National Water Quality Standard), the score for areas labelled as LPS was 31–69; the MPS was from 70 to 91, and HPS was 92. Results of HACA shows that seven stations were classified as Low Polluted Stations (LPS), which include 4KN06, 4KN08, 4KN09, 4KN10, 4KN11, 4KN12 and 4KN15. Six monitoring stations known as 4KN01, 4KN02, 4KN05, 4KN07, 4KN13 and 4KN14 were classified as Moderate Polluted Stations (MPS) and two stations namely 4KN03 and 4KN04 were classified as High Polluted Stations (HPS).

DA was applied for the three main groups obtained by HACA. Standard, forward stepwise and backward stepwise methods were tested. From the results, the accuracy of spatial classifications for Standard (13 variables), forward stepwise (6 variables) and backward stepwise (6 variables) methods were 83.61 % respectively. Adopting forward and backward stepwise mode, a few parameters have been identified to be the most significant variables in discriminating the river region, and these parameters were: DO, *E. coli*, pH, PO_4, COD, and Cl.

PCA was applied on the datasets to identify the most important parameters influencing the identified regions of the study area. The Spearman Correlation Test was used to identify the type of development that most affects the water quality in the Kuantan river basin. Tabulations of the population distribution, population alternative slope (PAL), farming, livestock, industrial area, the number of workers in industry, and the industrial areas are in accordance with the number of workers (AI/AW), which affect the dissolved oxygen (DO) based on 90 % of confidence interval.

Conclusion

Chemometric techniques were adopted to investigate the spatial variability of water quality in Kuantan river basin. HACA had successfully classified the Kuantan River basin into three parts based on the homogenetic characteristics, known as LPS, MPS, and HPS were purposely used to identify the most successful and significant parameters The most significant parameters in discriminating the river regions based on DA methods were DO, *E. coli*, pH, PO_4, COD, and Cl, with the accuracy of the spatial classification at 83.61 %. After the varimax rotation of the PCA method, ten contributing parameters causing the variations in the surface water quality along the river basin was identified. The 90 % confidence interval of

correlation test showed that population distribution, alternative population slope, farming, livestock, industrial area, number of workers in the industry, and area of industry over number of workers in the industry were considered as land use activities that affect water quality, based on *T*-test analysis. This study has illustrated the use of chemometric techniques for analysing and interpreting complex water quality data. The methods have been utilised successfully to determine the most polluted locations and to identify land use activities that contribute to the deteriorating water quality in Kuantan river basin.

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Chapter 55
Artificial Aeration for the Enhancement of Total Petroleum Hydrocarbon (TPH) Degradation in Phytoremediation of Diesel-Contaminated Sand

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Abstract Phytoremediation, one of the green technologies, is an alternative method to remediate contaminated soil. An important factor in the degradation of organic matter in phytoremediation is the availability of oxygen. Plants were known to enhance an aerobic condition especially in roots area. Therefore, to enhance the degradation of TPH in soil, one of the alternatives was to increase the oxygen concentration. Three treatments with different diesel concentrations (50, 1,525 and 3,000 mg/kg) and aeration rate (0, 1 and 2 L/min) were employed. After 72 days, the highest degradation of TPH in sand (73.7 %) was achieved in diesel concentration of 3,000 mg/kg and an aeration rate of 1 L/min. This degradation was higher than TPH

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degradation in bed with aeration rate of 0 L/min (65.4 %). TPH concentration in plant for all diesel concentration with aeration rate of 1 L/min was higher than aeration rate of 0 and 2 L/min even though *S. mucronatus* was observed to grow well at the aeration rate of 2 than 1 L/min. The highest TPH concentration in plant was achieved by *S. mucronatus* that grew on diesel concentration of 50 mg/kg, i.e. 416.6 mg/kg for aeration rate of 1 L/min. At the end of experiment, bacteria population on 50 mg/kg diesel concentration with an aeration rate of 1 L/min was 52×10^3 CFU/mL. These indicated that aeration with a higher rate did not always give a better result than a low rate.

Keywords Artificial aeration · TPH · Diesel-contaminated sand · Phytoremediation

Highlights

- Phytoremediation of diesel-contaminated sand using artificial aeration was tested.
- Three concentration of diesel-contaminated sand and three aeration rate were examined.
- Aeration rate of 1 L/min gave the highest degradation of TPH.
- Higher aeration rate did not always give a better result than a lower rate.

Introduction

Most of the methods to remediate soil contaminated with diesel were costly and non-eco-friendly. Phytoremediation, one of the green technologies, is an alternative method to remediate contaminated soil. Diesel oils, generally is more toxic to plants than crude oil because it contains higher concentrations of light hydrocarbon components than crude oils (Lin and Mendelssohn 2009).

An important factor in the degradation of organic matter at a reed bed is the availability of oxygen. Plants were proven to enhance the aerobic condition especially in roots area. In order to enhance the degradation of TPH in sand, one of the alternatives was to increase the oxygen concentration. Zhang et al. (2010) investigated the effect of using artificial aeration on constructed wetlands for domestic wastewater treatment. Chazarenca et al. (2009) also used artificial aeration in constructed wetlands to increase the biological activities and stimulate nitrifying/denitrifying mechanisms. In this study, the effect of artificial aeration on the performance of diesel-contaminated sand phytoremediation was evaluated using *S. mucronatus*, a native aquatic plant in Malaysia.

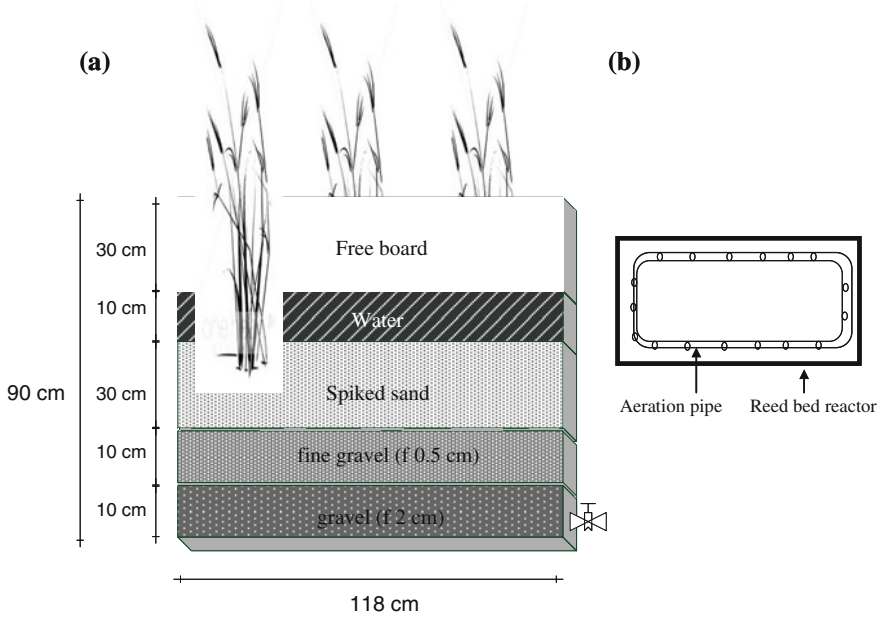

Fig. 55.1 Design of reed bed system. **a** Schematic of reed bed reactor. **b** Cross section of reed bed reactor

Materials and Methods

Different diesel concentrations namely 50, 1,525 and 3,000 mg/kg were employed for pilot scale experiment. The aeration rate was set at 0, 1 and 2 L/min respectively. Figure 55.1 shows the dimension and set up of pilot reed tank with the size of 1.18 × 0.9 × 0.9 m. The media used were gravel, fine gravel, and sand. The diesel fuel was mixed using acetone (R&M Chemical, UK) as a solvent. The sand was homogenised by stirring and left for two weeks prior to planting to let the acetone volatilize. After 2 weeks, the container was filled with tap water to maintain the wetness of the sand since the plants used were of wetland origin. The number of *S. mucronatus* planted in each tank was 60 plants to cover the whole surface area.

Approximately 10 g of sand samples was put into a 100 mL flask where anhydrous sodium sulfate (Merck, Germany) and 50 mL of Dichloromethane (DCM) (R&M Chemical, UK) was added later and stirred. Then, the samples in flask was put in an ultrasonic cleaner for 30 min at 50 °C. Later, the sample was filtered through glass wool and the extracted solution was poured into a 15 mL vial and left in fume hood for 3–4 days to allow evaporation process. The same procedure was conducted for 2 g of plant sample (root and stem). Analyses of the extracts (sand or plant) were concentrated to 2 mL in GC vials and analysed by Agilent 7890A Gas Chromatography (USA) with flame ionization detector (GC-FID). Percentage of diesel fuel degradation in sand was calculated from the TPH value of each sample

extracted from the sands at sampling time (TPH_t) subtracted from the TPH value of diesel fuel extracted from the sand at zero days (TPH_0).

Microbial population attached to the root sand was extracted. The population of living microorganisms in the rhizosphere of diesel-contaminated sand was determined by a serial dilution method, enumerated and reported in colony-forming units (CFU) per mL.

Results and Discussion

TPH degradation in sand with different diesel concentrations (50, 1,525, and 3,000 mg/kg) and aeration rates (0, 1 and 2 L/min) are depicted in Fig. 55.2. The highest degradation of TPH in sand (73.7 %) was achieved in diesel concentration of 3,000 mg/kg and aeration rate of 1 L/min. Meanwhile, the degradation of TPH in bed without aeration was 65.4 %. Sung and Chang (2004) investigated phytoremediation of diesel-contaminated sand in a column test planted with alfalfa for 100 days resulting in 98 % removal of TPH. They suggested that an air injection phytoremediation system can be used as a supplementary technique for the conventional phytoremediation.

Figure 55.3 shows TPH concentration in plant for all diesel concentrations on the last day of experiment (day 72). TPH concentration in plant for all diesel concentration with an aeration rate of 1 L/min was higher than aeration rate of 0 and 2 L/min even though *S. mucronatus* was observed to grow well in an aeration rate of 2 than1 L/min. The highest TPH concentration in plant was achieved by *S. mucronatus* that grew on diesel concentration of 50 mg/kg. These indicated that low aeration rate (1 L/min) was more suitable for phytoremediation of diesel-contaminated sand. According to Kang et al. (2010), the main mechanism in plant transpiration is the transfer of organic matter. Plants absorb organic compounds through the plant cell wall and then diffuse into the tissue sub-cellular.

Population of bacteria in *S. mucronatus* rhizosphere is shown in Fig. 55.4. Bacteria population from diesel concentration of 50 mg/kg with all aeration rates

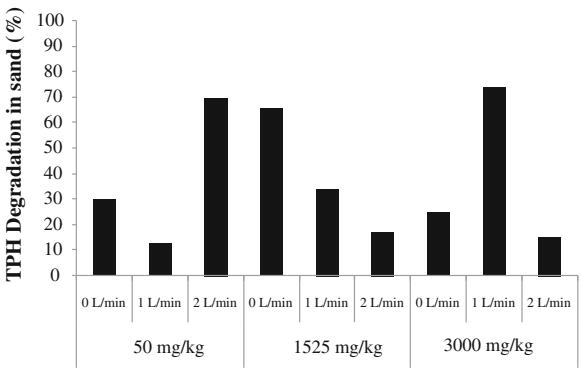

Fig. 55.2 TPH degradation in sand on the last day of experiment (72 days)

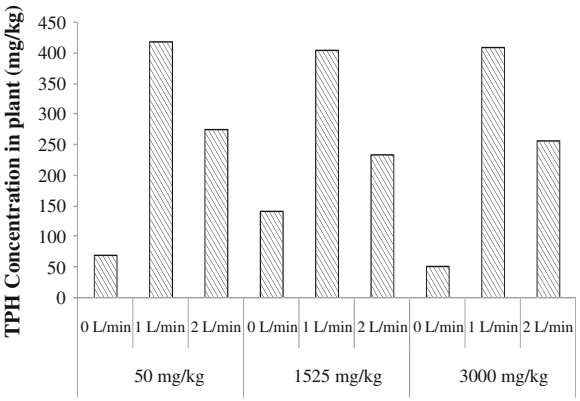

Fig. 55.3 TPH concentrations in plant on the last day of experiment (72 days)

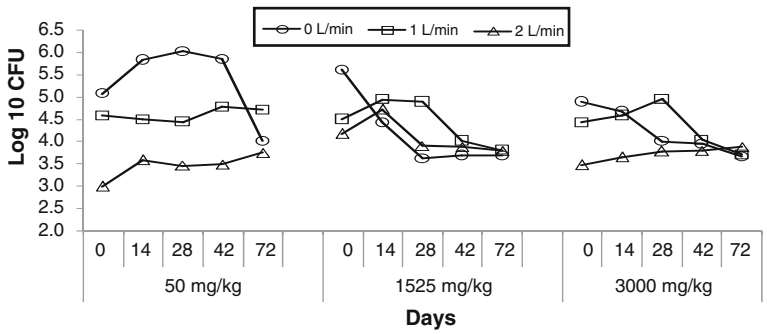

Fig. 55.4 Population of bacteria during 72 days of experiment

was higher than diesel concentration of 1,525 and 3,000 mg/kg. We calculated the population from diesel concentration of 50 mg/kg with an aeration rate of 1 L/min to be at 52×10^3 CFU/mL. Sung and Chang (2004) investigated phytoremediation of diesel-contaminated soil with an air injection system and found that an air injection could provide sufficient opportunity for microbial activity, increased microorganisms activity stimulated by plant root exudates and enhance biodegradation of hydrocarbon compounds via air provision.

Conclusion

After 72 days of phytoremediation, the highest degradation of TPH in sand for aeration rate of 1 L/min was 73.7 % for diesel concentration of 3000 mg/kg. The highest value of TPH concentration in plant was achieved on diesel concentration

of 50 mg/kg, with 416.6 mg/kg for aeration rate at 1 L/min. Population of bacteria in bed with aeration rate of 1 L/min (52×10^3 CFU/mL) was higher than 2 L/min (57×10^2 CFU/mL). Artificial aeration with different rates for phytoremediation showed that a higher aeration rate did not always give a better result than a lower rate.

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Chapter 56
Spatial Analysis of the Air Pollutant Index in the Southern Region of Peninsular Malaysia Using Environmetric Techniques

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Abstract Air pollution is becoming a major environmental issue in the southern region of Peninsular Malaysia. Environmetric techniques (HACA, DA, and PCA/FA) were used to evaluate the spatial variations in the southern region of Peninsular Malaysia, followed by API prediction comparison using ANN and MLR models. The datasets of air pollutant parameters for 3 years (2005–2007) were applied in this study. HACA clustered three different groups of similarity based on the characteristics of air quality parameters. DA shows all seven parameters (CO, O_3, PM_{10}, SO_2, NO_x, NO, and NO_2) gave the most significant variables after stepwise backward mode. PCA/FA identify that the major source of air pollution is due to combustion of fossil fuels in motor vehicles and industrial activities. The

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ANN model shows a better prediction compared to the MLR model with R^2 values equal to 0.819 and 0.773 respectively. This study concluded that the environmetric techniques and modelling become an excellent tool in API assessment, air pollution source identification, apportionment, and interpretation of complex dataset with a view to get better information about the air quality, and can be setbacks in designing an API monitoring network for effective air pollution resources management.

Keywords Air pollutant index · HACA · DA · PCA/FA · ANN · MLR

Highlights

- The stations has been categorized into three clusters: UHS, MHS and GHS.
- DA determines the most significant parameters that affected API in the study regions.
- Combustion of fossil fuels from motor vehicle are the major sources of air pollutant.
- ANN model shows better prediction compared to the MLR.

Introduction

Air pollution is becoming a major environmental issue in the southern region of Peninsular Malaysia due to the increasing number of transportations (mobile sources), trans-boundary pollution from neighbouring countries and the industrial activities (stationary sources), and they are the main sources of air pollution in Malaysia (Mutalib et al. 2013).

With increasingly of air pollution, it is important to investigate and predict air quality exactly for providing proper actions and controlling strategies so that the adverse effects to human health can be minimized. For predicting purposes, ANN and MLR were applied due to it has strong capability in predicting the complicated of data, can be trained accurately and gives a better performance compared to other models (Kamal et al. 2006; Karatzas and Kaltsatos 2007).

This study aims to identify the spatial variations on API in the southern region of peninsular Malaysia using environmetric techniques. This study also aims to perform comparative studies using multiple linear regressions (MLR) and artificial neural network (ANN) models in order to identify better air pollutant index prediction models.

Materials and Methods

Study Area

Eight stations were selected for this study-Pasir Gudang (CA0001: N01° 28.225 E103° 53.637), Bukit Rambai (CA0006: N02° 15.510 E102° 10.364), Nilai (CA0010: N02° 49.246 E101° 48.877), Johor Bahru (CA0019: N01° 29.815 E103° 43.617), Bachang (CA0043: N02° 12.789 E102° 14.055), Muar (CA0044: N02° 03.715 E102° 35.587), Seremban (CA0047: N01° 29.068 E103° 41.064), and Tampoi (CA0051: N01° 29.068 E103° 41.064).

Data Analysis

The data used in this study are daily concentration of Carbon Monoxide (CO), Nitrogen Dioxide (NO_2), Ozone (O_3), Sulphur Dioxide (SO_2), Mono-Nitrogen Oxide (NO_x), Nitrogen Oxide (NO), and particulate matter under 10 microns (PM_{10}) in eight stations for a 3 year period (2005–2007). All the data were provided by the Department of Environment (DOE). The methods of HACA, DA and PCA/FA from environmetric techniques were used to investigate the spatial temporal and variations of air quality. The MLR and ANN approaches were applied in the prediction model comparison. The correlation of determination (R^2) and root mean square error (RMSE) were chosen for measuring the network performance.

Results and Discussion

Classification of Sampling Station Based on the Air Pollutant Index

Data was analysed using HACA approach to classify the API stations based on its similarity. The eight stations were classified into three clusters-unhealthy site (UHS) represents CA006, CA0010 and CA0051, moderate healthy site (MHS) represents CA0001 and CA0019, and good healthy site (GHS) represents CA0043, CA0044 and CA0047.

Spatial Variations of Air Pollutant Index

DA was applied to the raw data into three main groups (clusters) defined by the HACA. The standard, stepwise forward, and stepwise backward modes were tested.

The spatial classification accuracy using standard (69.6 %), stepwise forward (91.0 %), and stepwise backward (94.4 %) mode DFA from seven discriminant variables were identified respectively. Seven variables (CO, NO_2, O_3, SO_2, NO_x, NO, and PM_{10}) were selected due to *p*-value of all parameters after stepwise forward and backward's test have high variation in terms of their spatial distribution.

PCA with FA was applied to the datasets in order to compare the compositional patterns between the examined ambient air quality parameters and to identify the factors that influence of the UHS, MHS, and GHS regions. The GHS region explains 70.2 % of the total variance, which comprises two PCs. The MHS and UHS regions which comprise three PCs, explain 79.3 % and 82.3 % of the total variance respectively.

GHS

VF1 explains 44.4 % of the total variance, showing strong positive factor loadings on NO_x (0.977), NO (0.886) and NO_2 (0.722), which related to the combustion of fossil fuels from motor vehicle exhaust, manufacturing industries, and food processing (Levine et al. 1984; Motallebi et al. 1990). VF2 explains 25.9 % of the total variance with strong positive loading on O_3 (0.740) and PM_{10} (0.869), which originated from burning of biomass and fossil fuels as well as from motor vehicles and natural emission sources (Mittal et al. 2007; Mutalib et al. 2013).

MPS

VF1 explains 43.3 % of the total variance, showing strong positive loadings on CO (0.775), NO (0.943) and NO_x (0.961), and could be considered by chemical components of various anthropogenic activities such as industrial, domestic, commercial and agricultural activities in the study area. VF2 explains 22.1 % of the total variance, showing strong positive loading on PM_{10} (0.751), which related to emission of fuels from motor vehicles and industrial activities. VF3 explains 13.8 % of the variance, showing a positive loading on SO_2 (0.983), which related to volcanoes activity from neighbouring countries and in various industrial processes such as combustion of coal and petroleum compound.

UHS

VF1 explains 39.8 % of the total variance and has strong positive loadings on NO_x (0.968) and NO (0.905), which related to the anthropogenic and natural activities such as burning of biomass and combustion of fossil fuels from motor vehicle

exhaust and various manufacturing industries. VF2 and VF3 explain 28.9 % and 13.7 %, respectively, of the total variance and shows strong positive loading on CO (0.851), PM_{10} (0.909) and SO_2 (0.956), which resulted from the motor vehicles combustions, coal powered power plants and uncontrolled burning of forests, volcano activities and dust storm from neighbouring country due to various activities (Mutalib et al. 2013).

Performance Comparison Between ANN and MLR Models

Performance indicators for ANN and MLR were used to compare for API prediction in the southern region of Peninsular Malaysia. From the findings, the API-ANN model ($R^2 = 0{,}819$; RMSE = 6.424) shows a better prediction compared to the API–MLR model ($R^2 = 0.773$; RMSE = 7.172).

Conclusion

Based on the analysis conducted, HACA grouped the study area (eight stations) into three clusters. The findings of DA in this study provide information that all parameters (CO, O_3, PM_{10}, SO_2, NO_x, NO, and NO_2) are the most significant variables and gave 94.4 % correct (after stepwise backward DA mode). For PCA/FA analysis, this method helped in identifying the sources or factors that responsible for API variations (which are mainly related to the combustion of fossil fuels, motor vehicle exhaust and natural sources such as volcanoes activity from neighbouring countries) in three different regions. Subsequently, receptor modelling in ANN and MLR of the API (API-ANN and API-MLR) provided apportionment by various sources in respective regions contributing to the air pollutants. The API-ANN model shows a better prediction compared to the API–MLR model. Thus, the application of environmetric techniques and modelling gave an excellent exploratory tool in API assessment, identification and apportionment of pollution sources, and interpretation of complex dataset in order to understand their spatial variations in the study area.

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Chapter 57
A Comparative Study of Groundwater Quality of Various Aquifer Systems in Malaysia

Mohammed Hatta Abd Karim, Hafizan Juahir and Ahmad Zaharin Aris

Abstract Groundwater resource has been exploited to a certain extent in Malaysia mainly to augment water supply to various needs of domestic, industry and agriculture. Many works have been concentrated to explore the optimum yield of groundwater in this particular area. Groundwater quality observations are merely to ensure they are within the required water quality standards. Studies on groundwater quality in Malaysia have not been in depth in terms of its origin, relationship to different types of aquifers, interrelationship with surface water, contamination possibilities as well as intrusion of saline water into the aquifers. The main objective of this paper is to examine the characteristics of groundwater quality in Malaysia particularly in alluvium and in hard rock layers. The study area will cover the Peninsular and East Malaysia comprising of 428 monitoring wells of various locations, sizes and types. A total of 267 wells are from the alluvium, while 161 wells are from the hard rock areas. Most of the shallow monitoring wells are from Sabah and Sarawak (East Malaysia) while the rest are from deep alluvium of Kelantan, Pahang, Perak, Selangor and Terengganu (Peninsular Malaysia). Hard rock wells are monitored mainly at Johor, Kedah, Negeri Sembilan and Melaka with some at Perak, Terengganu and Sabah. AQUACHEM is used to classify the types of groundwater present in Malaysia. Hierarchical Cluster Analysis (HCA) is to group the data into different clusters. Principal Component Analysis (PCA) is applied to get information on the most meaningful parameters due to spatial and temporal variations which describe the whole data set. Discriminant Analysis (DA)

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is used to construct the best discriminant function for each group of aquifers. Distinct differences are observed from samples of alluvium or hard rock aquifers of Peninsular Malaysia with East Malaysia. Based on the PCA, the most prominent variables of water quality of hard rock aquifers in the Peninsular Malaysia are Na, Ca, Cl, Cu and Pb, while in the East Malaysia are Na, SO_4, and Cl. For alluvial aquifers, the most prominent variables in the Peninsular Malaysia are Na, Mg and Cl, while in the East Malaysia are Na, K, Cl and CO_3.

Keywords Groundwater · Aquifer · Statistics

Highlights

- There are two classes of alluvial aquifer and hard rock aquifer each.
- Evidence of saline water intrusion in some places.
- High K groundwater quality of alluvial differed from hard rock aquifers.

Introduction

Groundwater is one of the nation's most important natural resources. The future large scale development of groundwater resources with accompanying decline in groundwater level, quality and negative impact to the environment has led to more concern among professionals and citizens with regards to the availability of groundwater in terms of quantity and quality. This paper examines the behaviour of groundwater quality of the country and to understand the characteristics of groundwater quality as well as its quantity. A comprehensive profile of groundwater in Malaysia can be used as a tool in effective decision making of managing groundwater resources in Malaysia.

The present groundwater utilisation covers only 3 % of the total water use in Malaysia which is 446 MLD (0.156 billion m^3/year). Water is mainly used for domestic needs (60 %), industrial sector (35 %) and agricultural sector (5 %) (Razak and Karim 2009). The wells are mostly vertical wells and distributed randomly throughout Malaysian. The natural allocation of water has been studied previously by JICA (1982), indicated that the annual groundwater recharge is 64 billion m^3. The rough estimate of groundwater storage in aquifers of Malaysia is 5000 billion m^3 (Mohammed 1999).

Groundwater has been used in Peninsular Malaysia since 1900s and to date only about 0.15 billion m^3 daily has been exploited. In Sarawak (part of East Malaysia),

groundwater is being extracted to about 0.05 billion m^3 daily while groundwater in Sabah (part of East Malaysia) is being pumped at about 0.02 billion m^3 daily.

In Malaysia, the alluvial aquifers are present mainly in many flood plains of major rivers that need to be studied in systematic manner to see their alluvial aquifer potentials. For hard rock aquifers favourable rock types with high fracture intensity are the most potential for groundwater. Unfortunately, there are still large areas in Malaysia that need to be explored. Effort is being made to use remote sensing tools together with selected geological parameters and use of GIS to earmark zones of most potential for groundwater in Malaysia (Manaf et al. 2012). This effort will make the nation-wide mapping of groundwater potential faster and cost effective.

Materials and Methods

The increase interest in groundwater development needs consistent monitoring followed by data analysis in order to see any intrusion, contamination and reduction of storage due to increase abstraction. The Minerals and Geoscience Department (JMG) has been monitoring the selected groundwater wells in all states (more than 3000 wells constructed) since year 1980. The data were compiled in JMG's groundwater databank named HYDRODAT. For this study, groundwater quality monitoring data from 2005 to 2012 for all states are taken into considerations. A total of 2985 water quality results are being used in the study. The parameters analysed are sodium, potassium, calcium, magnesium, ferrous, sulphate, carbonate, aluminium, flourite, bicarbonate, chloride, nitrate, arsenic, ammonia, manganese, copper, lead, zinc, strontium, barium, silica, nitrous oxide, pH, total solid, dissolved solid and conductivity.

This paper examines the patterns of groundwater quality in Malaysia; its classification, relationship between each element, in order to get information on the most important variables to the groundwater quality between various aquifer systems. From the geological point of view, the study area is divided into two major regions i.e. Peninsular Malaysia and East Malaysia. Due to distinct variations in properties of groundwater aquifers, the study has to do separate analysis for alluvial and hard rock aquifers.

This paper will focuses on using inferential statistics particularly the Multivariate Statistical Analysis (MVA) involving the use of HCA, PCA and DA. Many researchers have used the MVA for analysing groundwater quality, such as, Marengo et al. (2008) and Cloutier et al. (2008).

Results and Discussion

Hierarchical Cluster Analysis

For alluvial aquifers in Peninsular Malaysia, three classes are observed. Class 1 is more for the deep alluvium. Class 2 is those aquifers that are connected to saline water and Class 3 is those shallow aquifers that are within the boundaries of granite and sedimentary rocks.

For alluvial aquifers in East Malaysia, three classes are observed with one class showing distinct influence by saline water body while two other classes are have less chloride content and are within the fresh water zone.

For hard rock aquifers in Peninsular Malaysia, three classes are observed. Class 1 is more influence from igneous rocks. Class 2 is derived from younger sedimentary rocks and Class 3 is from the older sedimentary rocks.

For hard rock aquifers in East Malaysia, five classes are observed. Two classes are groundwater aquifer close to saline water bodies, two classes representing inland sedimentary rocks and one class is aquifer within mineralised surroundings.

Principal Component Analysis (PCA)

PCA of hard rock aquifer samples from Peninsular Malaysia shows that Na is correlated with Ca, Mg, SO_4 and Sr. Mg correlated with Cl, SO_4 and Sr while Cu correlated with Pb. The most contributing variables in F1 are Na, Ca and Cl, while in F4 Cu and Pb are prominent. These variables are mainly from the dissolution of parent rocks. Cu and Pb are from mineralised zones of the parent rocks.

Analysis using PCA is also applied to hard rock in East Malaysia and reveals that Na can be correlated well K, SO_4 and Cl. Ca is also correlated with HCO_3. The most contributing variables in F1 are Na, SO_4 and Cl. These variables are mainly from dissolution of parent rocks and probably some indication of saline water mixing.

PCA of alluvium in Peninsular Malaysia shows quite different result. Na is well correlated to Mg, HCO_3 and Cl. The most contributing variables in F1 are Na, Mg and Cl of which mainly comes from the alluvium itself.

Analysis using PCA to alluvium in East Malaysia shows distinct different from the other region. Na and K are correlated well with Cl. The most contributing variables in F1 are Na, K and Cl while in F5 CO_3 is prevalent. K most likely comes from the agricultural activities, while the rest can be from dissolution of minerals of the alluvium with calcareous member and/or derived from coral remnants of nearby saline water bodies.

Discriminant Analysis

The aquifers in Malaysia can be subdivided into shallow and deep aquifers. Seiler and Lindner (1995), distinguished the two aquifers using hydrodynamics concept. Near surface groundwater flows to the nearest river, while deep ones oriented their

flow lines deeper into a regional scale. Discriminant Analysis helps to get acceptable value for the depth of shallow aquifer. In all the four scenarios of shallow and deep aquifer boundary simulations, more than 64–95 % correct has been obtained when the shallow aquifer depth is not more than 15 m.

Conclusion

Groundwater aquifers in Malaysia can be divided into four main categories; alluvium of Peninsular Malaysia, alluvium of East Malaysia, hard rock of Peninsular Malaysia and hard rock of East Malaysia. Based on DA studies, the depth of the alluvium is generally within 15 m below ground level. From PCA analysis, the quality of groundwater in Malaysia is mainly from the dissolution of minerals of the respective geologic formation. There may be some indication of saline water mixing and probably some from fertiliser source especially in alluvium of East Malaysia. There is no evidence of any serious contamination from anthropogenic activities from the present study.

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Chapter 58
Extreme Value Theory for Modeling and Prediction of High PM_{10} Concentration in Johor

Nor Azrita Mohd Amin, Mohd Bakri Adam and Ahmad Zaharin Aris

Abstract When consider the extreme level of pollutant concentration, the Extreme Value Theory (EVT) is a best solution to model the extreme data and predict the level of dangerous concentration. This article analyzes the extreme PM_{10} concentration monitored at three monitoring stations in Johor. The diagnostic plots show that the GEV distribution of EVT with Frechet type is well fitted for modeling the monthly maximum PM_{10} concentration during the years 2001–2010, therefore, is sufficient for prediction. The application of EVT in air quality study is concerned on how well the mathematical theory further answer the question relating to the probability that the pollutant concentration will exceed a certain level in a period. In EVT, this quantity is often called return levels. The 10, 20 and 100-year return level is computed for future prediction. It is expected that the Muar station have high PM_{10} return level since it is located across the Malacca Strait from Sumatra, which is closest to the hot spots. The predicted return levels suggest that the intensity of coming pollution events for PM_{10} will worse in the future.

Keywords Extreme value theory (EVT) · PM_{10} · Gumbel distribution · Return level · Air quality index

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Highlights

- GEV distribution of EVT with Frechet type is well fitted to the extreme PM_{10} data.
- The trend for PM_{10} data for Pasir Gudang, Muar and Johor Bahru increase.
- Muar station has the highest prediction PM_{10} concentration level.

Introduction

High levels of air quality pollutant cause various impacts to human health and others materials and environmental damage. In order to minimize the adverse impacts of air pollutants, statistical models are commonly used to model and predict the air pollutants levels. Environmental risk studies are more concern with extreme situations than the average values due to its various dangerous impacts. However, most statistical methods are concerned primarily with the center of a statistical distribution, and not the tails of the distribution or the most extreme values at either ends. Therefore, this study will focus on the behavior of the tails of the distribution (extreme cases) and we call this as Extreme Value Theory (EVT). EVT is widely used in many fields ranging from environment, finance, insurance, geology, climate change, etc. Coles (2001) provide the necessary theoretical references for EVT as well as various application examples. At present, only a small number of literatures working on distribution fitting with consideration on extreme air quality concentration conducted in Malaysia (Hurairah et al. 2005; Yusof et al. 2011). Although there is no prior reason to make assumption of the probability distribution of air pollutants concentration, the choice of appropriate statistical distribution models is extremely significant (Jiang et al. 2011).

In the literature of extreme air pollution, Sharma et al. (2012) fit the Gumbel distribution for making predictions of the expected number of violations for monthly maximum sulfur dioxide (SO_2), nitrogen dioxide (NO_2) and suspended particulate matter (SPM) data. Lu (2004) claim that the monthly maximums of PM_{10} are well matched with Gumbel distribution and two-parameter exponential distribution and successfully predict the return period and exceedances over a critical concentration in the future year. Air quality study in Istanbul found that the usage of natural gas and higher quality coal improved the air quality of Istanbul after year 2000. However, this improvement has to be monitored wisely due to the increasing—population and associated traffic density. This work also considers the EVT to analyze air quality data and forecast future extreme events of SO_2 and NO_2 (Ercelebi and Toros 2009). Yusof et al. (2010) claim that the hourly average PM_{10} data for Seberang Perai area (industrialized area) fit the Lognormal distribution for 2000, 2001, and 2002 while 2003 and 2004 data fit to Weibull distribution model.

Materials and Methods

High PM_{10} level has been the common problem in Malaysia especially during dry season. During haze periods, PM_{10} was found as the main pollutant while the other air quality parameters remained within the permissible healthy standards (Payus et al. 2013). Therefore, this study focuses on extreme PM_{10} concentration based on block maxima approach which corresponds to GEV distribution. PM_{10} concentrations for Johor are stationaned at three locations: Johor Bahru (metropolitan area), Pasir Gudang (industrial town) and Muar (residential).

The EVT aims to characterize rare events and tails of distribution. The general designs of extreme value analysis are: first, extract a series of extreme values from the observations using block maxima or threshold method. Second, decide the model to be used and finally estimate the parameters. This work used monthly maxima series and estimates the parameters using MLE method in R software (ismev package). The monthly maxima series fit to GEV distribution based on EVT. GEV distribution function is given by:

$$G(z) = \exp\left\{-\left[1+\xi\left(\frac{z-\mu}{\sigma}\right)^{-1/\xi}\right]\right\};\ -\infty<\mu<\infty;\ \sigma>0;\ -\infty<\xi<\infty.$$

The parameters are location parameter, μ; scale parameter, σ; shape parameter, ξ. $\xi > 0$ correspond to Frechet distribution, $\xi < 0$ correspond to Weibull distribution and $\xi = 0$ correspond to Gumbel distribution. Prediction of the future extreme pollutant levels is extremely important in order to get prepared for their dangerous impacts. In EVT, the return level z_p used as the value that assume to be exceeded once every 1/p years. Return level for GEV is given by

$$Z_p = \begin{cases} \mu - \frac{\sigma}{\xi}\left[1-\{-\log(1-p)\}^{-\xi}\right], & \xi \neq 0 \\ \mu - \sigma\log\{-\log(1-p)\}, & \xi = 0. \end{cases}$$

Details on EVT can be referred to Coles (2001).

Results and Discussion

Table 58.1 provides the summary statistics of the monthly maxima PM_{10} concentrations. The highest recorded PM_{10} concentration was found in Muar with 532

Table 58.1 Data summary for monthly maxima PM_{10}

Stations	Min	Max	Mean	Std	Skewness	Kurtosis
JB	40	236	72.62	24.8461	3.0736	18.7571
PG	43	192	84.81	29.4802	1.5232	5.6192
Muar	45	532	95.45	57.8710	4.6461	31.3819

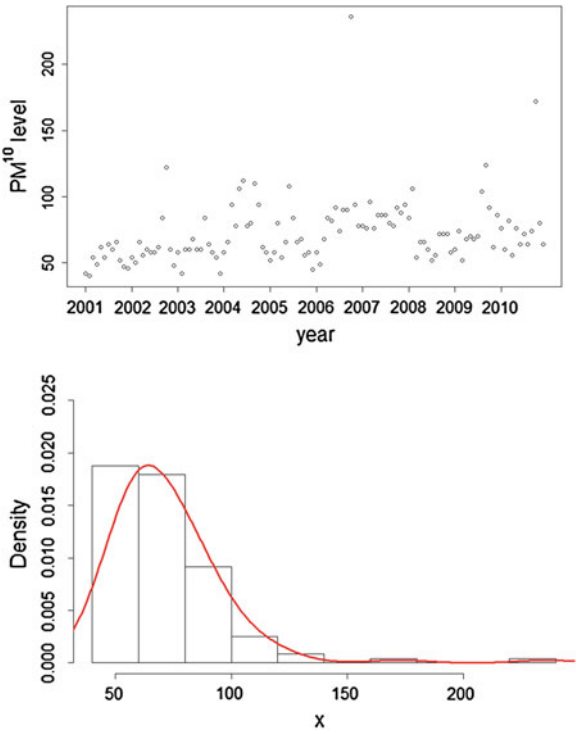

Fig. 58.1 Probability density for monthly maxima PM_{10} for Johor Bahru station

in year 2010. This is possibly due to the several haze episodes experienced in Muar and this situation will getting worse if there had been no rain in long periods. Figures 58.1, 58.2 and 58.3 show the probability density plot of monthly maximum PM_{10} data for three stations. These show that extreme PM_{10} concentration are positively skewed and supported by the descriptive statistics in Table 58.1 that the skewness greater than 0 and kurtosis greater than 3 implies the cases of extreme values. The extreme PM_{10} concentration for all the three stations fit the GEV distribution with $\xi > 0$ giving the heavy tailed case (Frechet type). From the plot, in 2006 Johor Bahru experienced 1-day high PM_{10} which exceeded 200 (very unhealthy) level while none for Pasir Gudang and 4 days for Muar in 2004, 2006, 2009 and 2010. The predicted return levels (Table 58.2) indicated that Muar showed higher return levels of PM_{10} in the future compared to others station. We also notice that the PM_{10} concentration for Pasir Gudang station will have higher concentration in the future compared to Johor Bahru although it does not experienced PM_{10} higher than 200 for the study periods.

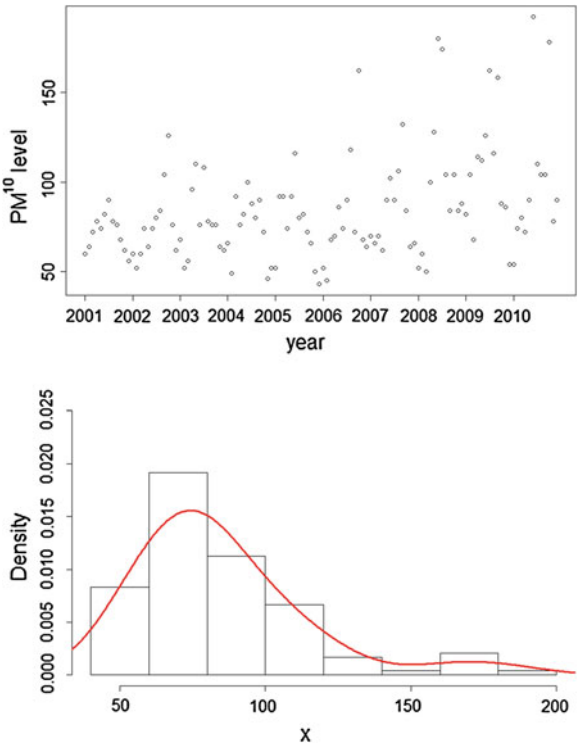

Fig. 58.2 Probability density for monthly maxima PM_{10} for Pasir Gudang station

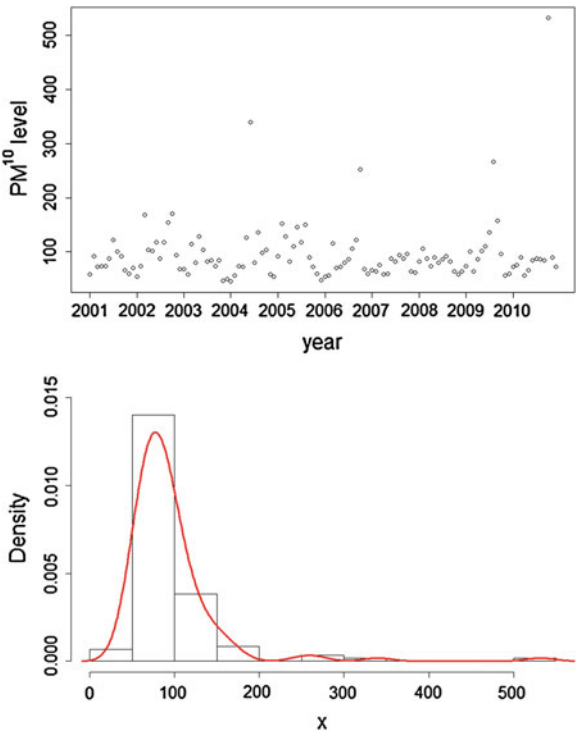

Fig. 58.3 Probability density for monthly maxima PM_{10} for Muar station

Table 58.2 Parameter estimates and return level for GEV model of monthly maxima PM_{10} data for three stations in Johor

Stn.	Parameter estimation			Return level		
	μ	σ	ξ	10 years	20 years	100 years
JB	62	14.6	0.131	100	115	154
	(59, 65)	(12.4, 16.8)	(0.007, 0.255)	(91, 109)	(102, 128)	(123, 185)
PG	72	19.3	0.126	121	141	191
	(67, 5)	(16.3, 22.3)	(−0.016, 0.269)	(110, 133)	(122, 159)	(147, 235)
Muar	73	21.1	0.303	141	176	284
	(69, 77)	(17.5, 24.6)	(0.158, 0.449)	(127, 157)	(149, 203)	(201, 373)

Conclusion

The EVT provides a sufficient model that can be used as a predictive tool for presenting future air pollution scenario and to help managing the future air pollution problem. Necessary actions must be taken to improve air quality and to prepare if the unexpected pollution happens.

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Chapter 59
Spatial Variations of Drinking Water Quality Monitoring in Water Treatment Plant Using Environmetric Techniques

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Abstract This research investigates the relationship between the physicochemical levels and the drinking water quality in Kuala Kubu Bharu, Selangor, Malaysia based on three different classes of drinking water. The environmetric techniques such as the discriminant analysis (DA), the principal component analysis (PCA) and the factor analysis (FA) were applied to analyze the spatial variation of the most significant physicochemical parameters of the drinking water quality and to determine the source of pollution. Seven physicochemical variables were analyzed. The forward and backward stepwise DA managed to discriminate six and two variables, respectively from the original seven variables. PCA and FA (varimax functionality) were to identify the origin of each water quality variable based on the three different drinking water classes. This study shows that environmetric method is the ideal way into provide meaningful information on the spatial variability of sophisticated drinking water quality data.

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Keywords Environmetric techniques · Discriminant analysis · Principal component analysis · Factor analysis · Drinking water quality

Highlights

- The drinking water quality at this study site is within the national standards.
- Color and turbidity are dominant physiochemical characteristics.
- Constructions, aquaculture and agriculture are sources of pollution.

Introduction

A safe, palatable and aesthetically appealing supply of drinking water to the public is vital. The National Standard for Drinking Water Quality has set a benchmark values for the drinking water parameters. The benchmark value for pH is 6.5–9.0. The benchmark value for Turbidity should be 5 NTU. The total suspended solids content is one of the most revealing properties of turbidity. Drinking water should not contain any settleable suspended solids. Next the benchmark value for colour is 15 TCU. Good drinking water should be colourless. The accepted benchmark values for Fe, Al, NH_3 and Mn are 0.3, 0.2, 1.5 and 0.1 mg/l respectively.

This study was carried out in the Kuala Kubu Bharu Water Treatment Plant by analyzing the secondary data of physicochemical levels of the drinking water quality. The data comprises of the monthly observations from January to December 2011.

In this study, the spatial analysis was conducted to identify the most significant parameters in the drinking water quality. The method that was used in this study is known as environmetric. Environmetric uses multivariate statistical modeling and data treatment. Environmetric also is known as chemometric (Simeonov et al. 2003). Environmetric helps to reveal and analyze multifaceted correlation in a broad range of environmental applications (Alberto et al. 2001). Environmentric has been widely used in analysing environmental data (Hafizan et al. 2010).

The objectives of this study are: (i) to analyze the physiochemical activities in the collected drinking water samples from the treatment plant, (ii) to identify the source of pollution for the significant parameters, and (iii) to compare the data of drinking water from the water treatment plant with the Drinking Water Standards set by the Ministry of Health Malaysia. This study could be a source of references for the future projects in the same field.

Materials and Methods

This study was carried out in the area of Kuala Kubu Bharu, situated in Hulu Selangor in the district of Selangor State in Malaysia. The geographical coordinates of this area is N3°34′ 0″, E101°39′ 0″.

The secondary data of physicochemical levels of the drinking water quality from Kuala Kubu Baru Water Treatment Plant were analyzed. The data comprises of the monthly observations from January to December 2011. The sampling stations are located at the Gerachi and Kubu River.

The data consist of three types of water samples: raw water, settled water and clean water. The source of the raw water is from Sungai Geraci and Sungai Kubu.

In this study, Discriminant Analysis (DA) was used to study the spatial variation between the different classes of drinking water such as raw water, settled water and cleaned water. The drinking water classes were used as dependent variables while the physicochemical parameters as the independent variables.

Principal Component Analysis (PCA) was applied for interpretation by identifying the latent factors that influence each class (Raw Water, Settled Water, and Cleaned Water). For this study, PCA/FA was applied to the standardized data sets (seven variables) for three diverse classes.

Results and Discussion

The physicochemical levels in water supply from the surface water intake in Kuala Kubu Bharu Water Treatment Plant are within the standards set by the Ministry of Health Malaysia (MOH), Privatization Cum Concessionaire Agreement (PCCA) and Internal guidelines (PNSB) (Standard Kualiti Air Wilayah Utara 2011).

The mean of the pH obtained for raw water, settled water, and clean water were 6.79, 6.64 and 7.37, respectively. The mean colour for raw water, settled water, and clean water were 26.52, 6.81 and 5.03 HU, respectively. The mean of turbidity for raw water, settled water, and clean water were 13.78 NTU, 3.57 NTU and 2.18 NTU, respectively. The mean concentration of Fe for raw water, settled water, and clean water were 0.035, 0.082 and 0.017 mg/l, respectively. The mean concentration of Al for raw water, settled water, and clean water were 0.017, 0.00, and 0.00 mg/l, respectively. The mean concentration of NH_3 for raw water, settled water, and clean water were 0.0096, 0.00 and 0.0035 mg/l, respectively. The mean concentration of Mn for raw water, settled water, and clean water were 0.046, 0.00 and 0.019 mg/l, respectively. From the results, the drinking water quality at this study site is within the national and international standards.

Spatial Variation of Physicochemical Parameters

The accuracy of spatial classification using standard mode of DA, forward stepwise and backward stepwise were 91.87 % (seven discriminant variables), 91.87 % (six discriminant variables) and 91.87 % (two discriminant variables) respectively. This shows that the classification matrix accuracy is excellent. The six discriminant variables in the forward stepwise analysis were found to be pH,

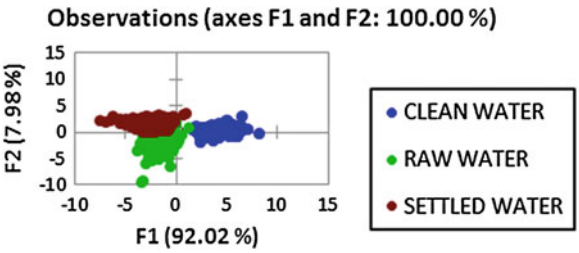

Fig. 59.1 The observation between three different classes of drinking water

Fe, Mn, Al, NH_3 and Turbidity. While for the two discriminant variables in the backward stepwise analysis shows only Fe and colour are the most significant parameters. The observations between three different classes of drinking water are shown in Fig. 59.1.

Source Identification of the Monitoring Area

From the study, VF1 has 28.06 % of the total variance and has strong positive loadings for colour and turbidity. The natural contributors are from anthropogenic sources (Tadesse et al. 2010). The runoffs from fields with high load of soil could lead to soil erosion which will eventually contaminate the Gerachi River and Kubu River. Construction activities nearby the Sungai Gerachi also can increase the turbidity level. The high loading of colour in the drinking water has been a major problem in drinking water quality (Aini et al. 2007). The high loadings of turbidity and colour are also contributed sewage waste from the aquaculture activity near Sungai Gerachi.

The total variance of VF2 is 27.35 % which shows positive loadings in pH and aluminium, and negative loading in iron, which it is caused by the acid rain. The strong loadings of iron and aluminium are due to the usage of fertilizers in agricultural industry near the Sungai Gerachi and Sungai Kubu.

VF3 explains 18.96 % of total variance and shows strong positive loading of ammonia (NH_4) and manganese (Mn). The high loading of ammonia and manganese can be attributed to the effluent waste from aquaculture industry near the Sungai Gerachi.

Conclusion

Based on the prolonged observation of the concentration of the physicochemical levels in the water distributed to the water supply system from the surface water and ground water intakes in Kuala Kubu Bharu, it shows that the produced water

are at par with the National Standards of Drinking Water standards. In conclusion, the multivariate statistical technique helped to provide significant input on the spatial variability of a large and multifaceted drinking water quality data.

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Chapter 60
Consortia Development of Hydrocarbon Degrading Rhizobacteria Isolated from *Scirpus grossus* in Diesel Exposure

Israa Abdul Wahab Al-Baldawi, Siti Rozaimah Sheikh Abdullah, Fatihah Suja', Nurina Anuar and Mushrifah Idris

Abstract The biodegradability of total petroleum hydrocarbons (TPH) as a diesel model by isolated rhizobacteria was investigated. We examined the biodegradability of diesel with n-alkanes chain (C8–C32) by mixed culture of rhizobacteria. Maximum biodegradation removal of TPH about 17.8 % achieved in mixed culture of Group A. Biodegradation is one of the appropriate techniques to reduce hydrocarbons contamination in the environment and it was an efficient method used to degrade hydrocarbons.

Keywords Biodegradation · Phytoremidaition · *Scirpus grossus* · Rhizobacteria · Diesel

Highlights

- The origin of the rhizobacteria in this study is from *Scirpus grossus* roots.
- Plant associated rhizobacteria can enhance contaminant degradation.
- Microorganisms consortia provides a promising strategies to clean the environment.

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Introduction

Water and soil pollution caused by petroleum hydrocarbons especially diesel from industrial wastes and oil spill accidents are extensive. The main process for the effective removal and elimination of total petroleum hydrocarbon (TPH) from contaminated water is via convergence of phytoremediation and microbial bioremediation strategies (Gerhardt et al. 2009; Zhang et al. 2013). The interaction between plants and bacteria enhances phytoremediation because plants can promote the degradation of available fractions by stimulating microbial activity, increasing the number of sites for the adsorption of contaminants, and exude compounds that increase the bioavailability of contaminants (Parrish et al. 2005). Biodegradation of petroleum hydrocarbons in different medium by bacterial cultures has been reported in both batch and field scale studies. This study was aimed to investigate the role of selected rhizobacteria for application in bioremediation of diesel contaminated wastewater.

Materials and Methods

Biodegradation Test of Isolated Rhizobacteria

Isolated rhizobacteria from rhizosphere zone for different treatments of diesel contaminated water were tested to determine their ability to degrade diesel. The biodegradation of selected rhizobacteria was evaluated under diesel stress in consortium (mixed culture). The diesel concentration used in this assay was 3 % (V_{diesel}/V_{water}) (Al-Baldawi et al. 2013). Mineral salts medium (MSM) containing diesel of 3 % (V_{diesel}/V_{water}) as hydrocarbon source was inoculated with rhizobacteria for biodegradation test. Four groups of mixed culture were tested for biodegradation: Group A (D8 + B7 + B12), Group B (B7 + B12), Group C (D8 + B7) and Group F (D8 + B12). The biodegradation test was done for 5 days using two conical flasks replicate for each sampling day (Ye et al. 2011). Physical and chemical parameters of culture medium such as pH, temperature (°C), oxidation reduction potential (mV) and dissolve oxygen DO (mg/L) were recorded.

Sample Analysis of Residual Diesel After Degradation Process by GC-FID

The ability of rhizobacteria to degrade n-alkanes (C8–C32) of 3 % diesel concentration (V_{diesel}/V_{water}) as sole carbon sources was tested. Two conical flasks of samples were harvested through centrifugation (Eppendorf/Centrifuge 5418) at

4000 rpm, 4 °C for 10 min. The supernatant was extracted at every 24 h time interval for 5 days. Dichloromethane (DCM) was used to extract the hydrocarbons from the sample. Samples were then dried over anhydrous sodium sulphate. The residuals were put into a 10 mL vial and then the remaining water was let to evaporate for 3–4 days in an overhead fume hood. The extract was then concentrated to 2 mL volume and analysed by gas chromatography GC–FID. The percentage of TPH Removal on each sampling day was determined by using the following equation:

$$\% \text{ Biodegradation} = \frac{TPH_0 - TPH_h}{TPH_0} \times 100$$

where

TPH_0 total petroleum hydrocarbon sampling on 0 h

TPH_h total petroleum hydrocarbon on each sampling hour

Results and Discussion

Biodegradation of Diesel by Isolated Rhizobacteria

Physicochemical parameters of pH (6.5–7.5), temperature (22–28) °C and ORP (−50)–(+50) mV remained constant along 5 days of experiment. There were no significant changes in pH, temperature, and ORP observed. Dell'Anno et al. (2012) found that temperature played major role in biodegradation in both aerobic and anaerobic conditions and may either promote or depress bacterial biodiversity depending on the redox potential conditions. An increase in the degradation rates of hydrocarbons was observed in aerobic conditions while in anaerobic conditions a decrease of hydrocarbon degradation rates was observed.

Mixed Culture

Four groups were tested for biodegradation: Group A (D8 + B7 + B12), Group B (B7 + B12), Group C (D8 + B7) and Group F (D8 + B12). The removal efficiency for each group was fixed (Fig. 60.1). The highest efficiency removal of n-alkanes was observed in Group A which include three rhizobacteria types D8 = *Bacillus aquimaris*, B7 = *Bacillus anthracis* and B12 = *Bacillus cereus* with degradation percentage of 17.8 %. The trend of total petroleum hydrocarbon (TPH) for the best performance of Group A is shown in Fig. 60.2 for 0 h and 120 h. Gargouri et al. (2011) used the mixed cultures (containing *Aeromonas punctate, Aeromonas caviae*, *Bacillus cereus*, *Ochrobactrum intermedium*,

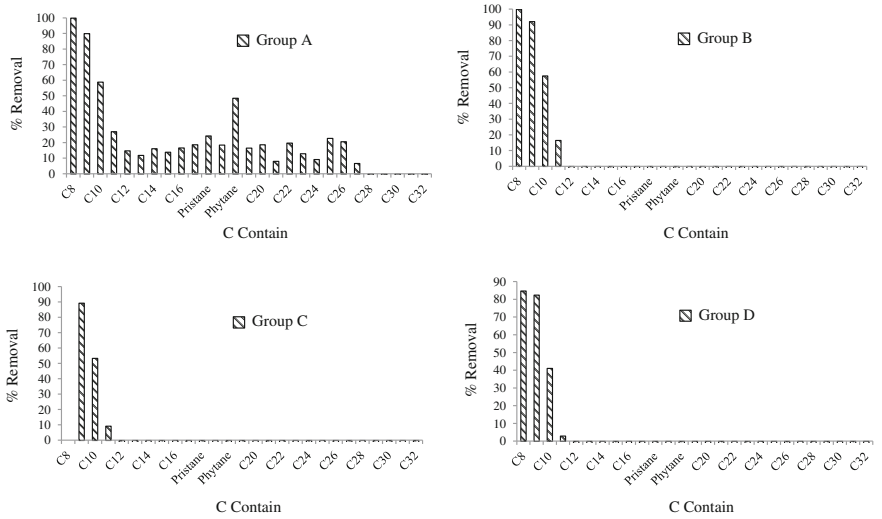

Fig. 60.1 Biodegradation removal percentage of C contain in mixed culture groups

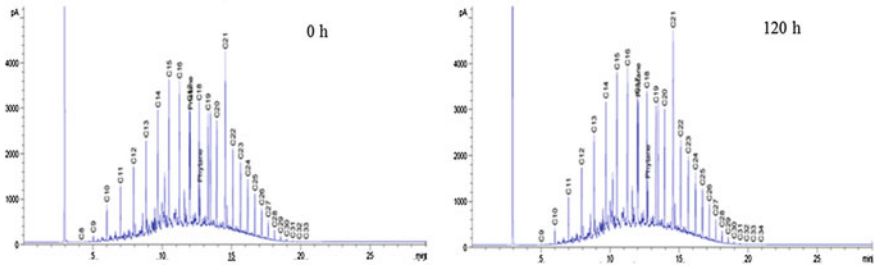

Fig. 60.2 Chromatogram of diesel extracted at 0 h and 120 h for Group A

Stenotrophomonas maltophilia and *Rhodococcus sp*) to degrade hydrocarbon-rich industrial wastewaters for hydrocarbons range n-alkanes (C10–C35) with an efficiency rate of more than 70 %. Bioremediation technology is a promising mechanism for treatment of water and soil contaminated with petroleum hydrocarbon (Taccari et al. 2012).

Conclusion

This paper discusses phytoremediation of diesel contaminated water using diverse groups of rhizobacteria from *Scirpus grossus* having different potential to degrade TPH. The highest efficiency removal for n-alkanes was observed from Group A

which include three rhizobacteria types D8 = *Bacillus aquimaris*, B7 = *Bacillus anthracis* and B12 = *Bacillus cereus* with degradation percentage of 17.8.

This mixed culture with degradation ability for a wide range of n-alkanes can be utilized and enhanced for bioremediation and phytoremediation of wastewater contaminated with diesel. The monoculture of the three strains had higher degradation percentages than the respective mixed culture. These results reveal that isolated rhizobacteria from contamination site are good sources for TPH-degraders which can be used for TPH bioremediation as a consortium.

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Chapter 61
Solid Waste Management Transition in Selangor: Issues and Challenges

Nurul Fadila Fadhilludin, Latifah Abd Manaf and Sabrina Ho Abdullah

Abstract Solid waste management in Malaysia has been facing many changes since a few decades ago. In September 1995, the Government decided to privatize the management of solid waste and in 2007 the Cabinet decided that the interim privatization is to cease for full privatization. With the Local Authorities (LAs) losing their authority, this privatization and enforcement of Act 672 has raised some dispute between the Federal Government and State Government in Selangor. Due to the conflict, Selangor has been exempted from the enforcement of the Act 672 and later terminate Alam Flora as their contractor. Therefore, the responsibility of managing the solid waste in each area will be under LAs and being monitored by the State Government. Based on the interview with several LAs officers in Selangor, this transition has positive and negative impacts to them. The termination of Alam Flora as their waste contractor can save a lot of money as they are managing the solid waste on their own. The LAs in Selangor is also directly involves with the process thus know the real situation of their solid waste scenario in their jurisdiction. Besides that, with the rotation system of hiring contractor in each LA, solid waste management can be improved. However, the LAs need to come out with their own plan for environmental program as Federal Government is not responsible for their solid waste management. Termination of Alam Flora has also increased workload for the LAs. Adaptation of new contractor has also caused time consuming and delay in solid waste disposal. This paper will discuss more on how this transition process gives impact to the LAs in Selangor.

Keywords SWM · LAs · Federal government · Transition · Issues · Challenges

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Highlights

- Transition of solid waste management in Selangor has positive and negative impacts.
- No uniformity between each local authority in managing their solid waste.
- Privatization of solid waste saves money.

Introduction

Solid waste management in Malaysia has been facing many changes since a few decades ago. Prior to privatization, solid waste management and public cleansing were the responsibility of the LAs, and were normally subcontracted to smaller waste management service providers. However, with the increasing costs of waste management, the situation resulted with subcontractors not being paid promptly, leading to drastically reduced efficiency (Periathamby et al. 2009). Therefore, in September 1995, the Government decided to privatize the management of solid waste and as an initial step; privatization is being carried out on an interim basis. On 1st January 1997, solid waste collection and transportation all over Malaysia has been taken over by Southern Waste Sdn Bhd and Alam Flora Sdn Bhd (Yahya and Larsen 2008). Then, in 2007 the Cabinet decided for full privatisation at the Southern and Central Zone to take place as soon as the Solid Waste and Public Cleansing Management Act 2007 come into force which adds on E Idaman Sdn Bhd as another concessionaire (Yahaya and Larsen 2008). The authority governing solid waste and public cleansing is shifted from state governments and LAs to the federal government and the management cost will be shared between these two parties. LAs will direct funds to a federal corporation that directly manages solid wastes. As an implication, all of this process has caused many reactions especially in Selangor. This led to many changes in Selangor solid waste management system and led to several issued and dispute between the Government of Selangor and other parties. As Selangor is generating the highest amount of solid waste in Malaysia, the solid waste management is very crucial and become a serious issue to all parties including public.

Issues of Solid Waste Management Transition in Selangor

Before privatisation, solid waste in Selangor was administrated by Local Authorities (LA), and solid waste is under Concurrent List (List 3) of the Ninth Schedule of the Federal and State constitution which stated both state and federal have jurisdiction over the solid waste administration. However, the government decided to

privatize the solid waste management and transferred the executive authority on solid waste management and public cleansing in Peninsular Malaysia from the Local Authorities to the Federal Government by enforcing the new act 672 on solid waste management. With the LAs losing their authority, this privatization and enforcement of Act 672 has raised some dispute between the Federal Government and State Government. LAs in Selangor are concerned that the enforcement of Act 672 will cause long term technical problem that will waste their resources and financial (Portal Dewan Undangan Negeri Selangor 2011). Besides that, the solid waste management in Selangor was being concession to Alam Flora before this. Unfortunately there are arrears that Selangor LAs faced with the Alam Flora which has reached to RM 133 millions. Therefore with the enforcement of this new act, the LAs need to settle this arrears which seems impossible as it involved a lot amount of money in a short time (Portal Dewan Undangan Negeri Selangor 2011). With all this obstacles Selangor has decided not enforcing the Act 672 and are allowed to be exempted (Hock 2011). They also terminated the Alam Flora services for solid waste cleansing and manage the solid waste themselves to save cost in managing the solid waste (Idris 2011). This has caused dispute between the Employee Union Congress and the Federal Government because the privatization lead to the termination of Alam Flora and cause 765 employees losing their job. However, fortunately the issue has settled by transferring these employees to another state where Alam Flora being concession under the Federal Government after enforcement of Act 672 (Idris 2011). With Selangor is being exempted from the enforcement of Act 672 and terminating their one and only solid waste management contractor, the LAs face bigger challenges in managing their solid waste. Therefore, the responsibility of managing the solid waste in each area will be under LAs and being monitored by the State Government.

Benefits of the Transition on Selangor Solid Waste Management

It is stated that there are many benefits from this transition process to the LAs. Firstly, the termination of Alam Flora as their waste contractor can save a lot of money as they are managing the solid waste on their own. With the increasing in solid waste generation in Selangor, it is necessary for the LAs to save their cost where possible as to use the budget appropriately where necessary. For example, in Petaling Jaya City Council, average cost for managing their solid waste management is from 45 to 60 million a year. By reducing cost for third party, this budget can be used for other green program or incentives to public in participating in city council program.

Besides that, by managing the solid waste collection themselves, the LAs in Selangor are directly involved with the process thus know the real situation of their solid waste scenario in their jurisdiction. LAs communication with public will be closer and every problem in community can be detected early to be solved.

LAs will also be more responsible for their jurisdiction as they are competing between each other to give the best service for their community. In addition, the LAs will also be more creative and active in conducting environmental program on their own in their jurisdiction and not being restricted by federal government.

Performance of contractor that is being hired by each LA can be monitored seriously and thus ensures high performance as they can be terminated if their performance is not satisfying. Unlike before, the contractor cannot be terminated therefore any unsatisfying performance by them will not cause severe impact and lead to lower performance. With the rotation system of hiring contractor in each LA, they will perform their best in order to not lose contract for waste collection service and improved the service.

Challenges of Solid Waste Management in Selangor

With the transition taking place, there are many impacts to the LAs in Selangor regarding their solid waste management. First of all, with the exemption of Act 672, the Federal has no authority in managing the solid waste in Selangor (Berita Harian Online 2011). Therefore, the LAs in Selangor needs to solved and conduct program on their own for their community such as waste separation at source program. In addition, if LAs in Selangor run out of funds and need more money for the work, they cannot apply to the Federal Government for funds (Hock 2011). This is a big risk for LA in Selangor. Hence, the LAs need to come out with their plan for such program of waste separation activity.

Besides that, there is no uniformity between each LA in managing their solid waste. As the state government is only monitoring the process, each LAs needs to figure out a plan for a better waste management. Therefore, it is hard to compare or each LAs progress in managing their waste. This lead to difference action between LAs where some are focusing on their technical matter and other LAs are focusing on their community participation.

In addition, termination of Alam Flora as a previous contractor has increase workload for the LAs. This is because; LAs needs to manage their solid waste collection and disposal by themselves. Therefore, they need to hire new contractor and deal with them in every aspect such as performance monitoring, monthly payment, and other aspects. They are also facing shortage of manpower and experts as solid waste is being managed by Alam Flora before. Termination of previous contractor has also lead to time consuming and delay collection as new contractor needs to adapt to the waste collection activities such as collection area map, rules, and process. Besides that, as LAs has no sources, tools, man power and equipment for waste collection, it is time consuming and for them to equipped themselves before taking care of the waste collection activities left by the previous contractor. This has caused a lot of problems such as improper and delay waste collections that lead to public complain. As the public complain increasing during early transition period, it has caused a bad reputation for the LAs.

Conclusion

As a conclusion, transition of solid waste management in Selangor has its positive and negative effects. Therefore, to improve solid waste management in Selangor, the government needs to evaluate and analyze each and every aspects of this new system. LAs should also cooperate with public in order to find the best way in servicing them. Lastly, the most important thing the Federal and Local Government should cooperate together in managing the solid waste in Malaysia.

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Chapter 62
Contribution Fuel Consumption of Fishing Vessel Operation to Greenhouse Gas Emission

Nurashida Saad, Ahmad Makmom Abdullah, Hafizan Juahir and Rosta Harun

Abstract Fishing vessel operation highly depends on fossil fuels such as gasoline, diesel to generate power. Combustion of fossil fuel would generate greenhouse gas emission such as carbon dioxide. However, the estimation of carbon dioxide emission from fishing vessel is rather scarce in Malaysia. This paper describes carbon dioxide emission estimation from fishing vessels operation in Selangor. This study was conducted at four fisheries districts in Selangor where fishing vessels anchored for operation. Fishing operation activities were divided into four fisheries operation zones (A, B, C, and C2). It involved 3,252 fishing vessels. Firstly, carbon dioxide emission for each vessel is determined by using tier 1 method waterborne navigation equation provided from Chapter 3 mobile combustion, volume two Energy, 2006 IPCC Guidelines for National Greenhouse Gas Emission Inventory. After the carbon dioxide emission estimation was calculated, an inventory of emission was carried out. Then, ANOVA test was used to determine the significant differences between fishing gear and fisheries zones. Total carbon dioxide emission from fishing vessels operation in Selangor is 295.44 Gg CO_2 for 2012. ANOVA test indicated there is difference in the mean carbon dioxide emission estimation between different types of fishing gear. There are also significant differences in the mean carbon dioxide emission estimation from four different fisheries zones in Selangor. Turkey Kramer Multiple Comparisons was applied to determine the pair of carbon dioxide emission of fishing vessels between types of fishing gears and fisheries zones. The burning of 89.35 Gg of fossil fuel by fishing operation released 295.4 Gg in 2012. Total amount of carbon dioxide emission from fishing vessel is low compare to latest Malaysia total carbon dioxide

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emission in 2000, 222,990 Gg CO_2. In conclusion, status of carbon dioxide emission by fishing vessel operation has been determined for Selangor.

Keywords Carbon dioxide emission · Fuel consumption · Fishing vessel operation

Highlights

- Fuel consumption of fishing vessels operation resulted low carbon dioxide emission.
- Active fishing gears vessels produced higher carbon dioxide emission.
- Lower Gross Rough Tonnage (GRT) class of vessel influenced carbon di-oxide emission.

Introduction

Fishing vessel operation highly depends on fossil fuels such as gasoline and diesel to generate power (Tydmers P and R Parker 2012). Combustion of fossil fuel would generate greenhouse gas emission such as carbon dioxide. Approximately, global fishing fleet was estimated to use 41 million tonnes of fuel per annum and release 130 million tonnes of carbon dioxide (World Bank and FAO, 2012). Selangor is one of the states in Malaysia that focuses on medium and small scale of fishing operation. It has a large number of fishing vessels operation in Peninsular of Malaysia after Johor and Perak (DOF, 2011). The operation of fishing vessel is licensed base on fishery zones (A, B, C, C2). Zone A is for distance 5 nm from shoreline which used by traditional fishing gear and anchovy purse seine with vessel size 1–19.9 GRT. While zone B for distance 12 nm from zone A line with fishing gear are trawl nets and fishing purse seine used by vessel in size 20–39.9 GRT. Distance for zone C is 12 nm from zone B line used by vessel in size 40–69.9 GRT with fishing gear similar to zone B. Zone C2 distance is more than 30 nm from zone C line. The size of vessel in zone C2 is more than 70 GRT. It was for deep sea fisheries. Since the fishing operation fully depends on fossil fuel, high consumption of fossil fuel will cause high carbon dioxide emission. However, the estimation of carbon dioxide emission from fishing vessel is rather scarce in Malaysia. This study can contribute to the baseline data in improving and enhancing sustainability of fishing activities. This paper describes carbon dioxide emission estimation by fishing vessels operation in Selangor.

Materials and Methods

This study was conducted at four fisheries districts in Selangor where fishing vessels anchored for operation. The fisheries districts were Kuala Langat, Pelabuhan Klang, Kuala Selangor and Sabak Bernam. Secondary data for the year 2012 from selected fisheries agencies were gathered for this study. Fishing operation activities was divided into four fisheries operation zones (A, B, C, C2). It involved 3,252 fishing vessels. Firstly, carbon dioxide emission for each vessel is determined by using tier 1 method waterborne navigation equation provided from Chapter 3 mobile combustion, volume 2 Energy, 2006 IPCC Guidelines for National Greenhouse Gas Emission Inventory. The guidelines consist of methods and equation on how to calculate direct greenhouse gas emission from various sources. In the guidelines, fishing vessels operation is listed using code and name 1 A4c iii fishing (mobile combustion) in detailed sector split for transportation sector. Carbon dioxide emission will be estimated by multiplied annual fuel consumption of each vessel with emission factor of fuel type (IPCC, 2006). Since there is unavailable specific emission factor for country, emission factors were obtained base on default emission factor which available in 2006 IPCC Guidelines for National Greenhouse Gas Emission Inventory. After the carbon dioxide emission estimation was calculated, an inventory of emission was carried out. ANOVA test was used to detect the significant differences in mean of carbon dioxide by fishing vessels between fishing gears and fisheries zones.

Results and Discussion

Total carbon dioxide emission from fishing vessels operation in Selangor is 295.44 Gg CO_2 for 2012. Drift/gill net vessels at Kuala Selangor has the highest emission of petrol consumer at zone A, 13.26 CO_2 Gg/year. While the highest emission of diesel consumer in zone A is drift/gill net vessel at Pelabuhan Klang, 11.00 CO_2 Gg/year. Zone B recorded Trawl vessels at Sabak Bernam is the highest emission of diesel consumption, 77.20 CO_2 Gg/year. It is similar to zone C where trawl vessels at Sabak Bernam has highest diesel consumption emitted highest emission, 39.55 CO_2 Gg/year. Zone C2 which has only fish purse seine as fishing gear used low diesel consumption, released emission 0.19 CO_2 Gg/year. Questions were asked to determine whether there is any significant differences between mean carbon dioxide emission of fishing vessel by different types of fishing gears and whether there is any difference in the mean carbon dioxide emission by fishing vessels at the four fisheries zones. ANOVA test revealed that there has significant difference in the mean of carbon dioxide emission between eight type of fishing gears $F(6,3252) = 1165.78$ greater than F critical 2.10 at $p = 0.00$. Then, ANOVA test also revealed that there has significant difference in the mean of carbon dioxide emission between four fisheries zones $F(3,3252) = 2719.47$ greater than F critical

2.61 at p value 0.00. Turkey Kramer Multiple Comparisons test was applied to determine the pair of mean carbon dioxide emission by fishing vessel between different types of fishing gears at fisheries zones. They have 12 pairs of fishing gear and five pairs of fisheries zones which have significant difference in mean of carbon dioxide emission. The burning of 89.35 Gg of fossil fuel by fishing operation released 295.4 Gg in 2012. Total amount of carbon dioxide emission by fishing vessel is still low compare to latest Malaysia total carbon dioxide emission in 2000, 222,990 Gg CO_2. Different types of fishing gear gave significant difference total to carbon dioxide emission. Thus, active fishing gear such as trawl net vessels produced the highest carbon dioxide emission compare to passive fishing gear such as drift net or purse seine vessels. A study by Driscoll and Tydmers (2009) found that global tuna fishing vessels burn 3 billion liter of fuel emitted 9 million tonnes of carbon dioxide emission equilibrium to air. Most of the fishing vessel operation in Malaysia including Selangor focuses on inshore fishing operation compare to deep sea (zone C and C2). Therefore, total carbon dioxide emission at zone A and B released high carbon dioxide emission compare to zone C and C2. The vessel technologies in Malaysia also play a role in the contribution to carbon dioxide emission. Most of the vessels operated in Malaysia are below GRT 70 compare to develop countries such as Norway, Korea, Japan which their fishing vessel exceed GRT 500. Hence, carbon dioxide emission by fishing operation in Selangor or Malaysia could not be really compared to developed countries.

Conclusion

Although Malaysia is a developing country which still does not have country emission factors for energy sector, the carbon dioxide emission estimation could be produced by using the waterborne navigation equation method. Thus, the status of carbon dioxide emission by fishing vessel operation has been determined for Selangor. Fuel consumption by fishing vessel operation released low carbon dioxide emission.

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Chapter 63
Garbage Enzyme as a Solution to Waste Minimization

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Abstract Garbage enzyme is obtained by fermenting fruit and vegetable wastes. This alternative method of biological recovery of organic waste may provide a solution to waste minimization and reduction since a large proportion of municipal solid waste consists of food waste. A study was conducted to assess the implementation of garbage enzyme making and usage as an initiative to reduce the amount of municipal solid waste generated by a hawker community. It was found that practical values, communal spirit and awareness of environmental consequences were among the factors that encourage the practice of garbage enzyme making, while ignorance, time and convenience factors hinder garbage enzyme making and usage. Taking these factors into consideration, municipalities could promote garbage enzyme as a viable method in reducing the amount of MSW generated.

Keywords Garbage enzyme · Biological recovery · Waste minimization · Municipal solid waste management

Highlights

- Some hawkers in Sibu Central Market recover their organic wastes.
- Factors that encourage GE making were awareness and environmental concern.
- Lack of time and knowledge were factors that hindered GE making and usage.

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Introduction

Solid waste management is a major environmental problem in Malaysia. The amount of solid waste generated continues to increase due to economic development and increasing population. Improved standard of living due to rapid economic growth has changed the consumption patterns of urban dwellers, thus resulting in an excessive generation of municipal solid waste (MSW). Increase in population growth has also brought about an increase in the amount of waste generated. The national average of waste generated is 0.5–0.8 kg/person/day, but in the cities the figures escalated to 1.7 kg/person/day (DOE 2006). On the average, over 23,000 tonnes of waste is produced each day in Malaysia, and this amount is expected to rise to 30,000 tonnes by the year 2020. Most of the wastes generated ended up in the landfill. Municipal governments are struggling to find the best methods for managing wastes for the growing volumes of refuse and a scarcity of disposal sites plaguing towns and cities everywhere.

Municipal Solid Waste (MSW) is defined as the useless and unwanted products in the solid state discarded by society. Putrescible food and organic waste form part of MSW and this biodegradable portion dominates the bulk of MSW. Food wastes contribute to about 45 % of solid waste composition in the municipal of Kuala Lumpur in 2006 (Abd Manaf et al. 2009). High percentage of food waste dumping is typical of developing countries whereas the developed countries have a high paper and cardboard content (Dhussa and Varshney 2000). Only less than 5 % of food waste is being recycled.

Not many are aware that garbage in the form of organic wastes from fruits and vegetable dregs are recyclable. The most traditional way of recycling organic waste is to compost the waste and used as fertilizer in the garden. When microorganisms metabolize the waste, organic waste gives off energy in the form of heat and loses between 40 and 75 % of its original volume in the process. The finished product is often used in landscaping, land reclamation, and landfill cover and to provide high-nutrient soil for farms and nurseries (Zarak and Adam 2009).

An alternative method of recycling organic wastes was introduced by Dr. Rosukon from Thailand (Polprasert 2007). In this method, organic waste is converted into useful enzymes through the fermentation process. The enzyme produced is known as garbage enzyme (GE). Garbage enzyme is known to have cleansing properties and has functional application as a multi-purpose household cleaner. Through this emerging method, garbage is turned into a useful and environmental friendly product which could substitute the use of chemical detergents. If well practiced, garbage enzyme making could help to reduce the amount of wastes disposed to the landfill. Therefore, garbage enzyme making may be a viable option for sustainable waste management in municipal planning.

One city in the state of Sarawak, Malaysia, had looked into this biological recovery method of organic waste reduction. The Sibu Municipal Council (SMC) has conducted numerous programs over the years to engage the local communities in pro-environmental activities. In its attempt to reduce the amount of solid wastes,

the local government conducted campaigns and projects to encourage local communities to practice garbage enzyme making and usage. To ensure success of the environmental programs, it is necessary to evaluate community responses and participation. Therefore a study was carried out to examine the practice of garbage enzyme making and usage among hawkers in Sibu, and to identify the factors that hinder or encourage these hawkers to practice making and using garbage enzyme.

Materials and Methods

This study was conducted among fruits and vegetable hawkers in Sibu Central Market, which is among the largest indoor markets in Malaysia. This venue was chosen as the location of study because of the large amount of organic wastes produced from this market daily. A survey questionnaire was used to collect data on participants' practices in the making and usage of garbage enzyme, and the factors that hinder or encourage their involvement. Interviews were conducted among Sibu's Municipal officers to gather information on municipal solid waste management. Descriptive analyses summarized the data and information collected.

Results and Discussion

From the interview held with the Senior Health Inspector in Sibu Municipal Council, it was reported that department records showed that the 18,704 m^2 building produced approximately five tons of waste per day. Waste generation in Sibu area is around 130 tonnes per day and waste generation per capita is 0.65 kg. The Sibu Municipal Council (SMC) spent RM4.6 mil per annum for solid waste management. The sanitary landfill of 13 acres costing RM0.5 million was in operation since 2001. The SMC is dependent on landfill as the core waste disposal method, therefore it is looking for sustainable alternatives to manage the increasing waste produced each year. Since 2007, the local government has foreseen the potential of garbage enzyme as a solution to the problem of insufficient landfill sites.

According to the Sibu Municipal Council's data record up to the year 2009, 49.5 % of the total waste disposed to the landfill sites consists of organic matters (Fig. 63.1) (Sibu Municipal Council 2009). This huge amount of organic wastes present a potential pressure on the environment. Not only do they produce bad odour and problems with vermins, as the organic matters rot, they also give off gases (mainly methane and carbon dioxide) which are potentially explosive and are greenhouse gases (GHG).

Survey results showed that 42 % of the hawkers recovered their organic wastes generated daily, through feeding them to livestocks, composting and garbage enzyme making. However, 58 % of them discard their organic wastes into the garbage bin. More than half (59.5 %) of the hawkers surveyed disclosed that they have never practiced garbage enzyme making.

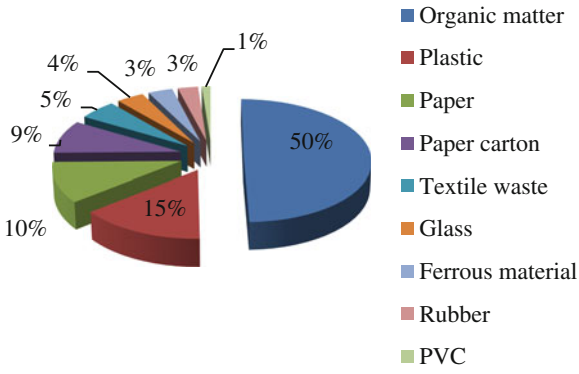

Fig. 63.1 Waste characterization in Sibu town, 2009

Factors that encourage the practice of garbage enzyme making and usage were having knowledge of garbage enzyme making and its usefulness. Many were influenced by communal practice, they do it because their friends and relatives are doing it. Altruistic values, awareness of the consequences to the environment, was also stated as a reason for practicing GE making. The main factor that hindered the hawkers from practicing GE making was the lack of awareness of the importance of GE. Others stated the lack of time and inconvenience as discouraging factors.

Conclusion

Effective recycling and recovery of organic wastes can mean a reduction in total wastes generated from the market. Garbage enzyme making is seen as a viable alternative solution in minimizing MSW sent to the landfill. Information dissemination and education is indicative in encouraging local communities to participate in the making and usage of garbage enzyme.

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Chapter 64
Distribution of Petroleum Hydrocarbons in Surface Sediments from Selected Locations in Kuala Selangor River, Malaysia

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Abstract A study has been conducted at selected locations along the Kuala Selangor River, Malaysia on seven surface sediment samples to determine the level of hydrocarbon pollution in the sediments. The homogenized sediments were extracted using soxhlet, fractionated and analyzed by using GCMS. PAHs were detected and were found in the range of 563–1,037 ng/g (dryweight). Ratio MP/P was used to determine the anthropogenic PAHs sources where seven stations were found to be polluted by petrogenic sources. Furthermore, MP/P ratios for sediment samples had values ranging from 1.752 to 18.6, while L/H ratios for the same samples ranged from 0.2978 to 1.393. There were 26 compounds of PAHs detected in the samples. Further analysis and more data is needed in order to identify the sources of oil pollution in seven sediment samples with unidentified oil sources.

Keywords PAHs · Petrogenic · Pyrogenic sources · MP/P ratio · Marine pollution

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Highlights

- The concentrations of the PAHs are distributed in all molecular weight range.
- PAHs were detected and were found in the range of 563–1,037 ng/g (dryweight).
- There were 26 compounds of PAHs detected in the samples.

Introduction

Rapid anthropogenic activities have brought about an increase in environmental pollution along the Malaysian coastal environment for decades. Malaysian coasts are subjected to various threats from petroleum pollution including routine and accidental oil spills from tankers, spillage of crude oils from inland and offshore oil fields and run-off from land-based human activities. Selangor is divided into nine administrative districts, one of those is the town of Kuala Selangor which lies in the lower reaches of Selangor River. The Kuala Selangor River is chosen for the study because the river flows through the hub of commercial, industrial and residential areas. Polycyclic aromatic hydrocarbons (PAHs) are example of hydrocarbon pollutants which may originate from sea and land-based. Petrogenic PAHs are hydrocarbons consisting of low molecular weight components and their presence is normally associated fresh input from lateral transport. Examples of petrogenic sources are crude oil, asphalt and gasoline are introduced to the environment through accidental oil spills, discharge from routine tanker operation, as well as municipal and urban run-off. Petrogenic sources with lower molecular weight PAHs (2–3 rings) are more water soluble and readily bioavailable for aquatic animals. Higher level of petrogenic PAHs were found to be accumulated in various organisms. Malaysian sedimentary PAHs impacted by petrogenic sources (Zakaria et al. 2002; Sakari et al. 2008) is unique compared to other industrial countries reported pyrogenic as the main source of sedimentary PAHs (Larsen and Baker 2003; Liu et al. 2009). On the other hand, pyrogenic sources are incomplete combustion of organic matter, biomass burning and mobile sources released to environmental in the form of exhaust and solid residue (Liu et al. 2009; Retnam et al. 2013). Pyrogenic PAHs are more toxic but less bioavailable due to their complex molecular structure and composition. Their concentration is usually high in urban zones but, due to their high diffusion rates and the ability to accumulate in particles, PAHs are easily transported through the air, and are subsequently deposited in soils and waters, sometimes far from the origin sources. Generally soil sites are located too near to potential sources of PAHs such as towns and oil tankers route especially along the Straits of Malacca. The purpose of this research is to determine the distribution of PAHs in the different sampling stations in Kuala Selangor river. Therefore, this study should be able to give some indication of the

concentration or level of PAHs in the Kuala Selangor region. In order to promote the understanding of PAHs distribution, this paper also discusses the relationship between sedimentary PAH levels and OC content in the sediments.

Materials and Methods

Selangor River is one of the major rivers in Selangor, Malaysia. It runs from Kuala Kubu Bharu in the east and empties into the Straits of Malacca at Kuala Selangor in the west. The total river catchment's covers an area of approximately 1,960 km^2. The map of sampling locations with detail data are shown in Fig. 64.1. Seven surface sediment samples were collected. 15 g of freeze-dried sediment samples were placed in pre-cleaned cellulose thimbles and soxhlet extracted for about 8–10 h with distilled dichloromethane (DCM). Clean up step is done by using 5 % H_2O deactivated silica gel to separate unwanted polar compounds and packed in the column until 9 cm in heights. The 2nd step column chromatography or fraction step is done using 100 % fully activated silica gel. The sample from first column was added to the column and charge through with 4 ml hexane to get alkanes and hopanes fraction, then 4 ml hexane added again to get LABs fraction, and finally 16 ml of Hexane/DCM (3:1 v/v) was added to get PAHs fraction. The extract was analyzed with GCMS.

Results and Discussion

The concentrations of 26 PAH and some related parameters are . The total concentrations of the 26 PAHs ($\sum$PAHs) in the sample sediments taken from Kuala Selangor River varied significantly ($p < 0.05$) among the stations and ranged from

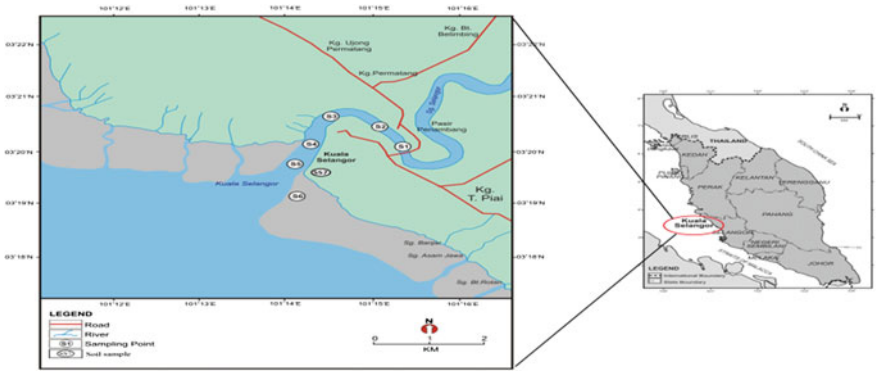

Fig. 64.1 Sampling stations along the coastline of Kuala Selangor River

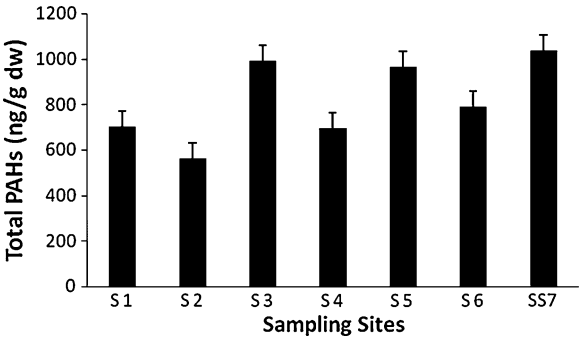

Fig. 64.2 Concentrations of PAHs in sampling stations in Kuala Selangor River

563 to 1,037 ng/g (dryweight) (Fig. 64.2). Moreover, it was found that the highest concentration of the total PAHs was recorded in stations three and five which are located near the Kuala Selangor Bridge and jetty (Fig. 64.1). Based on these results as, the concentrations of the PAHs in Kuala Selangor river stations are distributed in all molecular weight range (i.e. low and high molecular weight PAHs). N-Methylphenanthrene (n-MP) is the most abundant parameters which are relative to other PAHs in the samples.

This could be due to the fresh input of PAHs to the landfills such as illegal dumping of waste petroleum products although more data is needed to confirm this suggestion. The results also showed that those PAHs with low molecular weight are more volatile and more bio available than those PAHs having higher molecular weight. Therefore, the availability of Methylphenanthrenes in high concentration is a good indication of this fresh input. Previous research attributed such fresh input of a single diffuse source to the presence of high abundance of Methylphenanthrenes (Zakaria et al. 2005). However, regarding Benzo (k) fluoranthene (BkFl), Benzo (a) pyrene (BaPy), Indeno [1,2,3-cd] pyrene (IndPy) and Benzo [g,h,i] perylene (BghiPer), they were all available in relatively high concentrations. Such compounds are described as carcinogen and mutagen compounds which are capable of disrupting the endocrine system in human body. The results of this study also revealed that the second highest concentration of total PAHs was obtained from the samples taken from station one, four and six which are located in the coastal area of the Strait of Malacca facing the Kuala Selangor port. Furthermore, the samples from station two which is located at Kuala Selangor River displayed the lowest total concentration of PAHs. In this study, the PAHs compositions found in Station one which is located in the upstream of the mangrove estuary were compared for further analysis. SS7 known as soil sample around the sampling sites were collected and analyzed to identify the sources of PAHs. The results show that the high concentrations of PAHs in the sediment sample were 3-Methylphenanthrene (3Mp), 2-Methylphenanthrene (2Mp), Benzo (k)fluoranthene (BkFl), Indeno[1,2,3-cd]pyrene (IndPy) and Benzo[g,h,i] perylene (BghiPer), indicating extensive input of petrogenic PAHs. As proposed by Youngblood and Blumer (1975), many previous studies used the ratio of methylphenanthrenes to phenanthrenes (MP/P) was for the

purpose of distinguishing between petrogenic and pyrogenic sources of PAHs (e.g. Zakaria et al. 2002; Sakari et al. 2008; Bakhtiari et al. 2010). As for the methylphenanthrenes, they comprise 3-methylphenanthrene, 2-methylphenanthrene, 9-methylphenanthrene and 1-methylphenanthrene. These all are divided by the phenanthrene concentration. In this study, it was found that the MP/P ratios for all sediment samples (MP/P ratio) were >1.0. Such result implies that sedimentary PAHs in all stations mainly tend to be petrogenic PAHs (Table 1). The significant correlation between PAHs in the sediments and sediments' OC is achievable only in highly contaminated sites where the total PAH concentrations were >2,000 ng/g. For the current study, the sample sediments collected from all stations showed total PAH concentrations less than this value. Therefore, it can be concluded that the distributions and concentrations of PAHs in sediments of Kuala Selangor River are not controlled by the sediments' OC content.

Conclusion

The total concentrations of the 26 PAHs ($\sum$PAHs) in the sample sediments taken from Kuala Selangor River varied significantly ($p < 0.05$) among the stations and ranged from 563 to 1,037 ng/g (dryweight). Moreover, it was found that the highest concentration of the total PAHs was recorded in stations three and five which are located near the Kuala Selangor Bridge and jetty. The concentrations of the PAHs in Kuala Selangor river stations are distributed in all molecular weight range (i.e. low and high molecular weight PAHs).

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Chapter 65
Decolorization of Azo Dyes by Local Microorganisms

Wan Lutfi Wan Johari, Razlin Izwan Mohd Isa, Norhusna Ghazali, Noorliza Mat Arif and Mohd Yunus Abd Shukor

Abstract Several local microorganisms were isolated and screened for their capabilities to decolorize selected azo dyes. Two isolates, RII and NHG have shown their capabilities to decolorize azo dyes i.e. Metanil Yellow (monoazo) and Reactive Black 5 (diazo), respectively, under aerobic condition at room temperature. 96.0 % decolorization of Reactive Red 120 has been attained by the RII isolate. Crocein Orange G and Orange II, both have exactly the same molecular weights, were 23.7 and 68.5 % decolorized, respectively, by the same isolate under agitated conditions. 66.6, 61.4 and 11.4 % decolorization has been achieved by isolate NHG when tested with Direct Blue 71, Amaranth and Tartrazine, respectively. No correlation between degradation rate and molecular weight, number of azo bonds or presence of aromatic molecules has been observed.

Keywords Azo Dyes · Biodecolorization · Metanil yellow · Reactive black 5

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Highlights

- Local microorganisms capable of decolorizing azo dyes were screened and isolated.
- Isolates RII and NHG decolorized Metanil Yellow and Reactive Black 5, respectively.
- No correlation exists between rate and molecular weight or number of azo bonds.

Introduction

Azo dyes account for most of the overall dye produced. They are commonly used as colorant in pharmaceutical, textile, food, cosmetics, leather and printing industries. During the dyeing process, some percentage of dye used ended up in the effluents, and approximately 15 % may be found in wastewater (Spadarry et al. 1994). Azo dyes tend to persist in the environment due to the azo (N = N) and sulfonic ($-SO_3^-$) groups, which are less susceptible to aerobic oxidation. The presence of dye may affect the photosynthesis of aquatic life and the metabolites produced from the cleavage of azo bonds can be mutagenic and carcinogenic (Hu 2001). Metanil Yellow, which contains one azo bond, is still used in food, such as beverages and turmeric (Anjaneya et al. 2011). Consumption of this dye can cause various illness including intestinal disorders (Ramachandani et al. 1997). Reactive dyes, such as Reactive Black 5, are commonly used in textile industries and oftentimes these reactive dyes are not readily degradable.

Physicochemical methods such as advanced oxidation processes have been employed to decolorize and detoxify textile wastewater; however, the chemicals and treatments may be costly and produce chemical sludge (Sen and Demirer 2003). The reductive cleavage of azo bonds of reactive dyes through oxidation and phytocatalytic degradation may also produce toxic byproducts. The transformation of azo dyes through biological means, on the other hand, can be a better option for treatment of textile wastewater. The aromatic amines produced from the breakage of azo bonds can be further biodegraded by microorganisms.

In this work, local microorganisms capable of decolorizing selected azo dyes were screened and isolated. The selected isolates were then tested on structurally different azo dyes. The strain cultures were further studied on the biodecoloration rates of selected dyes.

Table 65.1 Decolorization of various azo dyes (50 mg/L) by isolates NHG and RII

Azo dye	Purity (%)	Molecular weight	Azo bond	λ_{max} (nm)	% decolorization NHG isolate
Reactive Black 5	55	991.82	2	597	99.2
Direct Blue 71	50	965.94	2	594	66.6
Amaranth	85–95	604.47	1	523	61.4
Tartrazine	>85	534.36	1	427	11.4
					RII isolate
Metanil Yellow	70	375.38	1	414	99.6
Crocein Orange G	90	350.32	1	482	23.7
Orange II sodium salt	85	350.32	1	483	68.5
Reactive Red 120	60	1469.98	2	517	96.0

The cultures were incubated with azo dye at room temperature, 24 h under agitated conditions

Materials and Methods

Chemicals and Media

Azo dyes, their percentages of purity, molecular weights, number of azo bonds, maximum wavelength used in this study are presented in Table 65.1. The mineral salt media (MSM) consisted of the following (per liter): 1.0 g yeast extract, 0.4 g K_2HPO_4, 0.2 g KH_2PO_4, 0.4 g $(NH_4)_2SO_4$, 0.1 g NaCl, 0.1 g $MgSO_4$, 0.01 g $MnSO_4$•H2O, 0.01 g Na_2MoO_4•$2H_2O$ and 0.01 g $Fe_2(SO_4)_3$•H_2O. The pH of the media was adjusted to 7 (Bai et al. 2007). For bacterial growth prior to decolorization tests, the MSM was supplemented with 10.0 g/L glucose.

Sample Collection, Screening and Isolation of Potential Decolorizers

Samples were collected from various places around Universiti Putra Malaysia i.e., soil samples from a pond in Kolej 15 and trench water near Faculty of Forestry. All of the samples were collected in sterile screw cap tube and the samples were tested within 24 h of collection. The enrichment was done using nutrient broth in 250 ml conical flask. Approximately 3.0 g of soil sample or 10 ml water sample was inoculated in the nutrient broth. The culture flasks were incubated on orbital shaker for 24 h at room temperature. Metanil Yellow and Reactive Black 5 were utilized during the screening process. The screening was carried out in universal bottles by adding 1 mL of bacterial sample, 9.0 mL of MSM supplemented with selected dye. Final concentration of Metanil Yellow and Reactive Black 5 were 35 and 27.5 mg/L, respectively. After 48 h of incubation, a loop-full of medium was streaked onto MSM agar containing dye and the plates were incubated at room temperature for 48 h. The colonies that show ability to decolorize dyes were isolated and streaked on new agar media.

For decolorization of various dyes, the selected isolates were further screened with different azo dyes as listed in Table 65.1. The cultures were grown in MSM with glucose for 24 h. 10 mL of culture was inoculated in 90 mL of MSM without glucose and 50 mg/L dye under agitated conditions. The decolorization of every dye was determined by using UV–Visible Spectrophotometer.

Results and Discussion

Two isolates, RII and NHG isolates, were chosen and have shown their capabilities to decolorize Metanil Yellow and Reactive Black 5, respectively. Isolate NHG was able to completely decolorize Reactive Black 5 in 12 h and the decolorization rate followed first-order reaction rate (Fig. 65.1).

The isolates RII and NHG have shown decolorization of various azo dyes with different molecular structure and complexity (Table 65.1). Apart from decolorization of Metanil Yellow by isolate RII, high decolorization activity was observed on Reactive Red 120, a sulfonated naphthalene-containing azo dye. Differences in molecular structure and weight or presence of sulfonic group may affect the decolorization rates of the dyes (Hu and Wu 2001). Nonetheless, when isolate RII was tested with both Crocein Orange G and Orange II, which both have exactly equal molecular weight, the isolate decolorized 23.7 % of Crocein Orange G and only 68.5 % of Orange II. Another study reported that molecular weight did not dictate the decolorization rate (van der Zee et al. 2001). The number of azo bonds may affect the decolorization rates and normally, longer times were required for compounds with high amount of azo bonds (Elisangela et al. 2009). Isolate NHG, on the other hand, was capable of decolorizing only 61.4 % of Amaranth (monoazo) while 99.2 % of Reactive Black 5 (diazo) has been decolorized.

Most of the initial step of azo dye biodegradation involves the cleavage of azo bonds and this happens under anaerobic conditions. When Metanil Yellow is transformed biologically, the products produced are metanillic acid and *p*-aminodiphenylamine (Anjaneya et al. 2011). The metabolites analysis of the anaerobic

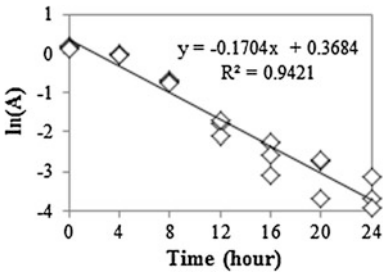

Fig. 65.1 Decolorization of Reactive Black 5 by NHG isolate measured value (◇) and first-order fit (—). The absorbance (A) readings were taken at 597 nm. Study was conducted in triplicates. initial concentration = 27.5 mg/L. Decoloration rate, k = 0.1704 h^{-1}

decolorization of Reactive Black 5 by *Rhodopseudomonas palustris* strain revealed that the production of various aromatic amines could be further degraded and detoxified under aerobic conditions (Wang et al. 2008).

Conclusion

Two local isolates were obtained and tested with structurally different azo dyes. These isolates were capable of decolorizing azo dyes under agitated conditions while most of the bacterial isolates in other studies were conducted under static conditions. Molecular weights, complexity of the structures, the presence of amino-aromatic molecules and number of azo bonds do not reflect the rate of decolorization by these microorganisms. Metabolite analyses should be conducted in the future for toxicity of decolorization byproducts, which may govern the decolorization rates of azo dyes, by local microorganisms.

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Chapter 66
Characterization and Source Apportionment of Fine Particulate Matter during 2011 Haze Episode in UKM Bangi, Malaysia

Norhaniza Amil, Mohd Talib Latif and Md Firoz Khan

Abstract This study aims to improve understanding of the haze episode particularly on $PM_{2.5}$ by investigating the mass concentrations and its relation to chemical compositions and related gaseous-meteorological parameters during 2011 haze episode at UKM Bangi. Overall, $PM_{2.5}$ mass concentrations for the haze episode averaged at 48.32 ± 10.07 $\mu g/m^3$ with 30.24 % portioned by 29 elements studied. The examinations of the relationships between $PM_{2.5}$ mass and gaseous-meteorological parameters shows that $PM_{2.5}$ mass within the study area is predominantly correlated with O_3, NO_2, NO_x and wind speed. The application of a receptor mode (PCA-MLR) to a database made up of chemical composition of $PM_{2.5}$ resulted with five factors identified as: (1) motor vehicle emission; (2) soil dust; (3) industrial; (4) sea-salt; and (5) undefined source. A synoptic wind stream for south-west period together with results of HYSPLIT backward trajectories for the sampling site-period traced to three locations at Sumatra. The results attained in this study highlights to us that whilst the trans-boundary smoke is the major contributor to the poor air quality of Bangi, local conditions, in particular traffic, may contribute a significant portion towards the haze event.

Keywords $PM_{2.5}$ · Chemical compositions · Haze episode · Source apportionment · PCA-MLR · Backward trajectories

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Highlights

- $PM_{2.5}$ mass concentrations exceeded the WHO recommended value.
- $PM_{2.5}$ mass correlated with O_3, NO_2, NOx and wind speed.
- PCA-MLR model successfully identified five sources of $PM_{2.5}$.

Introduction

Haze occurs during the southwest monsoon season because low-level winds over Malaysia are generally south-westerly and the weather is generally dry. A study by Abas et al. (2004) suggest that the concentration of air particulate matter in Malaysia is influenced by the southwest monsoon wind aside from the occurrence of biomass burning. Even though trans-boundary smoke is the major contributor to poor visibility in the Klang Valley, smoke from fires on Peninsular Malaysia is also a contributor (Keywood 2003). However, Afroz et al. (2003) conclude that air pollution comes mainly from land transportation, industrial emissions, and open burning sources with land transportation contributes the most. Fine particulate matter which primarily derived from direct emission from combustion processes has most concern towards the health effect due to its toxicological and physiological considerations which suggest that the fine particles may play the largest role in affecting human health (Pope III and Dockery 2006). Therefore, this paper aims to improve understanding of the haze episode particularly on $PM_{2.5}$ by investigating the mass concentrations and its relation to chemical compositions and related gaseous-meteorological parameters during 2011 haze episode at UKM Bangi.

Materials and Methods

Sampling Site Description

Universiti Kebangsaan Malaysia, Bangi was chosen as the sampling point with geographical latitude of 2°55′54″ and longitude of 101°46′37″.

Aerosol Sampling

Fine aerosol particles ($PM_{2.5}$) were collected for 8 days consecutively inclusive of one field blank during 24 ± 1 h from 8th August 2011 to 15th July 2012. $PM_{2.5}$ sampling was performed using Tisch High Volume $PM_{2.5}$ Sampler (Model TE-6070 V-2.5-BL) running at 67.96 m^3hr^{-1}.

Chemical Compositions

The water-soluble major ions analysed by Ion Chromatography (IC) were: anions (F^-, Cl^-, NO_2^-, Br^-, NO_3^-, and SO_4^{2-}); and cations (Li^+, Na^+, NH_4^+, Ca^{2+} and Mg^{2+}). In addition, trace elements ions were also determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS): Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, In, Mn, Ni, Pb, Rb, Se, Ag, Sr, Tl, V, U and Zn. For water soluble analysis, sonication method (60 °C, 60 min) was employed using Elmasonic S40 ultrasonic bath (Elma GmbH, Germany). For trace elements analysis, microwave—assisted extraction using acid digestion method (8:2 of HNO_3 and H_2O_2) was used. For both IC and ICP-MS analyses, six point calibration curves were performed and the regression for all elements was better than 0.999 that the analyses were then proceed. Black carbon (BC) analysis was done using Smokestain Reflectometer Model EEM43 M with calibration.

Meteorological and Gaseous Parameters

Meteorological data such as temperature and relative humidity were monitored continuously at the sampling site at 1 min interval using GRIMM 164 instrument. For the rest of related parameters, that is, the gaseous pollutants (CO, O_3, SO_2, NOx, NO_2), together with wind speed, wind direction and Air Pollution Index (API) were obtained from the Department of Environment Malaysia (DOE) for Putrajaya Station, which is the nearest DOE station to the sampling point.

Results and Discussion

$PM_{2.5}$ and Gaseous-Meteorological Parameters

On average, the $PM_{2.5}$ mass concentration was 48.32 ± 10.07 μg/m^3 with the highest concentration level recorded at 63.70 μg/m^3 on 11th of July 2013. For all 8 days campaign, the $PM_{2.5}$ mass concentrations exceeded the World Health Organization (WHO) recommended $PM_{2.5}$—24 hrs concentration at 25 μg/m^3. Correlation matrix run through the mass-gaseous-meteorological parameters shown predictable results since NO_x and VOCs are precursors of both O_3 and of a fraction of atmospheric particulate matter (Seinfeld and Pandis 2006). O_3 shown the highest significant correlation towards $PM_{2.5}$ mass with a strong 0.951 correlation followed by wind speed with 0.868 significance. NO_2 and NO_x on the other hand show a strong but negative correlation towards $PM_{2.5}$ mass with -0.907 and -0.776, respectively.

Chemical Compositions of $PM_{2.5}$

Overall, all elements studied summed up a total of 30.24 % of $PM_{2.5}$ mass concentrations. Black carbon portions the largest in $PM_{2.5}$ with 19.79 % followed by K^+ and SO_4^{2-} with 3.64 and 2.06 %, respectively. Na^+ and NH_4^+ come at number four and fifth biggest contribution towards $PM_{2.5}$ mass with 1.37 and 1.13 % each. Transformed from VOCs by photochemical reactions, SO_4^{2-} and NH_4^+ together with K^+ normally from biomass burning were in the top five biggest contributors towards $PM_{2.5}$ mass concentration. This results is consistent with findings from previous $PM_{2.5}$ study for 1998–2000 haze episode by Keywood (2003).

PCA-MLR Results

The combined Principle Component Analysis (PCA)-Multi Linear Regression (MLR) analysis were used to study the source information of environmental pollution. Following Dominick et al. (2012), the application of the PCA-MLR with varimax rotation using XLSTAT 2012 add-in software was applied into the normalized data matrix to predict source profile of the $PM_{2.5}$. Overall, five factors were determined summing 96.77 % of the total variance in the dataset for chemical compositions in fine particulate matter (Fig. 66.1).

Factor 1 which explains 57.58 % of the total variance and account for 70.20 % of $PM_{2.5}$ mass has been identified as motor vehicle emission. This factor presented with positive high loadings for F^-, NO_3^-, SO_4^{2-}, NH_4^+, K^+, Zn, As, Cd, Cs, Rb, V and BC. For the second source which contributes at 6.44 % of $PM_{2.5}$ mass concentrations, soil dust was presumed with positive loading of Al, Ba, Fe, Mg, Li and Sr. The third factor explains 8.75 % of total variance and show a strong factor loading of Ni and Cu, thus, identified as industrial. With 8.1 %, the fourth source was recognised as sea-salt while the fifth and final source was left undefined due to its unexplained factor loading.

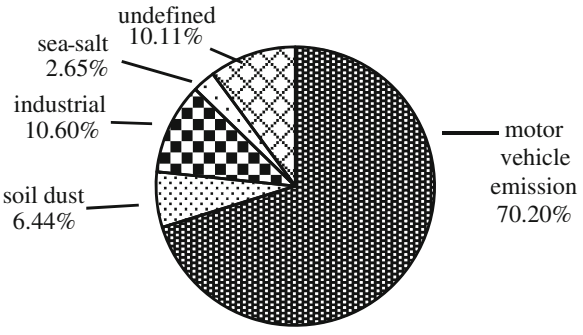

Fig. 66.1 Source apportionment of $PM_{2.5}$ identified by PCA-MLR

Conclusion

Overall, $PM_{2.5}$ mass concentrations for the haze episode averaged at 48.32 ± 10.07 μg/m^3 with 30.24 % portioned by 29 elements studied. The examinations of the relationships between $PM_{2.5}$ mass and gaseous-meteorological parameters shows that $PM_{2.5}$ mass within the study area is predominantly correlated with O_3, NO_2, NO_x and wind speed. The application of a receptor mode (PCA-MLR) to a database made up of chemical composition of $PM_{2.5}$ resulted with five factors identified as: (1) motor vehicle emission (2) soil dust; (3) industrial (4) sea-salt; and (5) undefined. A synoptic wind stream for south-west period together with results of HYSPLIT backward trajectories for the sampling site-period traced to three locations at Sumatra. The results attained in this study highlights to us that whilst the trans-boundary smoke is the major contributor to the poor air quality of Bangi, local condition, in particular, traffic source contribute a significant portion towards the haze event.

Acknowledgments This study was supported by Universiti Kebangsaan Malaysia with the research grants: Characterization and Source Apportionment of Fine Particulate Matter ($PM_{2.5}$) in the Klang Valley, Malaysia (FRGS/1/2013/STWN01/UKM/02/2). In addition, the authors would like to thank the Ministry of Education Malaysia and Universiti Sains Malaysia for supporting tertiary education of the first author.

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Chapter 67
Anoxic Limestone Drain for Treatment of Highly Acidic Water

Faradiella Mohd Kusin and Azmi Aris

Abstract Limestone has been widely used in the treatment of acidic water due to its capability of neutralizing acid and removing metals in water. This study investigated the efficiency of limestone treatment in treating acidic water in anoxic limestone drain at a laboratory scale. The anoxic limestone drain was basically designed to enhance limestone dissolution and alkalinity generation thus minimizing the potential of armouring, which may decrease the rate of acid neutralization. Actual raw water samples from two different locations within Sg. Bekok catchment which were highly acidic with low pH values were used in the experiment treated by 30 mm diameter of 112 kg of limestone. The conditions under which the pH increases, acidity decreases, alkalinity produced and metals were removed in the anoxic limestone drain have been determined. pH was significantly increased from initially 3.27–4.09 to 6.49–6.67 after flowing through the anoxic drain in 10 min of contact with the limestone. Acidity was reduced from 73–99 mg/L as $CaCO_3$ to 17–19 mg/L as $CaCO_3$ as pH were raised to reach near neutral levels. Iron and aluminium were also being removed in the anoxic limestone drain.

Keywords pH rise · Acidic water · Anoxic limestone drain

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Highlights

- The rate of acid neutralization is greatly depending on initial pH of the water.
- Alkalinity increased significantly due to higher rate of limestone dissolution.
- Iron and aluminium were removed by means of precipitation as metal hydroxides.

Introduction

There has been increasing river water quality deterioration over the country in the recent years. The deteriorating trend of river water quality has prompted the water authority to look into more effective means of improving them in a holistic manner so as to sustain their beneficial uses and demands. Intensive agricultural drainage activities in the riparian lowland between Bekok Dam and the town of Yong Peng has resulted in the deterioration of the river water quality, especially in terms of pH, iron and aluminium contents as what has experienced at Sg. Bekok, Batu Pahat in the recent years.

The water supply intakes within Batu Pahat district are unable to provide sufficient supply of raw water, which has led to water shortages problem. This is a result of water quality problems encountered at Sg. Bekok with high concentrations of iron (110 mg/L) and aluminium (290 mg/L) and pH values as low as 2.5 which exceed the limits set out by the National Water Quality Standard for Class II rivers (SAJ Holdings 2005). This has significantly caused interruptions in the operation of Yong Peng 2 and 3, Sri Gading and Parit Raja water treatment plants in producing sufficient potable water for the district needs. This study was implemented to investigate the viability of limestone treatment in treating acidic raw water prior to being used for water supply consumption. In specific, anoxic limestone drains (ALD), which operate at low oxygen concentration level, were studied. The ultimate aim of this study is to provide efficient on-site treatment system as an alternative solution to acidic raw water problem of Sg. Bekok, Batu Pahat.

Materials and Methods

River water samples from two different sources of Bekok Intake and Semberong Lagoon were used in the experimental work. Approximately 80 L of water samples were collected at the respective sites. The limestone used to treat the acidic water was of 30 mm in size and were used up to 112 kg (28 kg in each of the anoxic limestone reactor). Both the alkalinity and acidity of the samples were determined by titration with HCl and NaOH to pH 4.5 and 8.3 endpoints,

respectively based on Standard Methods for the Examination of Water and Wastewater (1999). Iron and aluminium were measured using HACH DR/4000 spectrophotometer and atomic absorption spectroscopy (AAS), respectively.

The anoxic limestone drains were constructed in series to receive the inflow from a holding tank of 30 L of acidic raw water. Water from the tank flowed through the anoxic drain via gravity to reach the effluent point at several contact times i.e. 10, 20, 30 and 60 min. Each of the limestone drain is of 20 cm in diameter with a length of 0.67 m and depth of 14 cm. The drain was made of PVC pipe in a semicircular form and was constructed with a slope of 1:50–100. A cling wrapper was used as the drain liner prior to place in the 28 kg of 3 mm limestone. The liner was wrapped over the top of the limestone to minimize O_2 from taking part in the treatment process. The flow rate was measured by recording the time to collect a known volume of water as it reached the drain outlet. pH was monitored at the inlet and outlet of each drain. Samples were taken at the outlet of final drain and analyzed for acidity, alkalinity, Fe and Al. Prior to experiment, oxygen was displaced from the drain by nitrogen gas until the O_2 content was <0.5 mg/L, which was considered as anoxic (Santomartino and Webb 2003).

Results and Discussion

Effect of Limestone Amount and Contact Time on pH Rise

The pH of the acidic water increased rapidly when first contacted with the limestone at the amount of 28 kg. This might be due to higher limestone dissolution rate at lower pH (pH $\sim$ 4) since the rate of limestone dissolution is directly proportional to the activity of H^+ (Plummer et al. 1978). The pH of Bekok Intake sample reached a near neutral level (pH 6–7) after contacting with 28 kg of limestone, whereas the Sembrong Lagoon sample needs 56 kg to raise its pH to the near neutral range. The pH was increased with increasing contact time, depending on the initial pH of the raw water. As the water flowed through the anoxic drains, pH increased due to the dissolution of limestone to reach near neutral level after 10 min of contact with the limestone. Initial pH of 4.09 for Bekok Intake rose to 6.67 in 10 min, whereas Sembrong Lagoon pH rose from 3.27 to 6.61 after 15 min of contact time.

Effect of Alkalinity on pH

A greater increase of alkalinity generation was found to take place during the early stage. Alkalinity was then increased with increasing contact time. When carbonic comes into contact with limestone, dissolution of limestone takes place. pH increased as the alkalinity was being generated to reach near neutral level in

10 min of contact time. It was also found that the alkalinity was significantly increased relative to low pH rise after it reached near neutral pH. It is because, dissolution takes place until a saturated solution of calcite is achieved, at which point equilibrium pH has been reached (Nuttall and Younger 1999).

The increase of alkalinity in relation to acidity reduction is given in Fig. 67.1. There was a strong correlation between acidity reduction in generating alkalinity in the raw water as given by the R^2 values. Sample of Sembrong Lagoon indicated a greater acidity reduction for a particular increase of alkalinity than that of Bekok Intake raw water. This was probably due to low initial pH and higher acidity of Sembrong Lagoon raw water, which tends to fasten the neutralization rate, as the dissolution of limestone is proportional to the activity of H^+.

Iron and Aluminium Removal

The concentrations of iron for both samples were reduced up to 69.52 and 71.28 % respectively even though oxygen levels within the drains were very low. Iron was removed due to precipitation at increased pH (pH $\sim$ 6) as a result of neutralization reaction between limestone and the raw water. Iron precipitation occurred as the water was being rapidly neutralized, reflecting the fact that iron precipitation is greatly accelerated at pH $>$ 4.5 (Singer and Stumm 1970). In fact, for iron precipitation to occur under the condition of anoxic drain, neutralization to pH $\sim$ 6 is required (Santomartino and Webb 2003).

The results indicated aluminium removal of 49.73 % up to 82.04 % due to precipitation of aluminium throughout the anoxic drains. It can be seen that aluminium was removed as the pH were increased to near neutral level with respect to different contact time since aluminium precipitated best at pH 6–7 (Wei et al. 2005). However, at the outlet aluminium concentrations were slightly higher than the recommended standard of 0.5 mg/L for 10, 20 and 60 min contact time.

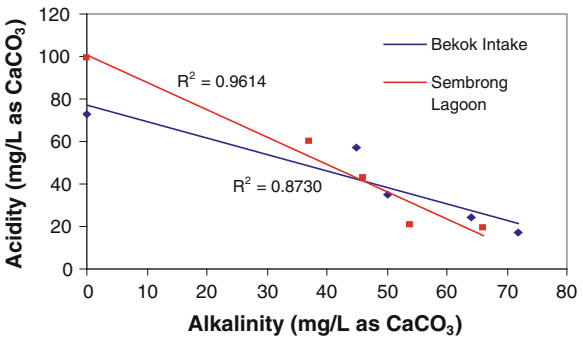

Fig. 67.1 Acidity reduction in relation to alkalinity production

Conclusion

Results indicated that the anoxic limestone drain is capable of reducing acidic condition of the raw water of Bekok Intake and Sembrong Lagoon. The required amount of limestone to neutralize acidic water and the contact time needed is much depending on the initial pH and acidity. Initial pH ranging from 3.27 to 4.09 with acidity of 73–99 mg/L as $CaCO_3$ could be enhanced up to 6.49–6.67 as the water flowed through the anoxic drain in 10 min of contact with the limestone. pH was found to be rapidly increased when first in contact with limestone since the dissolution of limestone is proportional to the acidity. Alkalinity increased significantly as the acidity reduced due to higher rate of limestone dissolution. The anoxic limestone drain was also found to be effective in removing iron and aluminium even though oxygen levels were very low.

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Chapter 68
Speciation: Determination of Methylmercury in Fish Samples with HPLC-ICP-MS

Kenneth Ong, Lilian Lim, S. Ghanthimathi, Norhidayu bt Ibrahim and Zalilah bt Nasir

Abstract Two mercury species in National Research Council of Canada Certified Reference Material (NRCC CRM) (i) TORT-2 and (ii) DORM-2 can be determined using high performance liquid chromatography (HPLC) in conjunction with inductively coupled plasma mass spectrometry (ICP-MS). A non-aggressive extraction method was employed to maintain the integrity of the species in samples. Chromatographic separation of Mercury species could be achieved in 6 min with a reverse phase (PerkinElmer C18 Aqueous) column using 0.1 % of L-cysteine as the mobile phase. The limit of detection for this method is 0.5 ppb (μg/kg), sufficient to determine the low level of Mercury in fish samples. The accuracy of the method was evaluated by analyzing marine biological certified reference materials (TORT-2 and DORM-2). The proposed method was then successfully applied in the determination of methylmercury compounds in "Ikan Kembung", a popular local fish for grilling also known as Indian Mackerel.

Keywords HPLC-ICP-MS · Methylmercury · Environment monitoring · Food safety

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Highlights

- A simple pre-treatment method was developed for rapid Mercury extraction.
- The method is quick, simple, repeatable and robust.
- Sensitivity, precision and LOD of this method complies with EU Commission regulations.

Introduction

Several forms of mercury occur naturally in the environment. The most common natural forms of mercury found in the environment are metallic mercury, mercuric sulfide (cinnabar ore), Mercuric Chloride and Methylmercury. Methylmercury is the predominant Mercury species in fish. The USEPA states in an updated Mercury overview paper that in most adult fish, 90–100 % of Mercury content is Methylmercury (USEPA 2001).

Methylmercury is also a well-documented neurotoxicant, which may, in particular, cause adverse effects on the developing brain. This compound passes both the placental barrier and the blood–brain barrier; as, such exposure during pregnancy is the main concern. Additionally, the overall evaluation for Methylmercury compounds is important since they are carcinogenic to humans.

The compound dealt with most extensively in toxicological research in recent years is Methylmercury. Generally, organic forms are much more toxic than the inorganic forms. Mercury is present in fish and marine mammals consumed by humans worldwide. Methylmercury is formed naturally (from anthropogenic sources and naturally released Mercury) by biological activity in aquatic environments, and is bio-magnified in the food chain, resulting in much higher concentrations in higher predatory fishes and mammals than in water and lower organisms. Most of the total Mercury concentrations in fish are in the form of Methylmercury (close to 100 % for older fishes).

Methylmercury has been found to have adverse effects on several organ systems in the human body as well as in animals. These include the nervous system (mental retardation, deafness, blindness, impairment of speech and etc.), the kidneys, the blood and the heart system (blood pressure, heart-rate variety and heart diseases). Other possible effects include cancer and genotoxicity. From research done on animals, there is evidence on its adverse effects on the immune system and the reproductive system. Methylmercury compounds as a whole are classified as possibly carcinogenic to humans.

In order to carry out the proposed studies, it was necessary to select the proper method for the determination of the methylmercury content in fish, which would meet the criteria of modern analytical methodology. The method had to have good reproducibility, repeatability and a high degree of recovery to ascertain good accuracy.

The methodology applied was based on extracting methylmercury with Toluene in an acidic medium. The extract was then back extracted into aqueous phase with L-Cysteine. Hydrochloride anhydrous (L-Cysteine.HCl). The methylmercury content in the aqueous extract was determined using HPLC-ICP-MS.

Materials and Methods

For speciation analysis, detection of the HPLC eluent was accomplished with PerkinElmer ELAN DRC-e ICP-MS instrument. The HPLC apparatus was equipped with PerkinElmer® Series 200 quaternary HPLC pump, autosampler, vacuum degasser and peltier column oven. All separations were performed at room temperature under isocratic conditions. The column used in this separation was a PerkinElmer C18 aqueous column 15 cm in length, with a 4.6 mm ID and 5 μm particles. 50 μL aliquots of samples were injected using a 200 μL PEEK injection loop. The coupling of HPLC to ICP-MS was accomplished by directing the eluent from the column to the Rheodyne switching valve. The sample was then transported to the ICP-MS for Mercury determination.

For sample extraction, 0.5 g of freeze dried sample was weighed into a 50 mL PP tube, followed by the addition 10 mL of Toluene. The content in the PP tube was stirred with a vortex mixer for five minutes to disperse the sample homogenously and to ensure that all methylmercury will be dissolved in toluene. Next, another 25 g of 0.1 % L-Cysteine. HCl was added as back-extraction solution. The tube was shaken to extract all forms of mercury into the aqueous phase. The sample tube was centrifuged at 800 rpm for 3 min to separate the Toluene layer from aqueous layer. By using a plastic syringe with needle, the aqueous (bottom) layer was collected and transferred to another clean PP tube. The tube with only the aqueous phase was centrifuged again at 4,000 rpm for 5 min. The solutions were transferred to the HPLC vials using a plastic syringe with a PVDF syringe filter attached. For analysis, an aliquot of this extract was injected into the HPLC-ICP-MS system.

Results and Discussion

In order to validate the HPLC- ICP-MS method, Mercury compounds were determined in the TORT-2 and DORM-2 reference sample. These two CRM were spiked with 4 ppb Mercury and 2 ppb methylmercury prior to extraction and compared with unspiked samples to calculate recoveries. The repeatability of the method was validated by conducting 3 parallel determinations (CRM Spike 1, and 2) of mercury with certified value of 0.27 ± 0.06 mg/kg and methylmercury with certified value of 0.152 ± 0.013 mg/kg contents in the TORT-2. The accuracy of the method was also determined on the basis of the analysis extracts from the certified reference

materials (DORM-2) which contained high level of total Mercury with certified value of 4.64 ± 0.26 mg/kg and methylmercury with certified value of 4.47 ± 0.32 mg/kg. Due to the high level of methylmercury in DORM-2, the abstracted solution was further diluted by another 25 times to avoid carried over effects. As such only methylmercury was determined in this case, the inorganic content (0.47 mg/kg) was much below than the detection level after the large dilution factors and thus not reported.

Conclusion

This work has demonstrated the ability to determine mercury species with the combination of HPLC and ICP-MS to offer excellent LOD, linear range, stability and accuracy for the analysis of trace levels of Mercury species in fish. In this study, a simple pre-treatment method was developed for the extraction of Mercury compounds in fish samples. The superb sensitivity, precision and excellent detection limits of this method easily meet the levels required by the EU Commission regulations. The speed and efficiency of the HPLC-ICP-MS allow a sample to be analyzed approximately every 6 min. The method is quick and simple to set up, yet offers a repeatable and robust analysis, providing an ideal solution for analysis of fish samples for potential Mercury contamination. Detection limits of various Mercury species obtained with this system are low enough for the Mercury speciation of many real samples without complicated sample pre-treatment.

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Chapter 69
Chemical Composition and Sources of Indoor and Outdoor PM_{10} in Primary Schools

Noorlin Mohamad, Mohd Talib Latif and Md Firoz Khan

Abstract Indoor and outdoor measurements of PM_{10} (particles <10 μm in aerodynamic diameter) and its compositions were carried out at two primary schools in Kuala Lumpur (S1) and Putrajaya (S2). Samples were collected using low volume sampler on Teflon filters over 8 h average sampling period. The water-soluble ionic species (WSIS) (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Ca^{2+}) were analyzed using ion chromatography. Elemental concentrations (Al, Pb, Zn, Cd, Cr, Co, Cu, and Ni) were determined using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Interpretations of the data were made based on enrichment factor (EF) and principal component analysis-multi linear regression (PCA-MLR). Results show that PM_{10} concentrations in S1 and S2 were higher indoor than outdoor. Overall, the concentrations of metals in indoor and outdoor PM_{10} are in the following order: Al > Zn > Fe > Ni > Cr > Pb > Cu > Co > Cd and Al > Zn > Fe > Ni > Cr > Cu > Pb > Co > Cd, respectively. The results of EF analysis found to be >1 for most elements studied. Results obtained by PCA-MLR indicate the dominance of earth crust sources (53 %), indoor activities (33 %) and corrosion product (14 %) in indoor PM_{10}. Soil (42 %) was dominant in outdoor PM_{10} followed by vehicle exhaust (39 %), secondary aerosol (12 %) and construction activities (7 %).

Keywords Particulate matter · Indoor/outdoor · School · Principal component analysis-multi linear regression · Enrichment factor

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Highlights

- Indoor to outdoor (I/O) ratio for PM_{10} in school classes was higher than 1.0.
- PCA-MLR identified sources and estimated source contributions for indoor and outdoor PM_{10}.
- Earth crust sources and soil dominated indoor and outdoor PM_{10}, respectively.

Introduction

Outdoor air pollution has been widely studied for many years owing to its potential impact on human health, atmospheric chemistry and climate change (Pope and Dockery 2006; Seinfeld and Pandis 2006). Indoor air pollution has also received great attention since studies indicate that pollutant levels could be higher indoors than outdoors (Janssen et al. 2001). In fact, children, a susceptible group to air pollutants effects, are believed to spend indoors more than adults. Thus, the environments such as school, nursery or home may lead children to potential health consequences as they have higher breathing rate and are still in the process of growing. Epidemiological studies have consistently shown an association between particulate matter pollutants and the number of deaths from cancer and respiratory diseases (Slaughter et al. 2005). The inorganic composition of outdoor and indoor particulate matter is important due to its association to children health (Almeida et al. 2011; Habil and Taneja 2011; Polednik et al. 2013). By taking this issue into account, the present study attempts to determine the mass concentrations of indoor and outdoor PM_{10} and its components in school buildings. Therefore, the aim of this study was to provide an indoor and outdoor relationship in term of atmospheric particle concentration in school buildings, as well as the information on the sources influencing the relationship between indoor and outdoor air quality.

Materials and Methods

Two public primary schools were selected on the basis of their feature as urban (Kuala Lumpur) and suburban (Putrajaya) sites as well as their accessibility. Sekolah Kebangsaan Jalan Raja Muda (S1) is located in the city centre of Kuala Lumpur, a busy commercial area with heavy traffic density. Sekolah Kebangsaan Putrajaya Presint 14 (S2) is situated in suburban residential area with medium traffic density. In this study, one classroom of each school was chosen as sampling site. Indoor air instruments were positioned close to the center of the classroom. The measurements were also taken close to the classroom as outdoor samples.

Loaded filter samples were divided into two portions. One portion was used for the analysis of water soluble ionic species (WSIS) and another portion was used for elemental analysis. WSIS extraction with ultra pure water were centrifuged and

Table 69.1 PM_{10} mass concentrations ($\mu g/m^3$)

Site	Indoor			Outdoor			I/O
	Min	Max	Mean ± SD	Min	Max	Mean ± SD	
S1	25.0	133.0	90.7 ± 44.9	33.3	129.0	78.8 ± 36.3	1.1
S2	16.7	129.0	89.5 ± 27.3	16.7	121.0	69.5 ± 33.9	1.3

sonicated to extract the filter material. The inorganic ions were analyzed using ion chromatography (IC). For elemental analysis, samples were digested with a mixture of HNO_3/H_2O_2 in microwave digestion system. Metal contents of final solution were determined by inductively coupled plasma-mass spectrometry (ICP-MS). Field and laboratory blanks were run using the similar procedures as the samples.

Results and Discussion

The mean concentrations of PM_{10} for both schools were higher indoor than outdoor. The PM_{10} concentrations ($\mu g/m^3$) ranged from 25 to 133 (indoor) and from 33 to 129 (outdoor) for S1, while, from 17 to 129 (indoor) and from 17 to 121 (outdoor) for S2 (Table 69.1). From the results obtained, indoor to outdoor (I/O) ratio for PM_{10} of both schools were found to be slightly higher than 1.0. This high I/O ratio can be related to the high occupancy levels and resuspension of particles from student activities during recess time such as moving and running.

Enrichment factors (EF) ware performed in this study to evaluate the crustal or natural and non crustal or anthropogenic origin of the elements in PM_{10}. Large variations of EF values (Fig. 69.1) are found for different elements indoor and outdoor PM_{10}. High EF values showed that anthropogenic sources contribute a major fraction in PM_{10}, while the EF close to unity showed that the elements are predominantly from soil materials (Han et al. 2007; Yongming et al. 2006).

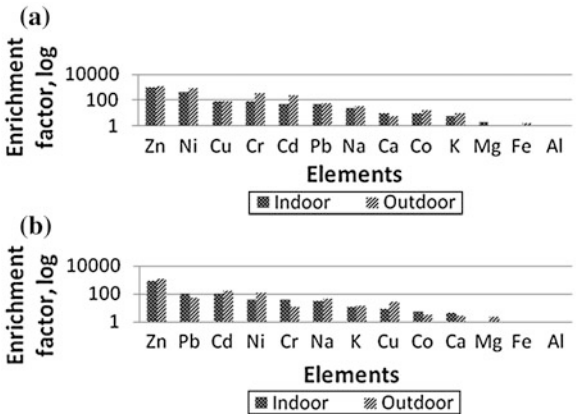

Fig. 69.1 Enrichment factor of elements in indoor and outdoor PM_{10}. (**a**) S1 and (**b**) S2

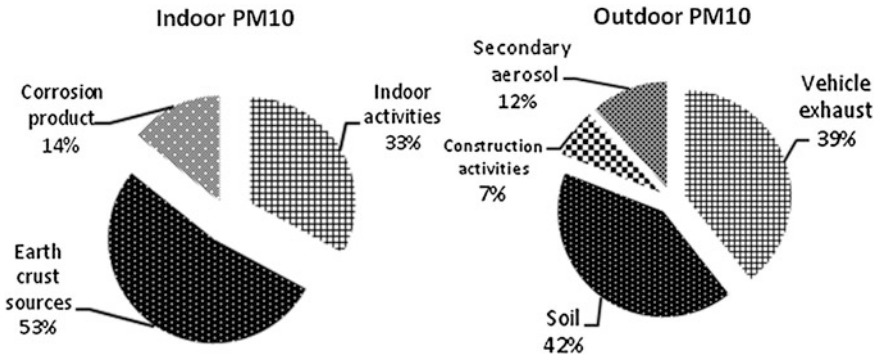

Fig. 69.2 Source apportionment of indoor and outdoor PM_{10}

Source apportionment for both indoor and outdoor PM_{10} was carried out by employing principal component analysis coupled with multi linear regression (PCA-MLR) using the WSIS and elemental concentrations datasets. The principal component accounted for 78.1 and 84.6 % of PM_{10} concentrations for indoor and outdoor, respectively. Three sources contributing to the indoor PM_{10} were identified such as earth crust sources (53 %), indoor activities (33 %) and corrosion product (14 %). The external sources included soil (42 %), vehicle exhaust (39 %), secondary aerosol (12 %) and construction activities (7 %) were resolved for outdoor PM_{10} (Fig. 69.2).

Conclusion

The mean concentration of indoor PM_{10} at S1 and S2 were higher than the outdoor. The high I/O concentration ratios suggested resuspension of particles are important factors that can influence indoor particle dispersion process and increased the level of earth crust sources indoors. The study also indicated that indoor activities and corrosion products in the classroom may also have significant impact on the indoor particle concentration. On the other hand, the outdoor PM_{10} concentrations were mainly contributed by soil, vehicle exhaust, construction activities, and secondary aerosol.

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Chapter 70
Concerns on the Threat of Environmental Hazards to Human and Environment in Malaysia: An Exploratory Analysis

Tengku Hanidza Tengku Ismail, Hafizan Juahir and Ahmad Zaharin Aris

Abstract A total of 1224 university students from Universiti Putra Malaysia, Malaysia, were asked to give a quantitative judgment about the threat to human and the environment with possible answers ranging from "no threat at all" (1) to "extreme threat" (7). This study was carried out from December 2007 to February 2008. Results from this study showed that students tend to rank 'threat 'as "high" for hazards familiar to them. The mean score for top five hazards were nuclear technology (6.07), global warming (6.04), drugs (5.92), earthquake (5.79), and tsunami (5.78). On the other hand, unfamiliar hazard such as genetic technology (4.74) and handphone (4.41) were perceived as 'least threatening'. The role of gender, year of study, race, and academic discipline on risk perception were also examined. Results show that gender plays the biggest role in shaping students' risk opinion. Female students were more concerned about threat of risk than male students. The differences in opinion follow this order: gender > year of study > race > academic discipline.

Keywords Risk perception · Threat · Environmental hazards · University students · Malaysia

Highlights

- Nuclear energy is perceived as most threatening to human and environment.

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- Unfamiliar hazards such as genetic technology were perceived as 'least threatening'.
- Females were more concerned about threat of risk than male.

Introduction

Under the 10th Malaysian plan, the national policy on environmental health includes sustainable development, socio- economic development, the protection of the environment and the promotion and protection of human health. Ten important environmental health areas of concern have been identified: hazardous waste management, rural water supply and sanitation, recreational water, safe drinking water, air pollution—outdoor and indoor, sewerage and urban sanitation, solid waste management, food safety, occupational health and safety, and soil contamination (Government of Malaysia 2010). Recent public protest and ongoing public concern about rare earth processing industries highlight the importance of understanding and knowing public concerns and sentiments on environmental issues. Individual interpretation of risk and its judgment are heavily influenced by life experiences, age, gender, culture, knowledge, and educational background. Individual acceptance of risk differs from place to place, and with time. What is acceptable by one person may not be true for other another. Society as a whole selects particular risk for attention and that risks are therefore exaggerated or minimized according to the social, cultural, and moral acceptability of each hazardous activity, substance and technology. Numerous articles on public perception of environmental health risks were published. These factors were heavily biased by socio-demographic factors and personal experiences; media coverage (including alternative media); proximity to the hazards; and other underlying factors which can lead to misjudgements of risk (Siegriest and Cvetkovich 2000; Miller et al. 2007; Van de Velde et al. 2011; He et al. 2012; Burger 2012). To date, published studies on societal risk perception on environmental health hazards in Malaysia are limited. This study examines various environmental hazards and measure threat to human and environment. The focus of this study is on the young educated group, since they are the potential leaders who will be involved in activities and decision making in environmental management.

Materials and Methods

The risk perception survey was carried at the main campus of the Universiti Putra Malaysia, Serdang, Selangor, Malaysia, from December 2007 to February 2008. The respondents were grouped according to gender, race, age group, enrolment year, and field of study. A total of 698 female and 526 male students participated in this study. Questionnaires were distributed to students residing in the University

residential colleges. These respondents represent students living in campus, which constitute 80 % enrolment at the university. To assess the risk perception, questions on the perceived threat to human and environment on 14 hazards were used. The questionnaire was adapted from other published studies carried out in Hong Kong (Lai and Tao 2003), and China (Xie et al. 2003). The hazards were: smoking, global warming, genetic technology, drugs, alcohol, nuclear energy, pesticides, tsunami, flood, earthquake, chemical pollution, hand-phone, microorganism, and loss of biodiversity. Respondents were asked to rate on a 7-points scale (1 = no threat at all, 2 = minimal threat, 3 = mild threat, 4 = moderate, 5 = strong threat, 6 = very strong threat, and 7 = extreme threat. Analysis of variance and multiple comparison tests were performed to test for differences in mean scores using SAS v 9.2. The statistical significance 0.05 was used in this study.

Results and Discussion

Perceived threats: The mean scores, standard deviations and hazard ranking for the given 14 items are calculated. The top five hazards that were perceived as threatening were nuclear energy (6.07), global warming (6.04), drugs (5.92), earthquake (5.79), and tsunami (5.78) while the less heard of hazards, such as, genetic technology (4.74) and hand-phone (4.47) were perceived as least threatening (Table 70.1).

In general, this study suggests that students tend to perceive environmental hazards as moderate to very strong threat. Items such as nuclear energy, global warming, tsunami and earthquake were perceived as higher threats compared to other issues such as smoking and alcohol use. As compared to Lim et al. (2008), their respondents were more concern with social issues while global warming and

Table 70.1 Hazard ranking as perceived by the respondents

	Mean	SD	Rank
Smoking	5.39	1.38	8
Global warming	6.04	1.11	2
Genetic technology	4.74	1.47	13
Drugs	5.92	1.32	3
Alcohol	5.35	1.38	9
Nuclear energy	6.07	1.30	1
Pesticide	5.21	1.20	11
Tsunami	5.78	1.33	5
Flood	5.32	1.28	10
Earthquake	5.79	1.26	4
Chemical pollution	5.67	1.2.9	6
Handphone	4.41	1.54	14
Microorganism	4.99	1.48	12
Loss of biodiversity	5.43	1.50	7

nuclear energy/waste were rank ordered lower. In this study, Tsunami and earthquakes were rank ordered higher, this was probably indicative of the heightened awareness after the great tsunami of 2004 that occurred in South East Asia. Although Malaysia was minimally affected, there were economic losses and fatalities. Prior to 2004, the word tsunami was far less heard of nor experienced. Unlike the tsunami, the Malaysians have had experienced with minor tremors when earthquakes occurred in Indonesia. However, the effects of these disasters on the respondents were not explored. A multinational comparison by Zhai and Suzuki (2009), indicated that global warming is rank ordered second highest (2 of 30). The people from Japan and China were more concern with the global warming and earthquakes compared to Korea (ranked 6 and 28 respectively). Tsunamis (ranked 26) and atomic power accident (ranked 25) was rank ordered lower, in contrast to our findings. As for the nuclear energy, a possible explanation was that since Malaysian has yet to have nuclear energy stations, the possible 'unknown' or 'public fear or dread' factors might have influenced their perception. This was reflective in the hazard profiling whereby upon examination of one of the risk perception attributes, 'known risk', the respondents judged both the nuclear energy and global warming as the two most threatening hazards but less known to those exposed compared to tsunami, earthquakes and flood. There is some similarity and difference from Lai and Tao (2003). Their respondents judged the natural disasters (earthquakes; flood and tidal waves) as well as radioactive fallout from nuclear power plant (we assume this falls under the same category as nuclear energy used in our study) as 'known' and 'dread' risk but the latter is 'less controllable' risk.

Comparison between groups: An ANOVA and multiple comparisons were conducted on the mean scores for each hazard on gender, academic discipline, and academic year of study and race variables. The effect of gender was significant ($p < 0.05$) for almost all hazards except for genetic technology. Female students (5.52) were more concerned about threat of risk than male students (5.28). The effect of academic discipline was not significant for almost all hazards except for loss of biodiversity ($p < 0.05$). The science discipline students' perceived loss of diversity is more threatening compared to the technical and social science students. The effect of academic year of study was significant for smoking, genetic technology, nuclear technology, earthquake, and loss of biodiversity ($p < 0.05$). In general, the first year students, majority of them between 19–20 years old, have lower risk perception compared to their seniors. The effect of race was significant only for drugs, alcohol, chemical pollution and loss of biodiversity ($p < 0.05$).

Conclusion

In this study, among the 14 listed hazards given to the respondents, the top five hazards that were perceived as threat to human and environment were nuclear energy (6.07), global warming (6.04), drugs (5.92), earthquake (5.79), and Tsunami (5.78). Unfamiliar types of risk, such as, hand-phone (4.37), genetic

technology (4.74), were seemed as having "lower threat". Of the four variables (gender, year of study, race, academic discipline) being examined, gender has a strong influence of the way they perceived threat. Results from this study support the conclusion that female students were more concerned about threat of risk than male students. The differences in opinion on individual hazards follow this order gender > year of study > race > academic discipline. Results from this study captured a highly specialized group, educated and knowledgeable.

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Chapter 71
A Review on Environmental Forensics and Environmental Law in the Malaysian Perspective

Maizatun Mustafa and Mariani Ariffin

Abstract Environmental law which is pertinent for the purpose of environmental protection and pollution control requires the assistance of forensic investigation and analytical sciences to investigate what is in the environment, where it has come from, and using that data to detect, prevent or prosecute environmental crime. In Malaysia and elsewhere, law enforcers are relying heavily on the scientific discipline of environmental forensics in order to prove, to the satisfaction of a court of law, who is responsible for instances of pollution. Specifically for Malaysia, environmental liabilities are generally the remit of the Department of Environment through enforcement of the Environmental Quality Act 1974. This Act is the main law enacted to help attain the objective of environmental policy which is to balance economic and environmental needs for the purpose of sustainable development. This Act is also the key piece legislation that has formed the basis of many prosecutions, and it contained various provisions that concerned directly or indirectly with environmental forensics. The objectives of this paper are to examine the Act, and to identify its relevance towards the application of environmental forensics within the legal process for the purpose of achieving the overall objectives of environmental protection and sustainable development. This research is very important because at the moment, there is a very limited number of other known researches in Malaysia that examine environmental forensics from the legal perspective. Thus this research should help policy makers, law enforcers, judiciary, scientists and other relevant stakeholders understand and expand their knowledge of environmental forensics in the context of law.

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Keywords Environmental law · Environmental liability · Environmental forensics · Judicial approach · Environmental protection

Highlights

- Environmental forensics is vital in solving environmental crimes.
- Outcomes derived from environmental forensics is essential in prosecuting polluters.
- Environmental law and policy directive have impacts on environmental forensics.

Introduction

In Malaysia, environmental law, notably the Environmental Quality Act 1974, plays vital roles in environmental protection including that of monitoring and preventing of pollution, as well as investigating, and prosecuting of environmental crime. Malaysia's environmental problems are diverse, ranging from land degradation due to earthworks and deforestation, to the pollution of water, marine and air due to industrial related activities. According to the Department of Environment (2011a), in recent years, industrial activities continue to become the major contributors towards environmental pollution in Malaysia. At present, main sources of water pollution include manufacturing and agro-based industries which is about 50 % of the total sources of water pollution (Department of Environment, 2011a). Gaseous emissions from industrial sources as well as motor vehicles continue to increase, with industries being the highest contributor for particulate matter (Mustafa et al. 2012). In coastal waters, oil and grease contaminations are widespread and increasing, with more restricted but important problems of heavy metals such as copper, mercury and lead levels exceeding proposed standards due to land-based uncontrolled industrial discharges (Department of Environment 2011a). Apart from that, high generation of toxic and hazardous wastes from manufacturing activities leads to cases of illegal dumping that can also results in soil and water pollution (Ariffin-Ho 2007).

The Act applies various strategies in order to deal with these issues, including that of "end-of-pipe" regulations, that restrict emissions of air and water pollutants from factories (Mustafa 2011b), and the application of contravention license to premises that discharge industrial wastes and sewage, or emit certain type of gases into the environment (Mustafa 2009). Other strategies introduced include environmental impact assessment and economic measures which are essentially

proactive approaches for preventing and reducing the environmental impact due to development related activities. The application of these and other strategies, which are based on accepted legal principles such as that of precautionary and polluter pays (Ansari et al. 2006), provide the basis for investigation in order to establish liability (Mustafa 2011a). According to the Department of Environment (2011b), in 2011, a total of 811 offenses were prosecuted under the Act. Out of this total, over 63 % involved offences related to air pollution, whereas nearly 12 % of these cases involved inland water pollution concerning effluent discharges exceeding the stipulated standards. The remaining cases were prosecuted under various other offences under the Act.

While the Act relies on criminal sanction for the purpose of prosecution, its objective is not just about prosecuting the polluter, but also determining preventive measures and highlighting specific needs. There are various provisions within the Act that require the involvement of environmental forensics in order to achieve its ultimate aim of environmental protection. Thus, the Department of Environment which is tasked to enforce the Act, must rely upon scientific evidence, including reports from the Chemistry Department, for the purpose of prosecution or prevention. At the same time, considering that forensics techniques may evolve in response to a specific law or type of environmental litigation, knowledge of environmental law, especially its rules and procedure affecting forensic processes, is vital. The fundamental focus of this research is therefore to examine the Act, and to identify its importance in relation to the application of environmental forensics within the legal process for the purpose of achieving the overall objective of environmental protection and sustainable development. Since there is a very limited number of other known researches in Malaysia that examine environmental forensic from the legal perspective, this research could help policy makers, law enforcers, judiciary, scientists and other relevant stakeholders understand and expand their knowledge of environmental forensics in the context of law.

Materials and Methods

The research used qualitative methods. In order to analyse the existing legal framework of environmental forensics, a targeted documentary analysis of primary and secondary sources was conducted. They include statutes, case law, textbooks, government materials and other relevant materials. Data gathered through library and desk-based research was analyzed using conceptual content analysis. In order to find out about the existing administrative process involving environmental forensics, non-doctrinal legal research of agencies' rules and guidelines and other resources was held. The findings were used to assess the existing legislation as a whole to see its strength and weaknesses towards environmental forensics.

Results and Discussion

For this research, the examination was done on the provisions of the Environmental Quality Act 1974 which are directly or indirectly relevant to environmental forensics, as well as on the relevant case law. Examination was also done to identify the link between environmental policy and the Act, and the implication of the former towards the application of environmental forensics within the law. These examinations revealed that the scope and jurisdiction of the Act are very wide pertaining to both the subject matter of environment, as well as what constitute "pollution", "pollutant", "environmentally hazardous substances", and "wastes". The understanding of the definitions of these terms, and how the court interprets them, would have, among other things, implications towards the scope and application of environmental forensics within the process of law. The examination explained that the Act applies various strategies in determining pollution offences, such as that of acceptable conditions under Section 21, thus relying on this and other types of evidence both for prosecution or defence. The Act is very clear about who has the power to prosecute, and whom should be liable in the event of crime and prosecution, and this is further strengthened by court's interpretation of the Act from decided cases, such as that of *Tenggara Gugusan Holidays Sdn. Bhd. v. Public Prosecutor* [2003] 1 MLJ 508. In relation to the protection of environment as a whole, examination of the Act indicated that the Act is designed to achieve the objective of environmental policy which is to balance the needs between economic development and environmental protection as evident from its provisions and regulations. Thus, on one hand, the Act imposes increased liability on industries for environmental damage that they have caused. On the other hand, pollution under the Act is not absolutely prohibited, but only restricted. Thus, industries can discharge their pollution as long as it is within the prescribed limit. In this regard, and from environmental perspective, the role of environmental forensics is important in helping the enforcement officer deducing evidence and submitting it to court during trial to ensure conviction. On the part of the court, its role is equally important to hear arguments from both sides of the parties proving and disproving liability for an environmental offence. The examination explains that, while the court is relying on specific chemical evidence to establish liability, the judge usually takes into consideration factors such as that of public policy in order to determine the amount of penalty imposed. The case in point, *Malaysian Vermicelli Manufacturers (Melaka) Sdn. Bhd. v. Pendakwa Raya* [2001] MLJU 359, illustrates the role of environmental forensic in assisting the court in making its decision especially the one involving serious pollution cases affecting public interest directly.

Conclusion

Within the legal framework of many countries, environmental forensics are developed and applied primarily due to the need to determine the environmental liability of an individual or group of parties in response to a legal provision. In Malaysia, the Environmental Quality Act 1974, which is the main legislation relating to environmental protection and pollution control, is the law most responsible for the development and application of environmental forensics. Based on the findings of the research, it is concluded that environmental forensics is a vital component within the whole of legal process relating to environmental crime. Among other things, outcomes derived from environmental forensics are essential in prosecuting polluters, determining preventive measures, and highlighting specific needs. The finding also found that existing environmental law and its provisions have implications on the way in which environmental forensics are being applied. This research concluded that, environmental policy directives, legal process, as well as judicial decisions help contribute towards the shaping of environmental forensic in Malaysia, and the overall development of environmental law in the country.

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Chapter 72
The Accumulation of Fe, Pb, Zn, Ni and Cd in *Nerita lineata* and *Thais bitubercularis* Obtained from Tanjung Harapan and Teluk Kemang, Malaysia

Nur Azyan Fathiah Adnan and Tengku Hanidza Tengku Ismail

Abstract The concentrations of selected heavy metals (Fe, Pb, Zn, Ni and Cd) were determined in the soft tissues and shells of two mollusc, namely, *Nerita lineata* and *Thais bitubercularis* taken from Tanjung Harapan and Teluk Kemang, Malaysia. Samples were collected in April 2012 and analysed using inductively coupled plasma mass spectrometry (ICP-MS). Fe is the most abundant metal in the tissue and shell compared to the rest of the metals. The concentrations of heavy metals in the soft tissues of *Nerita lineata* taken from Tanjung Harapan follow this order: Fe > Zn > Ni > Cu > Cd while in *Thais bitubercularis*, the metal concentrations were higher following the order of Fe > Zn > Cu > Ni > Cd. The samples taken from Teluk Kemang were higher and exhibited different trend for both organisms. For *Nerita lineata,* the concentrations were Fe > Cu > Zn > Ni > Cd > Pb while in the *Thais bitubercularis* the order was Fe > Zn > Cu > Cd > Ni > Pb. There was evidence of spatial difference where Fe was detected in large amount compared to other metals for both locations. Cd has the potential to be accumulated in *Nerita lineata* whereas for the *T. bitubercularis* Cu, Cd, and Zn were accumulated in the soft tissues.

Keywords Heavy metals · *Nerita lineata* · *Thais bitubercularis* · Biota-sediment accumulation factors (BSAFs) · Malaysia

Highlights

- There was an evidence of spatial difference in heavy metals concentrations.
- Fe is most abundant in both the organisms and sediments.
- Cu, Cd, and Zn accumulated in the tested organisms.
- *Thais bitubercularis* is a bettter heavy metal accumulator.

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Introduction

Elevated levels of metals in the sediments are attributed to anthropogenic activities. The Langat River (Negeri Sembilan) was heavily polluted with Zn and Cd. Areas along Tanjong Karang and the Johor Strait, the concentration of Pb and Zn were more than doubled than the global shale value, which was contributed to the usage of unleaded petrol (Pb) and tires (Zn) (Shazili et al. 2006). Sany et al. (2013) showed evidence of temporal and spatial distribution of heavy metals in water and in sediments of Port Klang. Their findings indicated that the concentrations of As, Cd, Hg, and Pb in sediment and As, Cd, Hg, Pb, Cr, and Zn in water were significantly higher than the background values. The main sources of heavy metal contamination in this area were industrial wastewater and port activities.

Bivalves (such as *Perna viridis* and *Saccostrea* sp) and gastropods (*Thais* sp.) are commonly used as bioindicators for heavy metal (especially for Cd, Cu, Pb, and Zn) (Shazili et al. 2006; Yap and Cheng 2009; Yap et al. 2009; Cheng et al. 2012). Another indicator of bioaccumulation property is the biota–sediment accumulation factors (BSAFs) which is the ratio of biota to sediment contamination concentration. Studies in gastropods showed that BSAF values >2 are classified as macroconcentrators, values $1 < \text{BSAF} < 2$ are microconcentrators, and BSAF value <1 are deconcentrators (Berandah et al. 2010; Yap and Cheng 2013). Yap and Cheng (2013) indicated that the soft tissues of *Nerita lineata* were microconcentrators of Cu and Zn while the shell and the operculum are classified as macrocentrators for Cd, Ni, and Pb.

This study aims at determining the distribution and concentrations of selected heavy metals (Fe, Pb, Zn, Ni and Cd) and the biota-sediment accumulation factor (BSAF) in two mollusk species (*Nerita lineata* and *Thais bitubercularis*) collected at Tanjung Harapan and Teluk Kemang.

Materials and Methods

Sample Preparation

Samples were collected from Teluk Kemang, Port Dickson, Negeri Sembilan and Tanjung Harapan, Selangor in April 2012. About 30–40 of each species of *Nerita lineata* and *Thais bitubercularis* were handpicked. The gastropods were dissected and separated into shells and soft tissues. These samples were dried in an oven at 60 °C until the constant dry weights were obtained. About 0.5–0.7 g of the dried tissues (Berandah et al. 2010) from each species of the gastropods were weighted. The tissues were digested in 10 ml nitric acid (AnalaR grade, BDH 69 %). Sample digestions were carried out following Yap et al. (2002). The instrument was calibrated with a blank and standards containing each element at 10 ppb, 20 ppb, 50 ppb, 100 ppb and 200 ppb.

Statistical Analysis

Biota–sediment accumulation factors (BSAFs) was determined. BSAFs are the ratio of biota to sediment contamination concentration. It is calculated based on the formula suggested by Berandah et al. (2010). The difference in the mean concentration of the heavy metals between locations as well as types and parts of the mollusks were determined using the Tukey test.

Results and Discussions

In general, the concentration of heavy metals in the soft tissues and in the shells for both species varied. *Thais bitubercularis* accumulated more Fe in the shells. The opposite pattern was observed from samples collected from Tanjung Harapan (Fig. 72.1).

The concentrations of heavy metals in the soft tissues of *Nerita lineata* taken from Tanjung Harapan follow this order: Fe (118.74 mg/kg) > Zn (11.47 mg/kg) > Ni (3.72 mg/kg) > Cu (0.15 mg/kg) > Cd (0.045 mg/kg) while in *Thais bitubercularis*, the metals concentrations were higher following the order of Fe (400.60 mg/kg) > Zn (372.10 mg/kg) > Cu (233.25 mg/kg) > Ni (0.258 mg/kg) > Cd (0.935 mg/kg). The samples taken from Teluk Kemang were higher for some metals and exhibited different trend for both organisms. For *Nerita lineata,* the concentrations were Fe (369.90 mg/kg) > Cu (7.26 mg/kg) > Zn (7.80 mg/kg) > Ni (4.08 mg/kg) > Cd (0.06 mg/kg) > Pb (0.09 mg/kg). For *Thais bitubercularis*, the

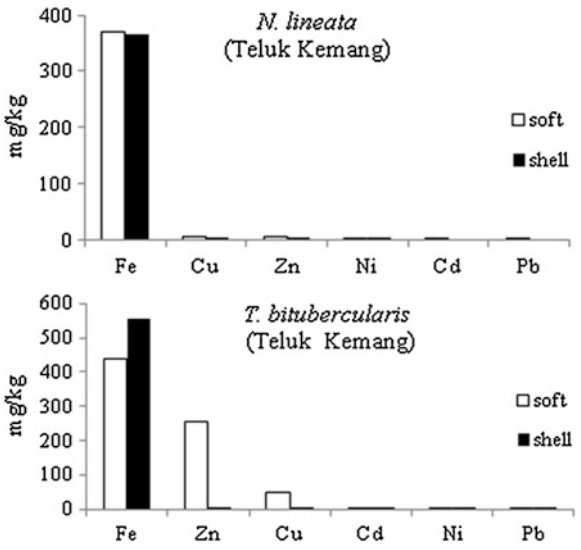

Fig. 72.1 The concentrations of heavy metals in *N. lineata* and *T. bitubercularis* taken from Teluk Kemang

order was Fe (436.64 mg/kg) > Zn (257.02 mg/kg) > Cu (50.81 mg/kg) > Cd (1.17 mg/kg) > Ni (3.11 mg/kg) > Pb (0.17 mg/kg). For the sediment samples, there was evidence of spatial difference where Fe is detected in large amount compared to other metals for both locations. The Fe concentration taken from Teluk Kemang was higher than Tanjung Harapan, 9718.75 mg/kg versus. 6187.41 mg/kg. The concentrations of Cu, Zn Cd, and Pb in *Nerita lineata* from this study are lower than that reported by Yap et al. (2009). In general, the calculated BSAF values for samples obtained from Tanjung Harapan were higher than Teluk Kemang. The highest BSAF was copper (Cu) in *T. bitubercularis* (91.186) while the lowest BSAF was iron (Fe) in *N. lineata* (0.028). The BSAF values for *N. lineata* follow this order; Cd > Ni > Zn > Cu > Pb > Fe. Only Cd has the potential to be accumulated. For the *T. bitubercularis* the order is Cu > Cd > Zn > Ni > Pb > Fe, where Cu, Cd, and Zn were accumulated in the soft tissues. The heavy metals concentration in the soft tissues of *T. bitubercularis* from Tanjung Harapan and Teluk Kemang exceeded the Malaysian Food Act 1983 for Cu and Zn. The concentration of Cd in the soft tissues of *T. bitubercularis* from Teluk Kemang also exceeded the Malaysian Food Act 1983. In contrast to Yap et al. (2009), they reported Cd exceeded the Malaysian Food Act 1983 for *N. lineata* in Tanjung Harapan.

Conclusion

Findings from this study showed that the concentrations of heavy metals in the soft tissue were higher than the shells for *Nerita lineata* and *Thais bitubercularis*. Fe is the most abundant metal in the tissue and shell compared to Cu, Zn, Ni, Cd, and Pb. The concentrations of heavy metals in the soft tissues of *Thais bitubercularis* taken from Tanjung Harapan were higher than *Nerita lineata* following the order of: Fe > Zn > Cu > Ni > Cd. The metal concentrations in *Nerita lineata* follow this order: Fe > Zn > Ni > Cu > Cd. The samples taken from Teluk Kemang were lower and exhibited different trend for both organisms. For *Nerita lineata,* the concentrations were Fe > Cu > Zn > Ni > Cd > Pb while in the *Thais bitubercularis* the order was Fe > Zn > Cu > Cd > Ni > Pb. For the sediment samples, different pattern was observed. There was evidence of spatial difference where Fe is detected in large amount compared to other metals for both locations. The Fe concentration taken from Teluk Kemang was higher than Tanjung Harapan. Cd has the potential to be accumulated in *Nerita lineata* whereas for the *Thais bitubercularis* Cu, Cd, and Zn were accumulated in the soft tissues.

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Chapter 73
Assessment of Water Quality Using Environmetric Techniques at Johor River

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Abstract In this study, the spatial water parameters of Johor River from 2003–2007 were analyzed by using environmetric techniques namely the hierarchical agglomerative cluster analysis (HACA), discriminant analysis (DA) and principle component analysis (PCA). These methods were used to determine the spatial variations and sources of pollutants in Johor River. There were 23 water parameters selected namely DO, BOD, COD, SS, pH, NH_3-NL, temperature, conductivity, salinity, turbidity, DS, TS, NO_3, Cl, PO_4, Zn, Ca, Fe, K, Mg, Na, E-coli and coliform. The HACA has grouped the water monitoring stations along the Johor River into three clusters; (1) the stations with low pollution sources (LPS), (2) moderate pollution sources (MPS) and (3) high pollution sources (HPS). Stations are classified into three clusters based on the similarity of each variable poses towards each other. Ten water parameters were being discriminated by conducting forward stepwise DA out of the 23 water quality variables. PCA were then conducted to identify the pollutant sources from the landuse of the area. Eight principle components (PCs) were obtained with 79 % variation of LPS region. Five PCs were obtained from MPS with the total variation of 84 % of the MPS region. The HPS has the most number of PCs which are nine PCs with a total variation of 83 % of its region. For the MPS and HPS, the pollutants were introduced by human activities such as discharge of chemicals, industrial wastewater, agricultural activities and urban development activities.

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Keywords Environmentric · Cluster analysis · Discriminant analysis · Principal component analysis · Heavy metals

Highlights

- Spatial water parameters of Johor River were analyzed using environmetric.
- Clusters of water monitoring stations based on their similarity of each variables.
- Water parameters were discriminate by conducting discriminant analysis.
- PCA identified the pollutant sources from the land use of study area.

Introduction

The quality of Johor River water in supplying potable freshwater has deteriorated (Sulaiman 2010). Therefore, due to the threat of pollutants released via anthropogenic activities, water quality prediction and assessment is essential for human development (Najah et al. 2011). In order to monitor the water quality along Johor River basin, Department of Environment (DOE) of Malaysia, Ministry of Natural Resources and Environment of Malaysia has installed telemetric stations. Water quality index (WQI) was developed from the data obtained during the monitoring program. WQI can be used to evaluate the water quality status and river classification for the entire river. It is useful in predicting the changes and trends in water quality by considering multiple parameters such as dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solid (SS), ammoniacal nitrogen (AN) and pH. WQI in the ranged of 0–59 corresponds to polluted river, 60–80 is slightly polluted or moderately polluted and 81–100 correspond to clean water classification (Juahir et al. 2011).

Materials and Methods

Johor River is located in central part of south Johor at longitude 1°27–1°49 N and 103°42–104°01 E (Fig. 73.1). The length of the main stream is 122.7 km, constituting a surface area of 2.636 km^2. The river originates from Mt Gemuruh, and discharges into the Straits of Johor. The main geological features of Johor River consists of intrusive rocks, Quaternary, Triassic, Permian, Cretaceous-Jurassic and Tertiary rocks. Johor River receives an average annual precipitation of 2,470 mm with mean annual runoff 37.5 m^3/s. The landuse along the river are urban (5.5 %), forest (16.4 %), oil palm and other crops (18.5 %), waterbody (0.5 %) and also swamps (11.6 %). The sampling for 23 parameters was done at 50 sampling stations along the river.

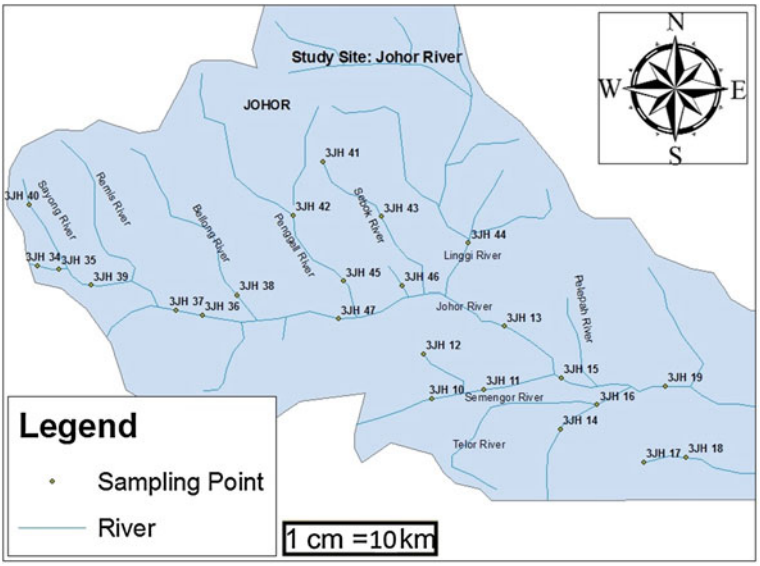

Fig. 73.1 Johor River showing sampling points

Results and Discussion

The first cluster represents low-pollution source (LPS) whilst the second cluster representing moderate-pollution sources (MPS) and the third represents high-pollution source (HPS). One monitoring station of each cluster is sufficient to represent a resonably accurate spatial water quality assessment for the entire Johor river. Cluster analysis technique can reduce the needs for numerous sampling stations.

For the standard mode DA, the correct accuracy is 90.91 % while for the forward stepwise mode, the correct accuracy is 90.73 % and for backward stepwise mode, the correct accurancy is 90.64 % respectively. In the standard mode DA, all the 23 water parameters were found to be significant. For the forward stepwise mode, DA, 13 variables were found to be significant in influencing the water characteristics. The 13 significant variables were DO, BOD, pH, NH_3NL, NO_3, PO_4, Zn, Fe, K, Na, OG, MBAS and E-coli. These parameters showed significant spatial variability. In the backward stepwise mode, 15 variables were significant in affecting the river water quality and the correct accuracy is 90.64 %. The forward stepwise mode was chosen because higher accuracy was obtained by this mode compared to the backward stepwise and the variables were less than backward stepwise mode. This can save cost in evaluating variables affecting the river water quality.

PCA was used to compare compositional patterns between water parameters and to identify factors that contribute to each region (LPS, MPS and HPS). Based on eigen values criteria, only PCs with eigenvalues greater than one is considered

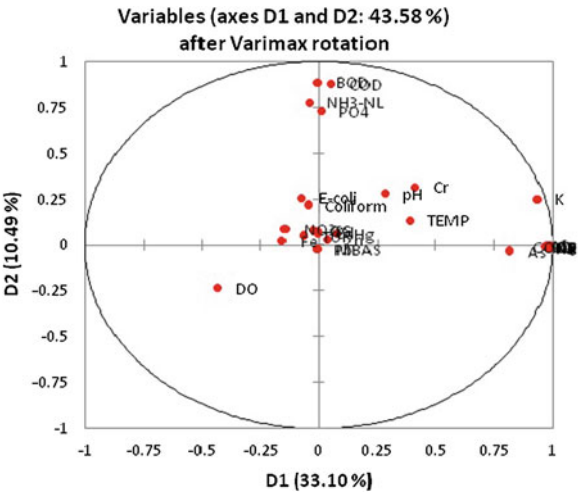

Fig. 73.2 PCA for 30 variables after conducting Varimax rotation with number factor of eight

important (Kannel et al. 2007). Eight PCs were obtained for LPS region,, five for MPS region and nine for HPS and these were based on eigenvalues greater than one which has a total summing variance of 79.2, 84.0, and 83.1 % respectively. Each total number of Varimax factors (VFs) was obtained based on their factor analysis (FA) that performed in PCs (Fig. 73.2).

Conclusion

The HACA has successfully classified the water monitoring stations along Johor River into clusters of low pollutant sources, moderate pollutants sources and high pollutants sources based on their water quality characteristics. The forward stepwise DA has also been able to discriminate ten variables correct accuracy of 90.73 % from the total 23 water quality parameters. In PCA, eight PCs were obtained with the total variation of 79 % from LPS region, five PCs were obtained from MPS for 84 % of the total variation of MPS region and nine PCs were obtained for HPS with 83 % of the total variation of HPS region. This technique had helped evaluating the spatial variation of Johor River based on selected monitoring stations and water quality parameters. Potential pollutant can also be identified from this techniques and this would contribute to a better river management.

Acknowledgments We would like to acknowledge the Department of Environment and Department of Irrigation and Drainage, Ministry of Natural Resources and Environment of Malaysia who have provided us with the secondary data of the Johor River Basin. We would also like to express our gratitude toward Dr. Hafizan Juahir for his advice and guidance for conducting this study. We would like to thank the Faculty of Environmental Studies for supporting us on this study.

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Chapter 74
Impact of Landuse on Seasonal Water Quality at Highland Lake: A Case Study of Ringlet Lake, Cameron Highlands, Pahang

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Abstract A study to find the relationship between landuse development and seasonal water quality changes in highland lake, Ringlet Lake, Cameron Highland, Malaysia was carried out. The study found that most of the parameter analyzed in both seasons shows that the Ringlet Lake is Class III in the Water Quality Index Due to high percentage of cleared area, as indicated by individual type of landuse, pollutants were transported through Bertam and Ringlet river and eventually to the lake.

Keywords Highland lake · Water quality analysis · Landuse impact · Seasonal variation · Water quality index

Highlights

- Landuse influence the deterioration of water quality at a highland lake.
- Landuse type influence seasonal variation of water quality.
- GIS analysis supports the relationship between types of landuse and water quality.

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Introduction

Landuse changes, policy and management practices, economic demand as well as environmental conditions may all lead to differences in pollutant transported into the aquatic ecosystem. According to Norhazni and Pauziah Hanum (1996) and UMCB (2001), the changes in landuse patterns in Cameron Highlands were recognized as the main contributor to the river water quality problems. Similar findings were reported by the Cameron Highlands District Council (2004) and Muhammad et al. (2009) that showed the Ringlet's main tributaries are at the lowest water quality class. Ringlet Lake was built for the generation of electricity and as a means of controlling floods. It is imperative that the life of the lake is sustained to ensure the efficiency of the dam, development of Cameron Highlands, the safety of the population downstream and for the benefits of the general public. The Ringlet Lake has been severely impacted and deteriorated as the result of intensive landuse development at higher region. These activities have directly and indirectly deteriorates the river water quality which finally affecting the lake water quality. This paper focuses on water quality analysis at the Cameron Highlands region, and examine the landuse pattern. The result from this study is important to prove intensive landuse development can be related to the water quality of the lake, focusing on the temporal/seasonal variation of the area.

Materials and Methods

Analysis of selected water quality parameters was conducted in two seasons at Ringlet Lake, Cameron Highlands, Malaysia, in June and September 2012 (dry and wet season, respectively). Landuse analysis for the landuse type and cleared area classification was conducted based on data acquired in 2008 by using GIS spatial tools. Standard procedure for water quality analysis was applied in accordance to APHA Standard Method Procedure (2000).

Results and Discussion

Spatial Analysis (Landuse Classification)

Based on the landuse type from the recent source (satellite image of 2008) as shown in Fig. 74.1, this manmade lake is affected from the landuse type within the three upper regions, namely, Upper Bertam, Middle Bertam and Lower Bertam.

The identification of potential causes of water quality deterioration at the lake can be identified in general, which include; topography, soils types, percentage of cleared area for agricultural activities, vegetation types, and indirect factors, such

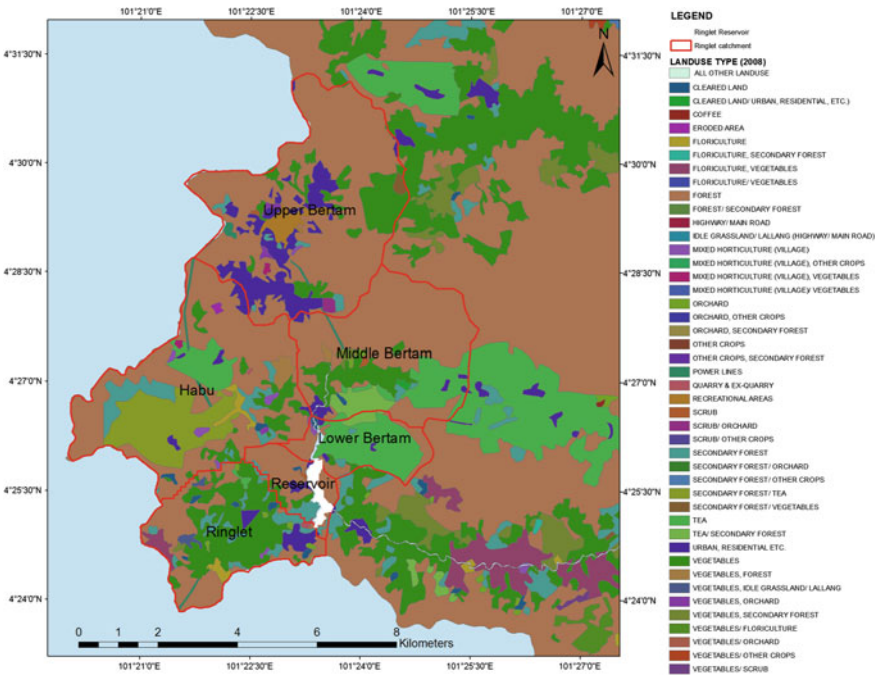

Fig. 74.1 Landuse map of Cameron highland area

as, the frequency of fertilizer and pesticides application, and the self-awareness of the farmers in managing their waste. Cameron Highlands is formed by elevated areas ranging between 1,070 and 1,830 m from sea level. The convex land surface and steep terrain pose a risk of erosion to the area if vegetation is cleared. In addition to the nature of farming activities, the soil type is also a significant factor that contribute towards severe land erosion. Within this area, 63.9 % is made of loamy type while 27.3 % is of laterite type. This type of soil with high sand content can be easily eroded, especially when exposed to agricultural activities. Other than tourism, highland agriculture is the main business activity in Cameron Highland. The increasing demand for highland agricultural products led to the clearance of more land for agricultural purposes, 3.5 % increase per year. From Fig. 74.1, the land conversion for growing main crops encompassed 52 % for vegetable, 41 % for tea, followed by flowers, fruits, spices and food crops at 4.92, 1.74, 0.51 and 0.45 %, respectively. This is evident by the significant increase in areas for growing vegetables and tea as the demand of this products increased over years. The types of vegetation affect the ability of the root system to hold the soil. The short and weak root system of the vegetables is almost functionless to protect the soil surface from erosion.

According to TNBR (2004), 87.2 % of the farmers grow vegetables which require a lot of water compared to the other types of plants. Excessive watering, ploughing, and tiling weaken and loosen the structure of the soil. Loose sand are then transported to the Ringlet Lake.

Water Quality Analysis on Selected Parameters

From the analysis, some of the main water quality parameters did not show any significant changes such as temperature (ranges from 21 to 22 °C) and conductivity (ranges from 45 to 3165 μS/cm), However, some important pollutants such as TSS, TDS, BOD, COD, pH, DO, selected nutrients (sulphate and nitrate) and oil and grease shows that the lake water is critically deteriorated as the seasons changes, due to flow variation and dilution factors. The problem of sedimentation of the lake is expected to increase and the negative effect on the nearby environment, the threat to safety of the population downstream and the reduction in viability of the dams itself are inevitable if no drastic action is taken to reduce the process of sedimentation. From the analysis undertaken by Zainal and Kia (1997), it has been found that the Ringlet location has the highest erosion risk/loss based on the *CP* factor of the USLE with a value of 0.0875. This result is supported by the fact that this location produced the highest ranking for residential (5.39 %) and construction (2.07 %) areas compared to other locations.

Artificial lakes, in effect, serve as sediment basins, trapping the eroded soil sediments by sharply reducing the inflowing stream's velocity and, therefore, its capacity to transport sediment loads. Eroded soil sediments suspended in flowing waters rapidly settle out and fall to the bottom in standing waters. Sedimentation reduces the effective life span of mainstream impoundments. Based on previous study TNBR (2004) and from this preliminary analysis and field observation, the lake water quality is lower than the river water quality. The Water Quality Index (WQI) of Ringlet Lake is summarized in Table 74.1.

Table 74.1 Water quality index at Ringlet Lake for dry and wet season

Station ID	Sg Bertam	Near Sg Lohai	lake	lake	Sg Ringlet
Ringlet (dry season)					
Sampling point	1	2	3	4	5
Class	II	III	II	II	III
WQI	79.76	76.04	79.76	77.69	71.99
Ringlet (wet season)					
Sampling point	1	2	3	4	5
Class	III	III	III	III	III
WQI	68.59	61.27	70.77	63.43	65.04

This study suggest that the degraded lake water quality is directly related to the percentage of cleared area for on the upper regions (water quality class shifted to Class II and III). The temporal variation shows that the lake receives more pollutant during wet season as surface runoff increases.

Conclusion

The study found that most of the parameter analyzed in both seasons shows that the Ringlet Lake is Class III in the Water Quality Index. Due to high percentage of cleared area, as indicated by individual type of landuse, pollutants were transported through Bertam and Ringlet river and eventually to the lake. A major management strategic plan to control the nutrients and other pollutant also needs to be addressed.

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Chapter 75
Polycyclic Aromatic Hydrocarbons (PAHs) in Sediments from Prai and Malacca Rivers, Peninsular Malaysia

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Abstract In this study the surface sediments of Malacca River (3 Stations) and Prai River (3 Stations) were analyzed to identify the distributions of PAHs. The concentrations of PAHs were quantified using Gas Chromatography–Mass Spectrometer (GC–MS). Total PAH concentrations varied from 716 to 1210 and 1102 to 7938 ng g^{-1}dw in sediments of Malacca and Prai Rivers, respectively. The concentrations of PAHs in sediments were classified as moderate in sediments of Malacca and high to very high level of pollution in sediments of Prai River. PAHs were dominated by high molecular weight (HMW) in sediments of Malacca River and low molecular weight (LMW) in sediments of Prai River. This indicates that petroleum hydrocarbon pollution in Malacca River is dominated by atmospheric input while that of Prai River is mostly fresh petrogenic input from lateral or horizontal transport via rivers and surface runoffs. The other diagnostic ratios of LMW/HMW, Fluo/(Fluo + Py), Fluo/Py and Comb/TPH in both rivers are consistent with the above statement.

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Keywords Polycyclic aromatic hydrocarbons (PAHs) · Petrogenic · Pyrogenic · Sediment · Prai river · Malacca river · Malaysia

Highlights

- The concentrations of PAH varied from 716 to 7938 ng/g dry weight.
- PAH values classified as moderate and high for Malacca and Prai Rivers, respectively.
- The sources were a mixture of pyrogenic and petrogenic in both rivers.
- Pyrogenic and petrogenic were dominance in Malacca and Prai Rivers, respectively.

Introduction

During the last few decades, Southeast Asian countries such as Malaysia have experienced a drastic increase in urbanization and industrialization, resulting in immense increase in petroleum hydrocarbon consumption. These changes had caused significant input of Polycyclic Aromatic Hydrocarbon (PAHs) to fresh-water and marine ecosystems in Malaysia (Zakaria et al. 2002). Recent studies indicated that rivers and coastal areas of this country are still receiving significant input of petroleum hydrocarbon pollution (Zakaria et al. 2002; Bakhtiari et al. 2009; Mirsadeghi et al. 2011; Sakari et al. 2012). PAHs are hydrophobic and their molecular structure is consisted of two or more fused benzene rings (Liu et al. 2009). Some members of this group are mutagenic, carcinogenic and can impose cascades of adverse effects to aquatic organisms (Karami et al. 2011) and human (Masiol et al. 2012). Based on the number of their benzene rings, PAHs are divided into two major groups namely Low Molecular Weight (LMW) with 2–3 fused benzene rings and High Molecular Weight (HMW) with more than three benzene rings (Achten and Hofmann 2009). LMW PAHs are more water soluble (Shahbazi et al. 2010), volatilizable and biodegradable (Xu et al. 2012) than HMW PAHs. The release of PAHs into natural environments is mainly governed by anthropogenic activities (Wang et al. 2011). Based on their source of release into natural environments, PAHs are divided into two groups, pyrogenic (incomplete combustion of organic matters) and petrogenic (unburned crude oil and its derivatives). This study was carried out to identify distribution and possible sources in surface sediments from Prai and Malacca Rivers.

Methodology

Surface sediment samples (the top 4 cm representing modern input) were collected from six locations in Prai River and Malacca River in January and May 2013, respectively (Fig. 75.1). The samples were transported (placed on ice in the cooler box) to the laboratory and stored at −20 °C until further analysis.

The samples were purified and fractionated according to the procedures described by Zakaria et al. (2002). In brief, sediment sample was extracted using Soxhlet extractor. The extract was eluted and fractionated using first and second glass columns to obtain PAHs. The PAHs fraction was evaporated to approximately one mL, subsequently concentrated to near dryness. The fraction was then re-dissolved in 200 μL isooctane containing 10 ppm internal injection standard (IIS), p-terphenyl-d_{14}. The PAHs compounds were analyzed using GC–MS.

Fig. 75.1 Locations of sampling areas showing Prai and Malacca Rivers in *red circles*

Result and Discussion

The concentrations of 16 PAHs were determined in sediment samples from Malacca and Prai Rivers. Table 75.1 shows the concentrations of total PAH in Malacca River which ranged from 716 to 1210 ng g^{-1} dw with the highest amount at Station 2 (1210 ng g^{-1} dw) and the lowest amount at Station 3 (716 ng g^{-1} dw). Total PAH concentrations in Prai River ranged from 1102 to 7938 ng g^{-1} dw with the highest amount at Station 1 (7938 ng g^{-1} dw) and the lowest amount at Station 3 (1102 ng g^{-1} dw). The levels of PAHs can be classified as low (0–100 ng g^{-1} dw), moderate (100–1000 ng g^{-1} dw) and high (1000–5000 ng g^{-1} dw) (Baumard et al. 1998). Based on this classification, PAH concentrations categorized as moderate in Malacca and high to very high in Prai Rivers.

In both rivers, it was observed that higher levels of PAHs occurred in upstream and lower concentrations were found in estuaries. This concentration pattern can be attributed to input from factories and industrial discharges and other anthropogenic input to the rivers. The gradual decrease of PAHs concentrations from the upper to lower stream is due to non-conservative behavior of PAHs. PAHs are normally partitioned to hydrophobic particles in the water column. As the particles are transported downstream, more particles clump together to form flocculation as the particle reach salinity regime in estuaries. The particles settle to bottom sediment which makes concentration of PAHs normally lower as it reaches estuary.

Table 75.1 Concentrations of PAHs and isomeric compounds for pyrogenic and petrogenic origins in sediments of different stations

	[a]TOC %	[b]∑PAHs	[c]LMW	[d]HMW	[e]LMW/HMW	[f]Fluo/Py	[g]Flou/(Fluo + Py)	[h]Comb/TPH
Prai station 1	1.97	7938	3646	2912	1.25	0.99	0.497	0.38
Prai station 2	2.47	4030	1687	1541	1.09	0.91	0.475	0.39
Prai station 3	1.74	1102	369	567	0.65	1.01	0.504	0.54
Malacca station 1	1.82	1142	326	589	0.55	1.00	0.498	0.55
Malacca station 2	2.20	1210	477	380	1.25	0.90	0.469	0.32
Malacca station 3	1.94	716	70	448	0.15	0.76	0.43	0.67

[a] TOC = total organic carbon; [b] ∑PAHs = the sum of the concentrations of naphthalene, cenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a] anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a] pyrene, indeno[1, 2, 3-cd]pyrene, dibenzo[a,h]anthracene, and benzo [ghi]perylene; [c] LMW = the sum of low molecular weight PAHs concentrations of acenaphthene, fluorene, phenanthrene, anthracene and fluoranthene; [d] HMW = the sum of high molecular weight PAHs concentrations of pyrene, benzo[a] anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a] pyrene, indeno[1, 2, 3-cd]pyrene, dibenzo[a,h]anthracene, and benzo [ghi]perylene; [e] LMW/HMW = the ratio of the sum of low molecular weight PAHs to high molecular weight PAHs; [f] Fluo/Py = the ratio of fluoranthene to pyrene; [g] Flou/(Fluo + Py) = the ratio of fluoranthene to fluoranthene +pyrene; [h] Comb/TPH 16 PAHs = the ratio of the sum of high molecular weight to ∑PAHs

The results show the abundance of HMW for Stations 1 and 3 of Malacca River and Station 3 of Prai River (Table 75.1). These stations may have received the input of pyrogenic sources particularly long-range atmospheric transport or the ubiquity of forest fires. For effective control of contaminant input, more detailed source identification of the contaminants is needed. The rest of the stations for both rivers displayed LMW PAHs indicating those stations may have received a fresh petroleum hydrocarbon input via lateral transport. The results of Fluo/(Fluo + Py), Fluo/Py and Comb/TPH ratios in both rivers are consistent with the result of LMW/HMW ratio.

Conclusion

Total PAH concentrations ranged from 716 to 1210 and 1102 to 7938 ng g^{-1} dw in sediments of Malacca and Prai Rivers, respectively. It can be concluded that the concentrations of PAHs in sediments can be classified as moderate in sediments of Malacca and high to level of petroleum pollution in sediments of Prai River. This study revealed that PAHs were dominated by high molecular weight (HMW) in sediments of Malacca River and low molecular weight (LMW) in sediments of Prai River which is consistent with the results of Fluo/(Fluo + Py), Fluo/Py and Comb/TPH ratios in both rivers.

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Chapter 76
Chlorination Disinfection Byproducts (DBPs): A Review of Malaysian Drinking Water Policy and Consumers' Perception

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Abstract Chlorine is used by water treatment plants (WTPs) in Malaysia to disinfect water from harmful microorganisms. However, chlorine can react with natural and organic materials and lead to the formation of disinfection byproducts (DBPs). DBPs are harmful to human health when exposed in sufficient quantities over a period of time. The objectives of this study are to examine Malaysian drinking water policy in relation to DBPs in the light of international guidelines especially the World Health Organization Guidelines for Drinking-Water Quality 2011 (WHO Guidelines) and to do a preliminary study of consumers' perception on drinking water quality in Selangor. In order to achieve these objectives, a targeted document review, and key-informant interview with officers from the Ministry of Health and a survey of consumers' perception were conducted. The study found that Malaysia adopts more stringent standard values for certain DBPs than the WHO Guidelines, but not in terms of monitoring and strategies for reducing the by-products. The survey result showed that 91 % of the respondents can tolerate minimal presences of DBPs, which have to comply to the regulations set by the Ministry of Health. Overall, 76 % of the respondents were satisfied with the drinking water quality at home.

Keywords Chlorination · Disinfection byproducts · Drinking water · Malaysian policy · Consumer perception

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Highlights

- Malaysia adopts stricter standard values for selected DBPs than the WHO guidelines.
- Most of the respondents had limited knowledge about DBPs and drinking water policy.
- 91 % of respondents agreed that a minimum concentration of DBPs is tolerable.

Introduction

Malaysia has several statutes that directly or indirectly protect the country's water sources from harmful pollutants. Nevertheless, raw water taken from these sources still contains some undesired contaminants and must be treated before distribution for consumer consumption. Generally, water treatment processes in a conventional water treatment plant (WTP) involves several key steps i.e., aeration, flocculation, sedimentation, filtration and disinfection (Latiff 2011). The focus of this study is on the disinfection stage. Disinfection is crucial to ensure drinking water is safe from microbial contaminants, which will consequently reduce the overall risk of water-borne diseases. Chlorine is widely used in water treatment due to its efficient disinfection mechanism and a cost-effective chemical. However, disinfection usually leads to the formation of DBPs due to chemical reaction between chlorine and natural or organic materials present in the raw water.

Individual can come into contact with DBPs via oral, inhalation and dermal (Backer et al. 2000). Although there are many groups of DBPs, including some possible yet unidentified DBPs in drinking water supply, the haloacetic acids (HAAs) and the trihalomethanes (THMs) typically occur at higher levels than other DBPs. It has been suggested that people who consumed chlorinated drinking water have a higher potential to develop cancerous cells and contribute to higher birth defects. In the United States, DBPs are associated with bladder and rectal cancer as well as reproductive and developmental problems (Duncan 2005). There have been also concerns about potential adverse reproductive health effects, such as stillbirth, low birth weight and congenital anomalies (Nieuwenhuijsen et al. 2000).

Nevertheless, the WHO (2011) states that the health risks from the DBPs are relatively small compared to the risks associated with inadequate disinfection and it warns that disinfection efficacy should not be compromised in order to control such by-products production. The burning question now is how can we use chlorine for disinfection while also ensuring that public drinking water is free from waterborne pathogens and therefore safe to drink? To overcome this problem, the WHO has issued the guidelines for drinking-water quality with the latest edition published in 2011. The WHO guidelines provide a reference and framework for safe drinking-water for many countries around the world including Malaysia.

The Malaysian Ministry of Health (2004) has set drinking water health-based thresholds in the National Standard for Drinking Water Quality 2004 (NDWQS). The NDWQS establishes maximum acceptance levels of several characteristics and constituents in drinking water which are hazardous to health or objectionable to the consumers. The quality of drinking water is measured based on its microbiological, physical, chemical and radioactivity characteristics. Apart from the NDWQS, Malaysia does not have a specific legislation on drinking water quality but a bill has been drafted and in the process of public consultation. Puncak Niaga Holdings Berhad and its subsidiaries are involved in the operation, maintenance, management, construction, rehabilitation and refurbishment of water treatment facilities, supply and distribution of treated water within the State of Selangor, Federal Territories of Kuala Lumpur and Putrajaya. Aini et al. (2007) indicated that color, odor and taste are among the main problems of drinking water. The problem of poor drinking water quality is partly due to the unprotected raw water sources. The jurisdiction on catchment areas and protection of water source falls under State governments. Another cause of poor drinking water quality is rustic pipes and improper maintenance of customer's internal piping system, water tanks and water filters (SYABAS 2013).

In this study, Malaysian drinking water policy in relation to DBPs is examined in the light of international guidelines especially the World Health Organization Guidelines for Drinking-Water Quality 2011 (WHO Guidelines). A preliminary result of consumers' perception on drinking water quality in Selangor is also presented.

Materials and Methods

This research used both qualitative and quantitative methods. The qualitative method involved targeted review of national and international policies and secondary resources concerning DBPs, as well as key-informant interview. The study used semi-structured interviews to allow new questions to be brought up during the interview based on what the respondents said. Content analysis was used to analyze the data. Questionnaire survey was also distributed as a preliminary study to investigate consumers' perception of drinking water quality. 100 respondents were selected randomly from a residential area in Selangor.

Results and Discussion

Concern about the safety and quality of Malaysia's drinking water prompted the government to come up with the NDWQS in the 1980s. Since then, the national guidelines have been reviewed a few times to keep it in tandem with international standards as stipulated in the WHO guidelines on drinking water. Malaysian policy

on drinking water only governs selected types of DBPs. A comparison of Maximum Acceptable Value (MAV) on DBPs between NSDWQ and WHO guidelines showed that Malaysia has lower MAV for total THMs and thus more stringent than the WHO guidelines. Similarly higher standard is set for dichloroacetic acid and trichloroacetic acid of HAAs.

Other than standards, Malaysia also has several recommended procedures, preventive measures and methods of treatment to achieve its drinking water quality standards in general. In addition, several national programs under various agencies have been launched to manage water quality and supply in Malaysia. There is a room for improvement in terms of monitoring and strategies in order to minimize the production of DBPs. Better institutional coordination and more cooperation among various agencies that are involved in water treatment and supply must be established. Furthermore, Malaysia will soon have a water safety plan that adopts comprehensive risk assessment and risk management approaches on the water supply from the catchment to the consumers when the Safe Drinking Water Quality Bill is passed.

With regard to the consumers' perception survey, it was found that most of the respondents had very limited knowledge about DBPs and drinking water policy in Malaysia. However, almost all of the respondents (91 %) would tolerate a minimum concentration of DBPs presence in their drinking water, if it is considered safe by Ministry of Health. Overall, 76 % of the respondents were satisfied with drinking water quality level at their homes.

Conclusion

Malaysia has been successful in providing microbiologically-safe drinking water and consequently the incidences of diarrhea and other waterborne diseases have been reduced. However, the threat of harmful DBPs in drinking water to human health has been given less attention in the Malaysian drinking water policy and its implementation. The developed countries such as the United States and European countries have invested a significant amount of energy and time to study the human health effects of DBPs and to restructure processes in WTPs. These efforts are made to reduce DBPs formation and to minimize any risk of cancer from long-term exposure (CDC 2004). Consumers in Malaysia have limited knowledge about DBPs. Despite, that they seem to have high level of confidence that Malaysian water authorities can provide clean and safe drinking water with minimum amounts of DBPs. This should give more reasons for Malaysian government to improve the existing policy on drinking water, which will further reduce the risk of adverse health effects.

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Chapter 77
Environmental Awareness, Attitude and Behavior Among Under Graduates in Malaysia

Kuang Hock Lim, Rosta Harun, Fiona GohSwee Ching and Lay Yen Yeo

Abstract This study was undertaken to evaluate the knowledge, attitude and behaviour on the environment among 650 undergraduates. The representative samples were selected through a two-stage sampling method. The validated questionnaires developed by the Focus Group Discussion (FGD) process and expert opinions were utilized in this study. The pre-testing of the questionnaire was carried out among 50 undergraduates. Explanatory Factor Analysis revealed three components existed in the questionnaire, namely knowledge, attitude and behavior. Each Component shows good reliability, awareness component (8 questions—Cronbach Alpha0.72), attitude (9 questions—Cronbach Alpha-0.78) and behavior (8 questions, Cronbach Alpha 0.70). This study revealed the level of environmental knowledge and attitudes among students was high 4:15(sd0.42) and 4:19(sd0.49), however, they score moderately on behavior component (3.20(sd0.46). There are no significant difference in awareness, attitude and behaviour between gender, However, different age groups differed significantly (4.24 vs. 4.14, $p = 0.013$). Meanwhile, the awareness score was also significantly different between undergraduates from different programs (4.11 vs. 4.20, $p = 0.005$). Multivariable Linear Regression indicates the positive association between high knowledge and attitudes with pro-environmental behavior.

Keywords Environmental Awareness · Attitude · Behavior · Undergraduates · Malaysia

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Highlights

- Respondents demonstrate high level of knowledge and attitude.
- Respondents scored moderately in behavioural aspects.
- There is significant difference on awareness between programs.

Introduction

Human and Environment Conference in 1972 was the turning point for global public awareness of the problem of environmental degradation that occurs as an effect of human activity (UNESCO 1972). While in 1992, the Earth Summit Conference in Rio has identified environmental awareness as one of the measures to overcome environmental problems such as global warming, ozone depletion and more (Andonova and Hoffmann 2012). This has prompted the adoption of Environmental Education activities by most countries in the world to raise awareness by impartation of general knowledge for the basic understanding of the environment, hence, this amend the attitudes and values to generate new environment through patterns of behavior. Malaysia also are not left behind in this aspect, as it was included in the school curriculum from primary up to tertiary education environmental awareness activities are also conducted by government agencies, such as, the Department of Environment (Harun et al. 2011). This study aimed to assess the awareness, attitudes and behavior towards Environmental among university students.

Materials and Methods

Samples and Instrument

The representative samples of this study were acquired using a two-stage stratified sampling method. First stage is the division of undergraduates according to program of study (science and art), followed by selection of undergraduates using simple random sampling. Three-hundred undergraduates from each program of study were selected based on the standard deviation score from previous study. However, to compensate the 15 % of non-response, 345 undergraduates from each program of study were selected. The Instrument of this study was the questionnaire developed through several stages. Focus Group Discussion (FGD) attended by all research members was the first stage, throughout the brainstorming process, all items related to environmental awareness, attitude and behaviour were developed. The draft questionnaire was then delivered to the content expert to verify the content validity. Pre-testing on 50 undergraduates was carried out; the construct

validity was established using Explanatory Factor Analysis which reveals three components. These components are Awareness (8 questions), Attitude (9 questions) and Behaviour (8 questions). The satisfactory internal consistency of each component are Cronbach Alpha 0.72 (Awareness), Cronbach Alpha 0.78 (Attitude) and Cronbach Alpha 0.70 (Behaviour).

All items in each component was evaluated using Likert Scale of 1–5, then the average score will be obtained through the division of scores by the number of questions. A high score indicates high awareness, attitude and pro-environment behaviour. Moreover, social-demographic variables such as age, education level and gender also obtained from the respondents.

Measures

The questionnaire was distributed to all selected respondents. The purpose of this study was explained to the respondents and those who agreed to participate in this study were required to sign the consent form which attached to the questionnaire. The completed questionnaire was then collected back by the research team members.

Statistical Analysis

Data was analysed using SPSS version 16.0. The characteristic of respondents (i.e. proportion of gender) was explained using Descriptive statistic. Independent-T test was used to test the mean score of awareness, attitude and behaviour between gender, program of study, age, and year of study, Multivariate Linear Regression was utilized to assess the real effect of social-demographic, awareness and attitude with pro-environmental behaviour. All statistical tests were performed at 95 % confidence level.

Table 77.1 Social-demographic characteristic of respondents

Variable	N (%)
Gender	
Male	137 (21.8)
Female	432 (78.2)
Program of study	
Science	387 (62.3)
Art	234 (37.7)
Year of Study	
1–2 year	393 (62.5)
3 year	236 (37.5)
Age group (years)	
18–20	322 (51.2)
21–25	307 (48.8)

Table 77.2 Awareness, attitude and behaviour score according to gender, course, year of study and age group

Variable	Awareness			Attitude			Behaviour		
	Score Mean (sd)	t value	p	Score Mean (sd)	t value	p	Score Mean (sd)	t value	p
Gender									
Male	4.17 (0.47)	0.55	0.58	4.16 (0.55)	−0.74	0.46	3.20 (0.49)	0.089	0.93
Female	4.15 (0.42)			4.20 (0.48)			3.20 (0.45)		
Program of study									
Science	4.11 (0.42)	−2.79	0.005	4.18 (0.52)	0.62	0.87	3.18 (0.46)	−1.33	0.18
Art	4.21 (0.40)			4.19 (0.45)			3.23 (0.45)		
Year of study									
1–2 year	4.13 (0.41)	−1.97	0.049	4.22 (0.47)	1.68	0.09	3.18 (0.43)	−1.60	0.11
3 year	4.19 (0.43)			4.15 (0.53)			3.24 (0.50)		
Age group (years)									
18–20	4.14 (0.40)	−0.336	0.74	4.24 (0.48)	2.48	0.013	3.19 (0.42)	−0.53	0.60
21–25	4.16 (0.43)			4.14 (0.51)			3.21 (0.50)		

Table 77.3 Coefficients values from the OLS regression on the behaviour of environment according to gender, education, program of study, year of study, age group, attitude and awareness of environmental score

Variable	Coefficients (standard beta)	t value	p
Attitude	0.314	7.914	<0.001
Awareness	0.082	2.08	0.04
Age Group	−0.013	−0.238	0.81
Gender	−0.009	−0.235	0.16
Year of study	0.075	1.78	0.06
Program of study	0.056	1.42	0.16
Adjusted R^2	11.5 %		
N	617		

Results and Discussion

A total of 629 respondents returned the questionnaire, with a response rate of 91.2 %. Of the 629 respondents, 492 (78.2 %) are female undergraduates, 236 (37.5 %) respondents are from the final year of study and 234 (37.7 %) are stream undergraduates (Table 77.1).

All respondents demonstrate high level of knowledge and attitude on environment. However, they only score moderately on behavioural aspects. In addition, analysis found a significant difference between awareness of environment between programs of study (4.20 for science program and 4.11 for art program, $p = 0.005$) and attitude score between different age group (4.14 for respondents aged 20 and above and 4.24 for respondents 18–20 years, $p < 0.05$) (Table 77.2).

Controlling for the other variables in model, social-demographic variables which are not significant in Univariate analysis show the similar trend in Multivariate analysis. Pro-environmental attitude and higher level of environmental awareness contributed significantly to pro-environmental behaviour, therefore, this has proven the correlation between these variables as the higher the awareness and attitude score toward environment, the more positive the behaviour towards the same component (Table 77.3).

Conclusion

All respondents demonstrate high level of knowledge and attitude on environment. However, they only score moderately on behavioural aspects. A significant difference on awareness between programs was noticed. For that reason, appropriate measures to enhance and inculcate pro-environment awareness and attitude should be planned and implemented throughout the university years in Tertiary Education.

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Chapter 78
Optimization of Coagulation Process for the Pre-Treatment of Biodiesel Wastewater Using Response Surface Methodology (RSM)

Nurull Muna Daud, Siti Rozaimah Sheikh Abdullah and Hassimi Hasan

Abstract The oily and turbid biodiesel wastewater is characterized by high chemical oxygen demand (COD), biological oxygen demand (BOD) and suspended solid (SS) contents. In this study, the ability of coagulation process to be used as pre-treatment process was investigated by considering several process conditions which includes pH, coagulant's dosage, mixing rate and settling time. Box-behnken design was used to optimize the operating conditions of coagulation process. The study shows that the coagulation process with pH 7.13, 2 g/L coagulant's dosage, 200 rpm mixing rate, and 65 min settling time managed to remove 34.5, 39.04 and 32 % of COD, SS and turbidity, respectively.

Keywords Biodiesel wastewater · Coagulation · Response surface methodology

Highlights

- Biodiesel production generates highly polluted effluent.
- Coagulation process is favorable for pre-treatment of biodiesel wastewater.
- RSM is used to obtain the optimum conditions of coagulation process.

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Introduction

For every 1000 L of biodiesel produced, about more than 200 L of wastewater was generated (Pleanjai et al. 2007). In 2011, approximately 29 million m^3 of biodiesel wastewater was generated worldwide (Veljković et al. 2013). Coagulation process has been widely used to treat various types of industrial wastewater, such as, pulp and paper mill wastewater (Ahmad et al. 2007), detergent wastewater (Aygun and Yilmaz 2010), and biodiesel wastewater (Rattanapan et al. 2011; Ngamlerdpokin et al. 2011). In coagulation process, coagulant is used to destabilize the small particle contents and flocculate into larger setlleable settleable flocs. The particles will be separated from the solution in a reasonable time.

In this study, alum was used as coagulant. To obtain the optimum conditions of coagulation process, response surface methodology (RSM) was used to create a set of designed experiments. Usage of RSM to design the experiments could help to reduce the number of experimental trials and evaluate the relative significance of variables and their interaction (Chavalparit and Ongwandee 2009).

Materials and Methods

The experiment was conducted using laboratory scale jar test apparatus. The wastewater sample was obtained from a commercial palm oil-biodiesel production plant located at Pulau Carey, Klang. The wastewater characteristics and analytical methods for each parameter are shown in Table 78.1.

The experimental design used four different factors; pH, coagulant's dosage, mixing rate and settling time. The responses investigated were COD, SS, turbidity and color. The number of experiments designated using RSM were found to be 29. The ranges and levels of each factor are shown in Table 78.2. In predicting the optimum condition for the process, the response surface regression analysis was performed and the quadratic equation model used (Ahmad et al. 2007) is expressed in Eq. (78.1):

$$Y_i = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j + \varepsilon \qquad (78.1)$$

where Y_i is the response, X_i represent the input factors, β_0, β_{ii} (i = 1,2,…,k), β_{ij} (i = 1,2,…,k; j = 1,2,…,k) are unknown parameters and ε is a random error.

Table 78.1 Characteristics of biodiesel wastewater

Parameter	Value	Analytical method/instrument
pH	3.85	pH meter (Metrohm, Switzerland)
COD (mg/L)	26820	Reactor digestion method (HACH DR 3900, USA)
SS (mg/L)	2064	Photometric method (HACH DR 3900, USA)
Color (PtCo)	9296	APHA Platinum-Cobalt Standard Method (HACH DR 3900, USA)
Turbidity (NTU)	2939	Turbidimeter (HACH 2100AN, USA)

Table 78.2 Ranges and levels of each factor

Factors (variables)	Range and level (coded)		
	−1	0	1
pH, x_1	4	6.5	9
Mixing rate (rpm), x_2	100	200	300
Coagulant's dosage (g/L), x_3	0.5	2	3.5
Settling time (min), x_4	10	65	120

Results and Discussion

The removal efficiencies for each experimental trial are listed in Table 78.3. The regression models which describe the removal efficiency of each parameter; turbidity (y_1), COD (y_2) and SS (y_3) are as in Eqs. 78.2, 78.3 and 78.4 respectively.

$$Y_1 = 69.47 - 6.45X_1 - 7.81X_2 + 41.43X_3 + 7.95X_4 - 20.97X_1^2 - 4.75X_2^2 + 0.68X_3^2 + 17.98X_4^2 - 6.42X_1X_2 + 0.93X_2X_3 + 14.72X_2X_4 - 0.45X_3X_4 \quad (78.2)$$

$$R^2 = 0.9106$$

$$Y_2 = 32.88 - 0.64X_1 - 0.97X_2 + 9.12X_3 + 2X_4 + 2.85X_1^2 + 1.87X_2^2 - 3.28X_3^2 - 1.77X_4^2 - 3.37X_3X_4 \quad (78.3)$$

$$R^2 = 0.8287$$

$$Y_3 = 24.99 - 0.47X_1 - 2.86X_2 + 23.33X_3 + 3.56X_4 - 10.63X_1^2 + 0.22X_2^2 + 12.28X_3^2 - 6.94X_4^2 - 2.17X_1X_2 + 5.16X_1X_3 - 0.82X_1X_4 + 2.72X_2X_3 + 5.15X_2X_4 + 5.92X_2X_4 \quad (78.4)$$

$$R^2 = 0.9740$$

Based on the optimization conducted using the regression models, the conditions for coagulation process was suggested at pH 7.13, 200 rpm mixing rate, 2 g/L coagulant dosage and 65 min settling time. The maximum removal efficiencies of turbidity, COD and SS are 67.27, 32.87 and 24.44 %, respectively. The comparison of removal efficiencies from the validity test and the calculated values obtained from Box-behnken optimization are shown in Table 78.4.

From the validity test, the turbidity removal differed from the calculated values with 55 % error. Meanwhile, the COD and SS removal obtained are higher than the calculated values, which means zero errors are obtained. The close removal values of these two parameters (COD and SS) imply that by using response surface

Table 78.3 Box-behnken design: Experimental and predicted removal efficiencies

Standard order	pH	Mixing rate (rpm)	Dosage (g/L)	Settling time (min)	Turbidity (NTU)		COD (mg/L)		SS (mg/L)	
					Experimental	Predicted	Experimental	Predicted	Experimental	Predicted
1	4	100	2	65	51.76	51.60	36.31	39.22	15.34	15.74
2	9	100	2	65	56.76	51.54	36.86	37.94	17.21	19.13
3	4	300	2	65	50.16	48.82	32.43	37.28	16.17	14.36
4	9	300	2	65	29.47	23.07	42.32	36.00	9.37	9.08
5	6.5	200	0.5	10	10.00	2.35	10.00	13.33	10.00	9.37
6	6.5	200	3.5	10	92.70	86.10	40.11	38.32	41.36	44.19
7	6.5	200	0.5	120	19.10	19.14	21.04	24.08	7.36	4.65
8	6.5	200	3.5	120	100.00	100.00	37.66	35.58	62.39	63.13
9	4	200	2	10	41.51	29.03	39.00	32.60	10.00	3.52
10	9	200	2	10	1.54	16.13	31.56	31.32	3.22	4.21
11	4	200	2	120	46.39	44.92	34.97	36.60	14.58	12.26
12	9	200	2	120	6.20	32.02	34.57	35.33	4.53	9.69
13	6.5	100	0.5	65	19.43	32.72	25.32	23.32	16.87	19.75
14	6.5	300	0.5	65	15.71	15.23	23.93	21.38	6.18	8.58
15	6.5	100	3.5	65	100.00	113.71	41.30	41.57	64.68	60.95
16	6.5	300	3.5	65	100.00	99.94	39.60	39.63	64.89	60.68
17	4	200	0.5	65	5.71	14.21	29.13	23.96	5.42	8.95
18	9	200	0.5	65	15.00	1.31	19.34	22.69	3.15	2.32
19	4	200	3.5	65	90.09	97.06	40.03	42.21	38.59	45.27
20	9	200	3.5	65	99.26	84.16	39.55	40.93	56.98	54.66
21	6.5	100	2	10	62.72	61.32	32.20	31.96	22.42	22.72
22	6.5	300	2	10	2.72	16.27	24.67	30.01	3.71	6.70
23	6.5	100	2	120	68.00	47.79	37.97	35.96	21.31	19.53
24	6.5	300	2	120	66.86	61.59	35.36	34.02	23.21	24.12
25	6.5	200	2	65	68.21	69.47	27.81	32.88	25.33	24.99
26	6.5	200	2	65	67.83	69.47	32.91	32.88	24.08	24.99
27	6.5	200	2	65	73.80	69.47	35.12	32.88	27.28	24.99
28	6.5	200	2	65	67.94	69.47	33.30	32.88	23.53	24.99
29	6.5	200	2	65	69.59	69.47	35.28	32.88	24.71	24.99

Table 78.4 Comparison of experimental values of validity test and calculated values of Box-behnken design

Process conditions	Removal parameter	Removal efficiency (%)	
		Calculated (Box-behnken)	Measured
pH: 7.13 Mixing rate: 200 rpm Dosage: 2 g/L Settling time: 65 min	Turbidity	67.27	32.00
	COD	32.87	34.50
	SS	24.44	39.04

methodology, the removal efficiency of coagulation process can be predicted while the optimum conditions be optimized.

Conclusion

The conditions of coagulation process in biodiesel wastewater treatment were optimized by applying Box-behnken design using response surface methodology. The target of having highest removal efficiency of multiple responses was achieved at optimum conditions of pH 7.13, with 200 rpm mixing rate using 2 g/L coagulant's dosage in 65 min settling time. Using the suggested optimum conditions, the overall removal efficiency turbidity, COD and SS obtained were found to be 32.00, 34.50 and 39.04 %, respectively.

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Chapter 79
Removal of Boron and Arsenic From Petrochemical Wastewater Using Zeolite as Adsorbent

Shamsul Izhar, Mohd Halim Shah Ismail and Lee Yuan Chuan

Abstract Petrochemical wastewater is one of the major industrial concerns due to the toxicity of heavy metals such as boron and arsenic. These metals must be progressively treated before discharged into receiving water. In this research, adsorption of boron and arsenic was conducted using natural zeolite (clinoptilolite). The arsenic and boron removal efficiencies using natural zeolite as adsorbents are 66 and 52 %, respectively, at its optimum conditions (pH 8, contact time 240 min and adsorbent dosage 480 g/L). Compared to various adsorbents, the adsorption using natural zeolite showed excellent boron and arsenic removal, thus has a great potential to be applied in industrial wastewater treatment plant.

Keywords Zeolite · Adsorbent · Wastewater · Heavy metal adsorption

Highlights

- Arsenic and boron removal efficiencies are 66 % and 52 %, respectively.
- Optimum conditions: pH 8, 240 min of contact time and 480 g/L of adsorbent dosage.
- Zeolite showed better boron absorption than activated carbon and activated alumina.

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Introduction

Among the heavy metals present in a wastewater treatment (WWT) system, boron and arsenic remain the toughest challenges for WWT system of petrochemical industry. Heavy metal treatment processes such as chemical precipitation, coagulation, flocculation, membrane filtration and reverse osmosis do not significantly remove boron and arsenic due to their high water solubility.

Some wastewater treatment technology such as filtration, precipitation, ion exchange and electro-coagulation can be used to remove boron and arsenic. However, these methods are less attractive due to high operating and maintenance cost, high production of toxic pollutant and low contaminants rejection. Some of the heavy metal, such as, boron was unable to be removed effectively via conventional wastewater treatment process. Alternatively, adsorption is a technology capable of achieving high boron and arsenic removal percentage with low operating cost. In this research, the adsorbent natural zeolite was used to remove boron and arsenic from petrochemical wastewater, due to its adsorption and ion exchange capabilities, easy available and low purchase cost. The optimum operating condition was determined by parameters such as pH of wastewater, dosage of adsorbent usage and contact time between adsorbent and wastewater sample.

Materials and Methods

The natural zeolite category used is a clinoptilolite type from Czech Republic which has low field strength and high Si content which is more selective for cations with lower charge density. The selectivity of clinoptilolite towards heavy metal ions (cations) exist in the series: $Pb^{2+}>Cd^{2+}>Cu^{2+}>Co^{2+}>Cr^{2+}>Zn^{2+}>Mn^{2+}> Hg^{2+}$ (Margeta et al. 2013). The zeolite was cleaned using deionized water, dried at room temperature and was used without surface modification or pretreatment. The surface of zeolite was scanned using Energy Dispersion Spectroscopy (Hitachi S-3400 N). The specific surface area of zeolite was determined using BET method (24.01 m2/g) while pore volume (0.155 cm3/g) and the pore radius (152 Å) were determined by BJH method.

Results and Discussion

Figure 79.1 shows the effect of pH on the removal of boron and arsenic. Both metals showed removal of less than 20 % below pH 4. However, at pH 7, metal removal was more than 20 % and at pH above 8, boron and arsenic removal was above 40 %. The percentage of boron and arsenic removal was higher at alkaline pH. The optimum pH for boron and arsenic removal was at pH 8 with a percentage

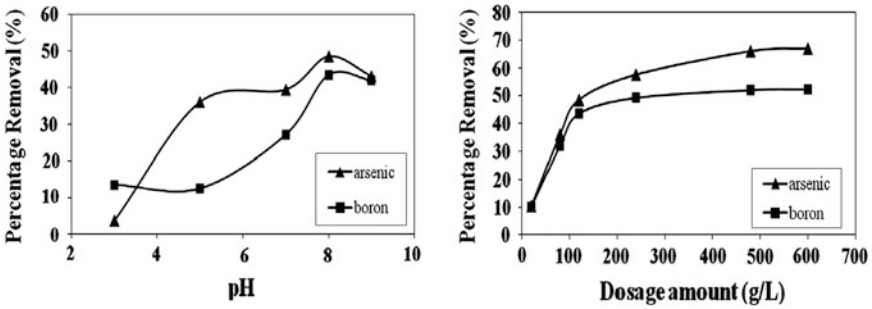

Fig. 79.1 Effect of pH (*left*) and zeolite dosage amount (*right*) on the removal of boron and arsenic. Agitation speed:150 rpm, contact time:240 min

removal of 43.5 and 48.5 %, respectively. The pH has a significant influence on the adsorption of boron and arsenic since pH can influence both the character of exchanging ions and the structure of the zeolite itself.

The maximum boron adsorption was obtained under alkaline conditions only at approximately pH 8–10. The natural zeolite has high cation-exchange capability due to its anionic framework structure. Thus at lower pH, the H^+ ions will compete with the arsenic ions As^{5+} and As^{3+} for the exchange sites on the natural zeolite surface. Besides, the electrostatic repulsion between the arsenic ions in solution and the protonated zeolite surface increases as more H^+ ions are adsorbed (Motsi 2010). Lower pH reduced the adsorption capacity of arsenic ions onto natural zeolite, hence, lowering the percentage of arsenic removal Moreover, the structure of natural zeolite may collapse in the presence of solution with pH lower than 4 (Singh et al. 2008).

The effect of adsorbent dosage on boron and arsenic removal was investigated by changing the natural zeolite dose between 20 and 600 g/L while the pH was held constant at pH 8. The speed of agitation used was 150 rpm and contact time of 240 min. Figure 79.1 (right) shows the effect of adsorbent dosage on boron and arsenic removal. It indicates that the removal of boron and arsenic increase with the increase in zeolite dose from 20 to 480 g/L and remains constant thereafter. For arsenic, the removal percentage increased from 10.44 to 66.33 % as the dosage amount increased from 20 to 480 g/L. Nevertheless, removal efficiency of arsenic only increased to 67 % when the zeolite dose was increased from 480 to 600 g/L. For boron, the removal efficiency varied from 10.05 to 52.01 % by increasing the zeolite dose from 20 g/L to 480 g/L. However, the removal percentage only increased to 52.26 % as the zeolite dose increased from 480 to 600 g/L.

The percentage of boron and arsenic removal can be improved by increasing the adsorbent dosage. Increase in adsorbent dose can increase the contact surface and adsorption sites between the heavy metals and zeolite. However, the boron and arsenic removal did not change significantly after 480 g/L adsorbent dosage since the equilibrium concentration difference caused the driving force for adsorption decrease for 480 and 600 g/L adsorption dosage (Ozturk and Kavak 2005). The

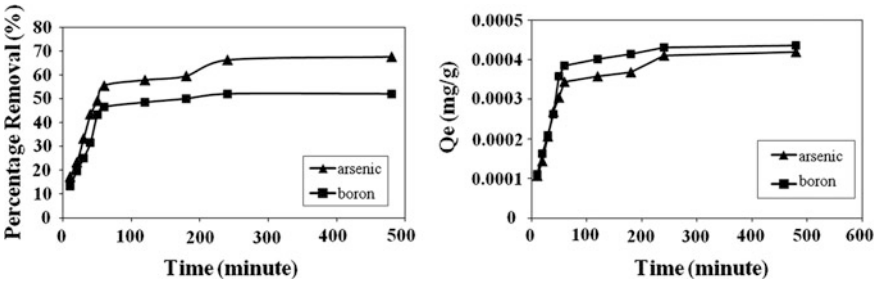

Fig. 79.2 Effect of contact time on adsorption of boron and arsenic (*left*), and adsorption capacities (*right*). Condition: pH 8, zeolite dose 480 g/L and agitation speed 150 rpm

effect of contact time on the percentage removal of boron and arsenic is shown in Fig. 79.2 (left). The percentage of metal adsorption also increases with the contact time. The adsorption rate of arsenic occurred rapidly during the first 50 min, and then decreased as the contact time increases. The equilibrium time was found to be 240 min. The percentage of arsenic removal at 480 min was 67.68 %, close to 66.33 % at 240 min, therefore, the contact time does not need to be longer than equilibrium time for time efficiency concerns. By comparing with other absorbent, the saturated contact time for arsenic adsorption is 1 h by palm oil mill boiler bottom ash and 8 h by activated carbon (Saad et al. 2006). For the removal of boron, adsorption rate occurred rapidly during the first 40 min and decrease afterward. The equilibrium time for boron adsorption was 240 min with the percentage removal of 52.01 %.

Activated carbon and activated alumina have been reported for their low boron adsorption efficiency. Figure 79.3 illustrates the comparison between adsorbents. Natural zeolite showed lower arsenic removal compared to fly ash and activated carbon. However, the zeolite showed a better efficiency for boron adsorption compared to activated carbon and activated alumina. The arsenic adsorption efficiency using activated carbon and activated alumina is higher compared to natural zeolite without presence of other metal ions and pollutants. Basically, the natural zeolite is a low cost adsorbent with a variety of applications including as

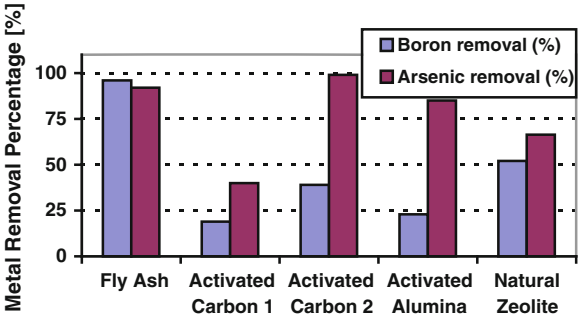

Fig. 79.3 Boron and arsenic adsorptions using various adsorbent. (*Carbon 1* salicylic acid impregnated activated carbon, *Carbon 2* Commercial grade)

adsorbents and ion exchangers and exhibits higher capacity than other adsorbents. Previous studies found that the zeolite was able to remove other pollutants such as phenol, mercury, cyanide, benzene, etc.

Conclusion

This study demonstrated the removal of boron and arsenic from petrochemical wastewater by natural zeolite with various pH, adsorbent dosage and contact time. The raw petrochemical wastewater contains 0.297 mg/L of arsenic and 0.398 mg/L of boron. The optimum condition for the adsorption of boron and arsenic was at pH 8. At these conditions, the optimum of adsorbent dosage for boron and arsenic was at 480 mg/L. The equilibrium time for boron and arsenic removal was at 240 min at optimum pH 8 by using 480 g/L adsorbent dosage. Under these optimum conditions, natural zeolite was able to remove 66.32 % of arsenic concentration and 52.01 % of boron concentration from petrochemical wastewater. In conclusion, zeolite can considered to be widely applied in WWT plant.

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Chapter 80
Composition of Surfactants from Sea-Surface Microlayer and Marine Aerosols along the Malacca Straits

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Abstract This study aims to determine the concentrations of surfactants on the sea-surface microlayer and in atmospheric aerosols from several coastal areas along the Malacca Straits. The concentrations of surfactants from the sea-surface microlayer (collected using rotation drum) and aerosols (collected using HVS) were analysed as Methylene Blue Active Substances (MBAS) and Disulphine Blue Active Substances (DBAS) by colorimetric method using a UV–visible spectrophotometer. The results of this study show the average concentrations of surfactants in the sea-surface microlayer ranged between undetected and 0.36 ± 0.34 $\mu molL^{-1}$ for MBAS and between 0.11 ± 0.02 and 0.21 ± 0.13 $\mu molL^{-1}$ for DBAS. The contribution of surfactants from the sea-surface microlayer to the composition of surfactants in atmospheric aerosols appears to be more dominant in coarse mode aerosols. Other anthropogenic sources such as regional biomass burning can also contribute to the amount of atmospheric surfactants as MBAS.

Keywords MBAS · DBAS · Coastal Area · Sea-Surface Microlayer · Atmospheric Aerosol

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Highlights

- Anionic surfactants dominated the concentration of surfactants.
- Surfactants in SML were contributed by anthropogenic sources.
- Biomass burning and sea spray are the main sources of atmospheric surfactants.

Introduction

Surface active substances or surfactants in sea-surface microlayer (SML) play important role on solubility and fate of chemicals in marine environment. Surfactants molecules reducing the surface tension of the water–air interface (Wurl et al. 2011; Lechtenfeld et al. 2013). Microorganism such as phytoplankton has been recognized as major contributor to the amount of surfactants naturally. The development and waste generation along the coastal areas has contributed to the high amount of surfactants from anthropogenic sources (Roslan et al. 2010). Evaporation processes from sea-surface microlayer will lead to the high amount of surfactants in marine aerosols along the coastal area. Surfactants in atmospheric aerosols can behave as cloud condensation nuclei (CNN) which can profoundly impact cloud properties, with important effects on local and global climate (Sareen et al. 2013).

This manuscript aims to determine the concentration of surfactants in sea-surface microlayer and surfactants in atmospheric aerosols along the busy coastal area of Malacca Straits. Using the Principal Component Analysis and Multiple Linear Regression (PCA-MLR) through the composition of anion and cation, the source apportionment of surfactants in atmospheric aerosols will be determined.

Materials and Methods

Sampling Site and Sea-Surface Microlayer

Samples of the sea-surface microlayer (SML) and atmospheric aerosols were collected between October 2011 and Mac 2013 from six locations with different background along the Malacca Straits. These sites namely Bayan Lepas (Penang), Kuala Selangor (Selangor), Port Dickson (Negeri Sembilan), Muar (Johor), Pontian (Johor) and Tanjung Piai (Johor).

Samples from SML were collected using a glass rotation drum as suggested by Harvey (1966). The surface collector uses a smooth, rotating cylinder whose surface is readily wet by water. Samples were stored in a vial at 4 °C prior to surfactant analysis.

Fine and Coarse Mode Aerosols

Samples from marine aerosol were also collected at each sampling stations. The samples were collected using a high volume sampler (HVS) (Thermo Scientific Model GS2313-105) in combination with a two-stage Cascade Impactor (Staplex) with slotted filter paper (Westech Instrument) to collect coarse mode aerosols (diameter size $>$ 1.5 μm) and backup filter paper (Whatman EPM 2000) to collect fine mode aerosols (diameter size $<$ 1.5 μm).

The sea-surface microlayer samples were filtered using 0.45 μm Whatman GF/C glass microfibre filters; the filtration process was conducted in the clean room. Then 20 mL of filtered samples were put into a 40 mL vial for surfactant analysis. For the aerosol samples, the filter paper containing aerosol particles was cut into small pieces (1 $\times$ 1 cm) in the laminar flow chamber (clean air station) before being extracted with 50 mL de-ionized water using ultrasonic extraction (Branson 3510, USA). The samples were then filtered using Whatman 0.45 μm GF/C glass microfibre filters and a vacuum pump (850 Air Compressor). Each 20 mL filtered sample was put into a 40 mL vial, ready for surfactant analysis. Blank filter papers for both coarse and fine mode aerosols were treated in the same way as the aerosol samples filter papers.

Surfactant Analytical and Statistical Analyses

The analytical method for both anionic and cationic surfactants is based on the formation of ion-association complex between the anionic or cationic surfactants and cationic (disulfine blue) or anionic (methylene blue) dyes, followed by spectrophotometric measurement of the intensity of the extracted coloured complex as applied by Latif and Brimblecombe (2004).

The concentrations of surfactants as MBAS were measured using the calibration curve established using sodium dodecyl sulphate (SDS) at the range of 0.05–2.00 μmol/L while the concentration of cationic surfactants as DBAS were measured using the calibration curve established using benzyl-dimethyl-tetradecyl-ammonium chloride dehydrate or Zephiramine at the range of 0.04–2.00 μmol/L for (DBAS) surfactants. Preliminary source identification study of surfactants using ionic compositions (F^-, Cl^-, $NO_3{}^-$, $SO_4{}^{2-}$, K^+, Mg^{2+}, Ca^{2+}) was carried out using Principle Component Analysis (PCA) together with multiple linear regression (MLR).

Table 80.1 Concentration of surfactants in sea-surface microlayer (n = 9)

Locations	MBAS (μmol/L)	DBAS (μmol/L)
Bayan Lepas	0.29 ± 0.04	0.14 ± 0.05
Kuala Selangor	0.36 ± 0.12	0.33 ± 0.02
Port Dickson	0.29 ± 0.11	0.20 ± 0.08
Muar	0.19 ± 0.03	0.21 ± 0.10
Pontian	0.29 ± 0.02	0.26 ± 0.03
Tanjung Piai	0.31 ± 0.13	0.25 ± 0.02

Results and Discussion

Surfactant in the Sea-Surface Microlayer

The concentrations of both anionic and cationic surfactants collected from the SML from the sampling stations are summarised in Table 80.1. Overall, the concentrations of anionic surfactants as MBAS in the SML were recorded higher compare to cationic surfactants as DBAS. Stations near to the river and urban areas show higher concentration of surfactants. There is no significant correlation ($p > 0.05$) between DBAS and MBAS in sea-surface microlayer.

The concentrations of both anionic and cationic surfactants from the aerosol samples are summarised in Table 80.2. The concentrations of anionic surfactants as MBAS were recorded higher compare to cationic surfactants as DBAS particularly at the station which influence by industrial activities such as Bayan Lepas.

PCA-MLR analysis using atmospheric aerosols major ions composition shows that the anionic surfactants as MBAS in fine mode aerosols are more related to anthropogenic sources such as biomass burning. Meanwhile, the composition of surfactants as MBAS in coarse mode aerosols and DBAS in both fine and coarse mode aerosols were related to sea spray.

Table 80.2 Concentration of surfactants in aerosol samples (n = 9)

Location	Aerosol size	Surfactants concentration ($pmolm^{-3}$)	
		MBAS	DBAS
Bayan Lepas	Fine	137.13 ± 34.91	62.49 ± 20.30
	Coarse	45.88 ± 9.62	29.60 ± 5.39
Kuala Selangor	Fine	120.13 ± 43.49	104.21 ± 18.02
	Coarse	45.80 ± 26.51	33.64 ± 12.03
Port Dickson	Fine	100.13 ± 33.49	76.72 ± 18.31
	Coarse	45.80 ± 26.51	33.64 ± 12.03
Muar	Fine	105.70 ± 32.51	88.33 ± 26.90
	Coarse	45.86 ± 14.90	48.03 ± 10.31
Pontian	Fine	93.98 ± 11.98	54.28 ± 4.16
	Coarse	45.78 ± 5.34	28.92 ± 0.60
Tanjung Piai	Fine	117.19 ± 15.49	52.25 ± 1.31
	Coarse	57.79 ± 5.18	29.49 ± 2.43

Conclusion

This study shows that the concentrations of surfactants in sea-surface microlayer are more related to anthropogenic sources particularly from river water intrusion. The composition of surfactants in atmospheric aerosols can be contributed by various sources. Regional biomass burning can contribute to the amount of anionic surfactants as MBAS in fine mode aerosols. On the other hand, concentration of anionic surfactants as MBAS and cationic surfactants as DBAS (in fine and coarse mode) are still influence by sea spray. Generation of surfactants in atmospheric aerosols from sea-surface microlayer can be eliminated with lower amount of surfactants especially from anthropogenic sources going into coastal areas.

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Chapter 81
Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in Sediment from Muar River and Pulau Merambong, Peninsular Malaysia

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Abstract Previous studies indicated that with increasing industrialization and urbanization, pollution problems have become more significant in Malaysia. West coast of Malaysia is more populated and urbanized than the east and therefore more susceptible to various pollutants. Surface sediment samples were collected from Pulau Merambong and Muar river, Peninsular Malaysia during May 2013 where 16 USEPA Priority Pollutants PAHs were analyzed using gas chromatography-mass spectrometry. Total PAHs in the sediments for Muar river ranged from 15.5 to 165.7 ng/g dw whereas the total PAHs for Pulau Merambong ranged from 38.6 to 122.8 ng/g dw. Due to rapid urbanization and motorization, Muar river showed an increasing trend of PAHs concentrations when compared to a study conducted about a decade ago. Pulau Merambong shows relatively lower PAHs concentrations as compared to other locations in Peninsular Malaysia. However, there is no previous data in Pulau Merambong to evaluate the trend in the petroleum hydrocarbons distribution and concentrations. In general, this study revealed that the lowest concentrations were detected in downstream of the Muar and Pulau Meranbong, respectively. This study also found abundance of high

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molecular weight (HMW) PAHs as compared to low molecular weight (LMW) PAHs suggesting predominance of pyrogenic PAH sources via atmospheric and long-range input. The ratio of LMW PAHs to HMW PAHs (LMW/HMW) were in the range of 0.05–0.33 indicating pyrogenic input and this is consistent with other diagnostic ratios.

Keywords PAHs · Malaysia · Sediment · Source identification · Pollution

Highlights

- Total PAHs in the sediment samples ranged from 15.5 to 165.7 ng/g dw.
- The lowest concentrations were detected in downstream of the rivers.
- High molecular weight PAHs were detected in sediment samples.
- The predominant source of PAHs is pyrogenic originating from long-range transport.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic pollutants consisting of two or more fused aromatic rings (Zakaria et al. 2002). Combustion of organic matter such as petroleum and petroleum products at a very high temperature give rise to PAHs in the environment (Youngblood and Blumer 1975). PAHs are of main concerns due to their wide distribution in aquatic environments (Zakaria et al. 2002), being persistent, mutagenic and carcinogenic. PAHs have a high tendency to attach to particulate matter and end up in the sediment (Guo et al. 2010).

Previous studies indicated that with increasing industrialization and urbanization, pollution problems have become more significant in Malaysia (Zakaria et al. 2002; Bakhtiari et al. 2009; Shahbazi et al. 2010; Sakari et al. 2011; Mirsadeghi et al. 2013; Raza et al. 2013; Retnam et al. 2013). West coast of Malaysia lies directly to the Strait of Malacca where a great deal of marine-based oil pollution occurs as a result of heavy oil tanker traffic. Furthermore, west coast of Malaysia is highly populated and urbanized with numerous rivers flowing through the region that receive land-based pollutants such as municipal effluents, agricultural effluents and industrial discharges. Therefore, rivers in this region carry pollutants from various inputs (Shahbazi et al. 2010). Nevertheless, the information on distribution of PAHs in this region is limited and scarce. Present research aims to assess distribution and source of PAHs in surface sediments in Muar and Pulau Merembong.

Materials and Methods

Surface sediment samples were collected from three locations including upstream, midstream and downstream of Muar and Pulau Merembong, Peninsular Malaysia during May 2013. Sampling locations are shown in Fig. 81.1. The sediment samples were transported on ice to the laboratory and stored at −20 °C until analysis.

Purification and fractionation of the sediment samples was performed using a method presented by Zakaria et al. (2002). Briefly, the previously freeze-dried sample was soxhlet-extracted using 250 dichloromethane (DCM) for 10 h. The extracts were rotary-evaporated to near dryness and were transferred onto the top of 5 % H_2O deactivated silica gel in a glass chromatographic column. Exactly 20 ml hexane/DCM (3:1, v/v) was used as an elution solvent for hydrocarbon fraction. The extract was rotary evaporated and reduced to near dryness and was sequentially fractionated with a fully activated silica gel column to get PAHs fractions using 16 ml hexane/DCM (3:1, v/v), respectively. The PAHs fraction was then transferred to a 2 ml amber vial and evaporated to near dryness using a gentle stream of nitrogen. GC–MS Shimadzu QP5050A model and BPX-5MS fused-silica capillary column (30 m by 0.25 mm i.d., 0.25-μm film thickness) was used to analyze PAHs. PAH concentrations were determined based on dry weight (dw).

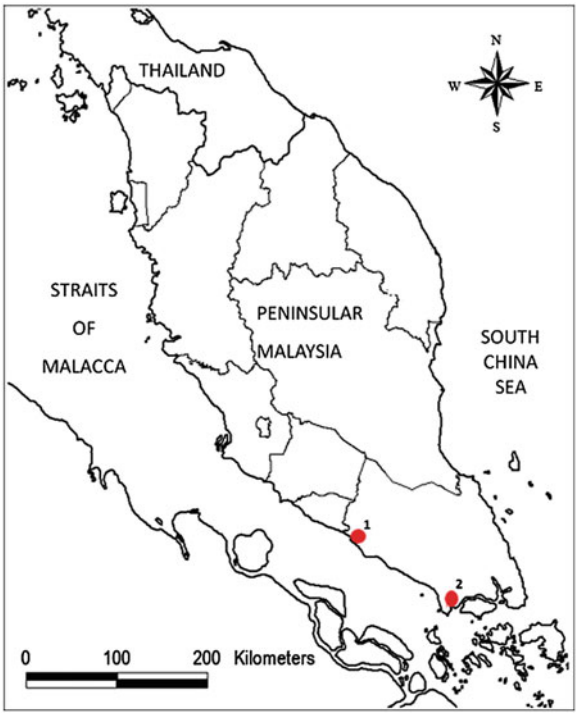

Fig. 81.1 Map of sampling locations in Peninsular Malaysia shown in *red circles*, *1* Muar, *2* Pulau Meranbong

Results and Discussion

The concentrations of total PAHs in Muar river ranged from 15.5 to 165.7 ng/g dw (Table 81.1). Total PAHs showed an increasing trend in Muar river compared to previous studies (Zakaria et al. 2002). The lowest PAHs concentrations were found in downstream in the river. It may implies that upstream urban runoff is probably the main source of PAHs although further study is needed to confirm this suggestion. It is interesting to note that, the same trend was recorded in Langat river, Peninsular Malaysia, where urban runoff from the industrial areas were recognized to play a pivotal role in higher PAHs concentrations of upstream (Bakhtiari et al. 2009). However, Rembau River and Linggi River in Peninsular Malaysia show much higher PAHs concentrations in downstream proximate to estuaries, indicating urban runoff near estuaries as possible source of PAHs (Raza et al. 2013).

The total PAHs for Pulau Merambong ranged from 38.6 to 122.8 ng/g dw. Pulau Merambong shows relatively lower PAHs concentrations as compared to other locations in Peninsular Malaysia. There is no previous data in Pulau Merambong to evaluate the trend in the petroleum hydrocarbons distribution and concentrations. Molecular ratios are known to be useful for source identification of PAHs. In present research, the ratio of LMW PAHs to HMW PAHs (LMW/HMW) are between the range of 0.05–0.33 indicating pyrogenic sources as probable sources of PAHs (Table 81.1). The result of LMW/HMW PAHs is consistent with that of Langat river where the range of LMW/HMW PAHs for surface sediment was reported from 0.17 to 0.39 (Bakhtiari et al. 2009). Dominance of HMW PAHs in surface sediments from west of Peninsular Malaysia was well documented in other studies (Raza et al. 2013; Retnam et al. 2013).

However, other studies suggested petrogenic sources as the main PAHs sources. In Peninsular Malaysia, sediments collected from urban areas were found to be highly impacted by petrogenic PAHs (Zakaria et al. 2002).

Table 81.1 PAHs concentrations and total organic carbon (TOC)

Sampling locations	[a]Total PAHs (ng/g dw)	[b]LMW/HMW	Total organic carbon (mg/g)
Merambong 1	51.5	0.21	1.05
Merambong 2	122.8	0.05	0.56
Merambong 3	38.6	0.08	1.64
Muar 1	165.7	0.07	2.21
Muar 2	45.5	0.33	1.23
Muar 3	15.5	0.29	1.91

[a] Total PAHs = the sum total concentrations of naphthalene to benzo(g, h)fluoranthene
[b] LMW/HMW = the ratio of sum of total concentrations naphthalene to Pyrene divided with the sum of total concentrations benz[a]anthracene to benzo[ghi]perylene

Conclusion

In conclusion, the highest PAHs concentration was detected in upstream of Muar river. The river near to estuary showed the lowest PAHs concentrations suggesting upstream urban runoff as the major source of PAHs. The ratios of LWM to HWM PAHs were found to be low in both Pulau Merambong and Muar river showing the dominance of HMW PAHs. There is no previous data in Pulau Merambong to evaluate the trend in the petroleum hydrocarbons distribution and concentrations. Since Pulau Merambong is situated in an ecologically sensitive areas bordering with Singapore Malaysia and Indonesia, the ecosystem requires continuous monitoring of possible contamination of petroleum hydrocarbon in the near future.

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Chapter 82
Identification and Development of Different Plumes of Chlorinated Hydrocarbons in Groundwater by Numerical Modeling Based on Carbon Isotope Dynamics

Caroline Schlegel, Johannes Michaelsen and Michael Heidinger

Abstract At Hamburg-Neuland groundwater monitoring revealed an area wide groundwater contamination by CHCs. The marshland is characterized by complex groundwater hydraulics. In order to understand plume development, a numeric groundwater flow and solute transport model has been set up. Unknown boundary conditions with respect to emission rate at the location of origin lead to the development of an innovative approach. The analysis of compound specific carbon isotope ratios revealed the complete transformation of PCE and TCE to ET and further on to CO_2. The isotope enrichment factor could be derived directly from the field data. The introduced sum parameter 'potential of source' was extrapolated from the sum of measured concentrations of PCE-VC (μmol/l) and the calculated amount of degradation. The emission rate over time at location of source was calculated based on the 'potential of source' determined for the monitoring wells. To achieve a decisive reduction of uncertainties, solute transport was calculated for the sum parameter 'potential of source' instead of considering PCE/TCE and their degradation compounds. Three distinct plumes were delineated and an area of unknown hydraulic characteristics identified.

Keywords Numerical modeling · Groundwater contamination · Carbon isotopes · Plume development · Potential of source

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Highlights

- Contaminant transport in aquifer is governed by hydraulics of groundwater flow.
- The sum parameter 'potential of source' reduce uncertainties.
- 'Potential of source' determines boundary conditions of solute transport.
- Three distinct plumes and an area of unkown hydraulic characteristics were identified.

Introduction

In the 80s and 90s of the last century large scale pollution of the upper Quaternary aquifer was detected at Hamburg-Neuland. The main pollutants identified were tetrachloroethene (PCE) and trichloroethene (TCE) and their degradation compounds *cis*- and *trans*-1,2-chloroethene (cDCE, tDCE) and monochloroethene (VC). The map—Fig. 82.2—exhibits an area-wide extent of groundwater pollution. Chlorinated Hydrocarbon (CHC) concentrations in groundwater covered a range from detection limits up to several mg/l. The presence of the degradation compounds of PCE/TCE indicated an ongoing biological degradation process. The final proof of anaerobic degradation was established by the detection of ethene (ET). The analysis of compound specific carbon isotope ratios revealed the complete transformation of PCE and TCE to ET and further on to carbon dioxide (CO_2). ET, VC and cDCE/tDCE were assigned to the primary substances PCE and TCE. Hamburg-Neuland represents a marsh land. Groundwater hydraulic is very complex in such areas. Such complex flow and hence solute transport regime can only be fully understood and evaluated by numerical groundwater modeling.

Groundwater sampling and analysis has been performed by Institut für chemische Analytik GmbH (ICA), Leipzig—Germany; analysis and investigations of isotopes and ethene has been performed by Hydroisotop GmbH, Scheitenkirchen—Germany.

Materials and Methods

A numerical finite element model was created with the Software Feflow 6.1 from DHI Wasy. The hydraulic part of the model was successfully calibrated (steady state) and validated (transient). The calibration results in the presented groundwater contour lines in Fig. 82.2.

The solute transport model requires a set of specific input parameters and boundary conditions (e.g. retardation, dispersion). For the immission of contamination the boundary conditions comprise the location of origin as well as the rate

of immission over time. In general, remediation projects may face three cases of state of knowledge:

1. Known location of source and known emission rate over time
2. Known location of source and unknown emission rates over time
3. Unknown location of source and unknown emission rates over time.

To overcome the lack of knowledge (location of source and emission rates over time) an innovative modeling approach is proposed. The functions of emission rates of contaminants are derived via compound specific isotope analysis (CSIA) investigations ($^{13}C/^{12}C$-ratios or $\delta^{13}C$-values) covering the whole area of interest. Numerous investigations (2004–2012, annual samples) proved that biological degradation of PCE/TCE and the associated enrichment of the $\delta^{13}C$-values in the CHC pool (PCE, TCE, cDCE/tDCE and VC) and ET. At two known sites of origin the primary $^{13}C/^{12}C$-ratio of the CHC-products (δ^{13}CsourcePCE/TCE) were determined using the most negative $\delta^{13}C$-value for the molar ΣPCE-ET at the site ($\Sigma\delta^{13}$C-PCE-ET-value). The isotopic enrichment factor (ε) could be derived directly from the field data using a correlation of molar ET portion (ΣPCE-ET) versus enriched $\Sigma\delta^{13}$C-PCE-VC-values and was found to be reliable throughout the investigation period. A sensitive quantification of biodegradation is therefore applicable using a Rayleigh Model, which is widely used to describe the fractionation effects of stable isotopes during degradation process by an exponential function.

The measured concentrations of CHCs in groundwater at the monitoring wells (ΣPCE-VC in µmol/l) represent the result of a specific immission at the site of origin (contaminant source) diminished by dilution, retardation and degradation during transport. Applying the measured and derived isotope data (δ^{13}CsourcePCE/TCE-values, $\Sigma\delta^{13}$C-PCE-VC-values, ε-value) and the quantification of biodegradation (Rayleigh Model) at the monitoring wells the 'potential of source' was extrapolated from the ΣPCE-VC-value (µmol/l) and the calculated amount of degradation (µmol/% transferred to µmol/l) for the time period of 2004–2012 (Fig. 82.1a). The introduced parameter 'potential of source' represents the concentrations of PCE/TCE at the monitoring well and the time of groundwater sampling for the case that no degradation would have occurred at all.

Time series of ΣPCE-VC in µmol/l (1992–2012), the measured isotope data/'potential of source' (2004–2012) at the monitoring wells and the travel time of contaminants from the source towards a monitoring well allow finally establishing the emission rates over time at the location of source (Fig. 82.1b).

Simulation of solute transport should consider the characteristic of transport and decay of PCE, TCE, cDCE/tDCE and VC; these complex processes require specific input parameters for each CHC, increasing the error of the model results due to parameter uncertainties. For the final calibration step the first order decay rates for only one substance (ΣPCE-VC) were introduced and assigned to differing parts of the environmental conditioning in the aquifer (methanogenic or not). These decay rates represent the proportionality factor between the "potential of source" and the measured ΣPCE-VC at a defined location (Fig. 82.1a, c). This procedure decisively reduces the error of modeling results and minimizes the degrees of freedom.

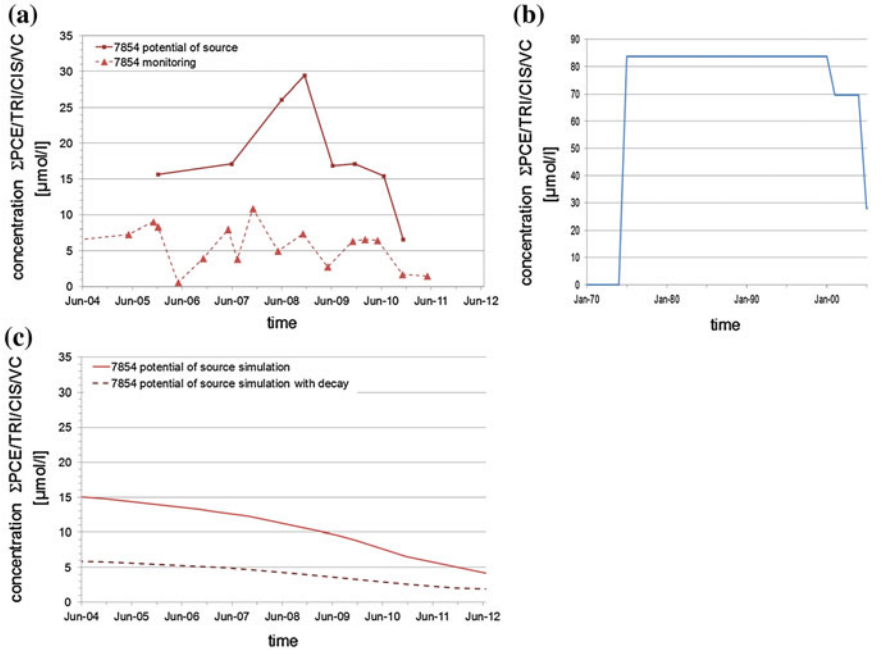

Fig. 82.1 **a** Concentration of CHCs and 'potential of source' over time in groundwater at oberservation well 7854, **b** concentration of CHCs in groundwater recharge over time at location of source, **c** model results—simulated 'potential of source' (concentration of CHCs) over time with and without taking into account decay at observation well 7854

Results and Discussion

The first step of calibration of the solute transport model was finished when the model outcome matched the height of "potential of source" as well as its temporal dynamics at all monitoring wells. The final outcome was reproducing the measured concentrations with the transport model at the monitoring wells (Fig. 82.1a, c).

The simulated plume distribution as well as the monitoring results are shown in Fig. 82.2. The simulation of the solute transport by the calibrated model allows separating the area delineated by the monitoring into two distinct plumes (case 2, Fig. 82.2). The immission of PCE/TCE into groundwater at a site in the south of Hamburg-Neuland led to the development of plume 1. The main axis of the plume 1 is directed south to north. CHC concentrations in groundwater at monitoring wells 9717, 9716, 9714, 9711, and 9705 are assigned to this source of contamination. The immission of PCE/TCE next to the harbor in the west of Hamburg-Neuland led to the development of plume 2. The main axis of plume 2 is directed from west to east. CHC concentrations in groundwater monitoring wells 7854, 5493 and 7853 are assigned to this source of contamination. The calibrated model

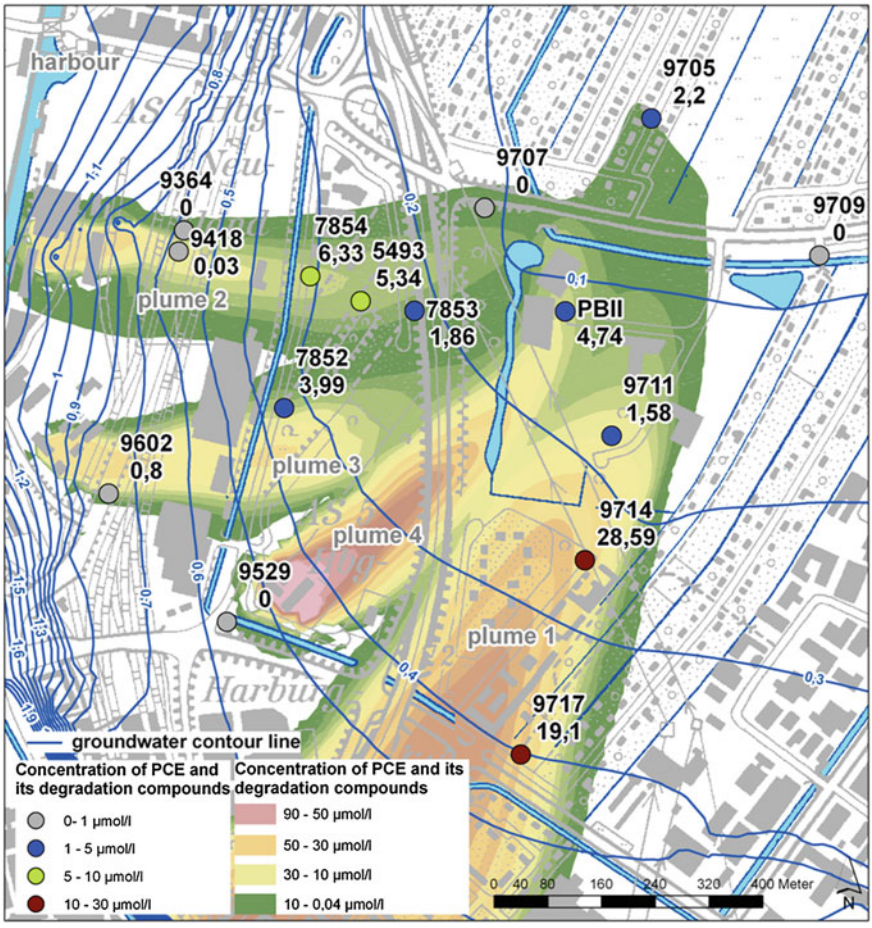

Fig. 82.2 Model results—map of simulated concentrations of CHCs in groundwater and contour lines of groundwater head and monitored concentrations of CHSs at monitoring wells

failed to reproduce the time series of CHC-concentrations measured at monitoring wells PBII and 7852 (case 3). The simulation software offers a so called backward calculation of pathlines. Starting from PBII and 7852 pathlines were calculated backwards. Results allowed establishing two additional plumes (plume 3 and 4, Fig. 82.2). The sites of origin are hypothetical. Besides unknown site of origin the isotope fingerprint of the primary products ($\delta^{13}C_{source}$PCE/TCE-value) are unidentified. A conservative $\delta^{13}C_{source}$PCE/TCE-value is given by analysis of groundwater samples of PBII and 7852 ($\Sigma\delta^{13}$C-PCE-ET-values). The chosen values for CHC concentrations at site of origin are based on reasonable assumptions. The simulation of plume 3 and 4 followed the procedure described above for plume 1 and 2.

After presentation and evaluation of the simulation results, an additional survey of groundwater chemistry was performed. Groundwater samples were taken and analyzed with respect to CHC and ET concentrations and their δ^{13}C-values. CHC concentrations above background level were only detected along the calculated streamlines of plume 3. A third plume has been delineated as the numeric model demonstrated after calibration. The results of the survey did not confirm the existence of plume 4. These findings lead to the assumption that groundwater hydraulic nearby PBII is not correctly implemented in the model at present stage. Further investigations on the unknown historical drainage patterns were recommended.

Based on interpretation of measured data of contaminants—chemical and compound specific isotope analysis—, the parameter 'potential of source' has been introduced. 'Potential of source' allowed to determine the function of immission rate at location of source and functioned as the only dependent variable for modeling. Applying this procedure minimizes uncertainties in the input data sets and hence error of model results. Simulations forecast successfully a so far unknown plume of contamination in groundwater. A gap of knowledge was identified with respect to local drainage patterns in the past. The developed and applied method proved to serve as an efficient tool in environmental forensic applied to groundwater remediation.

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Chapter 83
Distribution and Sources of Perylene and other Polycyclic Aromatic Hydrocarbons (PAHs) in South China Sea Sediments off Southern Terengganu Coast, Malaysia

Norhayati Mohd Tahir, Swee Yun Pang, Yii Siang Hii and Bernd RT Simoneit

Abstract Sediment cores from the South China Sea off Southern Terengganu were collected during May (post-Northeast monsoon) and September (pre-Northeast monsoon) 2007. The core sediments were cut into 2 cm sections, freeze-dried and then Soxhlet extracted. Extracts were fractionated using column chromatography and the aromatic hydrocarbon fractions were determined using gas chromatography mass spectrometry. The concentration of perylene varied between 0.43–5.01 ng/g and 0.42–9.79 ng/g in May and September, while the total 16 USEPA listed priority polycyclic aromatic hydrocarbon (TPAHs) ranged from 6.01–20.2 ng/g and 4.89–34.7 ng/g during the same respective periods. The PAH cross plots showed that pyrogenic PAHs dominated during May, whereas pyrogenic and lesser petrogenic PAHs dominated during September. Total organic carbon (TOC) showed strong correlation with TPAH and perylene near land, suggesting transport of terrestrially derived PAHs (biogenic or anthropogenic) into coastal sediments via surface runoff into rivers.

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Keywords Fluvial transport · PAHs · Perylene · Pyrogenic · Terrestrial input

Highlights

- Pyrogenic dominated over petrogenic PAHs in the Southern South China Sea (5–50 km).
- Correlation between TOC and PAHs suggesting surface runoffs from nearby landmass.
- Perylene is correlated with TOC suggesting possible from terrestrial input.

Introduction

Perylene is a five-ring PAH and has been well known as diagenetic products derived from its natural precursors, which are structurally related to perylenequinone (Jiang et al. 2000). Perylene can also be a key indicator for decayed organic matter reported from land to shelf, evidences have indicate a possible relationship between perylene with termite nests and/or its wood substrate in tropical top soils (Wilcke et al. 2002), dead wood (Krauss et al. 2005) and fossil wood remains (Bechtel et al. 2007).

In Malaysia, studies on anthropogenic derived PAH in sediment and on suspended particulate in riverine, estuarine and mangrove areas is well established (Mohd Tahir et al. 2011; Assim et al. 2009; Elias et al. 2007). However, understanding the extent to which the accumulation of PAHs in coastal core sediment is still limited (Sakari et al. 2010; Wu et al. 2009; Zakaria et al. 2009). This study has been initiated within the inner continental shelf (within 5–50 km) core sediments off Southern Terengganu coast to assess the distribution and sources of perylene and PAHs in an effort to gain a better understanding of various processes that control the burial of these compounds in marine sediments.

Materials and Methods

Three sediment cores (12–32 cm) were collected using gravity corer. Each core was sectioned into 2 cm intervals prior to freeze-drying. Freeze-dried sediments were then homogenized, sieved and were Soxhlet extracted using hexane/dichloromethane (1:1 v/v) as solvent and internal standards of phenanthrene-d_{10} and perylene-d_{12} were spiked into the sediment for recovery assessment. The sulphur content in the sediment was removed using mercury treatment (Beg et al. 2003).

The concentrated extracts were fractionated using solid–liquid column chromatography. Total organic carbon (TOC) of the sediments was determined by the Walkley and Black's titration method (Moris and Singh 1971). Identification and quantification of these aromatic hydrocarbons were carried out using a Shimadzu-QP2010 gas chromatography-mass spectrometer. The recoveries for phenanthrene-d_{10} and perylene-d_{12} ranged from 90.8 ± 5.38 % and 87.1 ± 4.63 %, respectively.

Results and Discussion

Perylene

The concentration of perylene ranged from 0.43–5.01 ng/g and 0.42–9.79 ng/g in May and September. The concentration of perylene was found to decrease with depth at ST1. Low concentration of perylene recorded might be due to a weak contribution of terrigenous organic matter, the rapid degradation of perylenequinones (Bertrand et al. 2013) or absence of binaphthyl as potential precursors (Silliman et al. 2000; Ricking and Schulz 2002). A significant correlation between perylene with TOC was only observed for core ST1, with $r = 0.927$ ($p < 0.05$). This suggests that perylene in core ST1 could be derived terrestrially (anthropogenic and/or biogenic) (Jiang et al. 2000) via river runoff into the coastal waters. On the other hand, no correlation was found between TOC and perylene at the other stations suggesting perylene in these sediments is derived from diffuse sources, such as anthropogenic activities or any other related unknown precursor carriers of perylene (Ricking and Schulz 2002; Jiang et al. 2000).

Polycyclic Aromatic Hydrocarbon

The vertical concentration profile of total 16 USEPA listed priority polycyclic aromatic hydrocarbon (TPAHs) ranged from 6.01–20.2 ng/g and 4.89–34.7 ng/g in May and September. The PAH concentration in SCS off Southern Terengganu are comparable to other reports in Malaysia such as coastal Rajang Sarawak (Assim et al. 2009), Dungun (Elias et al. 2007) and Penggerang, Johore (Mohd Tahir et al. 2004). Most samples for May 07 sampling period shows Fla/(Fla + Py) > 0.5 and BFl/(BFl + BeP) > 0.7, shows the predominance of combustion derived sources in study area (Luz et al. 2010; Yunker et al. 2002). On the other hand, ST1 core samples collected during Sept 07 sampling shows Fla/(Fla + Py) < 0.5 and BFl/(BFl + BeP) > 0.5, indicating that these PAHs are mainly derived from mixed biomass and fuel combustion sources; whereas cores ST2 and ST3 were dominated by both combustion sources and petroleum sources.

A strong relationship was only found between the TPAHs and TOC in core ST1 with $r = 0.821$, and $r = 0.913$ ($p < 0.05$), during the same respective periods. This observation could suggest that the PAHs in core sediment ST1 can be attributed to the deposition of both anthropogenic and biogenic onto soils, followed by surface runoffs into rivers and subsequently transported to the coastal environment.

Conclusion

The PAH concentration in the South China Sea sediments off Southern Terengganu, Malaysia (5–50 km) are considered not heavily polluted (below 100 ng/g). However, the result may not be conclusive because of the distance from land point sources and processes such as monsoon seasons, physical mixing, biodegradation and/or episodic input of PAH may influence the PAH concentration. The PAH cross plots indicate the distribution of PAHs is characterized by a dominant input from pyrogenic sources, and lesser petrogenic. The station near land received highest total PAH and perylene. These compounds were significantly correlated with total organic carbon content (TOC) which indicate the importance of surface runoffs from nearby landmass into rivers and subsequently transported to the coastal environment.

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Chapter 84
Case Study: Comparison of Air Dispersion from Solid Waste Incinerator Emission Using AERMOD and ISCST3

Luqman Chuah Abdullah and Yen Chen Tan

Abstract Combustion of municipal solid waste in a solid waste incinerator will generates flue gas emission consist of pollutants that may detrimental to human health. It was intended to observe the dispersion of the pollutants from the chimney of solid waste incinerator of Cameron Highlands using two air dispersion models, AERMOD and ISCST3. This study involves usage of 1 year hourly meteorological data, terrain data, chimney specification and pollutant emission rate as input in both models to predict the pollutants incremental concentration to the surrounding environment. It was found that AERMOD model simulates in a way similar to the real meteorological condition as compared to ISCST3. Higher concentration was predicted nearer to the pollutant source and at sensitive receptors in AERMOD as compared to ISCST3 prediction.

Keywords Air dispersion · AERMOD · ISCST3 · Incinerator

Highlights

- AERMOD predict higher concentration as compared to ISCST3.
- AERMOD model simulates similar to the real meteorological conditions.
- Prediction of air pollutants dispersion is influence by meteorological data input.

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Introduction

In view of rising solid waste generation in Cameron Highlands which in tandem with population and tourism growth (Department of Town and Country Planning 2007), the Ministry of Housing and Local Government of Malaysia has decided to construct and operate a municipal solid waste incinerator in Cameron Highlands. The solid waste incinerator comes with solid waste receiving and handling units, combustion process and pollution control units, which able to process up to 40 tonnes of solid waste a day.

Combustion of solid waste will generate flue gas that contains pollutants such as dust, sulphur oxides, nitrogen oxides, acid gases, heavy metal, dioxin, water vapour and carbon dioxide. The pollutants will be removed through a series of air pollution control consisting of cyclone, neutralisation reactor, and baghouse filter prior release into the environment as illustrated in Fig. 84.1 (ERE 2009).

Prior construction of the incinerator, a Detailed Environmental Impact Assessment (DEIA) was carried out in correspond with the requirement from the Department of Environment of Malaysia under Environmental Quality (Prescribed Premises) (Environmental Impact Assessment) Order 1987. The DEIA report entails the potential environmental impacts and mitigation measures to reduce the impacts. It was noted that ISCST3 model was used in the prediction of pollutants dispersion into the surrounding areas. In this case study, it was intended to observe the dispersion of pollutants from the chimney of the incinerator plant by using two different models, i.e. AERMOD and ISCST3. Both models are Gaussian plume air dispersion model. AERMOD uses vertical and horizontal turbulence variable with height while ISCST3 only use six discrete Pasquill–Gifford stability classes.

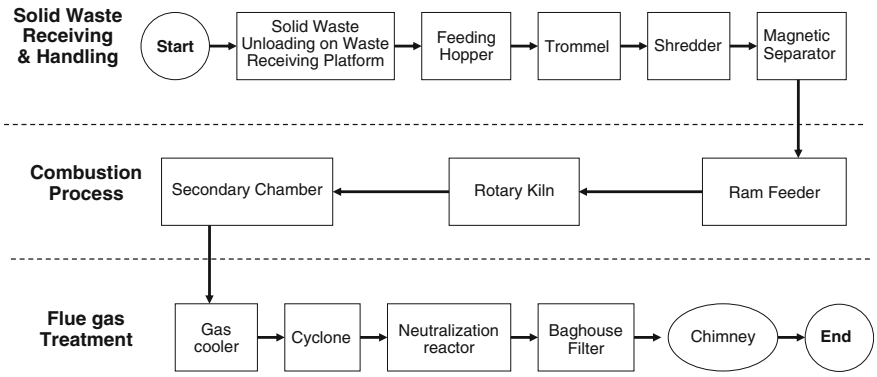

Fig. 84.1 Process flow of municipal solid waste incinerator

Methods

The models use steady state Gaussian equation that combines source emission, meteorological information, terrain, and dispersion coefficients to predict the maximum average incremental concentration (MAIC) of pollutants within the study impact zone. Cartesian receptor grid of 10 × 10 km and terrain elevation data of the Shuttle Topography Mission (SRTM) for Datum WGS 84 with resolution of 90 m obtained from National Aeronautics and Space Administration (NASA) were used. One year hourly meteorological data (year 2009) was obtained from Cameron Meteorological Station (4° 28′ N, 101° 22′ E; elevation of 1545 above m.s.l) and Sepang KLIA Meteorological Station (2° 43 ′N, 101° 42′ E; elevation 16.3 above m.s.l.). These stations were chosen because it was the nearest principal meteorological stations with the required data. The derivation of the output files for both models has been made reference to the methodology produced using local meteorological data, which is guided by User Guide of AERMOD, AERMET and ISCST3. Several assumptions have been made according to the methodology (Table 84.1).

The emission rate and chimney information were obtained from the DEIA report as tabulated in Table 84.2.

Results and Discussion

Summarized in Table 84.3 are the predicted MAIC from AERMOD and ISCST3 of air pollutants at the air sensitive receptors. It is observed that most of the predictions from AERMOD have higher MAIC compared to ISCST3. These were due to the lower convective and mechanical height calculated from the meteorological data preparation for AERMOD as compared to ISCST3. In ISCST3, the mixing heights were calculated from the wind speed that had been modified to 1 ms^{-1}, which is the minimum cut-off wind speed. Meanwhile, the lowest wind speed for AERMOD calculation was 0.2 ms^{-1}. Thus, AERMOD had a lower mixing height which less dilution of pollutants can take place. The result also implies that MAIC from AERMOD simulate to the real meteorological conditions as compared to ISCST3. Higher concentration values of pollutants from AERMOD prediction were observed at A1, which is nearer to the chimney as compared to prediction of ISCST3. The lower cut-off wind speed of AERMOD means more wind speed hour is retained to its original observation values and thus calm period is captured in the simulation. Stagnant air flow due to lower wind speed will have less dispersion to the surrounding and create a concentrated plume near source.

Table 84.1 Assumptions used in meteorological data preparation

Parameters	Assumptions
Upper air data (KLIA)	
Sounding	Morning sounding (0Z) is used
Levels, temperature, wind speed, wind direction	5 levels at the range of 50 m to 6000 m to be used
	Missing data in the 5 levels is replaced from the previous day record
	The 5 levels are assumed at hour 8, hour 11, hour 14, hour 20 and hour 6
	Hour 7 data is obtained from the surface data record for temperature, wind speed and wind direction
	Linear interpolation to replace the 19 levels
	Wind speed and direction in the 19 levels are replaced with 99.0 and 999
Standard deviation	Missing indicator of 99.0 and 99.00 for all hours
Surface data	
Missing data	Averaging for single missing data
	Replaced with the previous day's record for 2 or more sequences of missing data
	0 ms^{-1} and 0^{o} for missing wind speed and temperature
	Cloud cover obtained from KLIA station
Albedo, Bowen ratio and surface roughness	Value based on the wind direction and land use
Cloud cover	Change to basis of 10
Heat flux	Sunrise at 7.00 a.m.; Sunset at 7.00 p.m.
	Angle of sunrise and sunset are at 30^{o} while 90^{o} at 1 p.m.
u_* and L	Wind speed below 0.2 ms^{-1} is changed to 0.2 ms^{-1}
	Iteration only applies to positive heat flux
VPTG	Values taken from upper air data, minimum of 0.005 km^{-1}
Z_{ic} and Z_{im}	Early sunrise at 6 a.m., maximum of 4000 m
ISCST3	
Missing data	Cloud cover obtained from KLIA station
Wind speed	Wind speed below 1 ms^{-1} is changed to 1 ms^{-1}
Mixing height	Surface wind speed × 320

Adapted from: Chen 2010 and Chen et al. 2011

Table 84.2 Chimney specifications and emission rates

Chimney specifications		
Stack height: 30 m		Flow volume at NTP: 2.16 Nm^3/s
Stack diameter: 0.75 m		Exit temperature : 493 K (220 °C)
Exit velocity: 8.08 m/s		X, Y coordinate: 0, 0 m
Pollutants	Emission rate (g/s)	DOE emission concentration limit (g/Nm^3)
Particulate matter PM_{10}	0.065	0.03
Sulphur dioxide (SO_2)	0.432	0.20
Nitrogen oxides (NO_x)	0.864	0.4
Carbon monoxide (CO)	0.270	0.125
Hydrogen chloride (HCl)	0.216	0.10
Arsenic (As)	0.054	0.025
Cadmium (Cd)	0.032	0.015
Chromium (Cr)	0.108	0.050
Mercury (Hg)	0.022	0.010
Lead (Pb)	0.043	0.020
Dioxin/furan (CDD/CDF)	0.216 ng/s	0.1 ng/Nm^3

Table 84.3 Predicted MAIC from AERMOD and ISCST3–normal operation

Air pollutant	Time scale	Unit	A1		A2		A3		A4		RMAQG
			AER	ISC	AER	ISC	AER	ISC	AER	ISC	
PM_{10}	24-h	ug/m^3	0.10	0.01	0.04	0.03	0.03	0.03	0.02	0.02	150
SO_2	1-h	ug/m^3	6.72	1.62	3.43	2.07	2.35	1.12	1.15	0.95	350
	24-h	ug/m^3	0.64	0.10	0.23	0.22	0.22	0.2	0.10	0.10	105
NO_2	1-h	ug/m^3	13.43	3.23	6.87	4.13	4.69	2.24	2.31	1.90	320
CO	1-h	ug/m^3	4.20	1.01	2.15	1.29	1.47	0.70	0.72	0.6	35,000
	8-h	ug/m^3	0.97	0.2	0.43	0.41	0.21	0.26	0.19	0.16	10,000
HCl	24-h	ug/m^3	0.32	0.06	0.12	0.18	0.11	0.14	0.05	0.09	36
As	Ann.	ng/m^3	11.02	1.02	2.83	3.14	1.13	4.94	1.22	2.00	–
Cd	Ann.	ng/m^3	6.53	0.6	1.68	1.86	0.67	2.93	0.72	1.18	–
Cr	Ann.	ng/m^3	22.04	2.04	5.66	6.28	2.26	9.88	2.44	4.00	–
Hg	Ann.	ng/m^3	4.49	0.42	1.15	1.30	0.46	2.01	0.50	0.81	–
Pb	Ann.	ng/m^3	8.78	0.81	2.25	2.50	0.90	3.93	0.97	1.59	1,500
Dioxin	Ann.	fg/m^3	4.41	0.41	1.13	1.26	0.45	1.96	0.49	0.80	–

Notes RMAGQ = Recommended Malaysian Ambient Air Quality guidelines
A1 Project site; *A2* Ladang Blue Valley; *A3* Kg. Raja; *A4* Kg. Sungai Ikan

Conclusion

Both mixing height and wind speed which reflect the stability of the atmosphere, will affect the dispersion pattern of pollutants. It is observed that through the simulation carried out, AERMOD model simulates in a way similar to the real meteorological condition as compared to ISCST3.

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Chapter 85
Evaluation of Foam Stability in Decontamination Foam Stabilized by Silica Nanoparticles with Nonionic Surfactant

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Abstract The decontamination process was needed to remove the radionuclide in nuclear facilities under decommissioning. Among the decontamination techniques, the decontamination foam strongly decreases the amount of chemicals and the secondary wastes and, has wide application in nuclear facilities. The purpose of the present study is to investigate the effects of surfactants, silica nanoparticles (NPs) concentration, and pH for foam stability and oxide dissolution. The foam stability in acid pH has an effect on the concentration of nonionic surfactant, however, in neutral pH does not have concentration effect. The addition of 3 and 5 wt% silica NPs improves the foam stability by a factor of 3 and 5 at pH 2, compared to the foam stabilized with 1 % EM 100 surfactant only, indicating that the increase of silica NPs increased the foam stability. The oxide dissolution was evaluated for the decontamination foam containing 1 M HNO_3 using the corroded specimens. The results of an iron dissolution test showed that increased foam stability enhanced the iron dissolution owing to an increase in the contact time between the chemical reagents and the corroded surface.

Keywords Decontamination foam · Nanoparticles · Stability · Dissolution

Highlights

- The decontamination foam reduces the secondary wastes.
- Foam stability in acid pH has effects the concentration of nonionic surfactant.
- The silica nanoparticles increases the foam stability and oxide dissolution.

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Introduction

A large amount of liquid waste is generated from the decontamination that occurs when dismantling nuclear facilities. A process is needed to decrease the amounts of chemical reagents and secondary wastes produced during the decontamination process. Decontamination foam is a non-stable, two-phase fluid with aqueous and gas phases representing not more than 10 and 90 % of the total volume, respectively. This formulation can significantly decrease the amounts of chemical reagents and secondary wastes (Dame et al. 2005).

The advantage of decontamination foam has potentially wide application for metallic walls, overhead surfaces, and the elements of complex components in nuclear facilities (Nunez and Kaminski 2007). The disadvantages of decontamination foam systems include the relatively low decontamination factor with a one-time application (Nunez and Kaminski 2007). The decontamination efficiency can be enhanced by improving the contact time between chemical reagents and a contaminated surface through the addition of surfactants and viscosifiers to the decontamination foam (Dame et al. 2005).

Decontamination foam comprises a surfactant to generate the foam, a viscosifier to increase the foam stability, and chemical reactants to dissolve the contaminants on a solid surface. Silica nanoparticles (NPs) as viscosifier can be added to the foam formulation to increase the foam stability (Fig. 85.1). The hydrophilic particles remain confined in the liquid phase, and are able to enhance the foam stability. In addition, foams are stabilized by mixtures of surfactants and inorganic particles and foam stability increased by the change of NPs surface from hydrophilic to partial hydrophobic (Binks et al. 2008; Zhang et al. 2008). The objective of this study is to investigate the effects of surfactant and silica NPs concentration (visocisifer), and pH of solution (chemical reagents) for foam stability and oxide dissolution of corroded specimens.

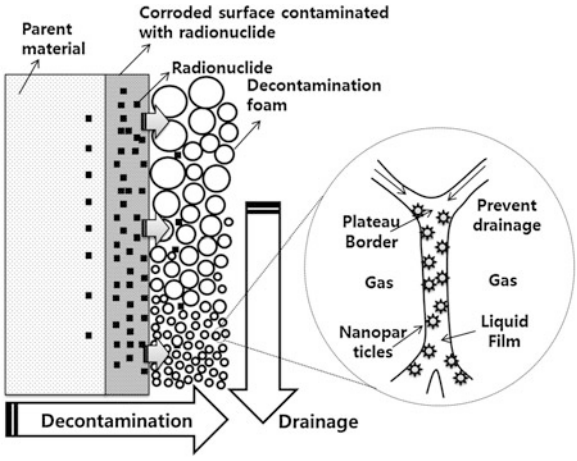

Fig. 85.1 The process of decontamination foam containing nanoparticles

Experimental Sections

For the experiments, commercial surfactants were used without further purification. Elotant™ Milcoside 100 (EM 100) as a surfactant is an alkyl polyglucoside supplied by LG Household and Health Care in the Republic of Korea, which contains 8–10 alkyl chains. All solutions were prepared using deionized water obtained from a Milli-Q water system. To investigate the effect of viscosifier, silica NPs (M-5, Cabosil) were selected to prepare the decontamination foam.

The foaming properties (i.e., foam formation and foam stability) were determined using a Foamscan instrument (Teclis/IT Concept, France). The foam was generated by blowing nitrogen gas at a flow rate of 200 ml/min through a porous glass filter at the bottom of a glass tube where 60 ml of the foaming aqueous solution (25 ± 1 °C) was placed. The foam was allowed to reach a volume of 200 ml. The bubbling was then stopped, and the evolution of the foam was analyzed using conductivity and optical measurements. Various silica NPs (0, 0.1, 0.5, 1, 3 and 5 wt%) were added to a high (1 %) and low (0.1 %) concentration of EM 100 surfactant at pH 6 and 2. All results of foam stability are given for the liquid fraction 2, which is located in the middle of the column.

SUS 304 specimens having 20 × 20 × 2 mm in size were used for dissolution test. The corroded layer of specimens was grown in a semi-loop filled with solution for 1 month, simulating the primary water in light water reactors. Various silica NPs of 0.5, 1, 3, and 5 wt% were added to a 30 ml of 1 % EM 100 surfactant solution containing 1 M HNO_3. About 100 ml of decontamination foam was prepared by shaking the 30 ml of decontamination foam for 10 s. The corroded specimens were located at the middle of the bottles. The concentration of dissolved iron from the corroded specimens was measured by Flame Atomic Absorption Spectroscopy.

Results and Discussion

In Fig. 85.2a and b, the decay of the foam volume is shown to solutions that contain EM 100 in high (1 %) and low (0.1 %) concentration of non-ionic surfactant at pH 2. The results showed that the foam volume in 1 % EM 100 increased with the increase of silica NPs and remained over 100 ml in the presence of NPs. However, the foam volume without NPs was significantly decreased below 50 ml. In Fig. 85.2b, the foam volume in 0.1 % EM 100 was significantly decreased after 1200 s in all concentration of silica NPs. The foam volume in acid pH has a significant effect for the concentration of nonionic surfactant. However, foam volume in neutral pH does not have concentration effect of nonionic surfactant (data not shown).

As shown in Fig. 85.3a, the liquid fraction was not observed until 1 wt% silica NPs, however, 2 and 4 % in liquid fractions were observed with 3 and 5 wt% silica

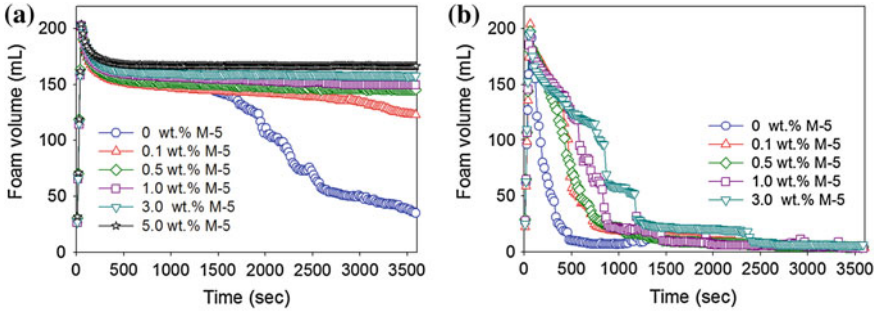

Fig. 85.2 Foam volume of **a** 1 % and **b** 0.1 % EM 100 containing various concentration of silica nano-particles (0, 0.1, 0.5, 1, 3, and 5 wt%) at pH 2 for 1 h

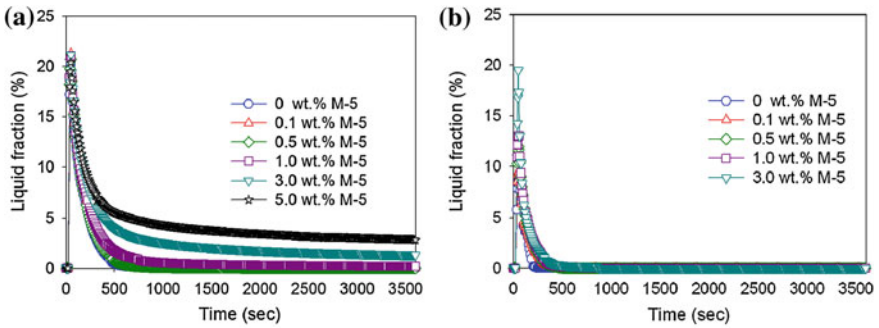

Fig. 85.3 Liquid fraction of **a** 1 % and **b** 0.1 % EM 100 containing various concentration of silica nanoparticles (0, 0.1, 0.5, 1, 3, and 5 wt%) at pH 2 for 1 h

NPs for 1 h, respectively. The addition of 3 and 5 wt% silica NPs increase foam stability (the liquid fraction of integration) by a factor of 3 and 5, compared to the foam stabilized only with 1 % EM 100 (Fig. 85.3a), indicating that the liquid fraction in 1 % EM 100 increased with the increase of silica NPs. In Fig. 85.3b, the liquid fraction in 0.1 % EM 100 was not observed in all concentration of silica NPs. These results indicate that it is difficult to use 0.1 % EM100 in decontamination foam owing to its deficiencies under acidic conditions. Alternatively, 1 % EM100 can be applied in acid pH containing chemical reagents.

The concentration of surfactant was important factor in acidic pH, therefore, the concentration of surfactant was determined to 1 % EM 100 for the oxide dissolution test containing chemical reagents (1 M HNO_3). In Fig. 85.4, silica NPs concentration was proportional to the integration of liquid fraction (left y-axis) as a factor of foam stability. In oxide dissolution test, the results showed that EM 100 foam containing 0.5 wt% and 1 wt% had approximately 1.25×10^{-2} and 1.29×10^{-2} mg of the level of dissolved iron (right y-axis), respectively (Fig. 85.4). The level of dissolved iron was 1.46×10^{-2} and 1.76×10^{-2} mg in

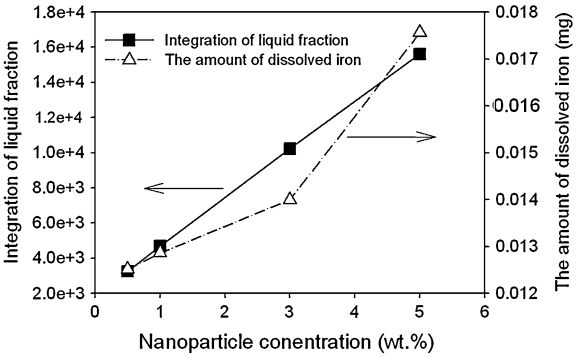

Fig. 85.4 The relationship of the integration of liquid fraction, the amount of dissolved iron and nanoparticle concentration (0.1, 0.5, 1, 3, and 5 wt%) in 1 % EM 100 at pH 2 for 1 h

the addition of silica 3 and 5 wt% NPs, respectively. The results showed that the increase of silica NPs increased the amount of dissolved iron of corroded specimens, suggesting that the increased foam stability enhanced the iron dissolution owing to an increase in the contact time between the chemical reagents and the corroded surface.

Conclusions

This study showed the effect of surfactant, silica NPs concentration, and pH on the foam stability and oxide dissolution to develop new formulations of decontamination foam. The foam stability of nonionic surfactant in low concentration (0.1 %) has a significant effect for pH. The result indicates that silica NPs increase the amount of oxide dissolution owing to the increase of the foam stability. In future studies, hot decontamination tests will be conducted using decontamination foam on a corroded surface adsorbed with radionuclides.

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Chapter 86
Separation and Characterization of Minerals from Centrifuged Waste Latex Sludge

Wirach Taweepreda

Abstract Waste latex sludge is generated during the production process of concentrated latex. The waste latex sludge is composed with both organic and inorganic materials which are the caused of pollution. In this research, the toxic waste latex sludge was digested using acids to separated and purified inorganic materials such as Boussingaultite mineral and phosphatic fertilizer. Minerals were removed from waste latex sludge after immersing in acid solution such as sulfuric and formic acid. The sulfate group of sulfuric acid reacted with magnesium of waste latex sludge formed precipitated Boussingaultite. The phosphate was removed after immersing waste latex sludge in formic acid and purifying with sodium hydroxide. Crystal structure and composition of occurred minerals were confirmed using power X-ray diffractometer (XRD) and X-ray fluorescent (XRF) combined with elemental analyzer, respectively.

Keywords Natural rubber · Latex sludge · Phosphate · Magnesium

Highlights

- Most of inorganic substance were removed after digestion with acid.
- Sulfuric acid digestion produced Boussingaultite mineral.
- The residue from formic acid digestion after treated with NaOH produced Stravite mineral.

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Introduction

The natural rubber latex (NRL), contain high magnesium ion (Mg^{2+}) content, is necessary to be treated with diammonium hydrogen phosphate (DAHP) to prevent blockade during the centrifugation of NRL. The Mg^{2+} react with DAHP result in solid waste latex sludge formation and precipitation from NRL. The waste latex sludge charateristics have been investigated and reported since the year 2002 (Okieimen and Okieimen 2002). Basic composition of this waste latex sludge are rubber hydrocarbon, nitrogen, magnesium, and phosphorus for 12.5, 3.3, 12.2, and 14.7 % by wt. (dry weight), respectively. Eventhough these material can be comparable used as commercial fertilizers but the limitations, heavy metal contamination, unsuitability to certain soils and crops must be concerned as well as the effect of rubber hydrocarbon which is not easily decomposed in soils. This waste latex sludge must be treated using landfill or digestion (Stark 2002).

In this research, the waste latex sludge was digested using acid for minerals recovery purpose. Acid type such as sulfuric acid and formic acid has different effects on recovered mineral type.

Materials and Methods

The waste latex sludge was kindly supplied by Chalong Concentrated Latex Company Limited and was used immediately. The waste latex sludge was grinded into small pieces before mixing with concentrated acid such as sulfuric and formic acid. The digested sludge was decreased in volume due to waste latex sludge decomposed and converted into gases resulted in lower specific gravity of waste sludge compared with water (Sakohara et al. 2011).

The Mg^{2+} was eluted from waste latex sludge after immersing in sulfuric acid. Mg^{2+} reacted with ammonium sulfate transformed to soluble magnesium ammonium sulfate. The saturated magnesium ammonium sulfate solution was crystallized after evaporation at 100 °C. The crystal structure and elements composition were characterized using X-ray Diffractometer (X'Pert MPD, Philips, Netherlands), X-ray fluorescence spectrometer (XRF) (PW 2400, Philips, Netherlands) and CHNS-O Analyzer (CE Instruments Flash EA1112 Series, Thermo Quest, Italy).

The digestion of waste latex sludge with formic acid was found that the rubber was separated and floated. Inorganic minerals were eluted and solute in formic acid solution as illustrated in Fig. 86.1. The solution was treated with sodium hydroxide (NaOH) solution resulted in canary yellow precipitated. The precipitated was separated and dried at 80 °C before characterized using X-ray Diffractometer (X'Pert MPD, Philips, Netherlands), X-ray fluorescence spectrometer (XRF) (PW 2400, Philips, Netherlands) and CHNS-O Analyzer (CE Instruments Flash EA1112 Series, Thermo Quest, Italy).

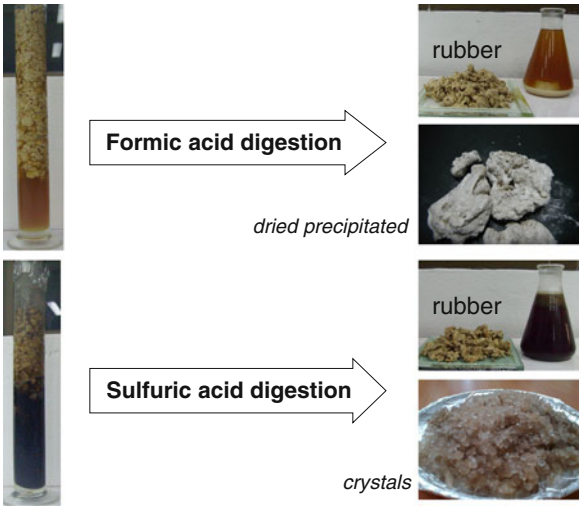

Fig. 86.1 Acid digestion of waste latex sludge

Results and Discussion

Most of inorganic materials were removed from waste latex sludge after digestion with sulfuric acid resulted in dark brown residue acid solution as shown in Fig. 86.1. The crystal was precipitated at flask bottom after evaporation of residue acid solution at 100 °C. The occurrence crystals are white to clear color and the gloss is vitreous. The powder X-ray diffraction pattern of the crystals as shown in Fig. 86.2 was in good agreement with Boussingaultite mineral (RRUFF ID-R070597.9) (Shimobayashi et al. 2011) and the refine unit cell parameters are $\boldsymbol{a}$ = 9.327(3) Å, $\boldsymbol{b}$ = 12.600(4) Å, $\boldsymbol{c}$ = 6.210(1) Å, and V = 697.6(8) Å^3. The crystal composition being $(NH_4)_2Mg(SO_4)_2 \cdot 6(H_2O)$ corresponded with elemental analysis as illustrated in Table 86.1. Adding sulfuric acid leaded to an increase of dissolved phosphate concentration by the spontaneous degassing of carbon dioxide

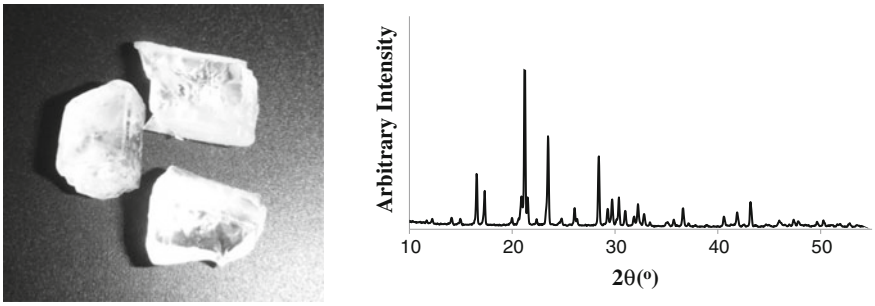

Fig. 86.2 Occurrence crystals and powder X-ray diffraction patterns from waste latex sludge digestion using sulfuric acid

Table 86.1 Elemental analysis of precipitated crystal from acid digestion

Elements	Concentration (% by weight)	
	H_2SO_4 digestion	Formic acid digestion
H[a]	5.250	4.440
C[a]	0.070	14.170
N[a]	7.090	3.740
O[a]	48.999	38.275
S[a]	29.661	0.179
Na	–	–
Mg	5.070	10.441
P	0.393	22.858
K	1.710	2.551
Ca	–	0.490
Fe	–	0.112
Zn	1.538	2.312
Rb	0.219	0.172

[a] Results from CHNS-O analyzer, CE instruments flash EA1112 series, thermo quest, Italy

(CO_2). The carbon and phosphorus contents of crystal from sulfuric acid digestion are lower than that from formic acid digestion. Most of phosphorus was still dissolved in waste water.

The digestion of waste latex sludge with formic acid was found white–gray precipitated mineral as shown in Fig. 86.1. The occurrence precipitated is white crystal with rectangular shape as shown in Fig. 86.3. The powder X-ray diffraction pattern of the crystals was in good agreement with Stravite mineral (RRUFF ID-R070597.9) (Anthony et al. 1990) and the refine unit cell parameters are $\boldsymbol{a}$ = 9.327(3) Å, $\boldsymbol{b}$ = 12.600(4) Å, $\boldsymbol{c}$ = 6.210(1) Å, and V = 697.6(8) $Å^3$. The crystal composition being $MgNH_4PO_4{\cdot}6H_2O$ corresponded with elemental analysis as illustrated in Table 86.1.

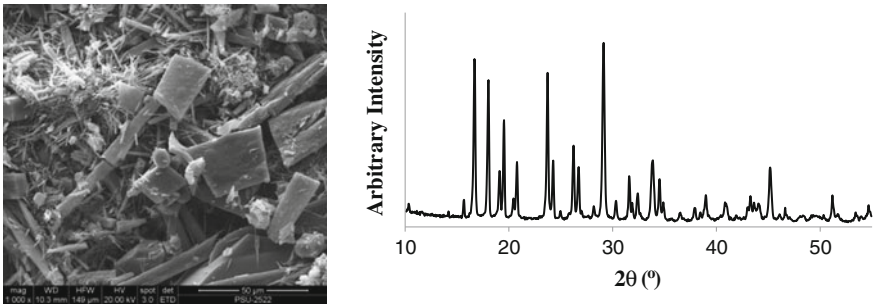

Fig. 86.3 The precipitate and powder X-ray diffraction patterns from waste latex sludge digestion using formic acid

Conclusion

The minerals removal from waste sludge using digestion method is feasible solution to solve the problem of waste disposal in the NR latex concentrated factories in any developing country like Thailand. It is not only to retrieve high value minerals which are essential nutrient in crop production, but also high quality rubber from null throw away materials.

Acknowledgments The authors are grateful to the financial supports from Office of National Research Council of Thailand (NRCT) (Project code: 50860).

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Chapter 87
Life Cycle Assessment at a Sawmill Manufacturing Company in Terengganu, Malaysia

Khairul Izzuudin Muhammad, Amir Hamzah Sharaai and Sabrina Ho Abdullah

Abstract Life Cycle Assessment (LCA) is known as a tool to evaluate and assessing the impacts of products towards the environment. It will include all the process or activities used and waste released into the environment. In detail, LCA involved the collection and evaluation of quantitative data on the inputs and outputs of material, energy and waste flows associated with a product over its entire life cycle. The objective of this study is to identify potential impact of sawmill manufacturing process. This study followed the four phases as stipulated in the International Organization for Standardization (ISO 14040 series of standard) for conducting LCA studies such as goal and scope definition, Life Cycle Inventory analysis (LCI), Life Cycle Impacts Assessment (LCIA), and Interpretation.

Keywords Sawmill manufacturing · Life cycle impacts assessment (LCIA) · EcoIndicator 99 evaluation method · Endpoints impacts

Highlights

- Sawmill manufacturing is potentially affected human health, ecosystem and resources.
- Logging activities are the biggest contributor in damaging the ecosystem quality.
- Transportation and electricity are the biggest contributors that destroy resources.

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Introduction

Timber production is an important activity in the housing industry and furniture production in the country. This activity accounted for most of the national income. If this activity is not well governed, there would be problems that would be detrimental to the country as illegal logging and environmental pollution problems. LCA is an environmental management tool and started to be used in 1960s in the USA (Curran 2006) that evaluates a product or service in detail from cradle to grave to identify the weaknesses of emissions and waste produced. This study is useful for displaying the potential impact generated so that corrective action can be made to save the environment.

Materials and Methods

This research is follows the LCA framework adopted from the International Organization of Standardization (ISO) guidelines specifically for life cycle assessment (LCA) (ISO 14044, 2006). There are four main phases in LCA: Goal and Scope Definition (ISO 14040); Life Cycle Inventory (LCI) (ISO 14041); Life Cycle Impact Assessment and Interpretation (LCAI) (ISO 14043).

Phase 1: Goal and Scope Definition

Goal: To analyse the potential endpoint impacts from a sawmill manufacturing at Terengganu, Malaysia.

Scope: System boundary that is covered in this study is only within the sawmill manufacturing including transportation, electricity consumption, and machinery.

Phase 2: Life Cycle Inventory

There are two types of data: Background and foreground data. Foreground data is the data collected from information obtained from the plants studied for example emissions, energy, water, and fuel consumption. While background data is obtained from secondary sources which is emissions from each process involved. The background data is obtained from EcoInvent database.

Phase 3: Life Cycle Impact Assessment

Inventory that is collected will be calculated and translated into midpoint and endpoint impacts as suggested by the EcoIndicator 99 method. For the purpose of this conference, only the endpoint impact is displayed. There are three types of endpoints proposed in EcoIndicator 99 that are Damage of environmental quality, Damages to human health and Damage to resource. Figure 87.1 is a normalization of the three types of endpoint (represent scale point (pt) and percent).

Phase 4: Interpretation

Analysis focused on demonstrating the shortcomings identified and suggestions are made to overcome the problem.

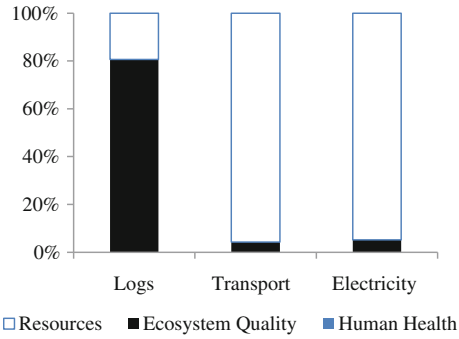

Fig. 87.1 Normalization of endpoint results of activities engaged in sawmill manufacturing

Results and Discussion

Analysis for this study focused on the three damages categories which are damages to human health, damages to ecosystem quality and damages to resources. Based on Fig. 87.1 analysis found that, logs activities show the highest impacts to damages to ecosystem quality which is 661.11 Pt (81 %). For the transportation and electricity, damages to the resources records higher value of impacts which are 2.46 Pt (97 %) and 172.0 Pt (95 %), respectively. Figure 87.1 also shows that there are two major contributors to these three damages categories. The logs activities contribute highest impact to ecosystem quality damages, while electricity generation contributes highest impact to human health. This research also detected a hotspot activity that is direct discharge to nearby river which potentially affected the quality of water of the Kenyir lake.

Conclusion

Timber production is one of the biggest profit of Malaysia revenue. Overexploitation of forest is among the environmental problem in Malaysia that needs solving wisely. LCA is an environmental management tool that can be recommended for use as a means of avoiding environmental shifting problems. Weaknesses or hotspot in the life cycle sawmill manufacturing are really helpful to the stakeholders to find ways to prevent and overcome the identified problems.

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Chapter 88
Noise Pollution Status in Central Mumbai: A Comparative Study

Prashant P. Bhave and Bisma Shaikh

Abstract Urban noise is mostly associated with urban development. Effect of noise can be temporary or permanent. In Mumbai where land area is a constraint, various land uses formally demarcated have overlapped and sound levels are observed to be above the permissible limits. A study of noise levels at various locations in a select area from Central Mumbai was carried out with noise mapping to get the current status of the noise pollution in the area. Noise maps are drawn with previous (2004) and current (2013) noise levels by overlying the sound level contours upon geographical information. This study gives a perspective of the current and previous noise levels in areas, which are above the recommended guidelines. This study also indicates a significant increase in the sound levels in the study areas over the study period. This study emphasizes on control of the increasing noise pollution at the earliest.

Keywords Sound level meter · GIS · Mumbai city · Noise map · dB

Highlights

- Noise levels exceeded the recommended guidelines in most areas.
- The Mumbai noise generated map is the basis for noise mapping for other cities.
- In the 2013 noise map, the 85 dB zone increases compared to the 2004 map.

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Introduction

Noise is commonly an unwanted sound and widely recognized as urban pollution. Mumbai being the fastest developing city of India, so are the problems associated with it. Particularly in congested urban areas of Mumbai the noise produced, is as a by-product of many activities. The noise pollution causes physical and psychological harm to inhabitants. To control noise pollution, provisions were made in Environment Protection Act 1986. The Noise Pollution (Regulation and Control) Rules, were enacted in year 2000. In Mumbai where land area is a constraint, various zones formerly demarcated have overlapped creating more urban noise. This creates an urgent need for the study of noise levels at various locations and mapping it. Urban areas close to busy roads, railways, airports are usually selected for initial implementation of mapping systems needed to draft noise control schemes (Tsai et al. 2009). de Kluijver and Stoter (2003) emphasized on the standardization of noise mapping tool. They also found that the implication of GIS in noise mapping studies enhances the performance of noise mapping studies and makes it easy, lucid and time effective. Based on the Norwegian socio-environmental survey database and a comprehensive national noise mapping effort, Klæboe et al. (2006) prepared noise impact maps so as to help experts, politician and the public to easily get an idea about the noise impact status in an easily accessible format. As per the studies conducted so far, it has been observed that transportation noise is a major source of noise exposure. The objective of this study is to measure and compare noise levels at various locations in selected areas from central Mumbai by generating noise maps during the study period.

Materials and Methods

The study area is approximately of 2.5 km^2 'Dadar-Matunga-Wadala', located in central Mumbai. The study area includes all types of areas as described in the Noise Pollution Rules, 2,000. Areas covered under this study are shown in Table 88.1 (Sule 2005).

For this study, 44 temporary noise monitoring stations in Dadar-Matunga-Wadala area were set up, to investigate noise levels during the morning (09:00–11:00 h) and evening (17:00–19:00 h) periods. Noise is measured using

Table 88.1 Various types of areas covered under study

Description	Areas under consideration
Highways	Dr. Ambedkar Road and Rafi A.Kidwai Road
Major roads	Laxmi Nappu Road, Mancherji Joshi Road, Katrak Road, Adenwala Road
Sensitive areas	Educational Institutes: VJTI, ICT, Khalsa, Poddar College, Ruia College, I.E.S. School, Don Bosco
Commercial area	Matunga Market, Suburban Railway stations
Residential area	Hindu Colony, Parsi Colony

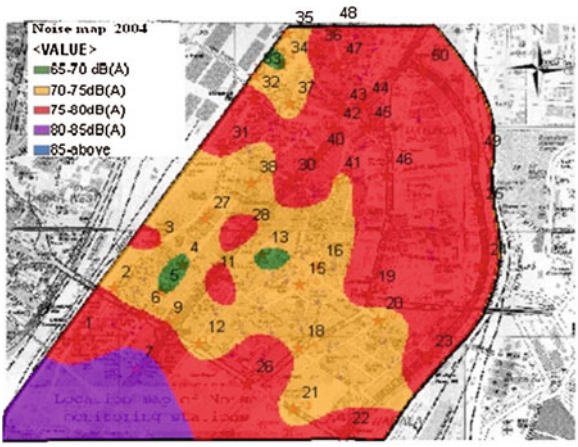

Fig. 88.1 Noise map for Year 2004

the digital sound level meters manufactured by Lutron in Taiwan. Figures 88.1 and 88.2 show the spatial distribution of monitoring stations. The GIS tools were used to overlay the noise maps on noise control zones to evaluate actual conditions compared to the noise control regulations.

'Leq' is defined as the constant noise level over a given time, expands the same amount of energy, as is expanded by the fluctuating levels over the same time (MPCB 2011). The equivalent noise level (Leq) constitutes an important parameter for evaluating the impact of fluctuating noises from all sources in the study area. ISO 1996-1 proposed the recognition of Leq as an international standard (Tsai et al. 2009; ISO 1981). Therefore, this study also adopted Leq as a standard for measuring environmental noise. Noise data in Dadar-Matunga-Wadala area (4 h monitoring) were collected from each noise monitoring station. Noise maps

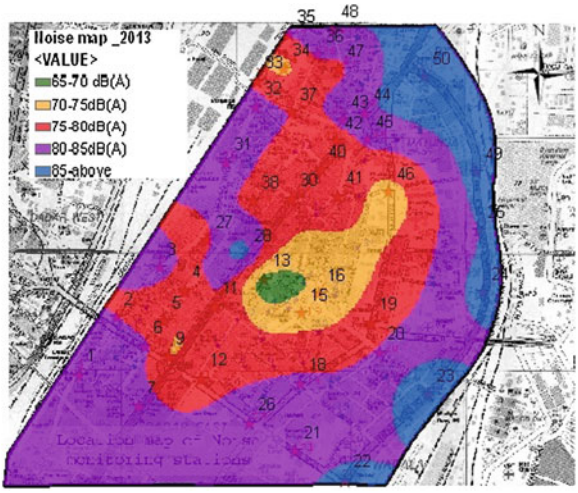

Fig. 88.2 Noise map for year 2013

were then generated using GIS to integrate the monitoring data with spatial information. Noise level contours were constructed by geo-statistical interpolation method. The current noise control zoning in Dadar-Matunga-Wadala area has four zones, namely, industrial, silence, residential and commercial. Based on the monitoring data, this study statistically summarized noise levels in these zones and compared the results with relevant noise regulation standards to evaluate present noise environments in the study area. Regulatory standards for noise control are based on noise control zoning. Table 88.2 demonstrates the maximum noise levels allowed by the Noise Control Standards (The Gazette of India 2000).

Results and Discussion

The noise levels were monitored on 44 locations as per methodology adopted. These parameters were recorded at an interval of 1 s for the monitoring duration of 4 h. Figures 88.1 and 88.2 show the noise map for year 2004 and 2013 noise data.

Highways: Along the stretch of Dr. Ambedkar Road from Maheshwari Udyan to Dadar Head Post Office (P.O.) it was seen that the Leq for year 2004 ranged between 75.7 and 82.2 dB at Dadar Head P.O. whereas for year 2013 it ranged between 75.25 and 84.26 dB. Similarly, on the Rafi A. Kidwai Road, the noise levels ranged from 76.1 to 77.2 dB, in 2004 as against 85.09–88.64 dB in 2013. Along the stretch of Dr. Ambedkar Road near Kapol Niwas the Leq of 76.19 dB as against of 77.5 dB, which is higher than that of current observations. Reduction in the present noise levels is due to the road/flyover development, thereby reducing traffic congestion in this area. Rafi A. Kidwai Road, the recorded higher noise is due to the movement of heavy vehicles and trailers throughout the day. The noise levels varied from 85 to 88 dB which is 25 dB higher than noise regulation standards. The Tilak road, which connects Khodadad Circle to Rafi A. Kidwai Road, the noise levels varied from 75 to 86 dB, which is 5–10 dB higher than the past reading and 20 dB higher than the noise regulation standards.

For the residential area and sensitive area viz. Hindu Colony, Parsi Colony with Nappu road, the recorded noise levels were above 79 dB, which is 29 dB more than applicable noise regulation standards. In the Matunga area, the educational institutes, such as, IES school, Ruia, Poddar, which are facing the Nappu Road,

Table 88.2 Standards of noise levels EPA (1986): noise pollution (regulation and control) rules, 2000

Area code	Category of area	Limits in dB(A) Leq	
		Day time	Night time
A	Industrial area	75	70
B	Commercial area	65	55
C	Residential area	55	45
D	Silence zone	50	40

"Night time" means the period between 22.00 and 06.00 h

were affected by noise mainly due to heavy traffic movement on this road. The Matunga Market area was observed to be noisy with Leq of 75 dB in the Year 2004 but in 2013 it is above 80 dB. This area recorded the highest noise level during study period (114 dB) during the monitoring period.

Conclusion

The generated noise maps for year 2004 and year 2013 gives an idea about the status of noise in the selected parts of the prime metropolitan area. In Mumbai, vehicular traffic is one of the major contributors to the elevated noise levels. The residential areas were observed to have high noise level sporadically. Overall, it was observed that the noise levels exceeded the standards prescribed by the regulatory authorities during the monitoring hours at all locations. This study which was an attempt to map the noises of Central Mumbai area would prove to be an important database/reference data for the urban noise pollution and would also help in formulating policies and control measures. Moreover, the basis of this study can be used to map whole metropolitan city like Mumbai or any other metropolitan city of India.

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Chapter 89
Weathering Product of Granite as a Possible Source of Strategic Mineral

Shaharin Ibrahim, Ahmadreza Ashraf, Elias Saion, Abdul Khalik Wood and Wan Abdullah Wan Yusoff

Abstract Several soil samples and granite bedrock samples from Cameron Highlands were analyzed for its elemental concentration using instrumental neutron activation analysis. A total of 34 elements were identified and their concentrations were determined in a single analytical session. Enrichment factor of elemental concentration in the top soil were computed. The findings indicate certain elements were enriched that may facilitates economic beneficiation.

Keywords Elemental concentration · Enrichment factor · INAA · Cameron Highlands Malaysia

Highlights

- NAA provides fast method to determine elemental concentration.
- Chemical weathering process of granite enriched certain elements in the top soil.
- Weathering enriched elements concentration that may facilitates exploitation.

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Introduction

Soil samples and the rock parent material were taken from the research plot of Malaysian Agriculture Research and Development Institute (MARDI) in Cameron Highlands, Malaysia. Their elemental concentrations were determined using Instrumental Neutron Activation Analysis in the laboratory of Malaysian Institute of Nuclear Technology Research (MINT), Bangi. Geologically, the area is underlain by granitic rock with grain size ranging from medium to coarse (KPU 1999).

In this work, the concentrations of elements in top soil and in the granite parent rock material were determined, and their enrichment factors were calculated. A total of 34 elements had been identified in a single analytical session.

Materials and Methods

Site location and Sample collection

The sampling sites and the area under study are shown in Fig. 89.1. The sample locations were recorded with a global positioning system Garmin model Rino530HC$_X$. Each sampling point is marked by Mx (x = 1, 2, 3…). A total of 10 soil samples were collected to a depth of 30 cm using standard Dutch auger. The samples were put into pre-cleaned glass bottles, labeled and transported to a laboratory in Universiti Putra Malaysia for sample preparation.

Sample Preparation

The sample was prepared in accordance to standard procedure as stipulated in (IAEA-TC-4 1992). Data reported in this study are calculated based on dry weight. A quadruplicate of samples (weight between 0.05 and 0.10 g) was used for short irradiation. Another quadruplicate samples (weight between 0.15 and 0.20 g) were used for long irradiation. The samples were put into a polyethylene vial and heat sealed. The certified reference materials (CRM) IAEA-SOIL-7 and (SRM) IAEA-SL-1 was prepared in identical conditions and used as reference material for each batch of short-lived and long-lived radioisotopes. The accuracy and precision of the analytical procedure were checked by comparing the concentration of the standard reference materials (SRM) obtained in the present work with those published by International Atomic Agency, Vienna, issued in September 1999.

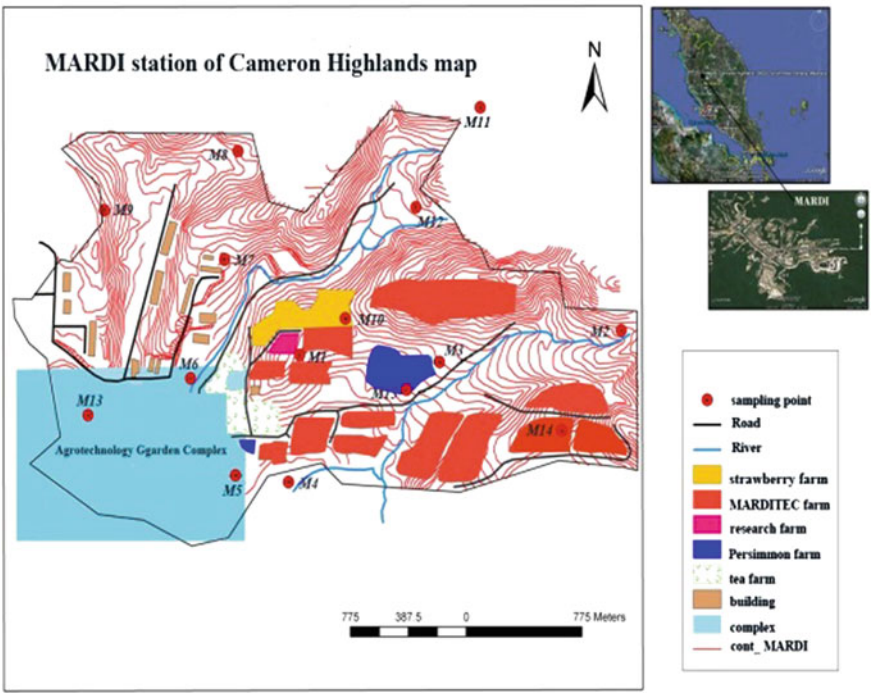

Fig. 89.1 Location map of the study area and sampling location

Instrumental Neutron Activation Analysis

Samples were irradiated at a thermal neutron flux of 4×10^{12} n cm^{-2} s^{-1} for short and long irradiation time of 1 min and 6 h, respectively. HPGe detector (ORTEC, 20 % relative efficiency, FWHM 1.8 keV at 1332 keV of ^{60}Co) was used for γ radiation coupled with a Multichannel Analyzer. Gamma vision software was used for the γ spectrum processing. Elemental concentrations in the samples were calculated using:

$$C_{sam} = \frac{A_{sam}}{A_{std}} \cdot \frac{W_{std}}{W_{sam}} . C_{std} \tag{89.1}$$

where A_{sam} and A_{std} are the activity of interested element in the soil sample and calibration standards respectively. C_{sam} and C_{std} are the concentration of the sample and calibration standards, W_{sam} and W_{std} are the weight of the sample and calibration standards, respectively. The enrichment factor was computed for each element using the following equation:

$$Ef = \frac{[M]_m}{[M]_{ref}} \tag{89.2}$$

Table 89.1 The mean concentrations of elements in the soil and enrichment factors (EF) for each sample at MARDI station Cameron Highlands

Station	Element	Mean concentration (%)	Enrichment factor	Element	Mean concentration (mg/kg)	Enrichment factor	Element	Mean concentration (mg/kg)	Enrichment factor
M1	Fe	2.92	1.26	Cs	17.20	0.36	Cr	52.60	2.54
M2		2.80	1.65		5.50	0.16		48.60	3.25
M3		2.90	1.53		12.30	0.31		64.50	3.80
M4		2.50	1.09		19.40	0.37		72.30	3.21
M5		2.60	1.07		17.50	0.36		63.70	3.02
M6		3.00	1.05		19.60	0.34		73.40	2.92
M7		2.50	1.18		13.00	0.27		79.50	3.80
M8		3.00	1.50		16.10	0.31		72.70	3.26
M9		2.80	1.21		12.60	0.33		80.40	4.78
M10		3.10	1.13		19.00	0.36		32.10	1.38

Station	Element	Mean concentration (mg/kg)	Enrichment factor	Element	Mean concentration (mg/kg)	Enrichment factor	Element	Mean concentration (mg/kg)	Enrichment factor
M1	Hf	15.30	1.62	As	23.00	0.30	Th	71.90	1.64
M2		28.80	4.23		19.90	0.36		62.00	1.96
M3		25.40	3.29		21.20	0.33		60.40	1.68
M4		15.00	1.46		13.40	0.16		47.40	0.99
M5		22.00	2.29		16.10	0.20		47.65	1.06
M6		14.50	1.27		16.40	0.17		49.70	0.93
M7		20.00	2.09		15.30	0.20		63.10	1.42
M8		14.70	1.44		26.80	0.32		60.50	1.28
M9		19.20	2.50		13.00	0.21		49.50	1.39
M10		11.20	1.06		14.80	0.17		48.30	0.98

where $[M]_m$ is the element concentration ratio to the Al concentration in the sample and $[M]_{ref}$ is ratio of the average concentration of the same element to Al concentration in the granitic parent material.

Results and Discussion

The result on concentration and enrichment factor of the elements found in the top soil of the study area is presented in Table 89.1. It can be seen that certain elements get depleted compared to the parent material upon development of top soil from the granitic parent material, while other elements get enriched. Elements that get enriched include Fe, Cr, Hf and Th, while those that get depleted include Cs and As. It has been pointed out by many researchers that the presence of elements in enriched quantity as compared to the parent rock from which they are developed may indicate input of the elements from external sources, mainly from anthropogenic activities and is indicative of pollution status. The proponent of this school of thought includes Pereira et al. (2007); Kamaruzzaman et al. (2008); Chatterjee et al. (2007); Sinex and Helz (1981) and Yousry et al. (2009). However, as pointed out by Reimann and De Caritat (2000), there is an intrinsic flaw in using the concept of enrichment factor in environmental chemistry, particularly when using the average elemental concentration of earth crust as a base line to which enrichment factors were calculated. In the present work, enrichment factor was calculated based on the concentration of the element present within the source rock from which the soil was developed.

The result of the present work indicated that Fe in the top soil is enriched up to 1.7 times the concentration of the same element within the parent rock material. Field observation indicated that the soil is not very much lateritic in nature. Here in Malaysia, normal chemical weathering of granite often produced lateritic soils, which have very high enrichment of Fe compared to the soil in the present study. Under such situation, if Cr, Hf or Th is also present within the granitic rock mass, then its concentration within the lateritic soil could be very substantial. Hence the opportunity to find source of strategic mineral could be high in region where tropical chemical weathering is dominant.

Conclusion

Tropical chemical weathering of granite may enrich certain elements in the soil up to the level that may cause the weathered product to be mineable for strategic elements.

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Chapter 90
Forensic Ecotoxicology

Tracy Kim Collier

Keywords Chemical contaminants · Environmental toxicology · Ecoepidemiology

Highlights

- Toxicology determines causal relationships between toxicants and effects.
- The vast majority of toxicology studies are laboratory studies.
- Forensic ecotoxicology focuses on determination of causation in natural ecosystems.
- Toxicology studies in ecosystems carry greater weight in support of management actions.

There have been a number of efforts over the past 50 years to explicitly recommend criteria for establishing causality between exposure to chemical contaminants and biological injury. Many of these efforts initially focused on human disease (Yerushalmy and Palmer 1959; Hill 1965; Hackney and Kinn 1979). In 1991, Glen Fox published a seminal paper suggesting criteria that could be used by wildlife toxicologists who were attempting to establish causality (Fox 1991). Some of the more comprehensive guidance documents on determining causality between environmental contaminants and biological effects were published by the US Environmental Protection Agency (USEPA) in 1998 and 2000 (USEPA 1998, 2000). In 2003, a special issue of Human and Ecological Risk Assessment was published on the subject of establishing causality in field studies, using a variety of case studies to test the utility of different causality criteria (Collier and Adams 2003). A book was recently published that also collected together a number of case studies, focusing on causal relationships between environmental contaminants and vertebrate wildlife (Elliott et al. 2011). It is an added feature of this book that the case studies are examined from both a technical as well as a social perspective.

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Collier and Adams (2003) proposed and evaluated a list of seven criteria for establishing causality in field studies. These seven, together with brief descriptions of each, were:

(1) Strength of association—there is a strong relationship between the stressor and the effect. For example, either a large proportion of individuals in an exposed area are affected, or perhaps a small proportion of individuals show a large effect. Alternatively, there may be a strong relationship seen between an effect in individual organisms and the presence or absence of a supposedly causal toxicant in their bodies.
(2) Consistency of association—the relationship between the stressor and the effect has been seen in other studies, especially in studies by other investigators.
(3) Specificity of association—the effect is diagnostic of exposure to the stressor, meaning that the effect is only observed after exposure to that specific stressor. Additionally, the stressor produces only that effect.
(4) Time order/temporality—the effect occurs only after exposure to the stressor. Alternatively, removal or reduction of the stressor results in a subsequent reduction in the effect.
(5) Biological gradient—there is a dose–response relationship between the stressor and the effect. As the magnitude of the stress increases or decreases, so does the magnitude of the effect.
(6) Experimental evidence—controlled exposure to the stressors (e.g., in laboratory or mesocosm studies) provide results that support the proposed causal relationship.
(7) Biological plausibility—The proposed causal relationship has a credible biological (or in this case toxicological) basis. Mechanistic linkages can be proposed linking stressor exposure to the biological effect.

For each of eight case studies conducted in natural ecosystems, investigators were asked to evaluate their specific study using the above criteria. A score was estimated for each of the case studies, as well as each of the criteria (Collier 2003), with scores ranging from 3 (convincing evidence presented in support of the criterion) to −1 (evidence argues against causality using that criterion). A notable result of this semi-quantitative analysis was that the third listed criterion, specificity of association, received only 2 points out of a possible 24. Thus it was recommended that, for establishing causality in natural ecosystems, expecting specificity of association is not appropriate or useful. Temporality, or time order, received the next fewest points, 11, but this was not unexpected because many field assessments are only conducted after an event, such as a release of chemicals, occurs. To subsequently determine temporality without baseline (usually pre-release) information is very difficult. When the scores of the individual criteria were summed, it was noted that the further up the scale of biological organization the studies went, the lower the scores received. This was also not unexpected, and demonstrates the difficulties of determining effects of specific stressors at the population or community level.

There is increasing recognition that even low levels of exposure to environmental contaminants can have unexpected consequences in natural ecosystems. Trying to understand these relationships well enough to support mitigation efforts is the reason that forensic ecotoxicology exists. In the United States, many of the recent advances in forensic ecotoxicology have come about as result of passage of the Superfund Act[1] in 1980 and the Oil Pollution Act of 1990. Under both of these Acts, two types of liability are assigned for releases of oil or hazardous substances: responsibility for cleaning up the environment, and responsibility for addressing injury to natural resources through appropriate restoration activities. Both cleanup and restoration can be exceedingly expensive to implement, with costs in the millions of dollars at many Superfund sites, and exceeding billions of dollars after major environmental releases, such as large oil spills. Forensic ecotoxicology is needed to help justify and guide these large expenditures.

Subsets of chemical contaminants have been termed contaminants of emerging concern, or CECs. Included in this category are those substances a) that are being detected in the environment in unexpectedly high concentrations, such as polybrominated diphenyl ethers; b) that are novel, and are being produced in large quantities, with little known about their persistence and toxicity; or c) for which there is new information about their harmful effects, such as polycyclic aromatic hydrocarbons and their developmental toxicity in fish (Incardona et al. 2011). Currently, many environmental monitoring programs focus on measuring contaminants in physical and biological matrices, and CECs are increasingly being reported (Klecka et al. 2010). However, whether such exposures will lead to adverse biological effects is unknown in many cases, which has led to recommendations for biologically-based monitoring and assessment (Collier et al. 2007), which is a component of forensic ecotoxicology.

Finally, environmental health is increasingly being linked to human health, thus forensic ecotoxicology also has value for protecting public health. If chemical contaminants are shown to be causing disease in wildlife populations, health practitioners can be alerted to be on the lookout for signs of similar exposures and disease states in humans who might also be at risk by virtue of their area of residence, or employment in certain industries. The term ‘sentinel species’ has been applied to this concept, and several examples are given in Trtanj et al. (2013).

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Chapter 91
Distribution of Heavy Metals, Organic Matter and Mean Size in Sediment at the Perlis River

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Abstract The distributions of heavy metals (As, Cd, Cr, Cu, Pb and Zn), organic matter and mean size were determined in the riverbed sediment by means of 10 sampling points in Perlis River. From this study, mean of heavy metals concentration in the sediment was dominated primarily by Cr with the concentration of 97.02 ± 9.34 mg/kg dry weight, followed by Zn (80.84 ± 31.68 mg/kg dry weight), Pb (58.67 ± 32.63 mg/kg dry weight), Cu (26.69 ± 10.34 mg/kg dry weight), As (24.52 ± 8.77 mg/kg dry weight) and Cd (0.11 ± 0.03 mg/kg dry weight). The distribution of organic matter ranged between 3.90 and 7.56 %, while mean size ranged between 6.95 and 7.55 respectively. The average of each heavy metal except Cd and Zn were found to be above the ISGQ standard which was proposed by Canadian Sediment Quality Guidelines. Correlation analysis showed that all metals except Cu were significantly correlated with the distribution of organic matter. This finding is crucial to determine the metals level in the sediment as well as to update the current status of metals pollution in the Perlis River.

Keywords Heavy metals · Organic matter · Mean size · Sediment · Perlis River

Highlight

- The trend of heavy metals found in sediment was: Cr > Zn > Pb > Cu > As > Cd.
- Mean size shows that sediment was dominated primarily by clay and silt.
- Significant correlation was found between all heavy metals and organic matter.

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Introduction

Sediment shows a strong tendency to accumulate pollutants in the water system as they are less likely to be influenced by water flow. Pollutants such as heavy metals were carried by water flow and eventually settle down or adsorbed by the sediment which depends on its physico chemical state and metals species. Since heavy metals are not biodegradable, it will slowly accumulate in various forms. Later, the accumulated metals embedded in the sediment will undergo various chemical reactions and can be released into the water column under due to several conditions such as pH changes, redox potential and sediment disturbance (Bartolli et al. 2011; Fortsner 1977).

However, elemental concentration of sediments was not only depending on by natural and anthropogenic sources but also upon the organic matter content, mineralogical composition and textural characteristic of the sediment (Filgueiras et al. 2004; Khalaf et al. 1981; Presley et al. 1980). Heavy metals are usually en-riched in the smaller grain size fractions (Ozkan 2012). Smaller particles have a large surface area over volume ratio which is associate to co-precipitation and complexation of metals on particles surfaces. Thus, the adsorption process of metals are higher in fine grain size which result in high metals concentration (Jain 2005).

There is not much data available on the heavy metals and grain size analysis in the sediment in North Western Part of Peninsular Malaysia especially in Perlis River. Contamination from anthropogenic sources such as domestic sewage, boat activities, agriculture and aquaculture run off can possess a serious threat to the food chain system in aquatic environment. Moreover, bioavailability of metals in sediment can be influenced by several factors including sediment characteristics such as grain size distribution, mineral composition and organic content (Bartolli 2011). Therefore, it is important to study the distribution of the potentially toxic metals and its factors that can contribute to the increasing load of metals in the sediment. This research was carried out to illustrate the distribution of selected heavy metals (As, Cd, Cr, Cu, Pb and Zn), organic matter and grain size distribution in the sediment of Sungai Perlis estuary.

Materials and Methods

Sampling was done in Perlis River estuary which is located at the northern west of Peninsular Malaysia. Samples were collected during Southwest, Pre-monsoon, Northeast and Post-monsoon season. Ten sampling stations were carried out sampled based upon the anthropogenic pollution sources nearby the location. Figure 91.1 shows the location of the ten sampling stations. The surface of sediments in each station was collected by using Van Veen Grab. Sediment samples were placed in clean Polypropylene (PP) plastic bags and all samples were properly labeled to avoid any cross contamination.

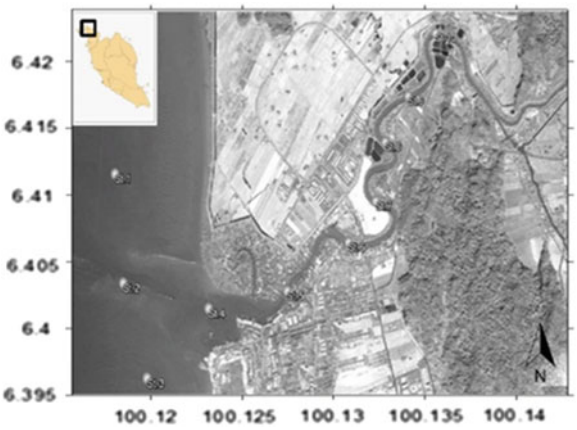

Fig. 91.1 Sampling stations in Perlis River

Sediment samples were dried in oven and grounded by using mortar and pestle. Then the samples were sieved through a 63 μm mesh size. For the analysis of total heavy metals, sediment samples were digested by following the published methods with some modifications (Jamil 2006; Noriki et al. 1980).

Mean size in sediment samples were determined by using laser diffraction method. Firstly, all carbonates were dissolved by using 4 M Hydrochloric acid solution (HCl). Then the organic components from sediment samples were removed by adding 50 % hydrogen peroxide (H_2O_2). Subsequently, the flocs of finer particles were break up by adding a dispersing agent (5 % calgon solution). Last but not least, the samples were later analyzed by using Particle Size Analyzer (PSA) system.

Results and Discussion

In general, the average heavy metals in sediment in at the Perlis River show the decreasing pattern as follows: Cr > Zn > Pb > Cu > As > Cd. It was found that Cr is the major metal component in the sediment of Sungai Perlis. Statistical analysis test (one way ANOVA) shows that there was no significant difference in both temporal and spatial distribution of As, Cd and Cu ($p < 0.05$) while for Cr, Pb and Zn were vice versa ($p > 0.05$). The result of recovery for each metal was in good agreement mostly between 100 and 115 %.

Fishing boats activities along the river may signify the source of Cr in the sediment. Primarily, Cr was used in paints especially on boat's hull in order to slow down the growth of organisms that attached to the hull (Ozkan 2012). Furthermore, runoff from the industrial areas and the main city of Perlis (Kangar) may be carried to the Sungai Perlis during rainfall which can be explained by the elevated level of Zn in the river. This result was in the line with the finding by

Water Monitoring Branch (2005) and Fortune (2006) where storm water from urban areas has increase the Zn loads to 60 times higher than background levels. Elevated concentrations of Pb were also found at a number of sites mostly at the upstream areas (St 8–St 9). Bridge oil from boats may be contributed to the Pb source which originates from leaded fuel use by fishing boat (Fortune 2006). Moreover, the sources of As was possibly byproduct from agriculture and aquaculture activities at St 7 and St 8 that uses As in pesticides and as additives in fish/shrimp food (Jain and Ali 2000). The average Cu and Cd concentration were much lower than average shale values of 14.00 mg/kg dry weight and 0.10 mg/kg dry weight respectively (Wedepohl 1995). This finding suggest that both metals may originate from the natural sources due to the weathering and geological process.

The average mean size for sediment along Sungai Perlis can be classified as medium to fine silt. The dominating of high percentage of fine silt may result from the low velocity depositional in the river (Fortune 2006). Generally the mean size gives a simple indication of the magnitude of the force, applied by water or wind which will affect the mean size of the grains.

The distribution of organic matter was ranged between 3.90 and 7.56 % in the Perlis River where higher percentage of organic matter was found at the upstream river. Upstream river hold various anthropogenic sources including domestic waste, aquaculture and agriculture activities, land development and industrial waste. Based on research by Galois et al. (2000), the origin of estuarine organic matter depends on the socio-economic environment through the effects of urbanization, industrialization and regional development.

In this research, the correlation of Pearson showed that the concentrations of heavy metals and grain size in the sediment varied independently from one another. From the data obtained, all metals have no significant correlation with the mean size but rather significant with the organic matter.

Conclusion

Data analysis shows that anthropogenic activities have greatly affect the heavy metals level in the sediment of Sungai Perlis. The spatial analysis also revealed that upstream river accumulating metals at significant level compared to downstream river. The significant correlation found between heavy metals and organic matter shows that organic matter has much more influenced on metals availability compared to grain size in the sediment in at Perlis River. This finding is expected to provides a new set of data for metals, organic matter and grain size in Perlis River as well as to update the current status of the river.

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Chapter 92
Impact of Poultry Manure and Ashed Sawdust in the Phytoextraction of Cadmium and Lead from Crude Oil Contaminated Soils

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Abstract The efficiency of composted poultry waste (CPW) and ashed sawdust (ASD), both singly and in combination as soil amendments for the remediation of Cd and Pb from crude oil contaminated soils was assessed. The CPW and ASD were mixed at different ratios [0:4, 1:3, 2:2, 3:1 and 4:0] to give five manure treatments, each was applied at 0, 4 and 8 t ha^{-1}. There were also three levels of crude oil soil contamination [0, 1 and 2 % (v/v)] and replicated thrice in a factorial completely randomized design. At full maturity, the harvested sunflower plants were separated into roots, shoots and grains, and thereafter analyzed for Cd and Pb uptake. Highest uptake for Cd was 0.63 mg kg^{-1} (shoot), 0.60 mg kg^{-1} (root) and 0.14 mg kg^{-1} (grains) and for Pb was 0.94 mg kg^{-1} (shoot) 0.79 mg kg^{-1} (root) and 0.17 mg kg^{-1} (grains) obtained at 8 t ha^{-1} of CPW application. Except for the soil acidity, total nitrogen and organic carbon; the relationship between Cd and Pb, and with other soil nutrients (Ca, Mg, K and Na) were inversely and significantly correlated.

Keywords Heavy metals · Phytoremediation · Crude oil · Composed poultry manure · Ashed sawdust · Sunflower

Highlights

- Composted poultry waste achieved better Cd and Pb uptake than ashed sawdust.
- Cd and Pb levels correlated positively with soil acidity, total N and organic.
- Sunflower can function in Cd and Pb uptake from crude oil contaminated sandy soil.

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Introduction

Crude oil is found in many parts of the world. Nigeria is one of the major producers of crude oil and the negative impact of oil exploitation on the environment is increasing tremendously. Presently in Nigeria, there is development strategies aimed at increasing crude oil production per day but with no pronouncement on the mitigating measures to combat environmental pollution arising from oil exploitation. Crude oil is a mixture of complex organic compounds, and also with variable concentrations of different metals (Overton et al. 1994). A large percentage of farm land in the oil-producing Niger Delta region of Nigeria had been degraded due to pollution from oil spills and pipeline leakages and thereafter, abandoned by their owners. The residue effects of crude oil pollution can reside in the soil for many years, if remedial steps are not taken to combat it. Any technique to remediate soil pollution must be eco-friendly, cheap and easy-to-use. Of all the remedial methods, phytoremediation; which is the use of plants to extract, sequester and or detoxify various kinds of pollutants (Zayed et al. 1998) has these qualities.

Several workers such as Dushevkov et al. (1995) and Adewole et al. (2010) had remediated heavy metal-polluted-soils with sunflower (*Helianthus annuus* L.). But these heavy metals were from the inorganic source. However, there is a dearth of information on the use of sunflower for the remediation of heavy metals from crude oil origin that had contaminated soil when composted poultry manure and ashed sawdust are used as soil enhancers. The choice of these organic materials as soil amendments was due to their abundance in Nigeria and the way they are incessantly burnt. This study therefore assessed the ability of sunflower to remediate Cd and Pb, constituents of crude oil from crude oil contaminated soil when different rates of composted poultry manure and ashed sawdust were used as soil amendments. The study also determined the effectiveness of these organic manures at different application rates for the remediation of Cd and Pb from crude oil contaminated soils.

Materials and Methods

The study was conducted in a screenhouse of the Obafemi Awolowo University (OAU), Ile-Ife, Nigeria. Surface soil was collected from an exhausted crop land within OAU, air-dried for 7 days, and sieved using a 2 mm sieve. Fresh poultry droppings were collected and aerobically composted for 3 months. Sawdust collected was also ashed. The composted poultry waste (CPW) and ashed sawdust (ASD) were mixed at different ratios (0:4, 1:3, 2:2, 3:1 and 4:0) to give five manure treatments. The crude oil, obtained from a local petroleum corporation was prepared to different levels of concentrations [0, 1 and 2 % (v/v)] as contaminants. Each of the one hundred and 35 polythene pots with drainage holes at the bottom

was filled with 5 kg of the sieved surface soil and placed on the tables in the screenhouse. The contaminants and manure treatments, also applied at three levels (0, 4 and 8 t ha^{-1}) were imposed to degraded surface soil, moistened with deionised water to field moisture capacity and allowed to equilibrate for two weeks. Each treatment was replicated three times and arranged in a factorial completely randomized design.

Viable seeds of sunflower purchased from the Institute of Agricultural Research and Training, Ibadan, Nigeria were planted at four seeds per pot and thinned to two stands per pot 2 weeks after sowing. The thinned stands were retained in their respective pots. The pots were maintained weed-free and regularly watered throughout the experimental period, but with caution to prevent leaching. At full physiological maturity stage, sunflower plants were carefully removed from the polythene pots by allowing the running tap water to flush out the attached soil particles. The plants were rinsed with deionised water. A clean and sharp knife was therefore used to separate the sunflower plants into roots and shoots, oven-dried for 48 h at 70 °C, weighed, ground, and stored. The harvested grains of sunflower were hand-threshed, dried and stored.

The pre- and post-soil tests were carried out to assess the selected properties and heavy metal content of the soil. Chemical compositions of composted poultry manure, ashed sawdust and crude oil were also determined. The particle size analysis of the soil was determined using hydrometer method (Bouyoucos 1951). Soil pH was determined potentiometrically in 1:1 soil–water ratio (McLean 1982). Organic carbon content of the soil and manure wastes was determined using Walkey-Black method (Nelson and Sommers 1982). The total nitrogen of the soil and manure wastes was determined by the macro-Kjeldahl method (Bremner and Mulvaney 1982). The available phosphorus in the soil and manure wastes was determined by Bray P1 method (Olsen and Sommers 1982). The Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} in the soil and manure wastes were extracted using 1 M ammonium acetate buffered at pH 7.0 (Thomas 1982). The concentrations of Ca^{2+} and Mg^{2+}in the extracts were measured using Buck Scientific 210/211 VGP (East Norwalk, Connecticut USA) Atomic Absorption Spectrophotometer (AAS), while K^{+} and Na^{+} were read on Gallenkamp flame photometer. The extractions of Cd and Pb in the crude oil, plant tissues and grains of sunflower were determined using Juo (1979) method and their concentrations read using an AAS. The mean concentrations in the root, shoot and grains were multiplied by their mean dry weight to obtain the uptake of Cd and Pb by the test plant.

Results and Discussion

The proportions of sand, silt and clay of the soil were: 860.0, 84.0 and 56.0 g kg^{-1} respectively, indicating a sandy soil texture. The soil used for the experiment was relatively slightly acidic (pH = 6.60) with high carbon/nitrogen ratio (77.50) indicating a slow nitrogen release soil. The cation exchangeable capacity

($Na^+ + K^+ + Mg^{2+} + Ca^{2+}$) was 1.49 cmol kg^{-1}. This confirmed the degraded state of the soil used for the study. The Cd and Pb concentrations in the soil were each 0.02 mg kg^{-1}; which was considered very low compared with 13.23 and 32.28 mg L^{-1} respectively for the crude oil. The composted poultry waste (CPW) had higher carbon/nitrogen ratio (7.14) than ashed sawdust (ASD) (220.41). This could have contributed to the better performance of CPW when singly applied than ASD. Organic manure with carbon/nitrogen ratio lower than 20 releases organic nitrogen for enhanced growth of crop better than those with carbon/nitrogen ratio greater than 20 (Olayinka 1996).

This superior quality of CPW over ASD as soil enhancer must have led to better dry matter yield of sunflower when the two were compared. With increasing CPW in the combinations, there was also increase in the dry matter yield of sunflower. The order of increase was: Control $< CPW_0ASD_4 < CPW_1ASD_3 < CPW_2ASD_2 < CPW_3ASD_1 < CPW_4ASD_0$. The manures applied enhanced the establishment and growth of sunflower as evident in the dry matter yield obtained. This result could be due to the unfavourable condition created by the crude oil on the soil physical properties. Parts of the soil pores might have been 'sealed up' by the sticky crude oil, thereby reducing the rate with which sunflower roots intercept and absorb the heavy metals. Njoku et al. (2000) earlier stated that the cell membrane of roots of plants for remediation was adversely affected in crude oil contaminated soil. At 8 t ha^{-1} of CPW when singly applied, 10.3 % of Cd and 5.9 % of Pb were optimally extracted from 2 % crude oil contaminated soil. The percent removal was however reduced at lower application rates of soil enhancers, and also when CPW was combined with ASD. The applied manures increased the soil acidity, and hence made the metals more available and mobile (Adewole et al. 2010). However, the control pots showed evidence of 'mining' of the soil nutrients as all the soil properties were lower than in the pre-cropping soil properties. Except for the soil acidity, total nitrogen and organic carbon; the relationship between Cd and Pb, and with other soil nutrients (Ca, Mg, K and Na) were inversely and significantly correlated. An inverse correlation implies that when the concentration of Cd and Pb increased with addition of manures; calcium, magnesium, potassium and sodium reduced.

Conclusion

The study concluded that sunflower could be effectively used for the remediation of Cd and Pb from crude oil contaminated sandy soil of Nigeria when 8 t ha^{-1} of composted poultry manure application is used.

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Chapter 93
The Invasive Weed, *Asystasia gangetica* as a Biomonitor of Heavy Metal Bioavailability and Pollution

Yap Chee Kong and Weiyun Chew

Abstract In this study, the weed *Asystasia gangetica* and surface soils were collected from six sampling sites in Peninsular Malaysia, including two landfill sites (Matang and Sg. Kembung), one industrial site (Juru) and three residential sites (Bukit Rasa, Ijok and Pagoh). The plants were separated into roots, stems and leaves. The ranges of metal concentrations (μg/g dry weight) in these pooled roots, stems and leaves were 0.03–1.01, 0.03–0.66 and 0.03–0.94, respectively for Cd; 12.1–27.9, 6.76–10.0, 9.92–19.8, respectively for Cu; 201.9–929, 27.8–579 and 87.1–1299, respectively for Fe; 1.01–3.36, 0.64–2.20 and 0.10–4.95, respectively for Ni; 4.58–8.28, 1.76–7.79 and 2.10–21.79, respectively for Pb; and 66.0–161, 52.6–148 and 35.7–159, respectively for Zn. Elevated metal levels were found in the industrial site at Juru and the landfill site at Sg. Kembung in *A. gangetica*, indicating high bioavailabilities to the weed. The accumulation patterns were Root > Stem > Leaf for Zn, Root > Leaf > Stem for Fe, Cu and Cd, and Leaf > Root > Stem for Ni and Pb. Based on the metal levels and clustering patterns, the different weed parts were shown to be potential biomonitors of heavy metal pollution. The Juru site was evidently found to be the highly metal-contaminated and had highest bioavailability of heavy metals. The Sg. Kembung site was found as the most metal-polluted site in which the levels of Cd, Cu, Ni, Pb and Zn in the soils exceeded the soil quality guidelines. The different weed parts could be used as biomonitors of heavy metal bioavailabilities and contamination of the sampling sites; in particular, the stem of the plant was a good biomonitor for Cu pollution.

Keywords Biomonitor · Heavy metals · Different parts · Soils

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Highlights

- Elevated metal levels in plants and soils in Juru and Sg. Kembung.
- The accumulation patterns in the plants were higher in the root.
- The metals in soils exceeded the soil quality guidelines.
- *Asystasia gangetica* could be used as good biomonitors.

Introduction

In this study, *Asystasia gangetica* was chosen due to the facts that this species has fulfilled most of the criteria for a good biomonitor as mentioned above. The plant was first introduced into Malaysia from India as ornamental plants in 1876 (Kiew and Vollesen 1997) but now this plant has become an invasive weed and can be widely found in urban and rural areas in Peninsular Malaysia (Kiew and Vollesen 1997).

There had been many studies on the plant as a biomonitor of the anthropogenic heavy metals (Junior et al. 2009). They demonstrated that metal concentrations in different parts of plants (e.g. leaf and roots) are able to reflect the urban areas ambient air pollutants concentrations, and even to discover the origin of the possible pollutants sources. The objective of this study was to determine the contamination and bioavailabilities of heavy metals of the sampling sites by using different parts of *Asystasia gangetica* as biomonitors.

Materials and Methods

The samples were collected between 21 April and 15 December 2011 from six sampling sites in Peninsular Malaysia and the samples information is given in Table 93.1. Four to six individuals of *A. gangetica* were taken from sampling location and immediately transported to the laboratory. About 1–10 cm of the surface soils were also sampled using a clean stainless steel soil sampler. The surface soils were dried and sieved through 63 μm test sieve in order to collect the clay and silt fraction of the surface soil. Washed plant samples were divided into leaves, stems and roots. The plant tissues and the soils were dried at 80 °C for 3–4 days. The metal analysis followed that as done by Yap and Pang (2011) for soils and Ong et al. (2011) for plant parts. The samples were then homogenized before being analyzed by using a flame Atomic Absorption Spectrophotometer Model A Analyst 800.

To avoid possible contamination, all the glassware and equipment used were acid-washed. Procedural blanks and quality control samples made from standard solutions (1,000 ppm) for all the six metals were analyzed once for every five

Table 93.1 Samples information of the present study

Sites	Sampling date	GPS-N	GPS-E	Plant height	Site description
Kg. Bkt. Rasa	21-Apr-11	3° 30′ 16.80″	101° 38′ 0.80″	93.0	Residential
Ijok	21-Apr-11	3° 19′ 38.00″	101° 25′ 8.00″	59.1	Residential
Matang	27-Apr-11	4° 49′ 16″	100° 40′ 44″	122.0	Landfill
Sg. Kembung	2-Jul-11	2° 53′ 8.30″	101° 49′ 20.80″	90.7	Landfill
Juru	2-Aug-11	5° 20′ 56.00″	100° 24′ 45.10″	54.5	Industrial
Pagoh	15-Dec-11	2° 10′ 59.00″	102° 44′ 46.00″	107.1	Residential

samples in order to check for sample accuracy. The quality of the methods used was also checked with Certified Reference Materials for Soil-5 (IAEA, Vienna) and the recoveries are being acceptable (80–120 %).

For the analytical procedures for four geochemical fractions of the surface soils, sequential extraction technique (SET) described by Badri and Aston (1983) was adopted. The SET included four fractions namely (1) easily, freely, leacheable or exchangeable, (2) acid-reducible, (3) oxidisable-organic and (4) resistant.

For statistical analysis, correlation analysis and cluster analysis based on "Single Linkage Euclidean distances was performed by using STATISTICA 99" Edition (Version 5.5). All the data were $\log_{10}(\text{mean} + 1)$ transformed in order to reduce the variance.

Results and Discussion

The metal concentrations in all sampling sites are shown in Table 93.2. For Cd, the highest levels were found in root and stems of Pagoh while Matang had the highest of Cd in leaf. For Fe, the highest levels were found in the root of Matang while Juru had the highest level of Fe in stem and leaf. For Cu, the highest levels in root, stem and leaf were found in Pagoh, Kembung and Juru, respectively. For Ni, the highest levels in root, stem and leaf were found in Ijok, Juru and Matang, respectively. For Pb and Zn, the highest levels in the three parts were consistently found in Juru. The accumulation patterns were Root > Stem > Leaf for Zn, Root > Leaf > Stem for Fe, Cu and Cd, and Leaf > Root > Stem for Ni and Pb. Generally, higher levels of Cd, Cu, Ni, Pb and Zn are found in Juru and Kembung. The highest Fe is also found in Juru, followed by Pagoh and other sites. The different accumulation patterns found in the plants indicated different accumulation uptake and sequestration of the different plant parts.

Based on the three plant parts of five common toxic metals (Cd, Cu, Ni, Pb and Zn), the clustering patterns clearly showed two major entities dividing into Juru and other sites. The clearly showed that the highest metal bioavailabilities to the three plant parts was found at Juru. This clustering pattern is slightly different when compared to the clustering pattern based on the same five metals in the four geochemical fractions, summation of four fractions and nonresistant fractions in

Table 93.2 Mean concentrations (μg/g dry weight) of metals in the roots, stems and leaves of *Asystasia gangetica* collected from all the sampling sites

	Cd			Cu			Fe		
	Root	Stem	Leaf	Root	Stem	Leaf	Root	Stem	Leaf
Rasa	0.03	0.40	0.03	14.12	7.49	17.25	408.41	27.87	87.08
Ijok	0.61	0.03	0.03	12.12	7.08	9.92	730.22	28.92	165.06
Matang	0.05	0.56	0.94	19.04	6.76	12.56	929.08	40.77	176.21
Kembung	0.07	0.52	0.92	20.34	10.02	16.18	201.99	81.08	287.93
Juru	0.03	0.29	0.03	13.20	9.72	19.77	431.40	579.24	1299.49
Pagoh	1.01	0.66	0.62	27.95	6.92	12.19	814.34	33.82	88.12
		Ni			Pb			Zn	
	Root	Stem	Leaf	Root	Stem	Leaf	Root	Stem	Leaf
Rasa	1.80	1.39	0.10	6.28	2.61	6.11	128.01	88.10	35.71
Ijok	3.36	1.31	2.27	5.56	1.76	7.90	66.01	54.23	38.71
Matang	2.52	1.27	4.95	5.75	2.59	3.87	144.17	78.36	64.16
Kembung	1.15	1.00	3.25	4.58	2.42	6.08	91.40	52.61	51.36
Juru	1.01	2.20	3.73	8.28	7.79	21.79	161.10	147.89	159.95
Pagoh	2.01	0.64	2.95	5.17	4.75	2.10	117.65	82.51	77.77

the surface soils of all sites. There are again two major clusters but one of the major clusters consisting of Juru and Kembung while the other including all the rest of the four sites. This shows that Juru and Kembung had high contamination of metals when compared to the other four sites. This could be related to its being a landfill site at Kembung and industrial area at Juru. However, only Juru was shown to have high metal bioavailabilities. Moreover, Juru has been constantly reported as being a heavy metal-polluted area in Peninsular Malaysia due to its heavy industrial activities (Yap and Pang 2011). Based on correlation analysis, the stem correlated significantly ($p < 0.05$) with soil Cu geochemical fractions, thus, the stem is a good biomonitor for Cu pollution.

The total concentrations of metals in soils of all sampling sites are presented in Table 93.3 and comparisons with established Soil Quality Guidelines (SQGs) are made. The highest levels of all the metals are found at Kembung, followed by Juru and other sites. For Cd, Cu and Zn, only the landfill site at Kembung exceeded all the SQGs including the intervention values for the three metals by Dutch Soil Guidelines (Vrom 2000) while Cd, Cu, Ni and Pb in Juru soils exceeded target values by the Canadian soil quality guidelines (CSQG) for Agricultural soils for the four metals (CCME 2001) but below the intervention values. However, Zn in Juru soils exceeded the intervention value for Zn. At the landfill site in Matang, Cd exceeded the target value for Cd and Pb exceeded both CSQG and target value. Other sites should not pose an environmental concern since the metal levels were all below the two SQGs.

Table 93.3 Comparisons of total concentrations (μg/g dry weight) of metals in the soils with soil quality guidelines

Sites	Cd	Cu	Ni	Pb	Zn
Rasa	0.23	6.62	3.44	17.1	11.03
Ijok	0.78	4.66	9.19	32.5	19.23
Matang	1.11	8.42	8.00	90.27	39.86
Kembung	12.43	1847.6	75.7	495.2	3820.4
Juru	3.98	88.2	24.8	261.9	2368.7
Pagoh	0.50	9.55	7.85	47.3	50.31
Overall	0.23–12.4	4.66–1848	3.44–75.7	17.1–495	11.0–3820
Canadian soil quality guidelines (agriculture) (CCME 2001)	1.40	63.00	50.00	70.00	200
Dutch soil guidelines (Vrom 2000)					
Target value	0.80	36.0	35.0	85.0	140
Intervention value	12.0	190	210	530	720

Conclusion

High metal levels were found in the industrial site at Juru and the landfill site at Sg. Kembung in *A. gangetica*, indicated high bioavailabilities of the metals to the plant. Based on the soils, the Juru and Sg. Kembung were found as highly metal-polluted sites that exceeded the soil quality guidelines. The different plant parts could be used as biomonitors of heavy metal bioavailabilities and contamination of the sampling sites; especially, the stem for Cu pollution.

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Chapter 94
Determination of Polycyclic Aromatic Hydrocarbons in Suspended Solid from Pengkalan Chepa River, Kelantan, Malaysia, Based on Weather Condition

Seyedreza Hashemi, Mohamad Pauzi Zakaria and Noor Zuhartini Md Muslim

Abstract Pengkalan Chepa River is located in the urban area that receives pollution loads from surronding area, sewage treatment and industrial garages and workshops. This research focuses on the determination of PAHs in suspended solid in Pengkalan Chepa River during rainy day, rainy season and sunny day. Total concentrations of PAHs in suspended solid in rainy day ranged from 323.5 to 1,153.1 ng/g while 7,421.2–1,786.71 ng/g in rainy season and 353.7–560.8 ng/g in sunny day.

Keywords Pengkalan Chepa river · PAHs · Suspended solid · Weather condition

Highlights

- PAHs concentration during rainy days was higher.
- Evidence of variations of PAHs concentrations with weather conditions.
- Low molecular weight PAHs (2-3 rings) were more abundant during sunny days.

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) is an ubiquitous pollution in the environment. Weather condition in most of the previous studies has affected the PAHs contamination (Delhomme et al. 2008; Zhao et al. 2008; Reinosdotter et al. 2006). PAHs do not dissolve in water but are attached to the suspended solid (SS) and settle down to become part of the sediment (Yoshida et al. 2002). Low molecular weight PAHs are water soluble and sensitive to microbial degradation and evaporation during the time in the environment (Pagni and Dabestani 2005). Biodegradation in aquatic is also depends on environmental condition (Bamforth and Singleton 2005).

The amount of PAHs in surface runoff from urban area will give impact to river water PAHs pollution (Zhao et al. 2008). Hydrophobicity also plays an important role that affects PAHs water pollution (Conte et al. 2001).

PAHs also affect the environment and living organism (Owabor et al. 2012). Health effect of PAHs from inhalation exposure is lung, gut, and skin cancer (Mastrangelo et al. 1996; Liu et al. 2008). PAHs pollution in Malaysia comes from a variety of sources, for example from dust road, tar ball and used oil.

In this research concentration of 16 USEPA PAHs (Na, Can, Ac, Flu, Phe, An, FLT, Pyr, BaA, Chr, BbF, BkF, BaP, BghiP, IcdP and BahA) in six sampling sites of Pengkalan Chepa River was determined. Pengkalan Chepa River is located in the urban area of Kota Bharu District, Kelantan State, Malaysia. The map of location is represented in Fig. 94.1.

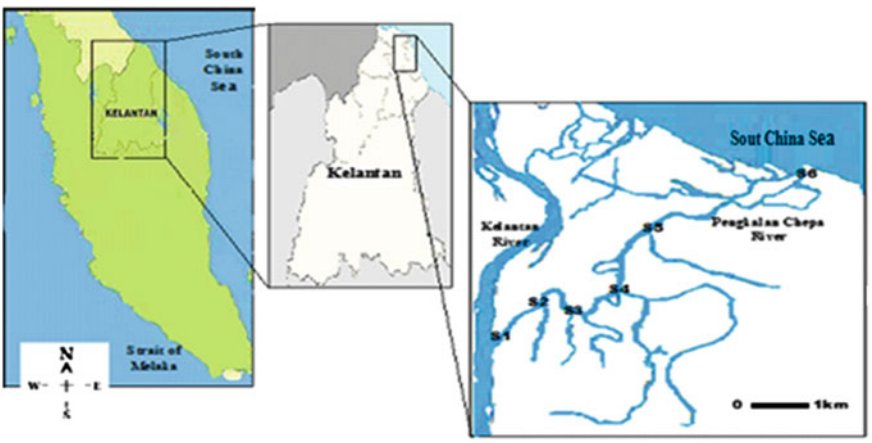

Fig. 94.1 Location of sampling area

Materials and Methods

The samples were collected during three weather condition, rainy season, rainy day and sunny day. Rainy season refers to 1 week of continuous raining while rainy day refers to 1 or 2 h of raining condition and sunny day refers to 1 week of no rain. During the rainy season, four water samples from four sampling sites (S2, S3, S4 and S6) of PCRB (one in each site) were collected while in rainy day, 12 samples from six sampling sites (two samples in each site) and in sunny day, 18 water samples from six sampling sites (three samples in each site).

Analytical procedure for PAHs extraction and fractionation follows the method described by Zakaria et al. (2002) and further analyses were done using Gas Chromatography Mass Spectrometer.

Results and Discussion

Results of suspended solid in water samples during rainy season, rainy day and sunny day were analysis and compared (Fig. 94.2). In rainy season the concentration of PAHs in the whole Pengkalan Chepa River were 20,702 ng/g dry weight. This concentration was about ten times more than PAHs concentration on sunny day which was 2,145 ng/g dry weight. During the rainy season, a high level of precipitation and high amount of urban runoff washed the pollutant, waste material and all contamination from surrounding area and causes direct and indirect river pollution (Berbee et al. 1999; Hoffman et al. 1984). The lowest concentration in PAHs was recorded in rainy day by 621 ng/g dry weight. On sunny day, sources of PAHs pollution were mainly from atmospheric PAHs pollution such as exhaust, air dust and wastewater discharge from work shop (Boonyatumanond et al. 2007). For PAHs composition (Fig. 94.3), in rainy season, Phe and Pyr were reported in high level, while on sunny day it was Phe and Na. According to Krauss et al. (2005), combustion of wood, grass, bio mass and fossil fuel are the main source of Na.

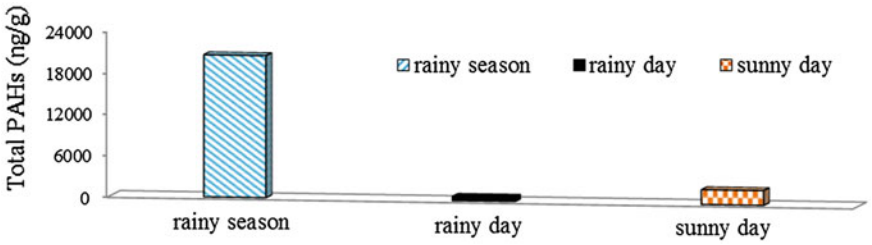

Fig. 94.2 Total PAHs in PCR in rainy season, rainy day and sunny day

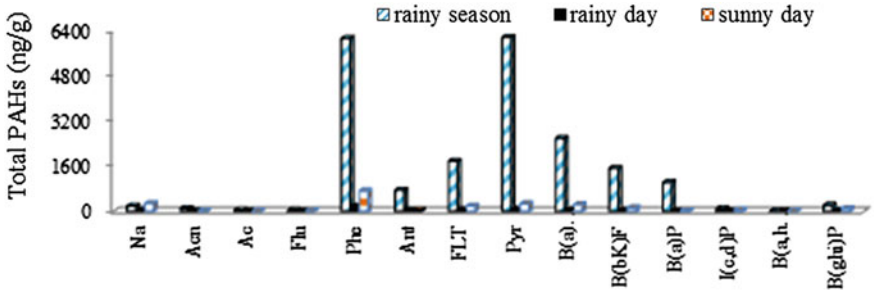

Fig. 94.3 16 PAHs in SS in rainy season, rainy day and sunny day

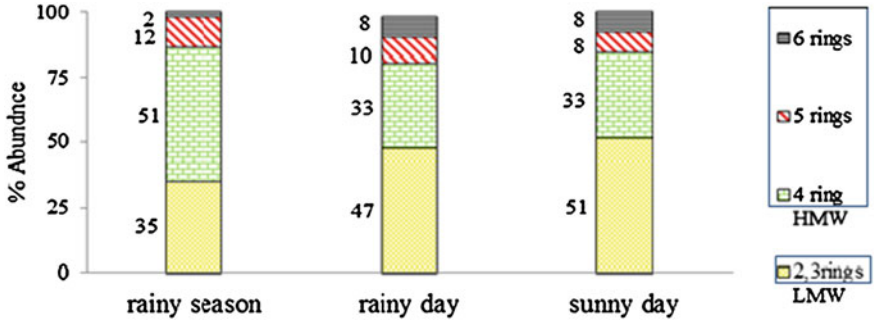

Fig. 94.4 LMW, HMW PAHs in SS in rainy season, rainy day and sunny day

Figure 94.4 reported the percent abundance of 2, 3-ring (LMW) to 6-ring PAHs from the Pengkalan Chepa River suspended solid in rainy season, rainy day and sunny day. From the graph, it shows that 2, 3 ring (LMW) PAHs was more abundant on sunny day by 51 % followed by rainy day and rainy season.

Conclusion

Results from water analyses in different weather condition, showed that PAHs concentration in rainy season was higher than rainy and sunny day. This is because high level of precipitation and high amount of urban runoff washed the pollutant, waste material and all contamination from surrounding area and causes direct and indirect river pollution. In the water sample, concentration of PAHs was measured via suspended solid because suspended solid has a significant role in transportation, biodegradation, preservation and hydrophobicity of PAHs. Result also showed that all 16 USEPA PAHs were present in the water bodies in all-weather condition with Phe and Pyr as the abundant concentration during rainy season. The high concentration of Phe in the river is because it is related to higher

water solubility and bioavailable properties of Phe compound. Urban runoff and street washout have shown significant role in high concentration of PAHs in rainy condition. In both rainy season and rainy day, HMW PAHs were recorded with the highest concentration. Low rate of microbial activity and high molecular affinity are the main reasons of abundant HMW PAHs concentration.

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Chapter 95
Arsenic Contamination in Groundwater and Human Health Risks in the Mekong River Basin of Cambodia

Kyoung-Woong Kim and Kongkea Phan

Abstract In order to investigate the human health impacts of arsenic in well water, groundwater and biological samples were collected from three provinces in the Mekong River basin of Cambodia and a health risk assessment model from U.S.EPA was applied. Results revealed that 98.65 % of respondents from the Kandal province study area were at risk of the potential non-cancer effect and an average cancer risk index was found to be five in 1000 exposure. The calculations also indicated that, in the Kratie province study area, 13.48 % of respondents were affected by non-cancer health risks and 33.71 % were threatened by cancer, whereas none of respondents in the Kampong Cham province study area appeared to have non-carcinogenic effect. Significant positive intercorrelations between groundwater arsenic concentration (As_w), arsenic in hair (As_h), fingernail (As_{fn}) and toenail (As_{tn}) suggested that As_h, As_{fn} and As_{tn} could be used as biomarkers of chronic arsenic exposure from consuming arsenic-enriched groundwater. Analytical results also showed that arsenicosis patients had significantly higher blood arsenic (BAs) and lower serum albumin (SAlb) than asymptomatic villagers. Arsenicosis symptom was 76.4 % more likely to develop among individuals having SAlb $\leq$ 44.3 g L^{-1} than among those who had SAlb $>$ 44.3 g L^{-1} and 117.6 % as likely to occur among those with BAs $>$ 5.73 μg L^{-1} than among those having BAs $\leq$ 5.73 μg L^{-1}.

Keyword Groundwater · Biomarker · Arsenicosis · Cambodia

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Highlights

- Arsenic concentrations in groundwater range from <0.03 to 1841.50 μg L^{-1}.
- Arsenic is predominantly found in the reduced form.
- As_h, As_{fn} and As_{tn} can be used as biomarkers of chronic arsenic exposure.

Introduction

Chronic exposure to arsenic-rich groundwater has created a substantial public health concern in Cambodia and many other parts of the developing worlds. Arsenic contamination in Cambodian drinking water sources was detected during the national drinking water quality assessment, conducted jointly by the Ministry of Rural Development and the Ministry of Industry, Mines and Energy between 1999 and 2000 (Feldman et al. 2007). To date, high arsenic concentrations in Cambodian groundwater have been reported. For instance, groundwater arsenic concentrations in the Mekong delta of Cambodia ranged from below the limit of detection up to about 900 μg L^{-1} with about 54 % of all the samples collected exceeding the WHO's drinking water guideline value of 10 μg L^{-1} (Polya et al. 2005; Stanger et al. 2005). In particular, arsenic concentrations in the groundwater in Kandal province ranged from 6.64 to 1543 μg L^{-1} with the average and median concentrations of 552 and 353 μg L^{-1}, respectively (Luu et al. 2009; Sthiannopkao et al. 2008). Arsenic was released from the near-surface, river derived sediments within the Mekong River delta and transported to the underlying aquifer by groundwater flow (Polizzotto et al. 2008). Although many populations live alongside surface waters in Cambodia, shallow groundwater is still the main source for drinking water. Therefore, this study aims to provide a comprehensive investigation of arsenic exposure pathway in the Mekong River basin of Cambodia. Health risk assessment of arsenic from groundwater, validation of exposure biomarker, factors controlling the development of arsenicosis symptoms can provide additional evidences of the impacts on human health and society from the environmental arsenic.

Materials and Methods

The design of the present study was a cross-sectional study. Sampling was carried out within three purposely selected areas with different arsenic exposure scenarios in the Mekong River basin of Cambodia. Kandal province was selected as an extremely contaminated area. Kratie province was selected as a moderately contaminated area, and Kampong Cham province was selected as an uncontaminated

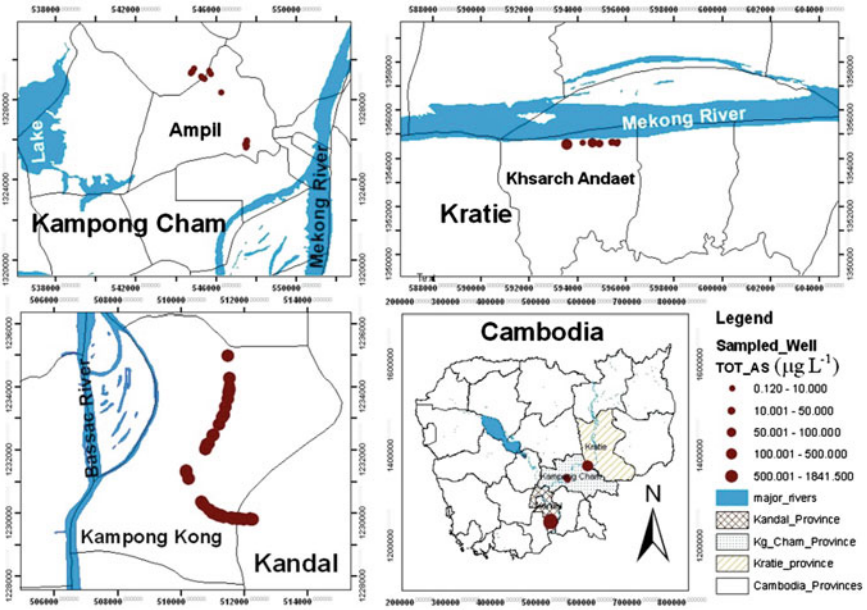

Fig. 95.1 Map of the sampling areas

area. Kratie and Kampong Cham provinces are located along the Mekong River upstream of Phnom Penh, whereas Kandal province is located between the Mekong and the Bassac Rivers, downstream of Phnom Penh (Fig. 95.1). Groundwater, hair fingernail and toenail samples were collected from residents in Kandal, Kratie and Kampong Cham provinces. In addition, spot urine and venous blood samples were also collected from arsenicosis patients and asymptomatic villagers in Kandal. After pretreatment, all chemical measurements of total arsenic concentration were performed by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7500 ce USA). Standard reference materials were analyzed in the same manners as samples to check the precision and accuracy of the analytical methods and analytical instruments. All statistical data analyses were employed by SPSS for Windows (Version 16.0). Significance was considered in circumstance where $p < 0.05$.

Results and Discussion

Analytical results of Cambodian groundwater samples show that the concentration of As ranges from <0.03 to 1841.50 µg L^{-1}. Arsenic was predominantly found in the reduced form, As (III) in the more reducing groundwaters of the Kratie and Kandal province study areas. In contrast, As (V) was mainly present in the oxidizing groundwaters of the Kampong Cham province study area. Health risk

Table 95.1 Percentage of residents exposed to toxic and carcinogenic effects in each of the study areas (%)

Study area	HQ > 1.00	Cancer risk probability (R)			
		>1 in 10^2	>1 in 10^3	>1 in 10^4	>1 in 10^6
Kandal (n = 297)	98.65	13.80	92.59	100.00	100.00
Kratie (n = 89)	13.48	0.00	0.00	33.71	97.75
Kampong Cham (n = 184)	0.00	0.00	0.00	0.00	93.48

HQ Hazard quotient; *R* Carcinogenic risk probability
1 in 10,000 is the highest safe standard for carcinogenic risk
1 in 1,000,000 is the safe standard for carcinogenic risk

assessment of inorganic arsenic intake through groundwater drinking pathway was presented in Table 95.1.

Biomarker study demonstrated that arsenic in hair (As_h), fingernail (As_{fn}) and toenail (As_{tn}) were highly elevated in the Kandal province study area. Concurrently, statistically significant positive intercorrelations between As_w, As_h, As_{fn} and As_{tn} were suggestive that As_h, As_{fn} and As_{tn} could be used as biomarkers of chronic arsenic exposure, in which As_h was more favorable than As_{fn} and As_{tn} due to the ease of sample processing and analytical measurements, respectively.

Binary logistic regression analysis was applied to assess the association between serum albumin (SAlb) and blood arsenic concentration (BAs) in both the presence and absence of arsenicosis symptoms in the study populations (Fig. 95.2). As a result, arsenicosis symptoms are 1.764 as likely to develop among those who have a SAlb $\leq$ 44.3 g L^{-1} (50th percentile of SAlb for asymptomatic villagers) than those with SAlb > 44.3 g L^{-1} (Odds Ratio = 1.764, 95 % CI = 0.999–3.114).

Similarly, the arsenicosis symptoms are 2.176 as likely to occur among those who have BAs > 5.73 μg L^{-1} (fiftieth percentile of BAs for asymptomatic villagers) than among those who have a BAs $\leq$ 5.73 μg L^{-1} (Odds Ratio = 2.176, 95 % CI = 1.223–3.872).

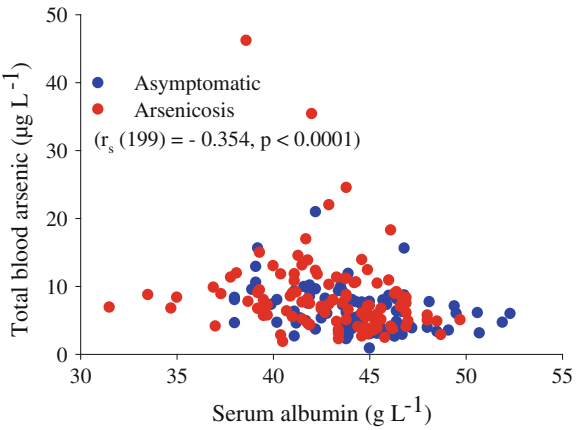

Fig. 95.2 Correlation between total blood arsenic (BAs) and serum albumin (SAlb) concentrations

Conclusions

Health risk assessment of arsenic intake through groundwater drinking pathway indicates that residents in the highly contaminated study area of Kandal are exposed to more toxic and carcinogenic risks than those in the Kratie and Kampong Cham provinces. Significant positive intercorrelations between groundwater arsenic concentration As_w, As_h, As_{fn} and As_{tn} suggest that As_h, As_{fn} and As_{tn} can be used as biomarkers of chronic arsenic exposure from consuming arsenic-enriched groundwater, in which As_h is more favorable than As_{fn} and As_{tn} due to the ease of sample processing and analytical measurements, respectively. Arsenicosis symptoms were found to be 1.764 more likely to develop among individuals having an SAlb ≤ 44.3 g L^{-1} than among those who have an SAlb > 44.3 g $^{-1}$ (Odds Ratio = 1.764, 95 % CI = 0.999–3.114) and 2.176 as likely to occur among those with BAs > 5.73 μg L^{-1} than for those having BAs ≤ 5.73 μg L^{-1} (Odds Ratio = 2.176, 95 % CI = 1.223–3.872).

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Chapter 96
Bridging the Gap: Research and Policy

Fatimah Mohamed Arshad

Abstract This paper examines the structural and cultural gaps between research and policy and the consequent under use of knowledge in environmental policy decision. The relationship is analysed from the perspectives of supply (research), demand (policy) and communication. The divide has to be rectified through structural adjustments particularly in establishing researcher-policy maker partnership in research as well as extending research scope that goes beyond examining a single constituent of a system, but a systemic view of the links between ecology, economic and institutional processes.

Keywords Research · Policy · Communication

Highlights

- Relationship between research and policy is not linear.
- Reductionist approach of environmental studies provide a partial view of the problem.
- Environmental policy research entails an integrated and multi-disciplinary study.

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Introduction

This paper examines the relationship between research and policy, that is, how research impacts policy, how policy impacts research and why they may not converge. Research produces and policy maker uses knowledge. Ideally, the two should be symbiotic, so that policy feeds on evidence based input and research feeds on policy needs. It is assumed that this relationship is linear and straightforward in that research is designed to meet the needs of the policy makers, and policy making is rationally based on relevant research findings or knowledge. However, in most cases, this relationship is weak and fraught. The two seem to be working independently with divergent goals or even when they meet, the interface is not smooth due to problems such as untimeliness, poor presentation and miscommunication.

The growing complexity of our environments calls for a closer knowledge sharing between the researchers and policy makers. There is a dire need of a greater understanding of the complex ecosystems often over long time frames, such as climate change, to provide solutions to environmental problems. However, these two elements; complexity and long time frames do not seem to augur well with the current society's economic chase and governance construct.

In explaining and seeking strategies to minimize the gap, the three major sectors are examined. They are; the supply of knowledge (research), demand (the policy makers) and communication (channels and effectiveness). The exchange and interaction between the supply and demand of knowledge holds the key to a better informed environmental policy decisions.

The Supply: Research

The Product

The nature of the product produced by the producers (researchers/scientists) determines its marketability. The most basic deliverable of scientific research is an individual peer-reviewed article published in an academic journal and rarely intended to guide policy decisions. Peer review is necessary to ensure the paper generates new data/knowledge, complies to the scientific norms and logical. In most cases, studies are carried out on a reductionist approach which is skewed towards a micro-perspective and partial view in contrast to the complexity nature of the environmental problem. Hence, it is almost always unwise to use these peer-reviewed papers as a basis for decision (Rogers and Gulledge 2010).

The other products include research reports and assessments, media writings, books, monographs, bulletins, though they may vary in quality, some are effective in sharing and relaying messages to policy makers and other stakeholders. Its infusion impact can be indirectly effective particularly in instilling values and

culture. Nevertheless, these types of publications receive poor ratings in the local academic incentive schemes as they are perceived as being non-scientific. Due to this, these outputs may not receive interests and commitment from the researchers/scientists and hence undermines their usefulness to the society.

Supply Problems

The followings are the major problems that "push" research findings away from the policy makers (Stone et al. 2001; Stone 2002; Nutley 2001).

(i) The public good problems—there is an inadequate supply of policy relevant research. The available literature is fragmented and predominantly small and ad hoc studies, often diverse in approach and the methodologies used are questionable. Majority of research are producer driven rather than user-oriented.
(ii) There is a lack of access to research, data and analysis by both parties.
(iii) There is a poor policy comprehension among the researchers about both the policy process and how research might be relevant to this process.
(iv) Researchers are not trained with communication skills of "selling" their findings to the policy makers.
(v) There is a lack of integration between the natural and social sciences in examining environmental issues when in reality there is a co-existence and interlinks between ecology, economic and institutional processes.
(vi) The nature of scientific research does not augur well with the premises and interests of the policy makers. For instance;

   a. Researcher chooses on making one change at a time, and holding other variables constant, compared to policy makers which emphasis on multiple changes and horse-trading between options (Heyman 2000).
   b. Researcher utilised randomised controlled trials as the best standard compared to the political difficulties of running trials on social policies.
   c. Researcher emphasise on central tendency while policy makers emphasise on the full diversity of the impacts of the policy.
   d. Researchers omit "outliers" while policy makers use them as a selling point.
   e. Researchers focus on maximum benefits while policy makers want general applicability.
   f. Researchers emphasise on the long term effectiveness while policy makers prefer short term results that fit within budgetary, electoral and other political concerns.

The Demand:Policy Makers

Policy Makers and Processes

The policy makers use a broad spectrum knowledge (research findings, expert advice, experiences etc.) to create policies. As for environmental policy, scientific knowledge is crucial in providing evidences and bases for decisions. The output of policy makers range from a general policy statement, sustainable development strategy, legislation (such as Environmental Quality Act), responses to actual or potential problems such as air and water pollution. It also includes the environmental aspects of policies in other areas such as agriculture, transport and energy. Policy processes are cyclical. It starts with problem definition and agenda setting, formal decision making, policy implementation and evaluation and identification of new problems. The cycle generates itself again over time.

The problems that hinder the policy makers in making optimum use of research findings are as follow (Stone et al. 2001; Stone 2002; Nutley 2001):

i. Policy makers provide a weak demand signal for knowledge as they are busy handling the problems of the day with little vision to plan about future information needs.
ii. Research uptake is undermined at times by the ignorance of politicians on the existence of policy relevant research.
iii. Policy makers and leaders may not be able to digest or absorb research work or output as they are driven by immediate political concerns.
iv. Politicisation of research distorts "true" knowledge to legitimise decision outcomes or reinforce existing policy preferences and decision.
v. The immediate timing decision of the policy makers do not synchronise well with the longer timelines involved in scientific inquiry which results in a mismatch and lag between knowledge production and its consumption.

Communication

The societal disconnection of both researchers and policy makers must be rectified through better communication. However, before presenting the information to the policy makers, it must satisfy the three critical characteristics, i.e., credible, salient and legitimate to ensure that it is effective in influencing social responses to public environmental issues (Taylor et al. 2004). The effective communication of science progresses in stages; conceptualization, documentation, and popularization (Scott 2000). Conceptualization involves translating ideas into concepts. Documentation refers to producing literatures to the intended audience. As for popularization, a third party may play an important role as the mediator between the scientists and policy makers.

A customized and effective marketing strategy must be adopted in selling "knowledge" to highly "politicized" users which have various stakeholders under their wings. A two-way communication system must be established to ensure continuous dialogues, knowledge sharing, research collaborations or partnerships. To communicate research findings to policy makers requires the researchers to build trust by being honest about underlying assumptions and other methodologies and explain the caveats of the model and its results and other methodological issues of the research.

Conclusion

Research is not a panacea to policy, but its knowledge applications may lead to a more informed policy decision. Facing a highly complex ecological problem, knowledge and evidences provide enlightened understanding and some clarities which improve policy debates and hopefully policy instruments. Research is an expensive affair for a developing country like Malaysia, hence, to optimize its utility in facing the environmental threats, research spending must yield an economic or social return in order development objectives in particular sustainability to be accomplished. It must demonstrate practical utility to the policy makers, industry and society at large. This requires a new investment approach in research, some rethinking of policy processes and the development of mechanism for bringing research and policy closer to one another. The current structure and culture gaps between research and policy are not conducive to a synergistic partnership of the two. The reductionist research may not provide the full picture of the problem to be of use to the policy makers who have a diverse of stakeholders under their wings. An integrated across discipline research is required to understand the interaction and circular causality between ecology, economic and institutional processes in the systems.

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Chapter 97
Application of a Monopole Sensor for Rapid *in situ* Water Quality Assessment: Theoretical Analysis

Mohamad Faiz Zainuddin, Zulkifly Abbas, Khairul Nizam Mohamed, Wan Mahmood Mat Yunus and Nurul Huda Osman

Abstract This initial study proposes a rapid and cost effective in situ water quality assessment based on reflection coefficient of a 1.749 cm long bare monopole senor. The reflection coefficient of the monopole sensor in air, water and ethanol were studied from measurement and calculations of Finite Element Method (FEM). FEM was used to calculate the reflection coefficient of the sensor in water/ethanol mixture solution.

Keywords Microwave · Monopole sensor · Water contamination

Highlights

- Good agreement between measured and calculated reflection coefficient.
- Dielectric constant decreases as water/ethanol ratio decreases.
- Reflection coefficient changes as water/ethanol ratio changes.

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Introduction

Currently, the standard procedure to assess water quality involves water sample collection and laboratory analysis. This procedure is highly accurate, but it is also tedious, slow, expensive, and can only be performed in a laboratory (Sun et al. 2011). Therefore, a rapid and cost-effective *in situ* water quality monitoring and assessment method is needed. Previous study has demonstrated that it is possible to detect water pollutants that exhibit high dielectric contrasts than water with microwave sensors such as monopole sensor (Shultz 2009). This is because the reflection coefficient (S11) of microwave sensors is dependent on the dielectric properties of a material under test.

This study aims to characterize the reflection coefficient (S11) of a 1.749 cm long bare monopole sensor in air, water, ethanol, and water/ethanol mixture solution. It is necessary to examine the sensitivity of monopole sensor to the presence of ethanol which was selected in this study to act as the "pollutant." The finite element method (FEM) was used in this study to estimate the reflection coefficient. FEM is a well-established numerical method to estimate S11 of a monopole sensor.

Materials and Methods

The experimental setup consists of the 1.749 cm long bare monopole sensor, the 50 Ohm low loss cable, the Agilent Field Fox network analyzer, beaker, retort stand and scissor jack. The Agilent 85070B open ended dielectric probe was used for permittivity measurement. The measurement was taken between 100 MHz and 4 GHz.

The relative permittivity (ε) of a material consists of dielectric constant (ε') and loss factor (ε''):

$$\varepsilon = \varepsilon' + j\varepsilon'' \tag{97.1}$$

The S11 is the ratio between reflected (P_t) and transmitted power (P_r) from the sensor:

$$\mathrm{S11} = \frac{P_r}{P_t} = \frac{Z_s - Z_o}{Z_s + Z_o} \tag{97.2}$$

Where

Z_s the characteristic impedance

Z_o the characteristic impedance

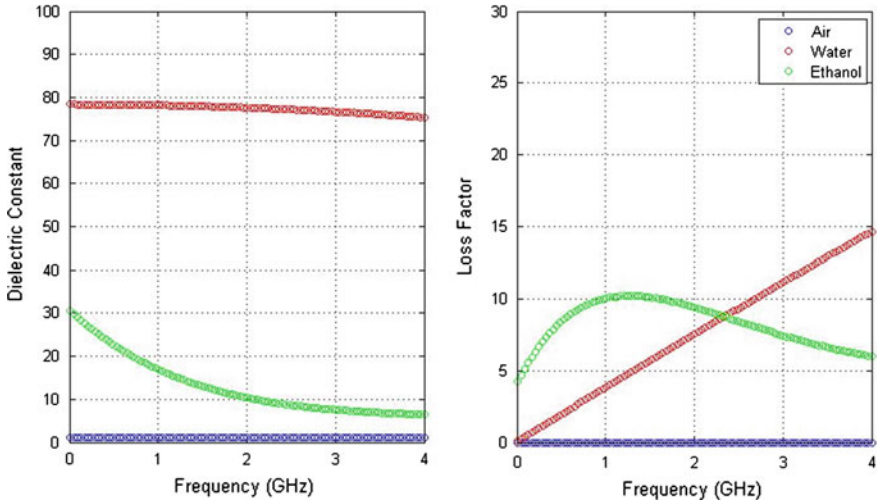

Fig. 97.1 The plot of permittivity values for air, water and ethanol obtained from Agilent 85070B measurement

Theoretically, the impedance Z_s is a function of ε and the detail on Z_s formulation can be found in (Olson and Iskander 1986). The impedance Z_o for low loss cable is 50 Ohm at all frequencies. The S11 consists of magnitude (|S11|) and phase angle ($\angle$S11).

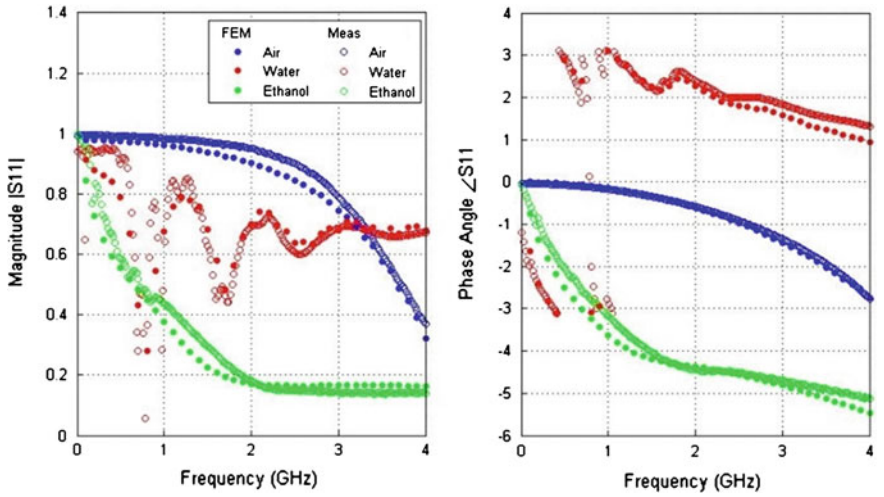

Fig. 97.2 The plot of measured and calculated S11 for air, water and ethanol

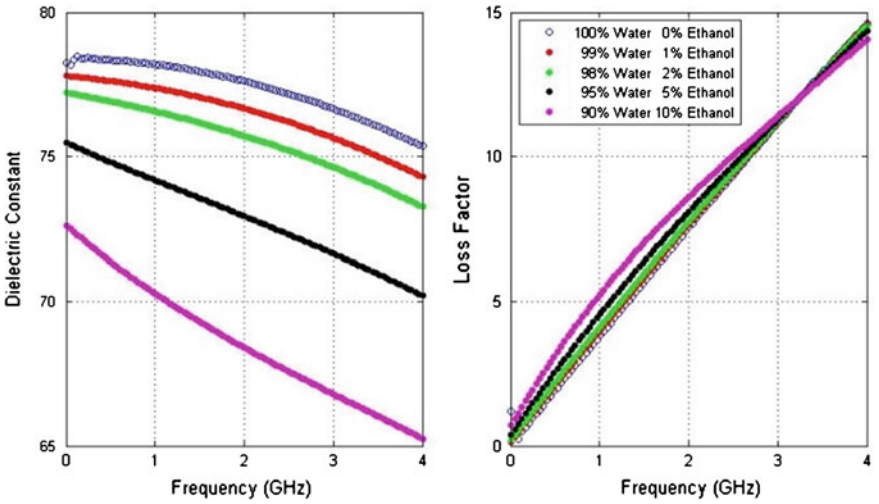

Fig. 97.3 The plot of theoretical permittivity values for selected ethanol/water ratio calculated from Eq. (97.3)

Results and Discussion

The permittivity of air, water and ethanol between 100 MHz and 4 GHz is shown in Fig. 97.1. The plot of permittivity highlights the dielectric contrast between air, water and ethanol. According to Eq. (97.2), permittivity affects the S11 of the monopole sensor which is evidenced in Fig. 97.2. This result provides a basis for

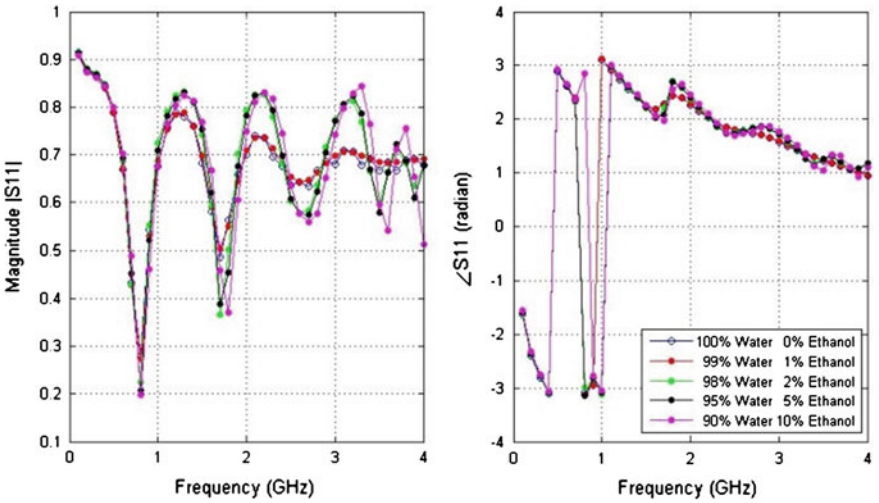

Fig. 97.4 The plot of theoretical S11 for selected ethanol/water mixture obtained from FEM

the measurement of the percentage of ethanol in water. Good agreement was generally found between measured and calculated values obtained from FEM.

The plot of theoretical permittivity values for selected water/ethanol ratio is shown in Fig. 97.3. The permittivity is calculated based on Kraszewski mixture model:

$$\sqrt{\varepsilon} = v_{\text{water}}\sqrt{\varepsilon_{\text{water}}} + v_{\text{ethanol}}\sqrt{\varepsilon_{\text{ethanol}}} \tag{97.3}$$

where v is the percentage volume of water and ethanol. The theoretical S11 of the sensor in water/ethanol mixture estimated with FEM is shown in Fig. 97.4, based on permittivity values plotted in Fig. 97.3. The change in S11 of the monopole sensor corresponds to the change in permittivity values due to different ratio of water/ethanol mixture. It can be observed that the sensitivity of the monopole sensor to percentage of ethanol is dependent on frequency. Between 100 MHz to 1 GHz, the difference in S11 between each water/ethanol ratio might be very marginal. Between 2 GHz to 2.5 GHz and 3 GHz to 3.5 GHz, the difference in S11 is more apparent. The magnitude |S11| is more sensitive to ethanol/water ratio than phase angle ∠S11.

Conclusion

Monopole sensors can be potentially used to detect water contaminants that possess high dielectric contrast than water. The S11 of the sensor is dependent on the water/ethanol ratio. Furthermore, the sensitivity of the sensor is also dependent on frequency. Other than alcohol, it is also possible to detect the presence of salts such as sodium chloride which also possess high dielectric contrast than water.

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Chapter 98
Assessment of Water Quality in Darwin Harbour Using Time Integrated Samplers and Biological Markers in Barramundi (*Lates Calcifer*)

Susan Codi King

Abstract A joint collaboration was undertaken to complement the existing Water Quality Monitoring Program in Darwin Harbour. The aim was to assess in situ environmental contaminants and their bioavailability at various sites around Darwin Harbour. Time integrated samplers known as semi-permeable membrane devices (SPMDs) for dissolved polycyclic aromatic hydrocarbons and diffusive gradients in thin films (DGTs) for labile dissolved metal species were deployed in four locations (Sadgroves Creek, Shell Island, Hudson Creek and West Arm) for a period of 10 days. In addition, at Sadgroves Creek and West Arm, biological monitoring was conducted using caged and wild caught barramundi (*Lates calcifer*). Several biomarkers, already established in barramundi, were evaluated and they included bile metabolites, cytochrome P450s and 7-ethoxyresorufin-O-deethylase (EROD) glutathione *S*-transferase (GSTs) and cholinesterase activity (ChE). Two other biomarkers were evaluated: vitellogenin in blood to assess potential impact from sewerage into Darwin Harbour, and sorbitol dehydrogenase (SDH), a potential biomarker of liver damage. Results highlight PAH concentrations at the West Arm site were below detection whilst PAH concentration at Sadgroves Creek, Hudson Creek and Shell Island were all similar. For labile dissolved metals, Aluminum, Manganese and Nickel were higher at impact sites as compared to the reference site. Mean concentrations of EROD activity, cytochrome P450, SDH activity, GST, ChE and vitellogenin were not significantly difference ($p > 0.05$) in barramundi from Sadgroves Creek and West Arm and they were comparable to basal levels measured in hatchery-reared barramundi ($T = 0$) used as a non-exposed reference. These results provided a baseline survey of PAHs and labile dissolved metals at several sites in Darwin Harbour, which compliments the data being generated from the Darwin Harbour Water Quality

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Monitoring Program. As development of Darwin Harbour progresses, impacts to the harbour can continue to be monitored and assessed in order to protect the environmental values for Darwin Harbour.

Keywords Water quality · Biomarkers · PAHs · Dissolved metals/metalloids · Darwin harbour

Highlights

- Evidence of human activity in a gradient moving away from the city of Darwin.
- DGT films results for Al, Mn and Ni were higher (urban/industrial sites).
- Concentrations of PAHs were low and pyrogenic in origin.
- All biomarkers were not significantly different between impact and reference sites.

Introduction

Darwin Harbour is one of Australia's largest deep-water harbours. With increased urbanisation around Darwin, there is growing concern that impact from localised point sources is having detrimental effects on this highly valued resource. There is growing public awareness for the need to improve our ability to detect exposure and potential adverse effects from man-made (e.g., anthropogenic) contaminants entering our marine systems and accumulating in aquatic biota. Assessment of water and sediment chemistry provides information on levels of pollutants in our waterways but offer very little information about the potential effects. A major tool in the detection and assessment of effects from anthropogenic contaminants is the development and use of biological markers (biomarkers). Biomarkers refers to any biochemical, physiological and histopathological indicator which signals exposure to, and possibly, adverse effects from anthropogenic pollutants within an organism and the magnitude of the response. Biomarkers can serve as early warning signals about an organism, the water quality of its environment and the potential health of its ecosystem before whole populations or communities are affected. Barramundi (*Lates calcarifer*) has been shown to be a good indicator species in rivers and coastal areas of northern Queensland, Australia (Codi et al. 2004, Humphrey et al. 2007). A number of biomarkers have already been developed and implemented in barramundi in Australian waters, which are relatively inexpensive, easy to use and provide results rapidly.

One of the aims of this study was to fill the existing knowledge gap and assess biomarkers in barramundi as an indicator of the water quality and potential

ecosystem health for Darwin Harbour. The goal was to establish baseline data on biomarker responses from anthropogenic contaminants as a reference, which can be used to measure future impact on the ecosystem of Darwin Harbour. Secondly, identify areas within Darwin Harbour that may be currently under stress from exposure to elevated levels of anthropogenic contaminants (both organic and metals) by comparing areas with varying degrees of pollution inputs.

Materials and Methods

For in situ environmental contaminants there were four study sites selected within Darwin Harbour (Fig. 98.1). The sites were selected based upon their relative proximity to anthropogenic activities in the harbour and classified accordingly as urban (Sadgroves Creek), industrial (Shell Island), residential (Hudson Creek) and unimpacted reference site (West Arm). In addition, biomonitoring was undertaken using both caged and wild caught barramundi (*Lates calcifer*). A controlled fish exposure study was conducted using hatchery-reared (10/cage) deployed in two cages at a references site (West Arm) and an impact site (Sadgroves Creek) (Fig. 98.1) for a period of two weeks. Wild caught barramundi were targeted from

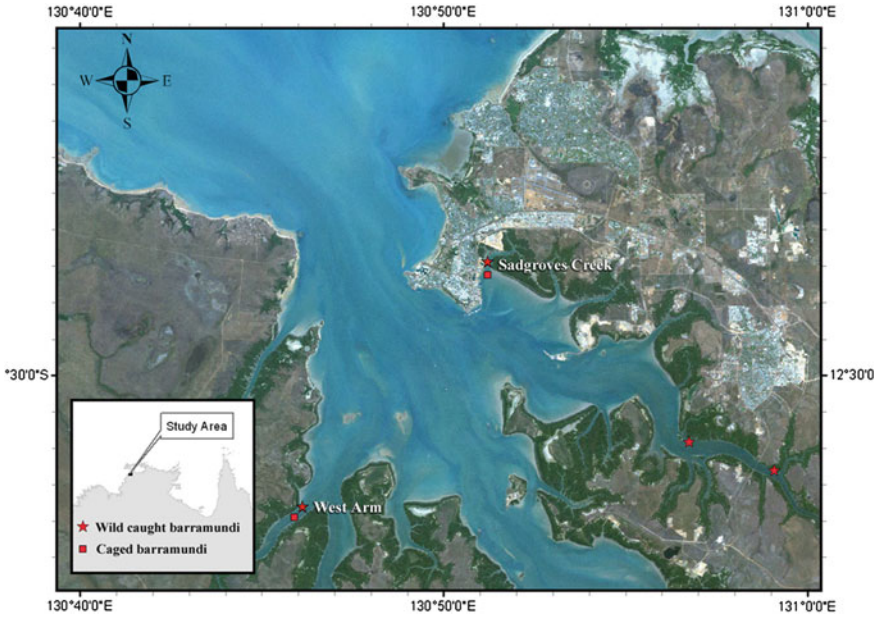

Fig. 98.1 Site locations for deployment of time integrated samplers (SPMDs and DGTs) and collection of wild caught barramundi (*red star*) and site for deployment of caged barramundi (*red squares*)

the same fours sites assessed for environmental contaminants (Fig. 98.1). Barramundi were collected with the aid of local fishermen using hook and line. Results were compared with biomarker responses in two month old hatchery-reared barramundi (Australian Barramundi Culture) as a baseline (T = 0).

Fish were sacrificed by cervical dislocation, and liver tissue (from the left lobe) was excised immediately, snap-frozen in liquid nitrogen and stored at −80 °C for later analysis of EROD and GST activity. Muscle was sampled for cholinesterase activity (ChE). Blood and plasma was collected as outlined in Codi and Hassell (2008). Bile was not collected as gall bladders were empty. Fork length (TL mm), total and gutted fish weight (g), gut and liver weight (g) were recorded for each fish. All fish were processed within 20 min to minimise handling stress.

EROD activity was determined using the fluorometric method with modifications described by (von Westernhagen et al. 1995) and optimised for use with barramundi as described in previous studies (Codi et al. 2004, Humphrey et al. 2007). GST activity was measured by Habig et al. (1974). Cholinesterase activity was determined spectrophotometrically by the method of (Ellman et al. 1961) as modified for a micro plate reader according to (Bocquené and Galgani 1998). Vitellogenin was determined by the method established for barramundi (Codi and Hassell 2008, Codi et al. 2008).

Time integrated samplers for both organics (SPMDs) and metals/metalloids (DGTs) were deployed on each cage to assess total exposure concentrations of organics and metals for the deployment period.

Results and Discussion

PAH concentrations measured by SPMDs were relatively low; however, there was a delineation in PAH concentrations moving from the eastern to western side of the harbour. PAH concentrations at the West Arm site were below detection yet PAH concentration at Sadgroves Creek, Hudson Creek and Shell Island were all similar (1.0, 0.674 and 0.729 μg/L, respectively). The main source of PAHs detected were pyrogenic PAHs typically associated with atmospheric deposition from combustion products (e.g., burning of fossil fuels), sewage and runoff. The data infers a higher input of pyrogenic PAHs in the water column closer to Darwin, an urbanised centre and where annual burning of native bush land is a common practice.

DGTs labile metals showed no distinctive pattern in concentrations for Gallium, Cadmium, Copper, Iron, Vanadium and Uranium. However, Aluminum appeared to be higher at Sadgroves Creeks and Manganese and Nickel were higher at Hudson Creek (data not shown) and Manganese, Cobalt, Copper and Cadmium represented the highest proportion of metals detected.

For the caged study, all fish escaped from the cages or were removed by other means so no results are presented. For the wild caught barramundi, mean concentrations of EROD activity, cytochrome P450, SDH activity, ChE and vitellogenin (not shown) were not significantly difference ($p > 0.05$) in barramundi

collected from Sadgroves Creek and West Arm and they were comparable to basal levels measured in hatchery-reared barramundi (T = 0) used as a non-exposed reference.

However, GST activity was the only biomarker which showed higher responses in barramundi from Sadgroves Creek (22.1 μmol/min/mg protein) as compared to West Arm (17.9 μmol/min/mg protein) and hatchery-reared (14.3 μmol/min/mg protein), albeit not signficant.

Conclusion

This study provides preliminary baseline data on the health of barramundi in Darwin Harbour. This information can help inform potential issues from anthropogenic contaminants especially as the region grows and industry and mining expand.

This initial study has led to an extensive research being conducting on the impact of sewage discharge and industrial discharges on the health of aquatic biota living in Darwin Harbour.

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Chapter 99
Water Quality and Enrichment of Sedimentary Polycyclic Aromatic Hydrocarbons (PAHs) Relation to Fish Culture in Malaysia

Ananthy Retnam, Hafizan Juahir, Mohamad Pauzi Zakaria, Ahmad Zaharin Aris and Mohd Fadhil Kasim

Abstract This study investigated the potential effects of the fish aquaculture on water quality and enrichment of PAHs in the aquaculture surface sediments. Water quality parameters and PAHs were determined at fish farms and reference sites. A significant decrease in dissolved oxygen at fish farms was observed ($p < 0.05$). Enrichment of total organic carbons (TOC) and PAHs in comparison to reference site were significant ($p < 0.05$). Enrichment of TOC had significant correlation with enrichment of PAHs ($p < 0.05$) especially carcinogenic PAHs. Cluster and principle components analyses revealed an additional source of PAHs (35 %) into the fish farm sediments. The finding of this study indicated fish farming is a significant source of dissolved oxygen deterioration and enrichment of PAHs. Therefore an appropriate monitoring system is required for the sustainable development of fish farming sector.

Keywords Fish farms · Dissolved oxygen · Enrichments · Polycyclic aromatic hydrocarbons · Total organic carbons

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Highlights

- Enrichment of total organic carbon and PAHs occurred at aquaculture.
- Total organic carbon had significant contribution to enrichment of PAHs.
- Enrichment prevalence at less antropogenic influences sites.
- Additional unknown source altered the natural input of PAHs at aquaculture sites.

Introduction

Aquaculture is an expanding food sector in many parts of the world meeting the demand for fish and fishery products. The global farmed fish production has increased by 85 % since year 2000. In Malaysia, fish cage aquaculture has been becoming more important with cages have increased by 5,000 cages/year since 1982. This type of culture system is the biggest revenue contributor in terms of economic value compared to other type of aquaculture system with RM 1,280,403/ha/year (Chong 2006). Besides the benefits, this industry causes environmental deteriorations such as enrichment of nutrients, organic matters (OM), heavy metals and organic contaminants. Aquaculture activities also cause bioaccumulation of various toxic pollutants added unintentionally into fish, which can pose health implication to human, who consume them (Blanco et al. 2011; Cheung et al. 2007; Foran et al. 2004; Kelly et al. 2008; Leeuwen et al. 2009; Padula et al. 2012; Salami et al. 2008). Decrease of dissolved oxygen and increase of sediment oxygen demand (SOD) also observed which could have impact on indigenous species and fish habitat (Bustnes et al. 2010; Gao et al. 2005; Hellou et al. 2005; Nghia et al. 2009; Russell et al. 2011; Sather et al. 2006; Wu 1995). Enrichment of OM is of particular interest since enhancement in OM tends to increase accumulation of pollutants such as heavy metals and persistent organic pollutants (POPs) such as PAHs. The objectives of this study are (1) to measure the water quality, the levels and characterization of PAHs in aquaculture and non-aquaculture sediments (2) to evaluate the enrichment level of TOC, total nitrogen and PAHs (3) to identify the possible sources and source apportionment in aquaculture and non-aquaculture sediments.

Materials and Methods

Sample were collected from aquaculture sites in Peninsular Malaysia covering West Coast which represent urban and industrialized areas and East Coast, which is relatively less polluted to evaluate the impact of aquaculture activities minus the anthropogenic sources. Sediment samples from fish aquaculture were collected

right underneath the cage farms. The natural marine or non-aquaculture (reference) sediments were collected about 1–2 km away from the cage farms (Wu 1995). Water quality parameters such as pH, temperature, salinity, dissolved oxygen and conductivity inside each fish farm were measured *in situ* at one meter below the water surface using multi parameter probe YSI 6600. The sedimentary PAHs were analysed by soxhlet extraction, followed by silica gel column clean-up and fractionation and determined by gas chromatography-mass spectrometer. Altogether, there were 24 PAHs compounds were being analysed. Total organic carbons and total nitrogen was measured using CHNS analyser.

Results and Discussion

The water quality impacts usually reflected by increase in biochemical oxygen demand (BOD) levels and lower dissolved oxygen (DO) around the sites. The level of DO at reference sites is significantly higher than fish aquaculture sites ($p < 0.05$). The use of trash fish and high density of fish in the cages produces high nutrient loadings causing an impact on water quality around the aquaculture sites (Wu 1995). The concentration of PAHs in aquaculture sediments ranged from low to moderately high. The levels of the individual PAHs in the surface sediments of fish farming is compared to Canadian Council of Ministers of the Environmental guideline (CCME) for marine superficial sediment (CCME 1999) for Interim sediment quality guideline (ISQGs). Acenaphthylene, fluorene and diben-za(ah)anthracene were found to be higher than the guideline value. This has raised concern not only to the safety of aquatic animals being raised at these sites but also human who consume them. Enrichment of total organic carbons (TOC) and PAHs were could be occurred at aquaculture sites with higher TOC and PAHs concentrations were observed at aquaculture compared to reference sites ($p < 0.05$). Enrichment of TOC has significant contribution to enrichment of high molecular PAHs especially carcinogenic PAHs ($p < 0.05$). The enrichment in less anthropogenic influence is more prevalence compared to sites with anthropogenic sources ($p < 0.05$). The major sources of PAHs in the aquaculture sediments are vehicular emission and mixed sources contribution about 50 and 15 % respectively. Molecular markers together with cluster and principle component analysis suggest that there is an additional source of PAHs pollution in the aquaculture sediments contributing to 35 % of total pollution loading.

Conclusion

The fish aquaculture has significantly contributed to deterioration of water quality and PAHs pollution compared to non-aquaculture sites. The dissolved oxygen at the aquaculture farms was significantly lower than reference sites ($p < 0.05$).

Enrichment of total organic carbons and PAHs were occurred ($p < 0.05$) with total organic carbons had strong significant contribution to enrichment of PAHs ($p < 0.05$) especially carcinogenic PAHs. The levels of PAHs individual compounds namely acenaphthylene, fluorene, and dibenza(ah)anthracene were found to be higher than the Canadian Interim Sediment Quality Guidelines These has raised some concerned of fish and other aquatic animals being raised at these sites and safety of human who consume them. Based on molecular ratio and patter recognition techniques, there is an additional unknown source of PAHs in aquaculture sites contributing to 35 % of total pollution loadings. The finding of study indicated fish farming is a significant source of PAHs in the marine environment and therefore an appropriate monitoring system is required for the sustainable development of fish farming sector.

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Chapter 100
Evaluation Approach in the Practice of Sustainability from Cultural Landscape Perspective: A Case Study of Masjid Kampung Kling, Malacca

Fadhilah Othman, Rosta Harun and Mohd Bakri Ishak

Abstract The purpose of this paper is to view sustainability practice from the perspective of cultural landscape by looking at Masjid Kampung Kling, Malacca. The selected mosque is a traditional building gazetted under National Antiquity Act (2005) and is located within the area of UNESCO World Heritage Site. A qualitative case study was used in uncovering the practice of sustainability. The cultural landscape approach has guided the study by questioning the meanings embedded within the traditional mosque's features thus providing a new angle of viewing the landscape as a social expression of symbols, icons, and metaphors. Concepts of sustainability and cultural landscape were reviewed for acquiring the sense of connection with each other. As for evidence, data was collected from several series of observation and interviews. Masjid Kampung Kling can be seen as a sub-cosmic from an enormous multi-culture of Malacca. Findings from the study suggested that the mosque has the portrayal of practical sustainability practice by both the contextual mean and testimonial proof. The sustainability practice can be viewed from three significance values of cultural landscape of the mosque namely (1) history (2) architecture and (3) archaeology. Current management should recognise Masjid Kampung Kling and other traditional mosques in general, for having the potential to present sustainability from cultural landscape perspective. Though Masjid Kampung Kling is already known as tourist attraction, concept improvement in the context of tourism will definitely add more values especially for academic and learning purpose.

Keywords Sustainability · Cultural landscape · Case study · Masjid kampung Kling

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Highlights

- New view in understanding sustainability perspective.
- Observation on intangible evidences of sustainability.
- Tracing out sustainability practices from history, architecture and archaeology.

Introduction

The most known definition on sustainability is popularized in Brundtland Report (*Our Common Future* 1987) that is a 'development that meets the needs of the present without compromising the ability of future generation'. Ever since, sustainability topic has become a major discussion along with the expanding awareness of environmental crisis. Adams (2006) has explained the concept of sustainability as a condition that is supported upon the three pillars of environment, society and economy. The concept is illustrated using the three interlocking models in which there is balance between the dimensions of sustainability (Fig. 100.1).

Cultural landscape can be understood as a simultaneous product of human interaction with nature (Lowenthal 1985). It is the result of people living with the physical environment, interacting with it and modifying it in myriad ways, modeling the worldview, ideology, and cognition upon the land. The outcome of cultural landscape is shaped by general mental template that the society use to understand the ways in which the world works as well as through people's actions and various physical and natural processes that shape the world. Therefore the practice of sustainability can be observed from the overlapping context of cultural landscape with sustainability dimensions (social and environment). Birnbaum (1992) added that cultural landscapes can be classified into historical sites, historical designed landscapes, historical vernacular landscapes, and ethnographic landscapes.

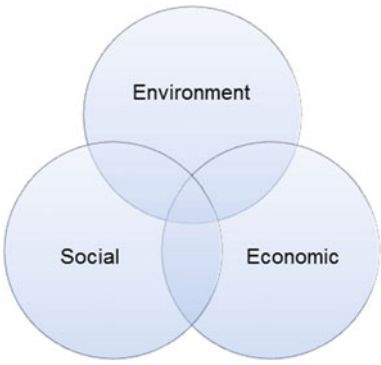

Fig. 100.1 Dimensions of sustainability (Adams 2006)

Materials and Methods

Masjid Kampung Kling, Malacca

The mosque was established near to Masjid Kampung Hulu on 1748. After that in 1872, the structure of the mosque was upgraded with briquette. Later in 1908, the roof was raised to the same level of Masjid Kampung Hulu. All the funding for mosque establishment came from money box and donation. The design of the mosque is influenced by Sumatera's mosques architecture with Hindu-like design. Nevertheless, Chinese design can also be seen at the mosque's minaret. The ornaments and interior decoration are observed to be the influence of Malay interpretation.

The mosque was gazzeted (National Antiquity Act 2005) as historical building by Department of Museums and Antiquity in 1999 and later was put under Perbadanan Muzium Melaka (PERZIM) management. Masjid Kampung Kling is located within the area of UNESCO World Heritage Site, exactly at *Jalan Tukang Emas*, adjacent to Sri Payyatha Viyanagar Moorthi temple and Cheng Moon temple. The road of which the mosque is located is known as *Jalan Harmoni* (Harmony Road) where it gathers religious buildings of Islam (mosque) Hindu and Budha (temples).

Case Study

This type of qualitative study has been widely used in cultural research. As in sustainability discipline, several examples of case study can be identified i.e. whole-system concept of sustainability (Greenhalgh et al. 2012; Nguyen and Bosch 2012; Isenhour 2010), good governance (Syed Muhammad and Anwar 2006), economic (Taplin et al. 2006) and architectural design (Bala 2010). The strategy used for data collection includes document analysis, interview, and observation.

Results and Discussion

Findings from the study suggested that Masjid Kampung Kling has the portrayal of practical sustainability practice by both the contextual mean and testimonial proof. The sustainability practice can be viewed from three significant values of cultural landscape of the mosque namely (1) history (2) architecture and (3) archaeology. The mosque has the potential to be expended within tourism and hospitality industry.

Heritage Tourism

Masjid Kampung Kling like other traditional mosques in Malacca can be seen as historical vernacular landscape and are advantageous for heritage tourism. Heritage tourism (under sub-class of cultural tourism) has been identified and highlighted in the new Tourism Policy by the Tourism Ministry as one of the new niche products to be developed extensively for the next 10 years (Mohamed and Mustafa 2005). Paralleled with the growing interest in heritage tourism and the global influx of the alternative tourists, tourist arrivals in the Malaysian historical cities, especially Penang and Malacca, have improved over the years.

Religious-Ecological Knowledge

A mosque must be interpreted from the prospect of its function and special characteristic of its form. According to Omer (2010), form of a mosque is a product of people interpretation from their surrounding and is influenced by existing environmental factors i.e. climate, topography, season, etc. Even though people can communicate with the environment as they wish, their interpretation are still bounded to the gist of Islamic pillar that they must not associate Allah as the only God with anything and by any mean. In a similar study Rosta et al. (2012) explained that despite the uniqueness of traditional mosque architecture in Malacca, none of ecological knowledge retrieved from the mosques are contradict with Islamic teaching.

Conclusion

Current management should recognize Masjid Kampung Kling and other traditional mosques in general, for having the potential to present sustainability from cultural landscape perspective. Though Masjid Kampung Kling is already known as tourist attraction, concept improvement in the context of tourism will definitely add more values especially for academic and learning purpose.

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Chapter 101
Contamination of Trace Elements (Cu, Pb, Cr) in Kong Ko Laut, Johor, Malaysia

Eddie Cheah Kee Wan and Ferdaus Mohamat-Yusuff

Abstract The aim of this study is to determine the contamination of trace elements (Cu, Pb and Cr) and to find the degradation or accumulation pattern of these elements in the sediments of Kong Kong Laut, Johor, Malaysia. Samples were collected from 9 different locations in 3 different months (i.e. February, March and April 2012). Samples were treated with acid digestion method to extract the trace elements. The elemental concentration was detected by using atomic absorption spectrophotometer. The average ranges of obtained trace element concentrations are as followed: Cu: 6.33–87.25 μg g^{-1} dry weight; Pb: 10.18–40.87 μg g^{-1} dry weight; Cr: 21.07–35.28 μg g^{-1} dry weight. Samples from Location No. 2 which received low water current were detected with relatively higher concentration of trace elements as compared with samples collected from site with higher water stream. However, concentrations of all trace elements were found below the threshold level stated in the Hong Kong Interim Sediment Quality Guideline (HK ISQG) except for concentration of Cu in sample from Location No. 2 collected in April, 2012. No significant value found between sampling period except for concentrations of Cu and Pb from Location No. 2.

Keywords Kong Kong Laut · Sediments · Trace elements · Contamination · Interim sediment quality guideline

Highlights

- Geographical condition and human activities were influencing the trace elements level.

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- No clear degradation or accumulation trend of each element were found in this study.
- Average concentration values of all elements were below the HK ISQG–low value.

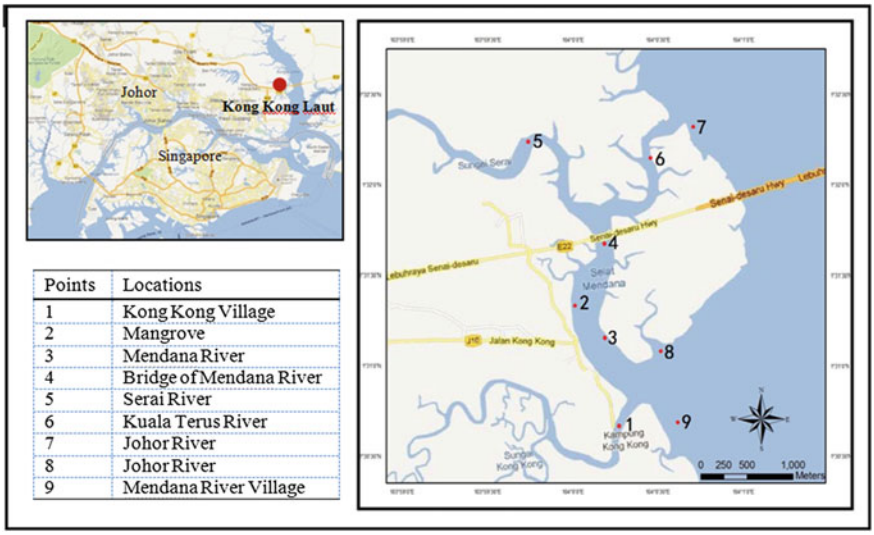
Introduction

Human activities usually have been recognized as the major source of excessive trace elements input to the environment. Streams and waterways are always a good transportation pathway to carry these pollutants along, and finally settled in sedimentation. Therefore, sediments played an important role in environmental studies, to monitor contaminants in the marine and aquatic environment, as it served as a reservoir of contaminants for bioaccumulation and trophic transfer (Burton 2002). Kong Kong Laut is a fishing village situated in Pasir Gudang, Johor, Malaysia. It is famous with fresh seafood supplies, aquaculture and tourism. In recent years, a few jetties and fishing spots have been constructed to fulfill the consumers' needs (Ang 2009). This area is expected to receive more publicity and human impact as the linkage of Senai-Desaru was developed recent years. With these construction and several minor developments conducted at Kong Kong Laut, this site of study is expected to associate with trace elements contamination. Improper waste management and river-top transportation might contribute to trace elements pollution in the site. Therefore, this study was design to investigate the source of trace elements introduction in the area, and also to understand the accumulation or degradation pattern of trace element in the sediments samples.

Materials and Methods

Samples Collection

Sampling activities were conducted in February, March and April 2012, where sediments were collected from nine locations around Kong Kong Laut (Fig. 101.1). Sediments were collected by using grab sampler, and were kept in Ziploc® bags. All the sediments collected were stored in a freezer at −20 °C until further analysis.



Points	Locations
1	Kong Kong Village
2	Mangrove
3	Mendana River
4	Bridge of Mendana River
5	Serai River
6	Kuala Terus River
7	Johor River
8	Johor River
9	Mendana River Village

Fig. 101.1 Sampling locations for sediments around Kong Kong Laut

Analytical Procedure

Samples were pre-treated to obtain a fine fraction for acid digestion. Pre-treated sediments were then digested with a mixture of hydrochloric acid and nitric acid (in a ratio of 3:1) to extract trace elements (ISO 1995; Zulkifli et al. 2010). The obtained suspension was then filtered through a 125 mm filter paper into a centrifuge tube, and diluted (DF = 10) prior to determination using atomic absorption spectrophotometer (AAS).

Statistical Analysis and Data Screening

Statistical analysis was performed using SPSS (version 17, SPSS Inc., Chicago, IL, USA) and Microsoft® Office Excel® 2007 (Microsoft Corporation, USA). Two-way ANOVA (analysis of variances) was conducted using Microsoft® Office Excel® 2007 to determine the difference between elemental concentrations form different location and months. The significant level was evaluated in 95 % confidence level ($\alpha = 0.05$). Hong Kong Interim Sediment Quality Guideline (HK ISQC) was adopted in this study for quick screening purposes.

Results and Discussion

Pooled concentration data of Cu, Pb and Cr obtained in this study were ranged as followed: 6.33–87.25 μg g^{-1} dry weight, 10.18–40.87 μg g^{-1} dry weight and 21.07–35.28 μg g^{-1} dry weight, respectively as shown in Table 101.1. Among these elements, the highest mean concentration was Cr (28.53 ± 0.74 μg g^{-1} dry weight), followed by Pb (21.93 ± 1.33 μg g^{-1} dry weight) and Cu (18.27 ± 3.19 μg g^{-1} dry weight) respectively (Table 101.1). The concentrations of Cu, Pb and Cr were generally low, as compared to the levels reported in the Strait of Johor and Peninsular Malaysia (Zulkifli et al. 2010). In general, none of these elements had an average concentration above the HK ISQG–low (Hong Kong Interim Sediment Quality Guideline—low) value (Fig. 101.2).

The concentration of each element from 9 locations was found to have strong significant differences between the stations at $p < 0.05$ as shows in Fig. 101.2. However no significant differences of all elemental concentrations found between the sampling months ($p > 0.05$) except for Cu and Pb in sample collected from Location No. 2 and Pb in sample from Location No. 8 (Fig. 101.2). This shows that only limited major trend of degradation or accumulation of each elemental concentration can be observed from this study.

Figure 101.2 showed the Cu value obtained in April from Location No. 2 was the highest among all the sampling points (87.25 ± 9.54 μg g^{-1} dry weight) and exceeded the low value stated in HK ISQG. Location No. 2 also showed the highest Pb concentration (40.87 ± 3.33 μg g^{-1} dry weight) among all sites (Fig. 101.2). Chromium was found to have the highest mean concentration and detected at all sampling site (Fig. 101.2). The main sources of Cr in this area is most probably due to the wide use of chromate copper arsenate (CCA) wood preservative for wooden structure of aquaculture, fishing spots and fishermen villages. This caused continuous contribution of Cr input into the aquatic environment (Kabata-Pendias and Mukherjee 2007).

Geographical condition found to play important role for high trace elements concentration. In example: samples from Location No. 2 showed higher value than sample from Location No. 1 even though Location No. 1 is in the vicinity of Kong Kong Village that expected to received human impact. This is because Location No. 2 is in Mendana Straits; a strong water flow was observed to move from the southern and northern part towards Mendana Strait and the water current tend to

Table 101.1 Range of pooled data (concentration of trace elements in μg g^{-1} dry weight) in monthly sediments from Kong Kong Laut

Elements	Concentration (μg g^{-1} dry weight)			
	February	March	April	Mean
Cu (n = 27)	8.38–21.41	11.1–57.32	6.33–87.25	18.27 ± 3.19
Pb (n = 27)	10.18–31.46	16.14–25.53	10.48–40.87	21.93 ± 1.33
Cr (n = 27)	23.41–35.28	25.00–34.51	21.07–31.43	28.53 ± 0.74

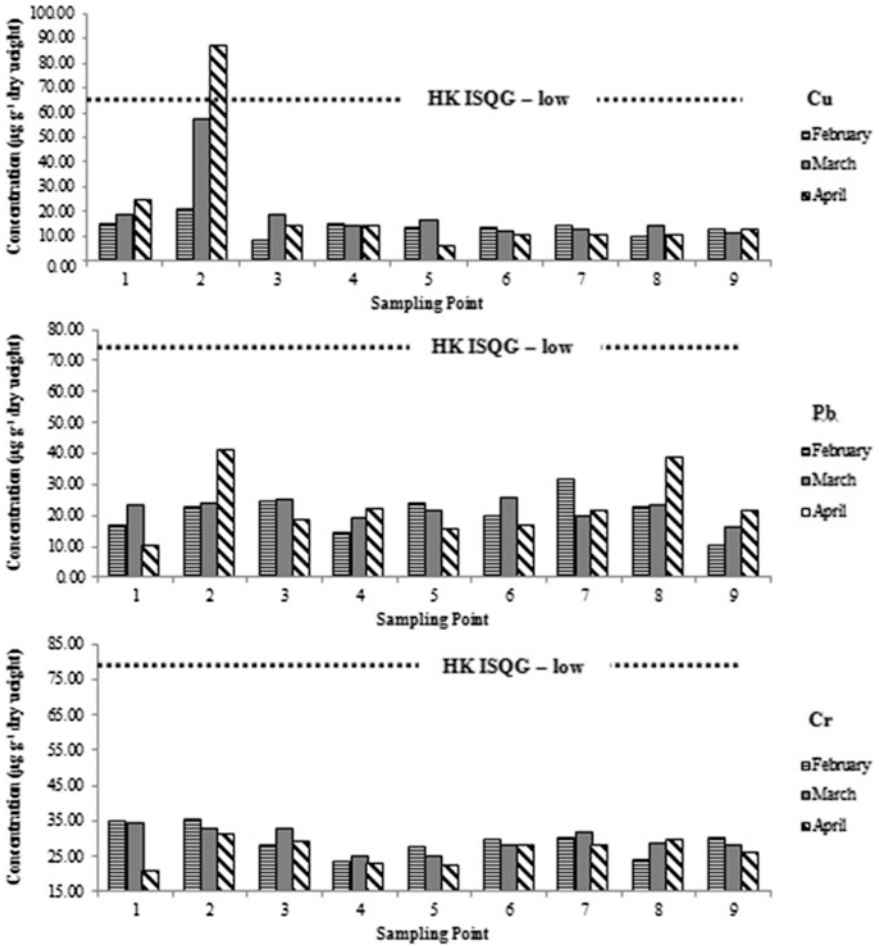


Fig. 101.2 Mean concentration of Cu, Pb and Cr (µg g^{-1} dry weight) in sediments collected in 3 months sampling series from 9 locations along Kong Kong Laut

slower down in the strait itself. Furthermore, the Mendana Straits is narrower at the northern part starting at Location No. 4. This creates a bottle neck condition in the strait and slow water stream at the area before reaching Location No. 4. Thus, this might encourage the sedimentation of suspended particles in the water column around Location No. 2 as reported by Haris and Aris (2012). Hence, sediment samples collected from Location No. 2 shows the highest amount of all elemental concentration among the others (Cu: 87.25 ± 9.54, Pb: 40.87 ± 3.33 and Cr: 35.28 ± 0.36; in µg g^{-1} dry weight). However further analyses are needed to confirm the influence of water flow and sedimentation of suspended particulate with accumulation of trace elements in these studies areas.

Conclusion

Contamination of Cu, Pb and Cr at Kong Kong Laut area are influenced by anthropogenic sources and geographical condition. The geographical condition plays an important role in producing unique elemental values between the sampling sites.

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Chapter 102
Heavy Metals (As, Cd, Cr and Pb) Concentration in Selected Freshwater Fishes and Health Risk Assessment Among Adults in Kluang, Johor

Saliza Mohd. Elias, Ana Mardhiah Marzuki, Hilaliyah Mokhtar, Christopher George, Noor Azianti Zakaria and Ahmad Zaharin Aris

Abstract A cross-sectional comparative study was conducted in two areas at Kluang, Johor to determine the heavy metals concentration in freshwater fish and health risk assessment among adults in the area. Kahang River is less polluted compared to Sembrong River. A total of 30 respondents from each area were randomly selected based on inclusion criteria. A set of pre-tested questionnaire was used to obtain the socio-demographic information, food frequency intake and health status of respondents. Three freshwater fish species from these rivers which were frequently consumed by locals were analysed for arsenic (As), cadmium (Cd), chromium (Cr) and lead (Pb) concentration using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The health risk of respondents was assessed through the calculation of HQ and LCR. Results showed that heavy metals concentration in freshwater fishes of polluted river (Sembrong River) were higher than the less polluted river (Kahang River).There was also a significant difference in the health risk of respondents of the two areas which indicated that respondents who consumed fishes from the polluted river may have higher risk of health problems associated with heavy metals exposure.

Keywords Sembrong River · Kahang River · Adults · HQ · LCR

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Highlights

- Heavy metals were detected in all fish samples from Sembrong River and Kahang River.
- Heavy metals level in fish from Sembrong River were higher than Kahang River.
- Consumer from Sembrong River face higher health risk than Kahang River.

Introduction

Fish is rich with vitamins, minerals and proteins which are beneficial to health (Alina et al. 2012). It contains omega 3 fatty acids and essential fatty acids (EFAs), known as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) which will reduce heart related disease (Hajep et al. 2009). However, fishes are endangered by contaminants transferred along the food chain. Heavy metals such as As, Cd, Cr and Pb have been recognized as strong biological poisons because of their persistent nature and cumulative action (Carbonell et al. 2009). These metals could reach food chain through various biochemical processes such as bioconcentration, bioaccumulation and ultimately biomagnified in various trophic levels and eventually threaten the health of humans by fish consumption (Agusa et al. 2005). Exposure to Cd and other "metalloestrogens" could result in an increased rate of breast and prostate cancer. The health hazards associated with exposure to Cr dependent on its oxidation state, ranging from low toxicity to the high toxicity of the hexavalent Cr. Hexavalent Cr is a toxic industrial pollutant and classified as the carcinogenic and teratogenic agent (ATSDR 2007). Pb is classified as very toxic that even low dosage of Pb may contribute to mental retardation and disrupting the learning process of children (CDCP 2002).

Materials and Methods

Study Location

Two areas in the state of Johor were chosen based on classification of river pollution level. Sembrong River is considered as polluted (Class III) and Kahang River is considered as less polluted (Class II).

Respondents

Thirty adults who consumed the fishes from these rivers were recruited from each village. Respondents with immune-compromised diseases were excluded. A set of pre-tested structured questionnaire was used to obtain socio demographic, health status, anthropometric measurement, food frequency intake, and other possible sources of heavy metals exposure. Respondent had signed consent letter in order to fulfill the ethical requirement prior to data collection.

Fish Samples

Based on modified Food Frequency Questionnaires (FFQ), three species confirmed to be the most frequently consumed fish in the two locations were *Leptobarbus hoevenii* (*Jelawat*), *Puntius gonionotus* (*Lampam Jawa*) and *Osteochillus hasseltii (Terubol*). Fishes were caught using cast net. The fish samples were then stored in sterile plastic bag and placed in cool box with ice packs for temporary storage at 4 °C before storage at laboratory freezer (−20 °C) for further analysis. Fish muscle tissues were treated with wet acid digestion prior to analysis. Inductively Coupled Mass Spectrometer (model ELAN 9000 Perkin Elmer ICP-MS, USA) was used to determine the heavy metal concentration (Irwandi et al. 2009). All samples were triplicates and reported in mg/L (ppb). The value of As, Cd, Cr and Pb concentration were applied into the following equation to obtain the actual heavy metals concentration.

$$\text{Heavy metals concentration in freshwater fish sample } (\text{mg/kg}) = [(\text{A} \times \text{B}) \times \text{C}]/\text{W}$$

where; A is the volume of extract (digested sample); B is the dilution factor (volume of diluted sample/volume of extract); C is the heavy metals concentration in the extraction (ug/ml) and W is weight of the sample (0.5 g).

Health Risk Assessment

The health risk assessment of the respondents was evaluated using Hazard Quotient (HQ) for non-carcinogenic health effects and Lifetime Cancer Risk (LCR) for carcinogenic health effects.

Table 102.1 The mean concentration of heavy metal (Ar, Cd, Cr and Pb) in freshwater fish samples of both areas (mg/kg)

Variable	Polluted river of Sembrong	Less polluted river of Kahang
	Mean	Mean
Ar	0.737	0.252
Cd	6.330	4.780
Cr	8.589	2.384
Pb	3.229	0.997

Mann-Whitney U test showed no significant difference of heavy metals concentration between both areas

Results and Discussion

Heavy Metals Concentration in Freshwater Fishes

Heavy metals (As, Cd, Cr and Pb) were detected in all fish samples from Sembrong River and Kahang River. Table 102.1 shows mean concentration of heavy metals in freshwater fish samples of both areas.

The results showed that the heavy metals contamination in fishes from Sembrong River were higher compared to Kahang River. The geographical nature of the river itself (Department of Fisheries Kluang 2013) coupled with pesticides and fertilizers pollution from palm oil and rubber plantations, improper waste management from the factories (sawmill, tissue papers, oil palm and wood processing) and sewage from pig farms might contributed to the heavy metals pollution at the area.

Health Risk Assessment

Table 102.2 shows the mean value of the Average Daily Dose (ADD), Lifetime Cancer Risk (LADD), Hazard Quotient (HQ) and Lifetime Cancer Risk (LCR) of respondents from both areas. Results showed that the health risk faced by the residents of Kampong Sedohok due to consumption of polluted fish were significantly higher compared to Kampung Punjut although all respondents fall into acceptable risk towards the carcinogenic and non-carcinogenic health risk at this moment. However, this condition may change in the future if the respondents continuously consumed polluted fishes.

Table 102.2 Mean of the health risk encountered by respondents from heavy metal exposure through consumption of freshwater fish

	Kampung Sedohok				Kampung Punjut			
	As	Cd	Cr	Pb	As	Cd	Cr	Pb
ADD	2.25×10^{-7}	1.78×10^{-6}	6.06×10^{-4}	23.88×10^{6}	3.19×10^{-6}	53.6×10^{-6}	1.72×10^{-3}	5.27×10^{-6}
LADD	1.03×10^{-7}	7.98×10^{-6}	2.06×10^{-4}	–	1.73×10^{-6}	22.3×10^{-6}	1.01×10^{-4}	–
HQ[a]	7.36×10^{-4}	2.8×10^{-3}	2.06×10^{-1}	9.33×10^{-5}	1.08×10^{-4}	1.07×10^{-3}	4.7×10^{-3}	5.33×10^{-5}
LCR[b]	1.54×10^{-7}	4.86×10^{-4}	4.3×10^{-6}	–	2.58×10^{-8}	1.35×10^{-6}	5.01×10^{-4}	–

[a, b] Mann-Whitney U test showed significant difference of HQ and LCR for every heavy metals between the two areas with $p < 0.05$

Conclusion

Heavy metals (As, Cd, Cr and Pb) were detected in all fish samples. The study indicated that fishes from the polluted Sembrong River showed slightly higher heavy metals concentration compared to less polluted Kahang River. The health risk indicated by HQ and LCR of respondents were also slightly higher in Kampung Sedohok compared to Kampung Punjut although all respondents fall into an acceptable risk towards carcinogenic and non-carcinogenic health effects. The increasing contamination level may lead to higher concentration of heavy metals in the fishes and posed greater health risk to respondents. It is recommended to perform biological monitoring of heavy metals exposure level to confirm the body burden of heavy metals on the respondents.

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Chapter 103
Patterns of Aerosol Over Malaysia from Multiple Satellite-Borne Sensors

Zulfa Hanan Ashaari, Grant Robert Bigg and Robert Gavin Bryant

Abstract Aerosols patterns over Malaysia are examined using two different satellite-borne sensors, namely the Moderate Resolution Imaging Spectroradiometer (MODIS) and the Ozone Monitoring Instrument (OMI), which have been providing continuous aerosol data since July 2002 and November 2004 respectively. The spatial and temporal distributions of aerosols detected by MODIS and OMI are described and compared with ground-based particulate matter measurements data. Data were analysed and discussed within the January 2005 until December 2008 time period. This period was chosen so as to compare multiple sources. Validation of MODIS and OMI with ground data for 48 months demonstrated that MODIS data product was more accurate in representing aerosols near the ground, while OMI data product was more accurate in detecting extreme emission events. An assessment of seasonal variability of MODIS, OMI and ground data revealed similar seasonal variability, where maximum values during the southwest monsoon season were found over all stations involved in this study. Therefore, these results suggest MODIS and OMI data product can be used as a proxy for regional aerosol studies.

Keywords Aerosols · Remote sensing · MODIS · OMI

Highlights

- MODIS AOD data product represents ground aerosol loadings better than OMI UVAI.
- MODIS AOD captured more aerosol properties than OMI UVAI.

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- All sensors possessed a strong correlation in the south Peninsular Malaysia.
- Both sensors and ground measurements showing strong seasonal cycle.

Introduction

Malaysia is well known as one of the regions affected by recurring air pollution phenomena on an unprecedented scale (Radojevic and Hassan 1999). However, despite the importance of air pollution issues in Malaysia, current understanding of this system in this region is hampered by data insufficiency and knowledge gaps. The understanding of aerosols patterns is essential for predicting future trend and assessing aerosols impact to the regional and global climate evolution. Previous studies show ground-based measurements coupled with remote sensing data sets have proved valuable for studying spatial and temporal aerosol distribution (Gassó and Hegg 1998; Hsu et al. 1999; Koukouli et al. 2006; Alam et al. 2010; Mélin et al. 2010; Alam et al. 2011; Guleria et al. 2011). Therefore, this study aims to evaluate the agreement and differences between different datasets and to determine and compare aerosol properties from different sources in the Malaysian region.

Materials and Methods

Satellite remote sensing datasets and ground-based measurements at 16 Malaysian Air Quality Monitoring Network stations (AQMN) has been collected for the period of 2005–2008. This study used MODIS Aerosol Optical Depth (AOD) and OMI UV Aerosol Index (UVAI) data provided by NASA and were conscientiously prepared, and analysed with the use of modern tools: Geographical Information System (ArcGIS). TOMS UVAI data was collected from TOMS version 8.5 algorithm collection 3 (OMTO3) and MODIS AOD was collected from Collection 5 (C005) of the Level 3 atmosphere products. Along with MODIS and OMI data product, this study also used ground-based particulate matter data prepared and provided by the Malaysian Meteorological Department (MMD) on a monthly basis. Ground-based particulate matter data was prepared on a point basis. Both MODIS AOD and OMI UVAI data product went through some treatment in order to get the point-based values. Erdas Imagine and ArcGIS software has been used to do this treatment.

Inter-Comparison Analysis

Lots of issues arose when analysing and comparing multiple datasets retrieved from multiple sources, such as sampling differences, data availability and instruments calibrations (Liu et al. 2008; Alam et al. 2011; de Meij and Lelieveld 2011).

However, temporal correlation analysis applied in this study is aimed at validating MODIS and OMI aerosol data and to gain a broader view of the sources of the concentrations over this region.

Results and Discussion

The correlation coefficient between ground particulate matter and MODIS AOD was found to be reasonably good ($r^2 = 0.5 - 0.7$), and significant in all stations located in the south peninsula with 95 % level of confidence. In contrast, the correlation coefficients between ground particulate matter data and MODIS AOD in the north peninsula stations were found lower. On the other side, stations located in Borneo exhibited significant and good correlation between ground particulate matter and MODIS AOD data ($R^2 > 0.36$). MODIS AOD may overestimate the values of low ground particulate matter. 3 out of 16 stations, which were found having insignificant relationship between ground particulate matter and MODIS AOD, exhibited small amounts of aerosol concentrations in the atmosphere, and thus there had been overestimates by MODIS AOD. In addition, MODIS AOD background values recorded in all stations vary between 0.15 and 0.4 μm. It is interesting to note, high correlation coefficients are mainly results of the good agreement between datasets when the AOD values are larger than 0.4 μm.

Correlation was found lower for ground particulate matter and OMI UVAI with 8 stations out of 16 stations exhibiting insignificant relationship. Most of the points are in expected accuracy when the OMI UVAI values are larger than 0.2 μm. This suggests stations with good relationship between ground particulate matter and OMI UVAI may contain high absorbing aerosol amounts in the atmosphere, probably contributed to by vegetation fires emission. Temporal correlation between MODIS AOD and OMI UVAI was good, with only 3 stations out of 16 having an insignificant relationship. Stations located in the northeast peninsula, show an insignificant relationship for all data products. This is due to these stations being located in a rural area and this suggests aerosol concentration over this area may vary and be affected by local pollution. In most of the stations, ground particulate matter and MODIS AOD were correlated well due to MODIS's high spatial resolution compared to OMI sensors.

The seasonal variation of ground particulate matter, MODIS AOD and OMI UVAI was analysed over a period of 4 years (2005–2008). Stations located in the south peninsula show maximum aerosol loading from July to October. These maximum values of aerosol concentration are clearly related to the dry background in this region due to the arrival of the dry season southwest monsoon during this period. The maximums in the late northeast monsoon also appear particularly in ground particulate matter and OMI UVAI datasets. The lowest values, which are associated with raining seasons, can be seen during December to February in all stations and datasets. On the other hand, a bimodal cycle can be clearly seen in the ground particulate matter and OMI UVAI datasets for stations located in the north

peninsula, where maximum loading was recorded in February and July. This is probably related to the bimodal annual cycle of rainfall over this region. MODIS AOD data set exhibited one peak cycle which occurred in summer. For the months presenting the highest mean value; (July–October), the ground particulate matter, MODIS AOD and OMI UVAI span a small range of value, 90 % of the monthly data are between 20 to 90 μg m^{-3}, 0.2 to 0.3 μm and 0.0 to 0.1 μm respectively.

The seasonal analysis showed that the station which is located in south-west Borneo, has the highest values of ground particulate matter, MODIS AOD and OMI UVAI, particularly during the southwest monsoon season and the lowest values were recorded during the northeast monsoon. This station is located close to biomass burning sources, thus the forest fires emissions are more persistent along with other local emissions. This is in contrast with what was found in the north Borneo station. These station recorded very little aerosol and showed bimodal cycle which peaks during inter-monsoon seasons (October–November).

Conclusion

Explanation of the differences and agreements between these different datasets is not straightforward. However, in spite of the instrumental differences, overall, MODIS is better than OMI in representing what happens on the ground. Values of OMI UVAI might be biased by aerosol from the ocean because positive values of AI will be associated with the UV absorbing aerosol from both local and trans-boundary aerosol. In contrast, MODIS AOD provides better estimates in terrestrial regions. Most of the ground particulate matter observations are in agreement with MODIS AOD and OMI UVAI when the ground particulate matter value is larger than 60 μg m^{-3}. On the other hand, MODIS AOD and OMI UVAI exhibited a good relationship for 80 % of the stations involved in this study.

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Chapter 104
Health Risk Assessment of Heavy Metals via Consumption of Bivalves Species in Kota Kinabalu, Sabah, Malaysia

Kamsia Budin, Sarva Mangala Praveena, Mahyar Sakari, Suriani Hassan and Elya Izzati Ibrahim

Abstract Bivalve organisms are more vulnerable to a variety of aquatic pollution. It has high adaptability to various levels of contaminations. It can accumulate pollutants such as heavy metal in its tissues and cause major concern on potential risk of heavy metal especially to the consumers. The objectives of this study were to determine heavy metal (Cu, Zn, Pb and Cd) concentrations in five most consumed and popular bivalve species among Kota Kinabalu community and to compare with the Food Regulation Malaysia (1985) and Food and Agriculture Organization. Five most consumed bivalves species are *Meretrix meretrix* (Kepah), *Anadara granosa* (Kerang), *Tridacna squamosa* (Kima), *Polymesoda erosa* (Lokan) and *Crassostrea gigas* (Tiram). Health risk associated with these heavy metals in the five bivalves species were estimated based on target quotients (THQs). The results indicated that the metal concentrations in the bivalves ranged from 3.21 to 36.22 mg/kg for Cu, 28.62–1771.12 mg/kg for Zn, 0.20–3.43 mg/kg for Pb and 0.44–7.27 mg/kg for Cd. These concentrations were significantly correlated with species and the size of bivalves. Some of the heavy metal concentrations exceeded the permissible level by Food Regulation Malaysia (1985) and Food and Agriculture Organization. However, based on the THQs value for adults, only metal concentrations in *Crassostrea gigas* (Tiram) exceeded, which indicates potential health risks associated with the consumption of this species.

Keywords Bivalves · Heavy metals · Health risk · Target hazard quotients (THQs)

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Highlights

- Zinc in *Crassostrea gigas* was the highest.
- Heavy metal concentrations were correlated with species and size.
- THQs value of heavy metal concentration in *Crassostrea gigas* feared may have a high risk.

Introduction

Generally, heavy metal enters the aquatic environment through atmospheric deposition, erosion of geological matrix and anthropogenic activities (Kaviarasam et al, 2012). Mining and industrial processing are some of the anthropogenic activities that cause the heavy metal contamination in the environment. These metals may accumulate in environment to a toxic concentration level which can lead to ecological damages (Alkarkhi et al, 2008). People can be exposed to these toxic chemicals that accumulate in seafood such as fish and shellfish taken from contaminated environment. Mollusks such as gastropods and bivalves are more sessile organisms as compared to fish. This makes them more susceptible to heavy metal accumulation through food intake and absorption from the environment and sometimes impose health hazard to consumers (Gupta and Singh, 2011).

Several methods have been used to estimate the potential health risks from heavy metals exposure. Current non-cancer risk assessment methods as typically based on the use of the target quotient (THQ), a ratio between the estimated dose of a contaminant and the references dose below which there will not be any appreciable risk (US EPA, 2000). If the ratio is less than 1, there will not be any obvious risk. This noncancer risk assessment method was also applied in this study.

The purpose of this study is to evaluate heavy metal concentration of Cu, Zn, Pb and Cd in the five bivalve species. This study also evaluates public health risks associated with five species of shellfish; *Meretrix meretrix* (Kepah), *Anadara granosa* (Kerang), *Tridacna squamosa* (Kima), *Polymesoda erosa* (Lokan) and *Crassostrea gigas* (Tiram), which are commonly consumed and popular among Kota Kinabalu community.

Materials and Methods

The fresh bivalves *Meretrix meretrix* (Kepah), *Anadara granosa* (Kerang), *Tridacna squamosa* (Kima), *Polymesoda erosa* (Lokan) and *Crassostrea gigas* (Tiram) were bought from four main markets in Kota Kinabalu. The five species were selected as they are common and the most popular bivalve among

community in Kota Kinabalu, Sabah. The samples were secured in clean plastic bags, kept on ice while being transported back to the laboratory for analysis. The location of the bivalve where they were collected by the fisherman was also recorded. The bivalve size was measured and the soft tissues were removed. Wet digestion method has been carried out using nitric acid (69 %) and detected with Inductively Couple Plasma-Optical Emission Spectrometry (ICP-OES).

One hundred and fifty customers were interviewed briefly and filled in a questionnaire on nutritional habits. The questions included on the preferable bivalves, amount, frequency of consumption, preparation methods and weeks of consumption. The locations where bivalves collected by the fishermen were recorded.

The methodology for estimation of target THQ used was explained in US EPA (2000). The models for estimating the THQ are:

$$THQ = \frac{EF \times ED \times FIR \times C}{RFD \times WAB \times TA} \times 10^{-3}$$

Where *EF* is exposure frequency (365 days/year); *ED* is the exposure duration (65 years) equivalent to the average lifetime; *FIR* is the food ingestion rate cephalopod mollusks: 9.8 g/person/day (FAO, 2005); *C* is the metal concentration in seafood (mg Kg^{-1}); *RFD* is the oral reference dose (Cd = 1 mg Kg^{-1}/day, Pb = 4 mg Kg^{-1}/day, Cu = 40 mg Kg^{-1}/day, Zn = 0.3 mg Kg^{-1}/day) (US EPA, 2000); *WAB* is the average body weight (65 kg). *TA* is the averaging exposure time for non–carcinogens.

Results and Discussion

The mean concentrations and standards deviations of all heavy metals analyzed is shown in Table 104.1. The heavy metal concentrations in bivalves were within the range of 3.21–36.22 mg/kg for Cu, 28.62–1771.12 mg/kg for Zn, 0.2–3.43 mg/kg for Pb and 0.44–7.27 mg/kg for Cd. Krusskal Wallis analysis shows that there are significant difference concentration of metals, where; *T. squamosal* > *C. gigas* > *A. granosa* > *M. meretrix* > *P. erosa*. However, there was no significant difference between the same species from different locations. This suggested that same species have a same mode of life and feeding may also have same uptake rate of metal concentration (Otchere, 2003). Still other factors such as geographical factors should not be excluded entirely (Peakall and Burger, 2003).

Spearmen test shows a significant correlation ($p < 0.05$) between Cu and Zn concentration and the size of bivalves. The bigger the bivalves, the more metal accumulated in the soft tissue.

Some of the heavy metal concentrations were exceeded the permissible level set by Food Agriculture Organization (Uzairu et al, 2009) and the Malaysia (Food Act Malaysia Food Regulation 1985, 2003). The present study showed that the Cd

Table 104.1 Mean concentrations (mg/kg w.w) and standard deviations of selected heavy metals (N = 45)

Market	Location collected	Species	Metal concentration (mg kg^{-1})			
			Cu	Zn	Pb	Cd
Donggongon	Kimanis	*M. merretrix*	8.49 ± 1.56	56.78 ± 2.83	56.78 ± 2.83	56.78 ± 2.83
	Kinarut	*P. erosa*	14.07 ± 2.36	211.2 ± 77.5	1.06 ± 0.63	0.49 ± 0.04
Night market	Semporna	*T. squamosa*	4.88 ± 1.13	99.5 ± 24.3	1.80 ± 0.17	3.82 ± 1.06
Kota Kinabalu	Sandakan	*M. meretrix*	3.21 ± 0.69	28.6 ± 6.84	0.20 ± 0.04	0.92 ± 0.39
		A. granosa	4.17 ± 0.41	58.4 ± 11.7	0.27 ± 0.03	7.27 ± 0.39
	Semporna	*A. granosa*	4.99 ± 0.28	50.4 ± 5.9	0.61 ± 0.59	2.56 ± 0.37
Putatan	Tanjung	*P. erosa*	27.09 ± 6.27	384.5 ± 85.6	3.43 ± 0.30	0.44 ± 0.03
	Dumpil	*C. gigas*	36.21 ± 6.88	1771.1 ± 350.3	0.94 ± 0.64	0.72 ± 0.09
Tuaran	Gayang	*P. erosa*	11.46 ± 3.37	103.5 ± 7.9	1.36 ± 1.03	0.51 ± 0.12

concentration in *T. squamosa*, and *A. granosa* exceed the Malaysia Food Act, 1985, which is 1 mg/kg, and the Food Agriculture Organization which is 0.5 mg/kg. Even though, most of the Pb concentration in the species were higher than the FAO standard which is 0.5 mg/kg, it is below the local regulatory (2 mg/kg). The zinc concentration in *C. gigas* was the highest concentration and exceeded more than 5x in comparison to both permissible limits. Other studies showed that *Crassostrea* sp. were able to accumulate Zn in its soft tissues up to extreme concentration without showing any sign of problem (Gupta and Singh, 2011).

The THQs value was calculated from the highest metal concentration recorded in the bivalves. The results show that the estimated THQ value for Zn concentration in *C. gigas* was the highest and exceeded 1. The Total THQ (Total of THQ for each metal concentration) in *G. gigas* was extremely high, which is 6.24. Findings from this study indicate that there is a possibility of health risk associated with eating these bivalves. The risk associated with Cu, Cd and Pb were only 4, 6 and 4 % of the Total THQ, respectively. The discrepancy of Total THQ may be primarily attributed to the distinct concentration of Zn.

Even though, the THQ value is alarming, Zn is categorized as micro nutrient and essential to living organisms. It involves in enzymes synthesis and metabolism activity. Other studies show that Zn are not considered as significant threat to human health as it can be easily regulated by man and low mammalian toxicity (Gupta and Singh, 2011; Nakisah et al, 2001).

Conclusion

The metal concentrations in the bivalves ranged from 3.21 to 36.22 mg/kg for Cu, 28.62–1771.12 mg/kg for Zn, 0.20–3.43 mg/kg for Pb and 0.44–7.27 mg/kg for Cd. The total THQ in *G. gigas* is 6.24 and the Zn concentration contributes to 85 % of the total THQ. Further studies are warranted as Zn is not considered as toxic metal as Hg, Cd or Pb.

The simple survey analysis shows that some ethnic groups in Kota Kinabalu may be at risk of exposure to high metal concentrations as the bivalves were the main source of protein in their diet.

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Chapter 105
Spatial and Temporal Distributions of Dissolved Organic Carbon in the Setiu River, Malaysia

Suhaimi Suratman, Yet Yin Hee and Norhayati Mohd Tahir

Abstract In general, higher concentrations of dissolved organic carbon (DOC) were measured at the downstream area of Setiu River basin, which associated with urban location. The high molecular weight (HMW, <100 kDa) DOC fraction generally was dominant consisting of 55–85 % of total DOC, within the DOC pool. Overall, HMW DOC dominance was associated with agricultural, aquaculture and urban areas, and was therefore likely to be a result of anthropogenic inputs. Re-suspension of bottom sediment in the river may have also played an important role in controlling the HMW DOC distribution in present study. The low molecular weight (LMW, <30 kDa) DOC, which constituted 34–70 % of total DOC, was generally showed the significant correlation with chlorophyll-a (chl-a), suggesting phytoplankton related processes may ifluence the LMW DOC in water column. DOC concentrations were climatological related with high values during the monsoon season and decreased significantly during non-monsoon season.

Keywords Chlorophyll-a · Dissolved organic carbon · Fractionation · Surface water · Southern South China Sea

Highlights

- Higher concentrations of DOC were found at downstream area.
- High molecular weight DOC fraction dominated the total DOC pool.
- HMW DOC fraction is from anthropogenic inputs and re-suspension of bottom sediment.
- LMW DOC fraction was associated with phytoplankton related processes.

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Introduction

Dissolved organic carbon (DOC) contains a large amount of organic molecules of low and high molecular weights. Hence, DOC can be divided into two classes i.e. High Molecular Weight (HMW) and Low Molecular Weight (LMW), operationally defined by ultrafiltration membrane cutoff. The size-based distinction between these fractions is more reasonably practical in understanding the sources and transformations of DOC. In general, HMW DOC could be terrigenous origin and sediment resuspension (Wang et al. 2004), while LMW DOC is from the biological origin (Suratman et al. 2009). In order to determine the seasonal and spatial variations of DOC, surveys of the spatial and temporal distribution of this parameter were carried out in the Setiu River basin, Malaysia. Size fractionation study was also carried out in order to identify the possible sources of DOC in the study area. The findings aim to comprehend the dynamics of organic C in aquatic system.

Materials and Methods

The study was carried out in the Setiu River Basin in the east coast of Peninsular Malaysia (Fig. 105.1). Land use within the river basin is expanding and is primarily associated with aquaculture and agriculture activities at the lower reaches of the river. Population density is concentrated at the middle and lower reaches of the river. This river basin is economically important since it provides water for

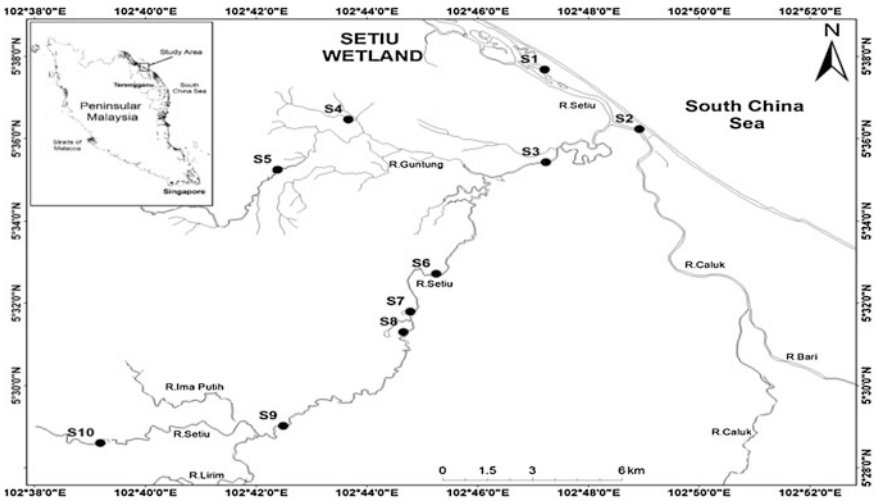

Fig. 105.1 Sampling sites of Setiu River basin

irrigation as well as services related to aquaculture, municipal water supply, and wastewater dilution. Wet Northeast (NE) monsoon from November to March and dry Southwest (SW) monsoon from May to September strongly influence the basin.

Samples were collected at monthly intervals for one year. The water samples were collected at 0.5 m depth using a Van Don sampler directly into polyethylene (PE) bottles. Samples for DOC determination were filtered immediately in the laboratory through pre-combusted (450 °C for 5 h) GF/F glass filter (pore size ~0.7 μm) and stored at −20 °C until analysis.

DOC was analysed by high temperature catalytic oxidation (HTCO) method using a Shimadzu TOC-V analyzer. Size fractionation of DOC was achieved by membrane ultrafiltration in a stirred cell (Amicon) under nitrogen pressure. The molecular weights of 30 kDa and 100 kDa were used as the cutoff point. The HMW DOC and LMW DOC in this study were operationally defined as the fraction with size below 100 kDa and below 30 kDa, respectively.

Results and Discussion

The DOC mean concentrations measured for Setiu River ranged from 1780 to 5400 μg/L C (Fig. 105.2). Two-factor without replication ANOVA test indicated that there was a significant difference for sampling sites ($p < 0.05$), reflecting that there was an obvious variation of DOC concentrations among the sampling sites. Relatively higher concentrations of DOC were observed at middle reaches of the river basin, which could be due to the domestic wastes from the urban area. The result reveals that there is a sharp increase of DOC concentration at station S2. Station S2 is located at downstream area with concentrated of agricultural and aquaculture activities, which could attributed to the anthropogenic inputs such as fertilizers used in the areas runoff toward the adjacent river. Royer and David (2005) have supported the claim that DOC from the agricultural area runoff to river

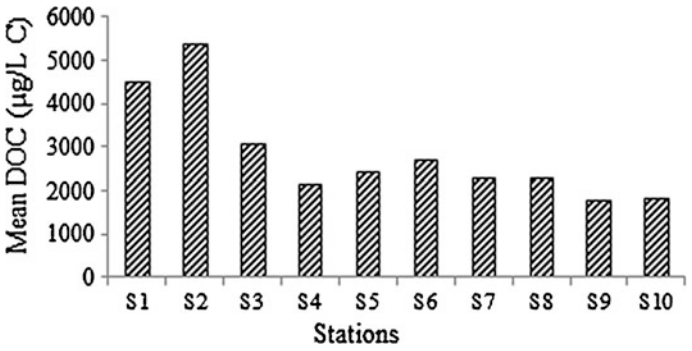

Fig. 105.2 Variation of mean DOC concentrations

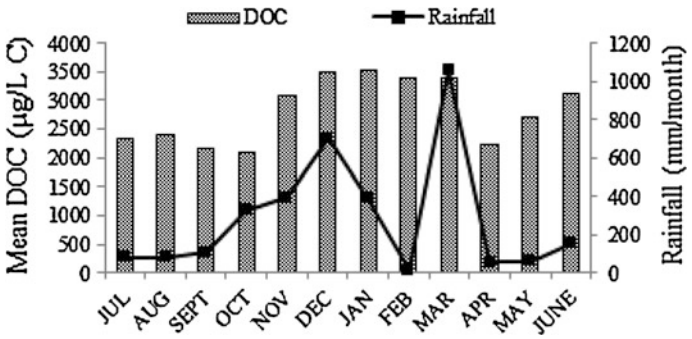

Fig. 105.3 Variation of mean DOC concentrations

was relative to the pool of soil organic carbon. Another elevated of DOC concentration at station S1 in present study may due to the location at Setiu Wetland. Aitkenhead and McDowell (2000) study found that the occurrence of massive amount of total organic C was more likely to found in wetlands. In present study, the saturated soils in station S1 (Setiu Wetland) probably inclined to retain organic C and therefore appeared higher DOC concentration.

DOC concentrations in Setiu River basin were generally responsive to the rainfall with DOC increasing during periods of high rainfall i.e. the NE monsoon season (October–March) (Fig. 105.3). From the ANOVA analysis, there was a significant difference between sampling periods ($p < 0.05$). The alternations of wet and dry seasons influence the retention and loss of chemical compounds. For example, agricultural runoff may result in excess organic C from non-point sources being washed out into the rivers by rain or leached into them through the soil. This runoff may result in high levels of organic C in present study.

The results show that the mean LMW DOC constituting 34–70 % of total DOC pool, while mean HMW DOC pool varied from 55 to 85 % of total DOC (Fig. 105.4).

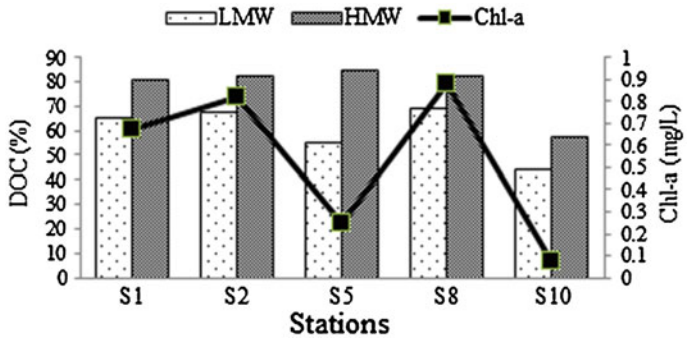

Fig. 105.4 Variation of mean LMW and HMW DOC (%) with chl-a

The weight distribution of DOC was used to aid source discrimination of the organic matter and to help understanding of the functional role of DOC in aquatic systems. In this study, stations with high percentage of LMW DOC were generally exhibited high chl-a concentration such as stations S1, S2 and S8. DOC may also be related with chl-a (Kragh and Søndergaard 2009) since the DOC can be attributed from phytoplankton exudation or decomposition (Lønborg et al. 2009; Suratman et al. 2009).

Of the five stations with high percentages of HMW DOC, three stations were associated with agriculture and urban areas (S1, S2 and S8). This relationship suggests that there may have been an anthropogenic source for the HMW DOC. This is in agreement with Wang et al. (2004). In this study, agricultural and urban land uses, affect the middle and lower reach of the river. Thus, input from sewage and sources and local anthropogenic inputs such as sewage inputs from urban runoff and sewage treatment plant outflow were contributed significantly to the HMW fertilizer runoff could be contributed to the high HMW DOC. The higher percentage of HMW DOC at station S5 caused by re-suspension of bottom sediments and releases the organic carbon into water column, due to ongoing sand dredging activities, which released the bottom sedimentary organic carbon.

Conclusions

This study shows that DOC concentration was relatively higher at the areas of agricultural, aquaculture and urban area. DOC pool was dominated by HMW DOC fractions and may be driven by the anthropogenic inputs and re-suspension of the organic matter from bottom sediment. Significant association of LMW DOC with chl-a was suggests that LMW DOC in present study was in part a result of by phytoplankton exudation or degradation. Moreover, DOC concentrations were linked to season, i.e. with higher during monsoon season and lower during non-monsoon season. This relationship was expected to be driven by higher runoff of DOC from soil into the river and the re-suspension of bottom sediment.

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Chapter 106
Discriminant Analysis of Water Quality Data in Langat River

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Abstract River monitoring processes usually generate large databases of water quality variables. These water quality variables are important to identify the status of the river. Due to multidimensionality of complex characteristics in river water, meaningful information from a large database can be extracted by using multivariate statistical methods, i.e., discriminant analysis (DA). Appropriate univariate transformation and data screening for multivariate outlier's detection were considered. The DA approach used in this study gave better information on river water quality, especially concerning the contribution of the variables in discriminating between the three spatial areas in Langat River.

Keywords Discriminant analysis · Water quality · Cluster analysis · Langat river

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Highlights

- DA approaches used gave better information on Langat river water quality.
- Thirteen significant variables were identified.
- The 13 variables statistically significant in discriminating among the sites cluster.

Introduction

Discriminant analysis (DA), is a multivariate method used to differentiate a particular classification variable using numerous characteristics. In river water quality analysis, the classification of variable refers to a particular type of land use or source pollution (Juahir et al. 2010), flow events (Shah Ali Charlie 2010) and also seasonal factors (Boyacioglu and Boyacioglu 2010). The DA approach used in most of water quality studies was limited to the accuracy of spatial classification, which is based on selected influential variables. Another approach, namely canonical discriminant analysis (CDA) can be used to identify most influential variables that discriminate effectively between one group and the other. From the CDA, the linear combinations of the quantitative variables, i.e., canonical variables, extracted and summarized between-group variation are in much the same way as the principal component analysis (PCA) (SAS 1999). However, the CDA approach is not widely used, especially in river water quality studies. Therefore, the CDA used in this study is to re-validate the DA as an alternative way to identify the most influential river water quality variables that best reveal the differences among the pre-identified group.

Materials and Methods

In this analysis, data for Langat River was collected based on the availability of recorded data from the period of 1995–2007. Five main monitoring stations were selected and the location is shown in Fig. 106.1 (Juahir et al. 2010). In this study, cluster analysis (CA) used hierarchical clustering procedure on the uncentered correlation distance was considered to group the most similar internal structure between objects. The proximities matrix between standardized water quality variables at station i and j,

$$D_{ij} = 1 - \left| r_{ij}^2 \right| \tag{106.1}$$

is calculated and it can be computed easily from statistical software, i.e. Minitab 1.5. The $\left| r_{ij}^2 \right|$ in Eq. (106.1) is the absolute value of the Pearson correlation coefficient. The initial classification information was then used in stepwise

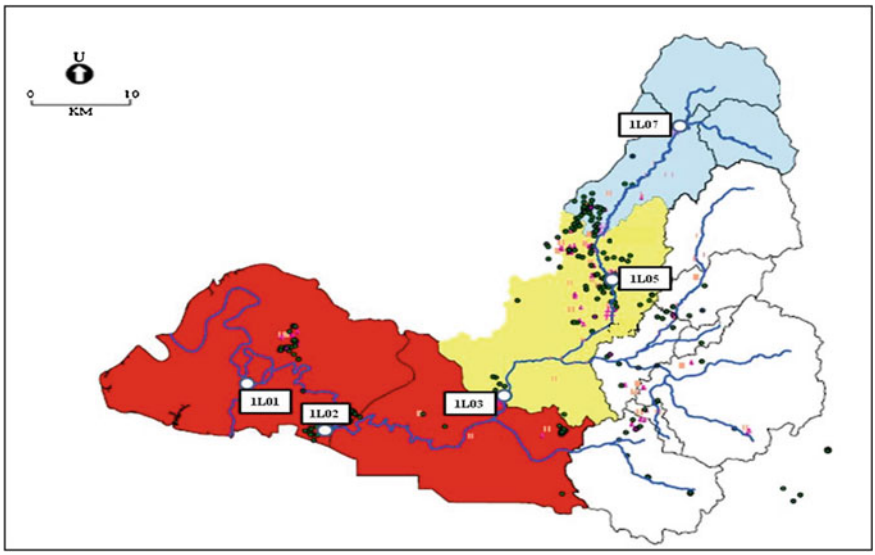

Fig. 106.1 Location of the selected sampling stations

discriminant procedures (SDA) to determine important discriminating variables. Those important variables were then used in canonical discriminant analysis (CDA) to confirm the inter-relationships between variables. In this paper, SAS software was used and the results were reported based on the treatment of raw data without standardization.

Results and Discussion

Based on cluster analysis, three groups of the five established existing stations were identified as shown by the dendogram in Fig. 106.2.

Three main groups defined by CA, i.e., high pollution-sources site (HPS), moderate pollution-sources site (MPS) and low pollution-sources site (LPS), were treated as dependent variables; and the water quality variables as independent variables. Based on SDA, 13 variables were found to be significant variables, i.e. Na, Turbidity, Ammoniacal Nitrogen, Ca, Dissolved solids, Electrical Conductivity, K, Temperature, Mg, pH, Dissolved Oxygen, Zn and Total Solids. On the other hand, the CDA results revealed that 13 variables were statistically significant in discriminating among the sites cluster, based on variance explained by two functions. The total amount of variances explained by the two functions is 100 % and the correlations of 0.97 and 0.84 indicate that the functions discriminate very well. The first and second canonical functions account for 85 and 15 %, respectively, for the variation in the discriminating variables. To aid visual interpretation

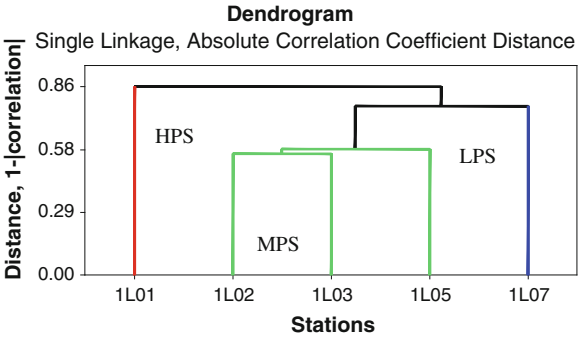

Fig. 106.2 Similarity dendogram obtained using Single Linkage method

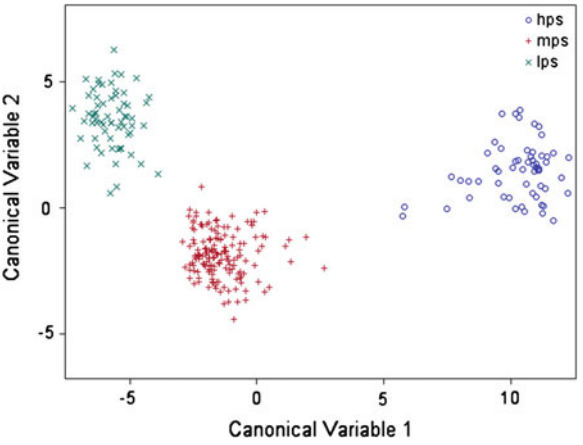

Fig. 106.3 Bi-plot display of 13 variables and the group discrimination

of group differences, the pairs of canonical variable scores in two dimensional bi-plots were plotted, as seen in Fig. 106.3. The plot shows the interrelationship among the 13 variables. The first canonical function with the largest loading on Conductivity, Dissolved Solids, Total Solids, Ca, K, Mg and Na successfully distinguished the HPS from the other two MPS and LPS groups. The second canonical function with the largest size loadings on Ammoniacal Nitrogen and Turbidity successfully discriminated between the MPS and LPS groups.

Conclusion

The results from the first canonical function, which has the largest loading on Electrical Conductivity, Dissolved Solids, Total Solids, Ca, K, Mg and Na, were consistent with the previous study (Juahir et al. 2010). Hence, the DA approaches

used in this study gave better information on river water quality, especially concerning the contribution of the variables in discriminating between the three spatial areas in Langat River.

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Chapter 107
Predictive Modeling of Chlorophyll a for Tropical Lake by Means of Hybrid Evolutionary Algorithm (HEA)

Mohd Yusoff Ishak, Hong Qing Cao and Friedrich Recknagel

Abstract This paper discusses the application of Hybrid Evolutionary Algorithm (HEA) model to simulate dynamics of Chlorophyll a in Lake Putrajaya, Malaysia for 7-days-ahead prediction using data from 2003 until 2008. Results are measured in term of closeness between predicted and measured data as well as the root mean square error value (RMSE) and r-square. The HEA achieved reasonable accuracy in predicting timing and magnitudes of algal blooms. Chlorophyll a concentrations levels at Lake Putrajaya were divided into low and high abundance in the water column depending on the pH threshold value of 7.9. Chl-a concentrations in Lake Putrajaya is predicted higher if pH of the water exceeds 7.9. Sensitivity analyses revealed that an optimal condition for algal growth and abundance is not only driven by physical and chemicals characteristics of the water body but also by impact of the monsoon season where a highest Secchi depth of up to 2.4 m was observed. The HEA has shown potential for utilisation in early warning and strategic control of algal blooms in tropical freshwater lake. Outcomes of this research offers an original contribution to the knowledge domain Ecology of Tropical Lakes by successfully applying data driven models (HEA).

Keywords Tropical lakes · Hybrid evolutionary algorithm (HEA) · Chlorophyll-a · Eutrophication

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Highlights

- HEA allows swift assessment of water quality and trophic status in Lake Putrajaya.
- HEA model is able to predict algal growth in tropical lakes ecosystem in Malaysia.
- HEA model forecasted a positive relationship between Chl-a and pH.

Introduction

Ecological key processes in tropical lakes are characterised by faster process rates as a result of higher water temperature conditions. The fluxes and transformation rates of tropical lakes are high and variable (Marotta et al. 2009) and information on nutrient cycling from temperate lakes cannot necessarily be extrapolated to tropical lakes, because of the fundamental difference in the physical and biological dynamics of the two type of systems (Gardner et al. 1998). The removal of planktonic biomass form in water storage reservoir for potability, efficient hydropower generation and safe water contact activities is costing a lot of money (Ho 1996; Omran 2011).

Intensive lake monitoring studies in Malaysia are not feasible due to the large numbers of lakes. Time series data from lake ecosystems parameters in this research were used to forecast algal blooms in the distant future such as 7-days ahead. Forecasting of both the timing and magnitude of an algal species were estimated by a set of rules. The adopted 7-day ahead for this predictive tool provides opportunities for proactive rather than reactive management regimes with regards to mitigating the effects of algal blooms in tropical lakes.

Results of this research have specified factors influencing the tropical lakes ecosystems and enhance understanding of these dynamic lakes. The Hybrid Evolutionary Algorithm (HEA) methods used in this research were also able to provide a model that would be able to be used operationally for tropical lakes.

Methods and Materials

Sampling procedures, including sample preservation and analytical methods for the measured parameters were carried out in accordance with APHA (1995). The software HEA was applied to develop models for Lake Putrajaya to allow 7-days-ahead forecasting of algal community dynamics reflected by chlorophyll-a data.

The HEA was designed to uncover predictive rules in ecological time-series data (Cao et al. 2006a) by combining genetic programming to generate and optimise the structure of rules and genetic algorithm to optimise parameters of rules (Recknagel et al. 2006). Rules discovered by HEA have the IF–THEN-ELSE structure and allow imbedding complex function synthesises from various predefined arithmetic

Table 107.1 List and definitions for input variables symbols

Input symbols	Definitions	Input symbols	Definition
WT	Water temperature	NO_3-N_{inflow}	Nitrate inflow
pH	pH	PO_4-P_{inflow}	Phosphate inflow
SD	Secchi depth	Turb	Turbidity
DO	Dissolved oxygen	Cond	Conductivity
NO_3-N	Nitrate	SR	Solar radiation
PO_4-P	Phosphate	Rainfall	Rainfall

operator (Cao et al. 2006b). The software HEA has been applied by means of the bootstrap training mode for 100 runs randomly picking 80 % of the data for training and 20 % of the data for testing. The list of input variables used for the experiment and their respective definitions are listed in Table 107.1

The polimictic shallow mesotrophic Lake Putrajaya is located at latitude 2° 55′ 11″ and longitude 101° 41′ 24″ with an average depth of 6.6 m.

Results and Discussion

The following model has been identified as the best performing model:

IF pH is equal or less than 7.9, THEN the chlorophyll a concentration is calculated by the equation;

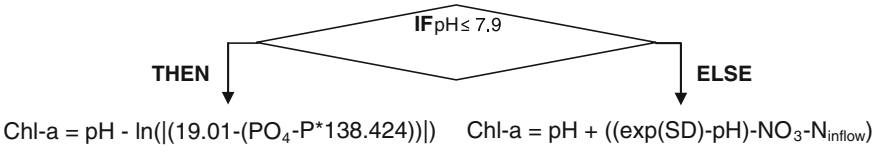
$$\text{Chl} - \text{a} = \text{pH} - \ln(|(19.01 - (\text{PO}_4 - \text{P}^{*}138.424))|)$$

Otherwise, the chlorophyll a concentration is calculated by the ELSE equation:

$$\text{Chl} - \text{a} = \text{pH} + ((\exp(\text{SD}) - \text{pH}) - \text{NO}_3 - \text{N}_{\text{inflow}})$$

The model achieved a root mean square error (RMSE) of 2.35 and an r^2 of 0.33

Conditions for Chl-a concentrations levels of Lake Putrajaya was divided into those for low and high abundance of the phytoplankton in the water column depending on the threshold value pH = 7.9. The ELSE branch of HEA forecasting model indicated a positive relationship between Chl-a and pH. Chl-a concentrations was higher if pH exceeds 7.9 (ELSE-branch) and lower Chl-a concentrations was forecasted for pH ≤ 7.9 by the THEN-branch. Shapiro (1973) has shown that pH is important in controlling algal dominance especially in determining the relative abundance of green and blue-green alga and believes this is associated with CO_2 availability.



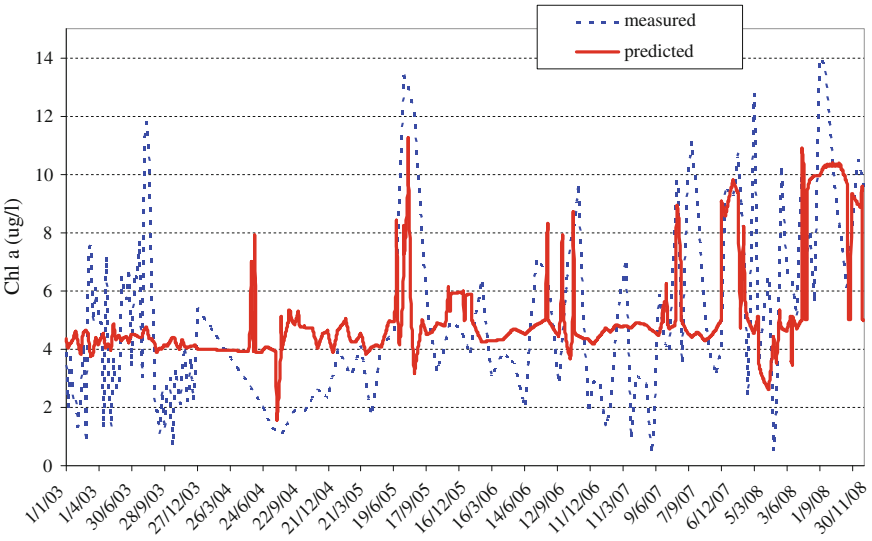


Fig. 107.1 Validation of the 7-days-ahead forecasting model for Chl-a (ug/l) in Lake Putrajaya for the years 2003 to 2008 (measured Chl-a = *blue dot*; predicted Chl-a = *red line*)

With regards to nutrient dynamics, the ELSE-branch was observed to reflect optimal conditions for phytoplankton growth outside the monsoon season where highest Secchi depths of up to 2.4 m and lowest NO_3-N_{inflow} concentrations coincide with highest Chl-a concentrations. However, the THEN-branch was reflecting sub-optimal underwater light conditions for phytoplankton growth during the monsoon season in the lake where the highest PO_4-P concentrations concurring with higher Chl-a concentrations.

The Chl-a model validation for Lake Putrajaya from the year 2003 to 2008 matches well timing and magnitudes of peak events except for Chl-a dynamics between 2003 and 2004 (Fig. 107.1). The model matches well peak events of Chl-a from 2005 to 2008 by predicting timing and magnitudes of such events. However the model fails to properly predict Chl-a dynamics between 2003 and 2004 even though matching the average Chl-a concentrations for that period of the year due to extreme hydrodynamic conditions during the early stage of the lake development. The shallowness of the lake in combination with intense management impacts added to the highly stochastic nature of this lake during these first 5 years.

Conclusion

The HEA has been successfully applied to develop and validate a forecasting model for Chl-a concentrations for tropical lake ecosystem of Lake Putrajaya. Chlorophyll-a was used as a proxy for algae growth. Results from this research have demonstrated that development of rule-based HEA model can forecast algal abundance in tropical lake ecosystem.

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Chapter 108
Heterogeneous Preferences for Domestic Water Quality Service Improvement: A Mixed Logit Approach

Suleiman Alhaji Dauda, Mohd Rusli Yacob and Alias Radam

Abstract This paper reports the findings from choice experiment (CE) study designed to estimate the economic value of domestic water quality and services attributes in Damaturu, Yobe State Nigeria. The Mixed Logit Model (MLM) was used in order to estimate the household preferences and personal interviews were made on a total of 300 households. The households were asked to select the best among the alternatives of the domestic water quality and service improvements. The attributes investigated were tab water quality (TWQ), total supply of water (TWS), tap water pressures (TWP) and water billing price (P). Findings of the study show that the household's preferred the highest changed in each attributes levels. The most significant variable in MLM model is TWQ attribute, which marginal rate of substitution (MRS) is 685 % for simple model and 572 % for interaction model. The findings of this study can assist the government in designing cost effective management and efficient tariff structure.

Keywords Choice experiment · Water quality · Willingness to pay · Mixed logit model · Heterogeneous attributes

Highlights

- MLM allows the variation of household's preferences for tab water attributes.
- The household's preferred the highest changed in each tap water attribute levels.
- MRS results can assist the government in designing tap water cost management.

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Introduction

This paper presents the findings of choice experiment (CE) study designed to estimate the economic value of domestic water quality and services attributes in Damaturu, Yobe State Nigeria. The mixed logit model (MLM) was used in order to estimate the household preferences and personal interviews were made on a total of 300 households. Each household was asked to select the best alternatives of the domestic water quality and service improvements. The attributes investigated were tap water quality (TWQ), total supply of water (TWS), tap water pressures (TWP) and water billing price (P). Findings of the study showed that the household's preferred the highest changed in each attributes levels. The most significant variable in MLM model is TWQ attribute, which marginal rate of substitution (MRS) is 685 % for simple model and 572 % for interaction model. The findings of this study can assist the government in designing cost effective management and efficient tariff structure.

Materials and Methods

Individuals are assumed to choose the alternatives which maximize their utility; we can apply probabilistic models to choose between the different alternatives available in each choice set, therefore, a good is valued in terms of its attributes (Hensher et al. 2005). In each choice set, attribute representing three alternative management options include a status quo option (Table 108.1). In this case, 300 samples of randomized households were selected and interviewed in Damaturu metropolitan, to state their willingness to pay for the improvement in the quality of their drinking water and supply services attributes.

Mixed logit model (MLM) is considered to be the most promising state of art discrete model currently available (Hensher and Greene 2002). The mixed logit models assumes a general distribution over individuals and alternatives for η_n and an IID extreme value type 1 distribution for ε_{int} that is, η_n can take on a number of distributional forms such as normal, lognormal and triangular. Denotes the density of $\eta_n f(\eta_n|\Omega)$ where Ω are the fixed parameters of the distribution. For a given value of η_n, the conditional probability for choice i is logit, since the remaining error term is IDD extreme value. Since η is not given the unconditional choice probability is this formula integrated over all values of η weighted by the density of η_i.

Model of this form are called Mixed logit, because the choice probability $Li(\eta)$ is a mixture of logit with f as the mixing distribution. The probability does not exhibit the well-known independence from irrelevant alternatives property IIA (Louviere et al. 2001). Ratios of marginal implicit price which can be translated as marginal rates of substitution (*MRS*) between price and water attributes, the

Table 108.1 Classification of attributes used in the study

Attributes	Levels		Descriptions
Tap water quality (TWQ)			
TWQ1	*Non-satisfactory*	*1*	*Poor quality tap water that needs treatment before consumption*
TWQ2	Satisfactory	2	Fairly good tap water, but treatment is highly recommended to make it safer for consumption
TWQ3	Very good	3	Poor quality drinking water which cannot be consumed without treatment
Total supply of water (TSW)			
TWS 1	*Very irregular*	*1*	*Daily interruption of water supply*
TWS 2	Irregular	2	Interruption of water supply at least once weekly
TWS 3	Regular	3	Regular water supply everyday
Tap water pressure (TWP)			
TWP 1	*Low*	*1*	*Low tap water pressure, cannot reach those in upstairs, wastes time in water collection*
TWP 2	Medium	2	Moderate pressure seldom reach those in upstairs
TWP 3	High	3	High water pressure can reach upstairs and minimizes wasting time
Water bill price (P)			
	N200		Average water bill per month

Note Italics present the status quo attribute levels. *N200*$^{\#}$ *is equivalent to USD1.30 Approximately*. Water bill refers to household monthly water bills charged by Yobe state Water corporation, presented as amount (percentage) increase over the current bill

coefficient β_m gives the marginal utility of income and is the coefficient of price attribute and β_k is the coefficient of the tap water attributes.

Results and Discussion

The estimated results of the MLM and marginal rate of substitution (in percentage) are presented in Table 108.2. The simple MLM indicates that, two variables of tap water quality (TWQ3 and TWQ2) are significant at 5 % level. Meanwhile, the variable of total water supply (TWS2 and TWS3) and water pressures (TWP2 and TWP3) are significant at 10 % level respectively. The payment vehicle for domestic water quality service improvement simply uses an increase in water billing price, measured as a percentage (%) and the household is required to trade off how many percents (%) they would be willing to pay as an increase over the water price they pay to obtain and enjoy a varying mix of water service attributes.

Table 108.2 Results for choice experiment models

	Mixed logit		Marginal rate of substitution (%)	
Variables	Simple model	Interaction model	Simple model	Interaction model
TWQ2	1.9426**	3.5059*	383.85	158.89
	(0.699)	(1.2039)		
TWQ3	3.4558**	0.9730**	685.26	572.50
	(1.301)	(0551)		
TWS2	1.0327*	2.0070	204.06	327.75
	(0.462)	(1.4400)		
TWS3	1.0271*	0.9917*	202.06	161.94
	(0.489)	(0.4278)		
TWP2	4.3778*	4.3138***	865.05	704.43
	(1.822)	(1.1375)		
TWP3	2.3025	0.5538*	45.49	254.06
	(1.172)	(0.9115)		
ASC	2.4809***	2.7420***		
	(0.653)	(0.4447)		
PRICE	−0.5607***	−0.6124***		
	(0.216)	(0.1520)		
TWQ2_EDU	–	0.7685***		
		(0.2323)		
TWQ3_EDU	–	0.5060***		
		(0.1604)		
TWP3_GEN	–	−1.2970*		
		(0.7251)		
N(Observations)	1500	1500		
Log likelihood	−1391.358	−1370.363		
R^2	0.155	0.168		
Adjusted R^2	0.151	0.136		

Note Standard errors in parentheses
* Significance at 10 % level, ** significance at 5 % level and *** significance at 1 % level

Conclusion

Based on findings of this study, it can be concluded that people in Damaturu are already paying more than the YSWC stipulated bills, hence so long as the promising improvement would be affected WTP would be higher. The Water service company or decision makers should take it as a matter of utmost priority to connect all households with portable water, improves the quality of drinking water by ensuring compliance with national water quality standards, this would justify any further increase over the existing tariff.

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Erratum to: Source Discrimination of PAHs in Industrial Soil of the Persian Gulf Coast

Fatemeh Valizadeh-kakhki, Mohamad Pauzi Zakaria, Ahmad Zaharin Aris, Mehdi Mohammadi and Hassan Tajik

Erratum to:
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The author name "Mehdi Mohammadi" is correctly placed in by-line, and missed to place the affiliation in both XML and PDF. Below given author name and affiliation should be included in both XML and PDF (in chapter opening page).

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