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Influence of Traffic and Land Use on Urban Stormwater Quality

Implications for Urban Stormwater Treatment Design

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ISSN 2194-7244 ISSN 2194-7252 (electronic)
SpringerBriefs in Water Science and Technology
ISBN 978-981-10-5301-6 ISBN 978-981-10-5302-3 (eBook)
DOI 10.1007/978-981-10-5302-3

Library of Congress Control Number: 2017945083

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Printed on acid-free paper

This Springer imprint is published by Springer Nature
The registered company is Springer Nature Singapore Pte Ltd.
The registered company address is: 152 Beach Road, #21-01/04 Gateway East, Singapore 189721, Singapore

Contents

Abstract

Urbanisation is a common phenomenon in most parts of the world as a result of increasing numbers of people moving into urban areas. This results in the increased use of motor vehicles and demand for living areas. The use of motor vehicles and other anthropogenic activities common to urban areas introduce a wide range of pollutants to the urban environment, including toxic species such as heavy metals and polycyclic aromatic hydrocarbons (PAHs). These pollutants are either directly deposited on ground surfaces such as roads or initially accumulate in the atmosphere and subsequently deposited on ground surfaces. When rainfall occurs, the deposited pollutants can be washed off by stormwater runoff and transported to receiving water bodies, undermining the urban water environment. In order to mitigate stormwater pollution, a diversity of treatment devices are employed and their effective design is dependent on an in-depth understanding of pollutant processes and pathways. Additionally, state-of-the-art knowledge is also required for the development of effective stormwater management strategies to minimise the adverse impacts on receiving water bodies due to urbanisation.

This book focuses on three important pollutant processes and transport pathways, namely, atmospheric build-up, atmospheric deposition (including dry and wet deposition) and build-up on road surfaces. Heavy metals and PAHs were the primary pollutants investigated in this study. Since traffic and land use are considered as the primary influential factors in pollutant generation, this research study selected a total of 15 study sites with varying traffic and land use characteristics in the Gold Coast, Queensland State, Australia. Three types of samples were collected at the selected study sites. These included atmospheric samples, atmospheric dry and wet deposition samples and road build-up samples. Univariate and multivariate data analysis techniques and mathematical modelling approaches were employed for the investigations undertaken and to create knowledge relating to the relationship between pollutants, traffic and land use, and for defining the linkages between pollutants in the atmospheric and ground phases.

It was noted that the concentrations of heavy metals and PAHs in the atmospheric phase are higher during weekdays when compared to weekends due to higher traffic volume on weekdays. Therefore, this could lead to increased human health risk during weekdays. Additionally, Zn was found to be the most abundant heavy metal species in the atmosphere, atmospheric (wet and dry) deposition and road build-up. This suggests that the presence of Zn in road stormwater runoff merits particular attention, compared to other heavy metal species. Light molecular weight PAHs (3–4 rings) showed higher concentrations and spatial variability compared to heavy molecular weight PAH species (5–6 rings) in both, atmospheric phase and road build-up. This is attributed to the volatile nature of light molecular weight PAHs. Heavy duty vehicle traffic volume is the primary source of PAHs and industrial land use tends to produce higher loads of PAHs than commercial and residential land uses. These outcomes demonstrate the important role atmospheric pollutants play in contributing to road stormwater pollution through atmospheric deposition.

Furthermore, a modelling approach was developed to estimate the annual loads of traffic-related pollutants in stormwater runoff from a given road site by incorporating a series of replication equations to a widely used computer model tool. Pollutant loads were modelled by assigning co-fraction coefficients of solids. The modelling approach developed can be used not only to estimate solids generation from road sites, but also as a planning tool to identify the enhancements required to improve urban stormwater quality.

Chapter 1
Primary Traffic Related Pollutants and Urban Stormwater Quality

Abstract Urbanisation introduces a range of pollutants to the urban environment. These pollutants include many toxic species. They are primarily sourced from traffic and land use related activities. The pollutants are directly deposited on ground surfaces or initially emitted to the atmosphere and subsequently deposited on ground surfaces via depositional processes. These pollutants are removed by stormwater runoff and transported to receiving water bodies, undermining the urban water environment. This chapter discusses the primary traffic related pollutants and their transport pathways. Pollutants discussed include solids, heavy metals, polycyclic aromatic hydrocarbons and airborne particulate pollutants while their transport pathways include atmospheric build-up, dry and wet deposition, build-up and wash-off on road surfaces.

Keywords Urbanisation • Stormwater pollutant processes • Stormwater quality • Pollutant transport pathways • Traffic related pollutants

1.1 Background

Urbanisation is a common phenomenon witnessed in most parts of the world. Among a range of urban characteristics, increased traffic volumes and a diversity of land use are the primary characteristics imposed on the environment. Traffic and land use developments introduce a range of pollutants into the urban environment. These pollutants include many toxic species such as heavy metals and polycyclic aromatic hydrocarbons (PAHs). These pollutants remain distributed either in the atmosphere in association with dust particles or deposited on urban surfaces such as roads and roofs. During rainfall events, these pollutants can be scavenged by rainfall and transported to receiving water bodies by stormwater runoff, undermining the urban aquatic environment. For example, Davis and Birch (2010) noted that road surfaces in an urban area can contribute up to 26% of the total runoff volume and up to 40% of the total heavy metal loads. Considering the area occupied by road surfaces, this is a disproportionally high contribution in pollutant load.

J.M.A. Gunawardena et al., *Influence of Traffic and Land Use on Urban Stormwater Quality*, SpringerBriefs in Water Science and Technology,
DOI 10.1007/978-981-10-5302-3_1

In this context, use of treatment measures to mitigate the adverse impacts of stormwater pollution is essential to safeguard the water environment. Effective design of these measures closely relies on an in-depth understanding of pollutant processes and pathways. Stormwater pollutants are subjected to a range of processes after being emitted from sources such as traffic and land use related activities. These processes include atmospheric accumulation, dry and wet deposition, build-up on urban surfaces, wash-off during rainfall events and transport with runoff into receiving waters. The processes are influenced by a range of source characteristics such as traffic volume, traffic mix and land use activities and climate characteristics such as antecedent dry conditions and rainfall characteristics. It is critical to have accurate estimates of pollutant loads produced by traffic and land use related sources. At the same time, a sound theoretical understanding of pollutant sources and generation, pollutant processes and their key influential factors is essential for the design of effective stormwater treatment systems to mitigate the impacts on the receiving environment.

1.2 Rationale for the Publication

The key objective of this publication is to contribute to an in-depth understanding of the linkages between primary pollutant processes and influential parameters and, thereby, to develop quantitative relationships to define how traffic, land use and climate factors influence the chain of pollutant processes and pathways of atmospheric pollutants build-up, dry and wet deposition and build-up on urban surfaces. The in-depth knowledge presented in this publication is based on a comprehensive research study which is presented in three phases: (1) state-of-the-art field investigations to characterise air quality in relation to targeted traffic generated pollutants, namely, particulates, heavy metals and PAHs, atmospheric dry and wet deposition and pollutants build-up on road surfaces; (2) comprehensive data analysis using multivariate data analysis techniques to create new knowledge and to develop empirical predictive equations relating to primary pollutant processes and influential factors and for understanding how changes in traffic, land use and climate factors influence these processes; (3) development of an innovative modelling approach for stormwater quality prediction by integrating the empirical process equations.

This publication consists of the following chapters:

Chapter 1: Provides a summary of critical information presented in published literature related to this topic. It provides the necessary background information to support the content presented in the rest of the chapters.

Chapter 2: Provides the research design and the study methodology for the comprehensive field investigations conducted. This chapter explains the content, context and quality of the data obtained to support the subsequent analysis presented in the remaining chapters.

Chapter 3: Provides the outcomes from the data analysis in relation to atmospheric build-up, dry and wet deposition and road surface build-up investigations. This chapter also provides a detailed discussion on the linkages between pollutant loads, sources and underlying land use, traffic and climate parameters.

Chapter 4: Provides details of the development of a modelling tool to predict heavy metals and PAHs loads which are the key traffic related pollutants. This chapter also presents the interpretations of simulation outcomes.

Chapter 5: Outlines the practical implications of the study outcomes and recommendations for treatment design and future research directions.

1.3 Traffic Related Pollutants in Urban Stormwater

Traffic related pollutants are primarily sourced from exhaust emissions, tyre and brake wear, road surface abrasion and lubricants and engine oil leakages. These pollutants can be in the form of solids, heavy metals, PAHs and airborne particulate matter.

1.3.1 Solids

Solids deposited on road surfaces are heterogeneous. Other than traffic related activities (Gunawardana et al. 2014), atmospheric deposition (Sabina et al. 2006; Gunawardena et al. 2012) and surrounding soil (Qian et al. 2011; Zhang et al. 2015) also contribute solids to the urban road environment. Solids deposited on road surfaces are subjected to complex mixing processes which occur during transport. Furthermore, due to frequent traffic activities, traffic related solids commonly combine with soil mineral components and produce unique mixtures (Gunawardana et al. 2012).

Among a number of physical and chemical properties, particle size of solids is critical due to the fact that this parameter has a significant influence on the adsorption of heavy metals and PAHs to solids (Bian and Zhu 2009; Li et al. 2015). This is because, conditions favourable for pollutant adsorption to solids such as specific surface area (Gunawardana et al. 2012), organic carbon content (Krauss and Wilcke 2002), effective cation exchange capacity (Gunawardana et al. 2013) and clay forming mineral content (Gunawardana et al. 2014) increase with the decrease in particle size. In this regard, solids can be considered as an important pollutant present on road surfaces.

1.3.2 Heavy Metals

Heavy metals have received significant research attention due to their potential toxicity to human health. Although there are a number of heavy metal species present in the urban environment, cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), chromium (Cr) and zinc (Zn) have received particular attention due to their potentially acute or chronic toxic effects on flora, fauna and humans.

Traffic activities such as vehicle tyre and component wear, exhaust emissions, and engine oil leakages play important roles in the generation of heavy metals in the urban environment. Table 1.1 gives the possible sources of heavy metals related to vehicular traffic. Liu et al. (2016a) noted that heavy metal loads deposited (build-up) on road surfaces increase with increasing traffic volume while their variability decreases. This concept is illustrated in Fig. 1.1. This phenomenon is due to the fact that higher traffic volume leads to more frequent vehicular activities and consequently produces higher loads of heavy metals. Additionally, the deceased variability of heavy metal build-up loads with increased traffic volume in turn indicates the important role of traffic activities in influencing heavy metals build-up. The influence of higher traffic volume outweighs other influential factors such as land use and atmospheric deposition, leading to lower variability in heavy metals build-up.

Toxic heavy metals associated with stormwater can accumulate in waterways, exerting adverse impacts on living organisms. As stormwater is receiving significant attention as a viable alternate water resource for reuse (Liu et al. 2015), the presence of heavy metals in stormwater can pose human health risk, seriously undermining reuse safety (Ma et al. 2016).

Table 1.1 Primary heavy metals related to traffic activities

	Fuel	Engine oil	Tyre wear	Brake wear	Chassis	Road surface wear	Road paint
Al			X		X	X	
Cd	X	X	X	X			
Cr	X	X	X	X	X	X	X
Cu			X	X		X	
Fe			X	X	X		
Mn	X		X	X	X		
Ni	X	X	X	X		X	
Pb	X		X	X		X	X
Zn	X	X	X	X		X	

Refer to Tiarks et al. (2003), Adachi and Tainosho (2004), Fatemi et al. (2006), De Silva et al. (2016), Huber et al. (2016), Mummullage et al. (2016)

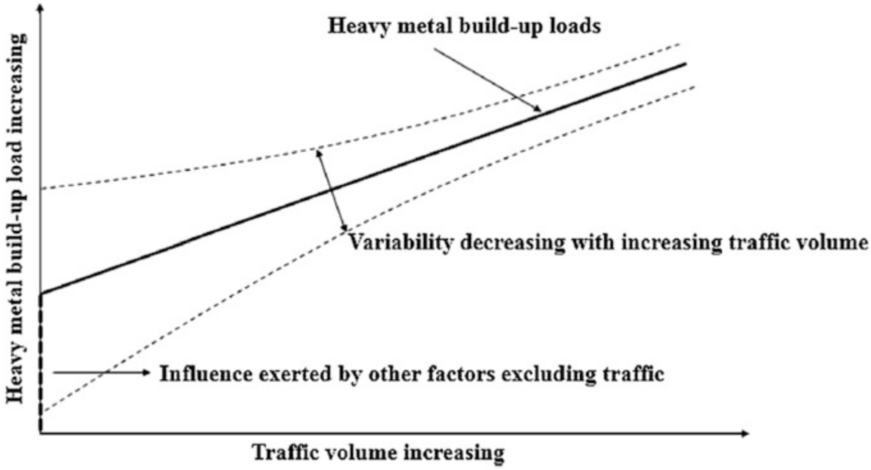

Fig. 1.1 Conceptual illustration of the variability of heavy metals build-up with traffic volume (Liu et al. 2016a)

1.3.3 Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds made up of carbon and hydrogen atoms with at least two fused benzene rings in different configurations (Gayen and Sinha 2013). They can be divided into two categories: low (light) molecular weight compounds containing up to four rings and high (heavy) molecular weight compounds containing more than four rings (Liu et al. 2016b). USEPA (1984) identified 16 PAHs as priority pollutants due to their toxicity, especially carcinogenic properties, potential for human exposure and prevalence in the urban environment. PAHs are highly hydrophobic and their aqueous solubility decreases with increasing number of rings (Wu et al. 2013). Consequently, PAHs are liable to associate with particulates in the aqueous environment rather than being soluble in water.

Traffic is a dominant source of PAHs on urban road surfaces. The two primary traffic sources of PAHs are vehicle exhaust and abrasion of road surfaces. Therefore, higher loadings of PAHs can be attributed to higher traffic volumes (Takada et al. 1990; Krein and Schorer 2000). Traffic characteristics affect not only PAHs loadings, but also the species composition. For example, heavy-duty diesel vehicles are the primary source of lighter PAHs while light-duty gasoline vehicles are the major source of PAHs with heavy molecular mass (Miguel et al. 1998; Boonyatumanond et al. 2007; Wang et al. 2011; Gunawardena et al. 2012). Therefore, vehicle mix in urban regions can be a determining factor in PAHs composition.

In addition to traffic volume, urban land use characteristics also have an impact on the concentration of PAHs in stormwater runoff. Hoffman et al. (1984) investigated the loading of individual PAHs, and they found that industrial and highway areas contribute comparatively larger amounts of PAHs to urban stormwater runoff than residential and commercial areas. This is attributed to the nature of industrial activities, relatively greater abrasion and higher automobile emissions.

The presence of PAHs in stormwater poses ecosystem and human health risks, especially species having heavy molecular weight. It is noted that PAHs with 5–6 benzene rings, especially dibenzo[a,h]anthracene (D[a]A) and benzo[a]pyrene (B[a]P) in stormwater, contribute most to human health risk (quantitatively more than 90%) (Ma et al. 2017). Liu et al. (2016b) observed that heavy PAH species pose high ecosystem risk and exert a negative influence on the safety of stormwater reuse. PAHs with heavy molecular weight generally are more toxic, and hence, pose a higher risk even in low concentrations (Burkart et al. 2013).

1.3.4 Airborne Particulate Pollutants

The combustion of fossil fuel by vehicles results in the emission of particulate pollutants into the atmosphere. Although these pollutants may initially be suspended in the atmosphere, dry and wet deposition processes can deposit them on ground surfaces and eventually transport to receiving waters during storm events. Therefore, these particulates also contribute to road surface stormwater pollutants and receiving water degradation.

Vehicular emissions are one of the most prominent sources of ultrafine particles (<2.5 μm), contributing between 25% to 35% of $PM_{2.5}$ to the urban atmosphere. This particle size poses a significant human health risk (Pohjola et al. 2002). For example, $PM_{2.5}$ can lead to high plaque deposits in arteries, causing vascular inflammation and atherosclerosis (Chow et al. 1996). Particularly, diesel vehicles and non-combustion emissions from road traffic are two key sources of airborne particulate pollutants (Jandacka et al. 2017).

Vehicle-generated airborne particulate pollutants are highly dependent on the vehicle type and the operating conditions (Kanabkaew et al. 2013). Operating conditions are a significant factor as vehicle emissions rely on fuel consumption, which in turn is influenced by the vehicle speed. Traffic congestion, leading to frequent vehicle stop–start activities, can cause the incomplete combustion of fuel and generate high pollutant loads such as particulates. This means that traffic congestion will influence the generation of airborne particulate pollutants.

1.4 Pollutant Transport Pathways

1.4.1 Atmospheric Pollutants Build-Up

Atmospheric pollutants build-up refers to pollutants accumulation in the atmosphere. In the urban road environment, climate-related factors such as rainfall and antecedent dry days and urban traffic characteristics are important factors in atmospheric pollutants build-up.

1.4.1.1 Rainfall and Antecedent Dry Period

Airborne particulate mass is influenced by rainfall as particulates are absorbed by raindrops and removed during rainfall events (Guo et al. 2014). This process reduces the atmospheric particulate load. As shown in Fig. 1.2, reduction in atmospheric particle concentrations can be more than 50% depending on the time of day and amount of rainfall received. In fact, other soluble gases such as NO_2 and SO_2 in the atmosphere also follow similar trends as particulate pollutants in the atmosphere (Luo et al. 2016). During dry periods, atmospheric pollutants can undergo dry deposition. Dry deposition is considered as directly proportional to the atmospheric pollutant concentration. Due to this, dry deposition is highly influential in fluctuations in atmospheric pollutant concentrations and maintains a dynamic balance by acting opposite to atmospheric accumulation.

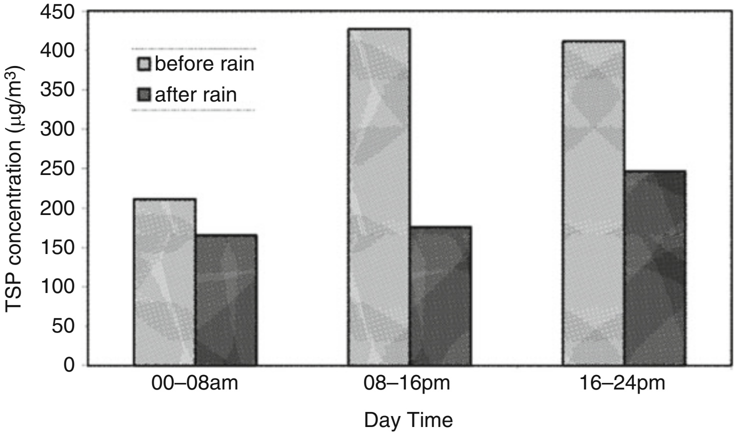

Fig. 1.2 Airborne particulate (TSP) concentrations before and during rainfall in Delhi, India (Ravindra et al. 2003)

1.4.1.2 Urban Traffic

Increase in traffic volume contributes higher pollutant loads to the urban atmosphere. Emissions from an individual vehicle can be related to fuel consumption, vehicle class, vehicle age, traffic flow, road surface condition and traffic congestion. These factors play a significant role in contributing pollutants to the atmosphere. Additionally, compared to light duty vehicles, heavy duty vehicle traffic is a major source of suspended particulate matter to the atmosphere. This means that not only total traffic volume, but also heavy duty traffic volume should be a focus in relation to the investigation of airborne pollutants into the urban environment.

Furthermore, traffic-related atmospheric pollutants build-up has temporal variation. Pohjola et al. (2002) investigated the seasonal variation of vehicle induced atmospheric particulate matter and found relatively high concentrations during spring. Gunawardena et al. (2012) found traffic-related particulate PAHs in the atmosphere have a higher concentration during weekdays while traffic sources play a less important role in generating PAHs during weekends. This means that atmospheric pollutants build-up is significantly influenced by traffic characteristics along with temporal factors.

1.4.2 Atmospheric Deposition

Atmospheric deposition is a process by which atmospheric pollutants are transferred back to ground surfaces. Atmospheric deposition has two forms, namely, dry deposition and wet deposition (Wang et al. 2016). Dry deposition occurs during the dry periods while wet deposition takes place with rainfall. However, there are only a limited number of studies focusing on pollutant contribution by atmospheric deposition to urban stormwater runoff (Sabin et al. 2005). Additionally, wet deposition has received more research attention than dry deposition. However, dry deposition fluxes are almost always predominant for major traffic related pollutants such as heavy metals, compared to wet deposition (Gunawardena et al. 2013). This underlines the equal importance of dry deposition and wet deposition in contributing pollutants to urban stormwater.

Dry deposition could remove higher loads of pollutants from the atmosphere than wet deposition due to its prolonged operation during dry weather. Wang et al. (2016) noted in their study that 69% of PAH loads were removed from the atmosphere by dry deposition while the corresponding percentage was 31% for wet deposition. This highlights the important role of antecedent dry days in influencing stormwater runoff quality via pollutants build-up on ground surfaces.

Wet deposition depends on the rainfall characteristics such as rainfall intensity and duration. Shannon and Voldner (1982) found in their study that the maximum wet deposition of 80% of airborne mass occurs during a 6-h rainfall event. Tsai et al. (2011) noted that rainfall duration and frequency influence pollutant concentrations in wet deposition. Longer duration and more frequent rainfall events lead to low concentrations of pollutants due to dilution.

It is noteworthy that there is no experimental approach available to link air quality and atmospheric deposition to stormwater quality. This leads to a knowledge gap in relation to the contribution of atmospheric pollution to stormwater runoff quality, which could result in the underestimation of pollutant loads from urban road surfaces.

1.4.3 *Pollutants Build-Up on Road Surfaces*

Pollutants build-up refers to the accumulation of pollutants on road surfaces during dry periods. The build-up process on road surfaces is influenced by a range of external factors such as traffic volume (Gunawardena et al. 2014), antecedent dry period (Wicke et al. 2012; Wijesiri et al. 2016a), road cleaning frequency (Walker and Wong 1999), and road surface roughness (Liu et al. 2016a, b) as well as internal factors such as particle size distribution (Wijesiri et al. 2015). Among the external influential factors, antecedent dry period is an important factor governing pollutants build-up. Generally, a longer antecedent dry period produces higher loads of build-up since pollutants have a longer time to accumulate. However, when the antecedent dry period is greater than around 7–9 days, the pollutants build-up loads show signs of reaching a constant value. Once it reaches a constant value, the build-up process is in an equilibrium state (Egodawatta and Goonetilleke 2007).

In terms of internal factors, it has been noted that a longer antecedent dry period can lead to higher loads of large particles during the build-up process. This is due to the accumulation of larger particles and the re-distribution of smaller particles with increased antecedent dry period (Egodawatta et al. 2006). Therefore, a higher fraction of small particles is more likely to deposit outside the road surfaces. Figure 1.3 illustrates the change in particle size distribution with increasing antecedent dry days. Furthermore, previous researchers (Mahbub et al. 2011) have

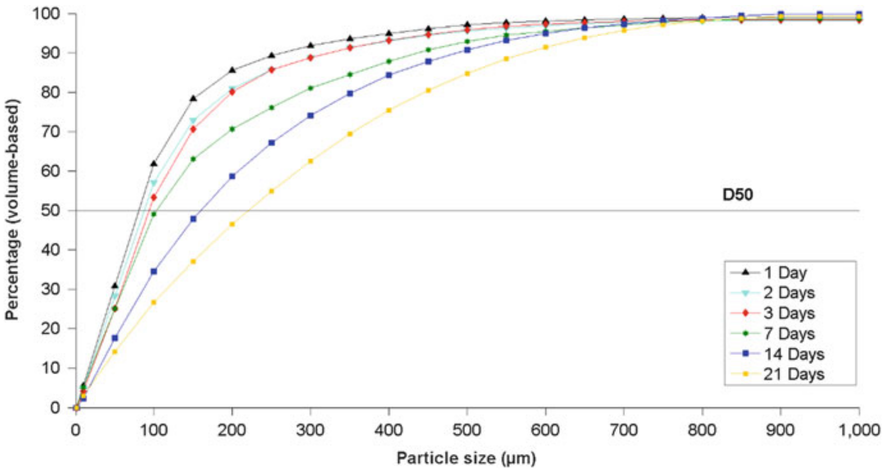

Fig. 1.3 Change of particle size distribution with antecedent dry days during the build-up process

noted that the influence of traffic on the re-suspension of larger particles is more significant than smaller particles. This phenomenon can be attributed to the fact that there is a thin laminar airflow at the road surface on which a traffic-related turbulent airstream flow is present (Wijesiri et al. 2016b). Fine particles smaller than the thickness of this laminar airflow are barely subject to turbulent eddies while larger particles are potentially subject to turbulent eddies, resulting in their re-suspension.

A number of empirical equations have been proposed to simulate pollutants build-up. Although these equations have different forms, they all represent the trend of increasing pollutant loads with increasing antecedent dry period, then reaching a relatively constant value after a period of time. These typical equations are as follows:

- Reciprocal form: $y = a + \frac{b}{x}$
- Logarithmic form: $y = a + b \ln x$
- Exponential form: $y = a\mathrm{e}^{-bx}$
- Power form: $y = \min(c, ax^b)$

where:

x—Antecedent dry days
y—Build-up load accumulated
a, b and c—Coefficients

(Ball et al. 1998; O'Loughlin and Stack 2003; Egodawatta 2007; MIKEURBAN 2008).

As pollutants build-up is significantly influenced by a range of factors, these coefficients in the build-up equations could vary under different conditions. For example, Egodawatta (2007) noted that the coefficients of the power build-up equation were different for catchments with high population density and low population density. In an investigation into the coefficients of the exponential build-up equation in the MIKE URBAN model, Liu et al. (2010) found that the input parameters applicable to Southeast Queensland, Australia, were significantly different from the default values given in the software, which was developed in Denmark. This implies that pollutants build-up varies significantly with regional characteristics such as local traffic and land use.

1.4.4 Pollutants Wash-Off

Pollutants wash-off refers to the process where pollutants build-up during dry weather is mobilised due to rain drop impacts and stormwater runoff during rain events. The process of pollutants wash-off can be considered as a combination, including pollutant separation from the ground surface and transportation. Firstly, rain drops reach the ground and wet the surface dissolving water soluble pollutants and dislodging particulate pollutants. Secondly, the separated pollutants are transported by stormwater runoff.

Rainfall characteristics such as rainfall intensity and rainfall duration are the most important influential factors in relation to the pollutants wash-off process. Liu et al. (2012) divided natural rainfall events into three types in terms of their influence on pollutants wash-off, namely, high intensity-short duration (Type 1), high intensity-long duration (Type 2) and low intensity-long duration (Type 3). Compared with Type 3, Type 1 and Type 2 rainfall events tend to have a higher capacity for detaching pollutants from road surfaces and resulting in higher pollutant concentrations in stormwater runoff. This can be attributed to the higher kinetic energy of rainfall with higher intensity and the dilution effect of long duration events.

Typically, an exponential equation is employed to replicate the pollutants wash-off process based on the rainfall intensity. There are two types of equations commonly used as given below:

- Exponential form $W = W_0(1 - \mathrm{e}^{-KIt})$
- Modified exponential form $F_\mathrm{W} = \frac{W}{W_0} = C_\mathrm{F}(1 - \mathrm{e}^{-KIt})$

(Sartor et al. 1974; Egodawatta et al. 2007)
where*:*

W—Weight of the material mobilised after time t
W_0—Initial weight of the material on the surface
I—Rainfall intensity
K—Wash-off coefficient
F_W—Fraction of wash-off
C_F—Capacity factor

Although the exponential form has the ability to replicate pollutants wash-off, Egodawatta et al. (2007) found that a rainfall event has the capacity to wash-off only a fraction of the pollutants present on the surface and that fraction varies with rainfall intensity, kinetic energy of rainfall and pollutant characteristics. Therefore, they suggested a modification to the exponential form by introducing a Capacity Factor (C_F) which is defined as the capacity of rainfall to transport pollutants. According to Egodawatta et al. (2007), C_F varies between 0 and 1 depending on the rainfall intensity. When rainfall intensity is less than 40 mm/h, capacity factor (C_F) will increase linearly from 0 to 0.5, which is followed by a constant value of 0.5 for 40–90 mm/h and then varies from 0.5 to 1.

Same as for pollutants build-up, particle size also exerts a significant influence on pollutants wash-off. Wijesiri et al. (2015) found that particles larger and smaller than 150 μm follows three different wash-off processes, which are closely related to their build-up processes. Figure 1.4 illustrates the three scenarios. The remaining >150 μm particle loads on road surfaces are lower than <150 μm particles in scenario 1 and 2. This is dependent on rainfall wash-off capacity. This means that stormwater quality estimation should be based on different particle sizes,

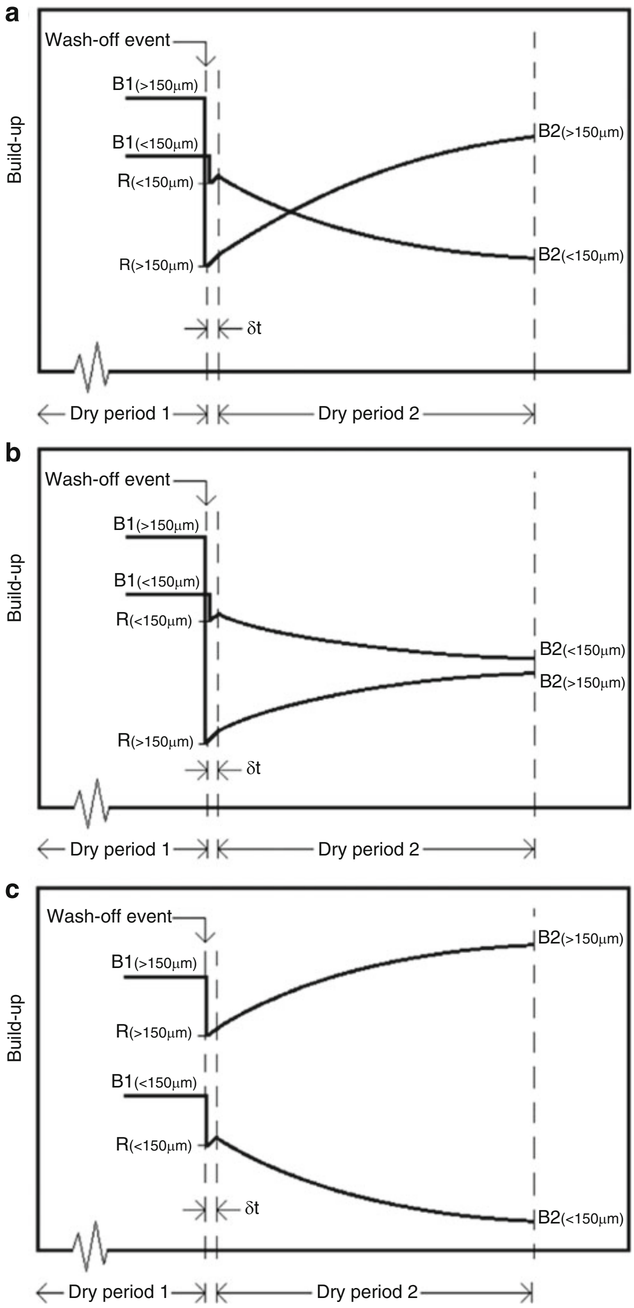

Fig. 1.4 Three scenarios related to build-up and wash-off processes (Wijesiri et al. 2015) (**a**, **b** and **c** represent scenario 1, 2 and 3; $B1_{(<150\ \mu m)}$, $B1_{(>150\ \mu m)}$ and $B2_{(<150\ \mu m)}$, $B2_{(>150\ \mu m)}$ are particulate build-up available at the end of dry period 1 and dry period 2, respectively; $R_{(<150\ \mu m)}$ and $R_{(>150\ \mu m)}$ are particulate loads remaining after the wash-off process; δt is duration of build-up that occurs immediately after wash-off event)

which is not taken into consideration in current stormwater quality modelling approaches.

1.5 Summary

This chapter focused on traffic-related pollutants and their transport pathways. The primary pollutants related to urban traffic are solids, heavy metals, polycyclic aromatic hydrocarbons (PAHs) and airborne particulate pollutants. These pollutants are produced not only by vehicle exhaust emission but also by other factors such as vehicle tyre and brake wear, combustion of fossil fuel and engine oil leakage. During rainfall events, these pollutants (particularly toxic pollutants such as heavy metals and PAHs) are transported to receiving waters, posing ecosystem and human health risks.

Additionally, pollutants in the atmosphere can contribute to road stormwater quality degradation. This is because dry and wet deposition processes can deposit them on ground surfaces and will wash-off with stormwater runoff. Unfortunately, there are only a limited number of research studies focusing on the influence of air pollution on stormwater quality. This is an impediment to the accurate estimation of pollutant loads on urban surfaces.

In order to link air pollution to stormwater quality, four important pollutants transport pathways are essential to be understood. These are atmospheric pollutants build-up, atmospheric deposition (including dry and wet deposition), pollutants build-up on road surfaces and pollutants wash-off by stormwater runoff. Although each pathway is influenced by different factors, urban traffic as the primary pollutant source plays a significant role in influencing the transport pathways. This means that any appropriate mitigation strategies for the treament of urban stormwater runoff need to be implemented based on traffic characteristics and their relationships with each pollutants' transport pathway.

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Chapter 2
Research Program

Abstract Investigations into pollutant processes of atmospheric build-up, dry and wet deposition and build-up on urban surfaces require a scientifically robust research program. This chapter primarily discusses strategies adopted for study sites selection, the field sampling program and laboratory testing. Discussion of the sampling program includes sample collection methods for atmospheric pollutant build-up, atmospheric deposition and build-up on road surfaces.

Keywords Field sample collection • Sample testing • Study site selection • Laboratory testing

2.1 Background

Stormwater pollution due to traffic generated pollutants is complex since it involves a number of interlinked processes and influential factors. Urban traffic generates a range of pollutants, a portion of which accumulates in the atmosphere while the remainder will deposit directly on ground surfaces. Pollutants emitted to the atmosphere will eventually deposit on the urban surface through dry and wet deposition. Pollutants build-up on ground surfaces is dynamic since it is dependent on direct and atmospheric depositions and potential re-suspension due to wind and traffic induced turbulence. The dynamic nature also stems from the fact that the built-up pollutants undergo periodic wash-off during rainfall events. Pollutants removed by wash-off are eventually transported to receiving water bodies with stormwater runoff. Consequently, it is evident that traffic generated pollutants are subjected to a complex chain of processes which are influenced by a range of land use, traffic and climate parameters.

Investigating the complex chain of pollutant processes and influences exerted by land use, traffic and climate factors requires a technically robust research program. Chapter 1 described the outcomes of past research undertaken which provided the basis for this research study. This chapter outlines the design of the comprehensive research program developed to investigate the chain of processes discussed above including identification of study sites, the field sample programme and laboratory

J.M.A. Gunawardena et al., *Influence of Traffic and Land Use on Urban Stormwater Quality*, SpringerBriefs in Water Science and Technology,
DOI 10.1007/978-981-10-5302-3_2

testing techniques adopted. Outcomes of this chapter provided the essential data for subsequent analysis and interpretation discussed in the subsequent chapters.

2.2 Study Sites

As the research focus was on traffic related pollutants, typical urban road sites were selected. The selected study sites were located at Gold Coast, Queensland State, Australia. Gold Coast is among the cities with high population growth rates in Australia, leading to high traffic growth.

A total of 15 study sites were selected for sampling. Out of the 15 sites, 11 were road sites with different land uses and traffic characteristics, while 4 sites consisted of urban centres having intense anthropogenic activities. Sites were selected such that they represented the typical land use and traffic variations within urban regions. Land uses considered for sampling were residential, commercial and industrial, while different traffic characteristics such as traffic volumes and traffic congestion conditions were considered within each land use. Sites were selected such that an in-depth sampling programme for atmospheric pollutants, dry and wet atmospheric depositions and build-up on road surfaces could be undertaken. Figure 2.1 shows the study sites, while Table 2.1 provides the traffic and land use characteristic of these study sites.

2.3 Sample Collection

2.3.1 Atmospheric Build-Up Sampling

As discussed in Chap. 1, atmospheric pollutant build-up is influenced by the antecedent dry days subsequent to a rain event, time of the day and traffic and land use activities. Based on the hypothesis that the day of the week also influences atmospheric pollutants build-up, the sampling was carried out during both, weekdays and weekends. A total of 30 air samples were collected at the 15 study sites on weekdays and weekends.

Atmospheric build-up samples were collected using a calibrated air sampler. The sampling flow rate was set at 15 m^3/h. Oven dried quartz filter papers and pre-extracted polyurethane foams (PUFs) were used for air sample collection. Pre-extracted PUFs were spiked with field surrogate standards before being used for sample collection. This was to monitor unusual matrix effects and sample recovery. After setting up of PUFs and filter papers in the sampler, it was programmed for an 8-h sampling period in order to cover morning and evening traffic emission peaks. A total of 120 m^3 air were sampled to collect pollutants from each site. Figure 2.2 shows the air sampling in the field.

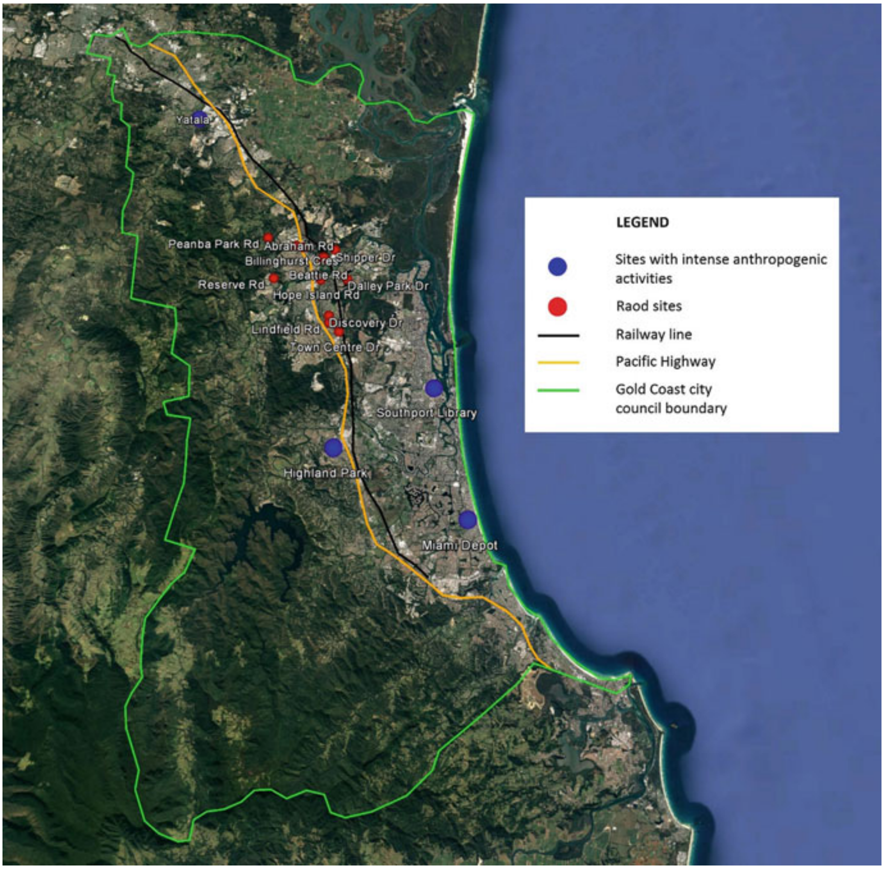

Fig. 2.1 Study sites

2.3.2 Atmospheric Wet and Dry Deposition Sampling

Atmospheric deposition sampling was conducted at eight study sites (four road sites and four sites within urban centres, having intense anthropogenic activities). Sampling was conducted as shown in Fig. 2.3. A detailed schematic of the sampling device is illustrated in Fig. 2.4. One set of funnel and bottle was used to collect dry deposition and the other set to collect bulk deposition (dry and wet deposition together) samples. The device was placed at 3 m above the ground to ensure that road dust due to vehicle induced turbulence was not collected.

For dry deposition sample collection, the funnels and bottles were installed in the field immediately after a rainfall event since the atmospheric pollutant load is minimal at that stage. The selected sampling periods were 3, 4, 5, 6 and 7 days after a rain event. This was to capture the changes in deposition due to variations in pollutant concentrations in the atmosphere. Accordingly, a total of 40 dry

Table 2.1 Traffic and land use characteristic of the study sites

Study sites	ID	Land use	Average daily traffic volume (DTV)	Average daily heavy duty vehicle traffic volume (HDTV)	Traffic congestion parameter (V/C)
Abraham Road	Ab_c	Commercial	8742	270	0.57
Beattie Road	Be_i	Industrial	4633	107.5	0.46
Billinghurst Crescent	Bi_r	Residential	1964	220	0.14
Dalley Park Drive	Da_r	Residential	10,690	312	0.26
Discovery Drive	Di_r	Residential	997	90	0.39
Hope Island Road	Ho_c	Commercial	25,578	177	0.64
Lindfield Road	Li_c	Commercial	8599	280	1.21
Peanba Park road	Pe_r	Residential	30	3.5	0.76
Reserve Road	Re_r	Residential	10,027	391	0.61
Shipper Drive	Sh_i	Industrial	958	1139	0.39
Town Centre Drive	To_c	Commercial	5931	35	0.31
Highland Park	Mi_hd	Intense anthropogenic activities, comprising different land use types			
Southport Library	So_hd	Intense anthropogenic activities, comprising different land use types			
Yatala	Ya_hd	Intense anthropogenic activities, comprising different land use types			
Miami Depot	Mi_hd	Intense anthropogenic activities, comprising different land use types			

deposition samples were collected from eight study sites for five different antecedent dry days.

Direct sampling of wet deposition was not possible. Therefore, the bulk deposition samples were collected instead. The funnel and bottle set reserved for bulk deposition sampling was removed and replaced after a rainfall event. Consequently, the samples collected consisted of dry deposition as well as wet deposition. The total sampling period for each event was dependent on the time between two consecutive rainfall events. Three rainfall events were sampled at each site in order to calculate the average bulk deposition for the site. Accordingly, a total of 24 bulk deposition samples were collected at the eight study sites from three rainfall events.

Fig. 2.2 Air sampling in the field

Fig. 2.3 Atmospheric deposition sampling at the field

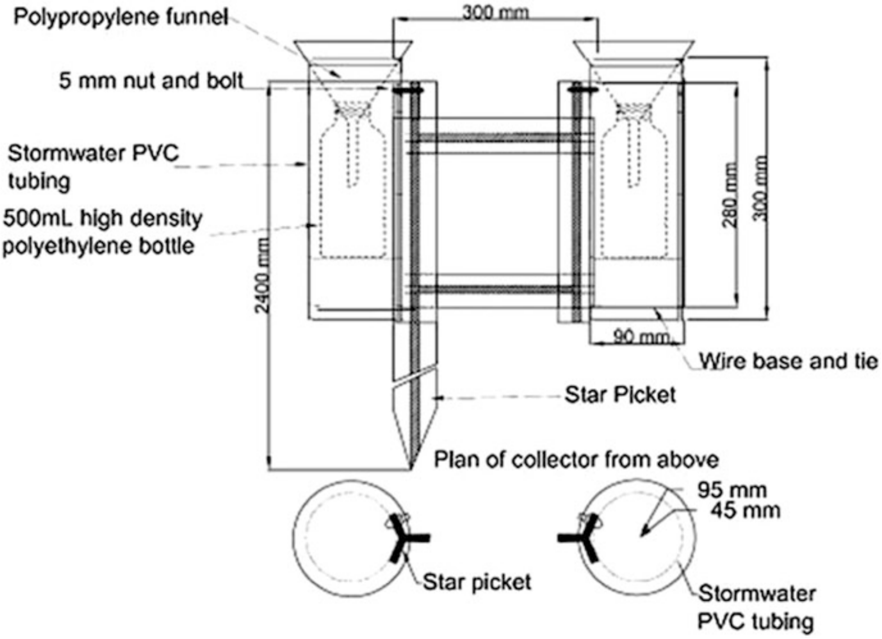

Fig. 2.4 Atmospheric deposition sampler (Adapted from Gunawardena et al. 2013)

2.3.3 *Road Build-Up Sampling*

The road build-up sampling was undertaken at periods longer than seven antecedent dry days. This is due to the fact that road surface pollutants build-up rate increases rapidly and then asymptotes to an almost constant value after around 7 days as discussed in Chap. 1 (Egodawatta and Goonetilleke 2007). Eleven road surfaces out of the 15 sites were selected to conduct road build-up sampling. These road surfaces were asphalt paved.

Build-up sample collection was undertaken using a vacuum system as shown in Fig. 2.5. A dry and wet vacuuming collection method was used while a 1.5 m × 2 m frame was used to demarcate the test plot (Liu et al. 2012). The frame was placed between the kerb and the median strip of the road which had previously been cleaned. Only one sample was collected at each study site based on the assumption that pollutants build-up is uniform throughout the study site. There were 11 build-up samples collected from the road surfaces. Before using the vacuum system, all component parts including the water compartment, hoses and foot were cleaned with deionised water. A volume of 3 L of deionised water was poured into the water compartment as the filtration medium. Another sample of deionised water was taken as a field blank. The process of dry sample collection was to vacuum the surface three times in perpendicular directions.

Fig. 2.5 Road build-up sampling

Before wet sample collection, the surface was dampened with a sprayer without creating any wash-off. The wet sample collection was undertaken to ensure that fine particles, the pollutants strongly adhering to the surface as well as those within crack and pores on the road surfaces were collected. The same vacuuming procedure used for the dry sample collection was applied. As the last step, the water compartment, hoses and brush were washed with deionised water thoroughly in order to remove any particulates adhering to the surfaces of the equipment. The collected water sample was transferred into a polyethylene container.

In summary, three types of samples were collected in the research study, namely, atmospheric build-up samples, atmospheric depositions samples (dry and bulk) and road build-up samples. The sampling scheme, including the number of samples collected and relevant study sites, is summarised in Table 2.2.

2.4 Pollutants Selection and Sample Testing

As discussed in Chap. 1, heavy metals and PAHs are the primary traffic related pollutants. Therefore, these two pollutant species were the focus of the research study. Heavy metals investigated in the study included lead (Pb), Zinc (Zn), Cadmium (Cd), Chromium (Cr), Nickel (Ni), Manganese (Mn) and copper (Cu) since these are primarily generated by traffic (Mahbub et al. 2010; Mejia et al. 2013; Liu et al. 2016). PAHs tested included 14 out of the 16 priority species

Table 2.2 Sampling scheme

		Number of samples collected				
		Atmospheric build-up		Atmospheric deposition		
No.	Site name	Weekdays	Weekends	Dry	Bulk	Road build-up
1	Abraham Road[b]	1	1	5	3	1
2	Reserve Road[b]	1	1	5	3	1
3	Peanba Park Road	1	1			1
4	Billinghurst Cres	1	1			1
5	Beattie Road[b]	1	1	5	3	1
6	Shipper Drive	1	1			1
7	Hope Island Road	1	1			1
8	Lindfield Road	1	1			1
9	Town Center Drive	1	1			1
10	Dalley Park Drive	1	1			1
11	Discovery Drive[b]	1	1	5	3	1
12	Southport Library[a]	1	1	5	3	
13	Miami Depot[a]	1	1	5	3	
14	Highland Park[a]	1	1	5	3	
15	Yatala[a]	1	1	5	3	
Total sample no.		30		64		11

[a] These sites were referred as Group 1 sites in Sect. 3.3

[b] These sites were referred as Group 2 sites in Sect. 3.3

identified by US EPA (EPA 1999), namely, acenaphthene (ACE, 3 rings), acenaphthylene (ACY, 3 rings), fluorene (FLU, 3 rings), anthracene (ANT, 3 rings), phenanthrene (PHE, 3 rings), fluoranthene (FLA, 4 rings), benzo(a)anthracene (BaA, 4 rings), chrysene (CHR, 4 rings), pyrene (PYR, 4 rings), benzo(e)pyrene (BeP, 5 rings), benzo(a)pyrene (BaP, 5 rings), dibenzo(a,h)anthracene (DbA, 5 rings), benzo(ghi)perylene (BgP, 6 rings) and indeno(1,2,3-cd)pyrene (IND, 6 rings) and alkylated PAH, 2-bromonapthalene (NAP-2B, 3 rings). The detailed testing methods for heavy metals and PAHs are provided in Appendix.

Physico-chemical parameters such as total suspended particulate matter (TSP, for air samples), total organic carbon (TOC) and total solids (TS) were also tested as these parameters influence the behaviour of heavy metals and PAHs in atmospheric build-up, atmospheric deposition and build-up on the road surfaces (Silke et al. 2000; Wang et al. 2010; Gunawardana et al. 2013; Mejia et al. 2013; Liu et al. 2015). Table 2.3 gives details of the laboratory testing of the samples collected.

Table 2.3 Laboratory testing for the three transport pathways

	Atmospheric build-up	Atmospheric deposition	Build-up on road surfaces
Total particulate matter (TSP)	√	×	×
Heavy metals	√	√	√
PAHs	√	√[a]	√
Total solids (TS)	×	√	√
Total organic carbon (TOC)	×	√	√

√ tested; × not tested

[a] Although PAHs were tested for atmospheric deposition samples, all results were below limits of detection. Therefore, PAHs were not included in the analysis of atmospheric deposition

2.5 Summary

This chapter has discussed study site selection, sample collection, pollutants selection and sample testing. A total of 15 study sites (11 road sites and 4 sites with intense anthropogenic activities) were selected to collect atmospheric build-up, atmospheric deposition and road build-up samples. The study sites selected have different traffic and land use characteristics. This facilitated the investigation of traffic related pollutants and their processes.

Due to high toxicity and close relationship with urban traffic activities, heavy metals and PAHs were selected as the primary pollutants targeted in the research study. In addition, other physico-chemical parameters which can influence the behaviour of heavy metals and PAHs in the urban road environment were also tested.

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Chapter 3
Influence of Traffic and Land Use on Pollutant Transport Pathways

Abstract This chapter discusses the influence of traffic and land use factors on atmospheric pollutants build-up, dry and wet deposition and build-up on urban surfaces. Heavy metals (HMs) and polycyclic aromatic hydrocarbons (PAHs) were the focus of discussion in this chapter as these pollutants are ubiquitous in the urban environment, being commonly associated with traffic and anthropogenic activities common to urban areas and are toxic to human and ecosystem health. The research outcomes presented in this chapter confirm the influential role played by atmospheric pollution in stormwater pollution. The study outcomes also highlight the linkage between pollutants species with their potential sources and influential factors. Furthermore, the linkages between pollutants in the atmospheric phase, depositions and build-up on urban surfaces are also identified. For example, Zn was found to be the most abundant heavy metal element present in atmospheric build-up, atmospheric deposition and build-up on road surfaces, whilst light molecular weight PAHs have a higher concentration and spatial variability in both, atmospheric and road surface phases. The analysis also highlighted the influence exerted by heavy duty vehicle traffic on pollution in the urban environment, particularly in industrial land use areas. The knowledge created will contribute to informed decision making for minimising urban stormwater pollution and thereby safeguarding the urban water environment. In addition, these outcomes can also be applied in urban transport planning in order to enhance urban liveability.

Keywords Traffic pollutants • Atmospheric build-up • Atmospheric deposition • Pollutants build-up • Urban traffic • Pollutant pathways

3.1 Background

Urban stormwater pollution is influenced by a range of pollutant processes and pathways, which consist of atmospheric build-up, atmospheric deposition and build-up on road surfaces for eventual wash-off by stormwater runoff. These processes and pathways are interrelated and interdependent. In this context, an in-depth understanding of their characteristics is important for designing mitigation strategies to minimise the impacts of urban stormwater pollution and thereby for safeguarding the urban water environment.

J.M.A. Gunawardena et al., *Influence of Traffic and Land Use on Urban Stormwater Quality*, SpringerBriefs in Water Science and Technology,
DOI 10.1007/978-981-10-5302-3_3

This chapter focuses on key outcomes generated by analysing the data obtained from the comprehensive field investigations presented in Chap. 2. Heavy metals (HMs) and polycyclic aromatic hydrocarbons (PAHs) are the focus of discussion in this chapter as these pollutants are ubiquitous in the urban environment, being commonly associated with traffic and anthropogenic activities common to urban areas and are toxic to human and ecosystem health. In this chapter, analysis for atmospheric build-up, atmospheric deposition and build-up on road surfaces are presented individually. This is followed by the presentation of the outcomes of the investigation into the linkages between these three pathways.

3.2 Analysis of Atmospheric Build-Up

3.2.1 Analysis of Total Particulate Matter

As a number of pollutants in the atmosphere are associated with total particulate matter (TSP), it is essential to investigate the influence of urban traffic on TSP. In the research study, as the TSP concentrations were measured for weekdays and weekends separately, a comparison between the two data sets was also undertaken. As evident from Fig. 3.1, TSP concentrations during weekdays are comparatively higher than for weekends. This is due to the fact that traffic volumes are higher during weekdays, resulting in relatively higher atmospheric emissions. As the traffic volume increases, traffic induced wind can re-suspend particles which are

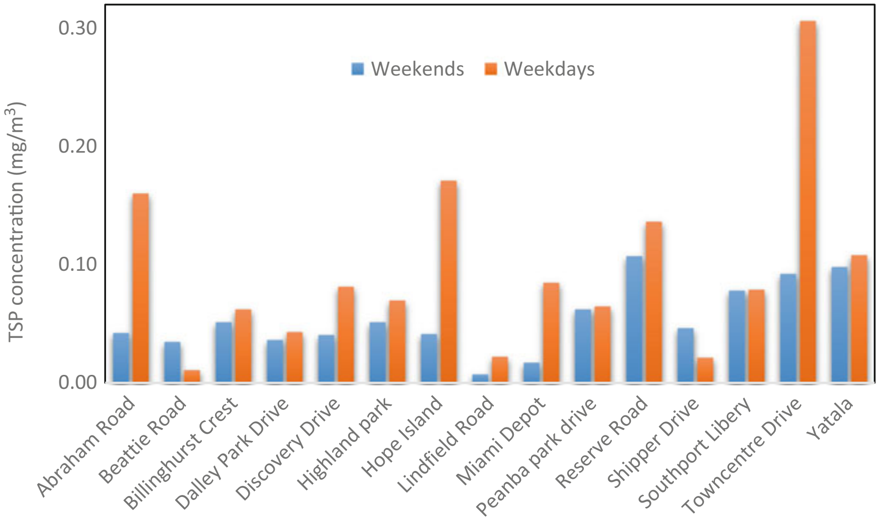

Fig. 3.1 TSP concentrations during weekdays and weekends

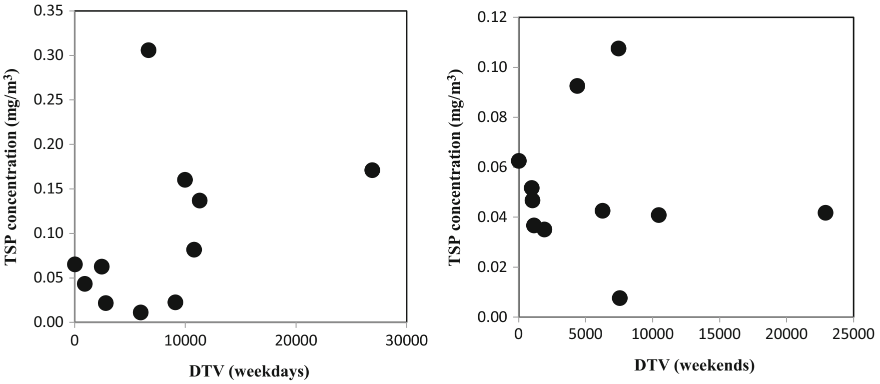

Fig. 3.2 Relationship between TSP concentrations and traffic volume

already deposited on the ground and increase the TSP concentrations in the atmosphere.

Based on the data collected, Fig. 3.2 shows the change in TSP concentrations with traffic volume (DTV, average daily traffic volume) for weekdays and weekends. It was found that TSP concentrations are generally proportional to DTV for weekdays, but this phenomenon was not evident for weekends. This means that atmospheric TSP concentrations are more influenced by traffic volume during weekdays rather than weekends. This can be attributed to a higher traffic volume at weekdays compared to weekends. It can also be inferred that heavy duty traffic volume which is a primary contributor of particles to the atmosphere (Jayaratne et al. 2005) is less frequent during weekends. This also contributes to lower TSP concentrations on weekends.

3.2.2 Analysis of Heavy Metals

Heavy metal concentrations in the atmosphere during weekdays and weekends are shown in Fig. 3.3. As Ni and Cd were not detected in almost all of the samples, they were not included in the analysis. Generally, atmospheric heavy metal concentrations are higher during weekdays than weekends. Same as for TSP, this can be attributed to the higher traffic volume on weekdays. Zn was consistently detected in relatively the highest concentration during both, weekdays and weekends, while Pb had the second highest concentration. As discussed in Chap. 1, the main sources of Zn are vehicle related lubricants, engine oil and tyre wear while brake pad wear and tyre wear are the primary sources of Pb (Hussain et al. 2015; Mummullage et al. 2016). Furthermore, resuspended soil dust enriched with Pb from previous decades of leaded fuel usage can also be a contributor of Pb to the urban environment (Gunawardena et al. 2013; Hussain et al. 2015). This can also be supported by the

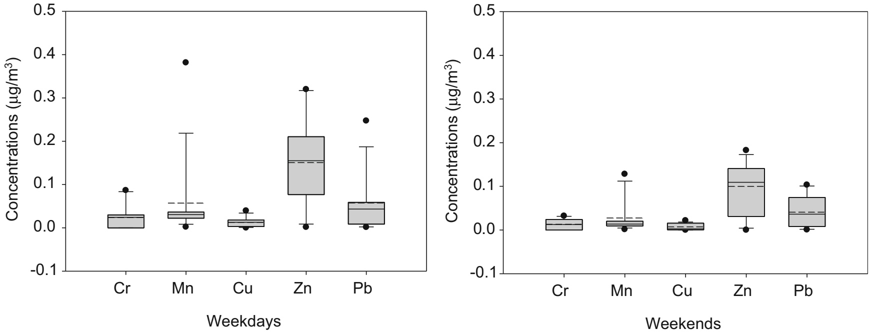

Fig. 3.3 Heavy metal concentrations in the atmosphere during weekdays and weekends (*dashed lines*—mean; *solid lines*—median)

fact that the adsorption of heavy metals to soil particles is in the order of Pb > Cu > Zn > Ni > Cd (Usman 2008).

As evident in Fig. 3.3, the range of concentrations for Zn and Pb are wide. This suggests significant spatial variability of heavy metals in the atmosphere near roads with different traffic characteristics and land use. In this context, it was considered important to investigate the influence of traffic and land use on atmospheric heavy metals. For this purpose, principal component analysis (PCA) was employed. Four of the study sites, namely, Highland Park, Miami Depot, Southport Library and Yatala, were not road sites. These sites were selected due to the intense anthropogenic activities in the surroundings. As such, traffic data was not available for these four sites, which were excluded from the analysis. A matrix (11 × 9) was created, where the objects were the remaining 11 road sites and variables were the five heavy metals (Cr, Mn, Cu, Zn and Pb), traffic related factors (total average daily traffic volume, DTV and heavy duty traffic volume, HDTV), TSP and wind speed. Selecting heavy duty traffic volume rather than total traffic volume only was due to the dominant contribution of heavy duty vehicles to heavy metal generation, compared to light duty vehicles (Liu et al. 2015a, b). This selection can also be supported by the discussion on atmospheric TSP concentrations during weekdays and weekends (see Sect. 3.2.1). TSP is an important atmospheric pollutant as other pollutants such as heavy metals are generally attached to particulates (Tartakovsky et al. 2016). Wind speed is a significant influential factor in relation to atmospheric pollution as higher wind speeds result in the dispersion of pollutants (Grundstrom et al. 2015).

Figure 3.4 gives the PCA biplots for weekdays and weekends. According to the biplot for weekdays (Fig. 3.4a), Cu and Cr form acute angles with HDTV, implying close correlation between these variables. This means that Cu and Cr are primarily generated by heavy duty vehicles. It is evident that Mn and TSP are closely correlated, but not with traffic parameters. This implies that Mn would be mainly generated from surrounding soil. Interestingly, TSP does not show a strong correlation with both traffic related parameters (DTV and HDTV). This observation

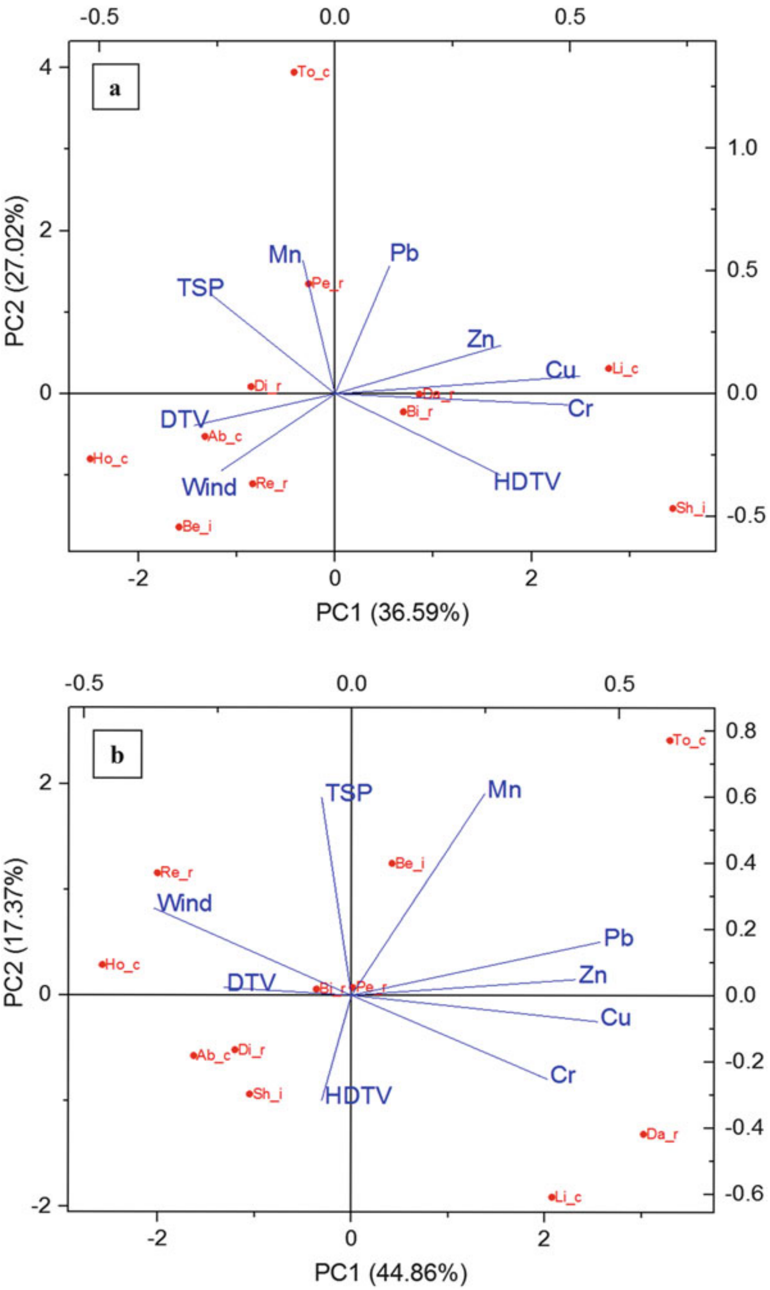

Fig. 3.4 PCA biplots of atmospheric heavy metals during: (**a**) weekdays and (**b**) weekends (the first two letters represent road names while r, i and c represent residential, industrial and commercial land uses. For example, Ab_c represents Abraham Road which is located at commercial areas)

suggests that traffic is not the dominant source of atmospheric TSP and alternate sources also contribute. This can be supported by the outcomes of the study by Tippayawong et al. (2006) where three primary sources of atmospheric TSP were identified. The first being long-distance sources such as wind transported particulates; the second being short-distance sources such as re-suspension of road deposited solids and the third being unknown sources with low influence of traffic emissions. The above outcomes confirm that the prominent sources of atmospheric pollutants are related to wind transported particles, traffic and re-suspended soil.

Figure 3.4b is the PCA biplot results for weekends. It can be noted that neither traffic related variables nor wind is correlated with any of the investigated heavy metals. This means that other sources such as surrounding soil might be dominant during weekends as traffic volume is low compared to weekdays. Therefore, atmospheric heavy metal concentrations are generally not highly influenced by traffic during weekends. This could lead to a relatively uniform distribution of heavy metals in the atmosphere at weekends.

It can be noted that residential road site objects are relatively clustered close to the origin while commercial and industrial road site objects are positioned away from the origin and relatively scattered. This is particularly evident in the biplot of weekdays. This can be considered to signify the influence of land use on heavy metals in the atmosphere. Atmospheric heavy metal concentrations are higher at the commercial and industrial areas (commercial and industrial road site objects are located far from the origin while residential objects are relatively near to the origin) and have a higher spatial variability (commercial and industrial road site objects are scattered while residential objects are clustered around the origin), compared to residential areas. This is attributed to more frequent and diverse traffic activities at commercial and industrial land use areas when compared to residential land use areas. For example, commercial and industrial areas generally include heavy duty vehicle loading–unloading activities and normal light duty vehicle traffic while private vehicles are the primary form of traffic in most residential areas.

3.2.3 *Analysis of PAHs*

The boxplots given in Fig. 3.5 provide comparisons of particulate and gaseous PAH concentrations during weekdays and weekends. Generally, PAH concentrations in the atmosphere during weekdays are higher than weekends, and it is more evident for gaseous PAHs. This is attributed to the higher traffic volume during weekdays compared to weekends. Light molecular weight (LMW, 3–4-ring) PAHs show higher concentrations than heavy molecular weight (HMW, 5–6-ring) PAHs. This is attributed to the volatile nature of LMW PAHs.

It is noted that gaseous PAHs are generally in higher concentrations than particulate PAHs, and this is independent of the PAH species. This suggests that atmospheric PAHs in the urban environment could pose potential human health risk via inhalation. This can also be supported by the fact that gaseous pollutants are less likely to deposit on road surfaces than particulate forms (Liu et al. 2015a, b).

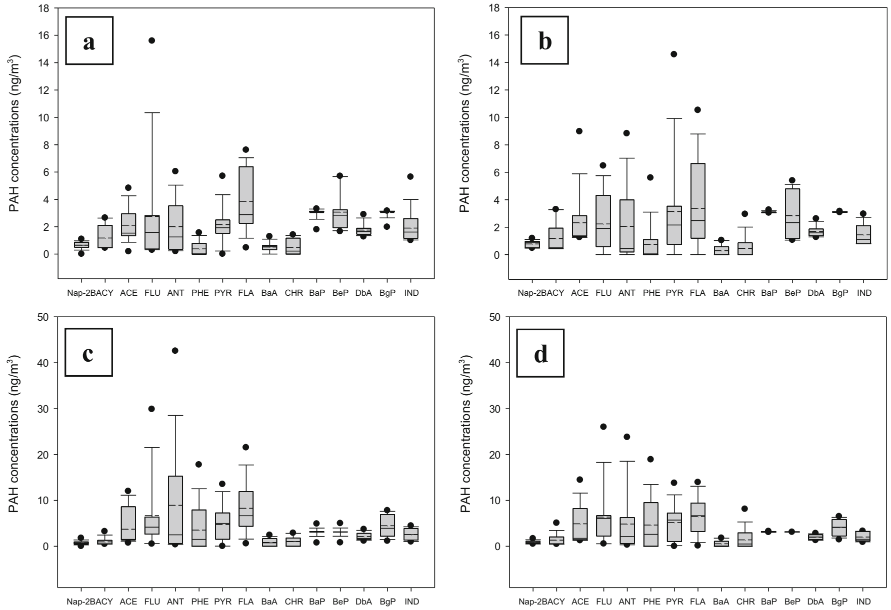

Fig. 3.5 Particulate and gaseous PAH concentrations in the atmosphere during weekdays and weekends (**a**: particulate, weekdays; **b**: particulate, weekends; **c**: gaseous, weekdays; **d**: gaseous, weekends; full names of PAHs refer to Sect. 2.4)

In terms of data ranges shown in Fig. 3.5, LMW PAHs indicate relatively wider data ranges than HMW PAHs and is independent of PAHs species and day of the week (weekdays or weekends). This means that LMW PAH concentrations in the atmosphere are highly variable at road sites, which have different traffic characteristics and land use while HMW PAH concentrations are relatively similar throughout those road sites. LMW PAHs are generally volatile and hence more influenced by factors such as wind and traffic turbulence, resulting in more frequent re-distribution and thereby, higher variability.

PCA was also undertaken to further investigate the relationships between atmospheric PAHs and traffic and land use. Figure 3.6 gives the biplots for particulate and gaseous PAH concentrations in the atmosphere during weekdays and weekends. In the case of weekdays, for particulate PAHs, it can be noted that the vectors which are closely correlated with HDTV, DTV, TSP and wind are LMW PAHs (3–4 rings) such as ACY, ACE, PYR, FLU and Nap-2B. On the contrary, in terms of gaseous PAHs, the PAH species which are strongly correlated with HDTV, DTV, TSP and wind are BgP, DbA, IND and FLU, three of which are HWM PAHs (5–6 rings). This means that external factors such as traffic and wind tend to influence particulate LMW PAHs and gaseous HMW PAHs.

Compared to weekdays, PAHs are less correlated to traffic, wind and TSP during weekends regardless of particulate and gaseous forms since most of PAH vectors are located opposite to HDTV, DTV, TSP and wind in the biplots for weekends (Fig. 3.6b, d). This means that external factors such as traffic are not the dominant

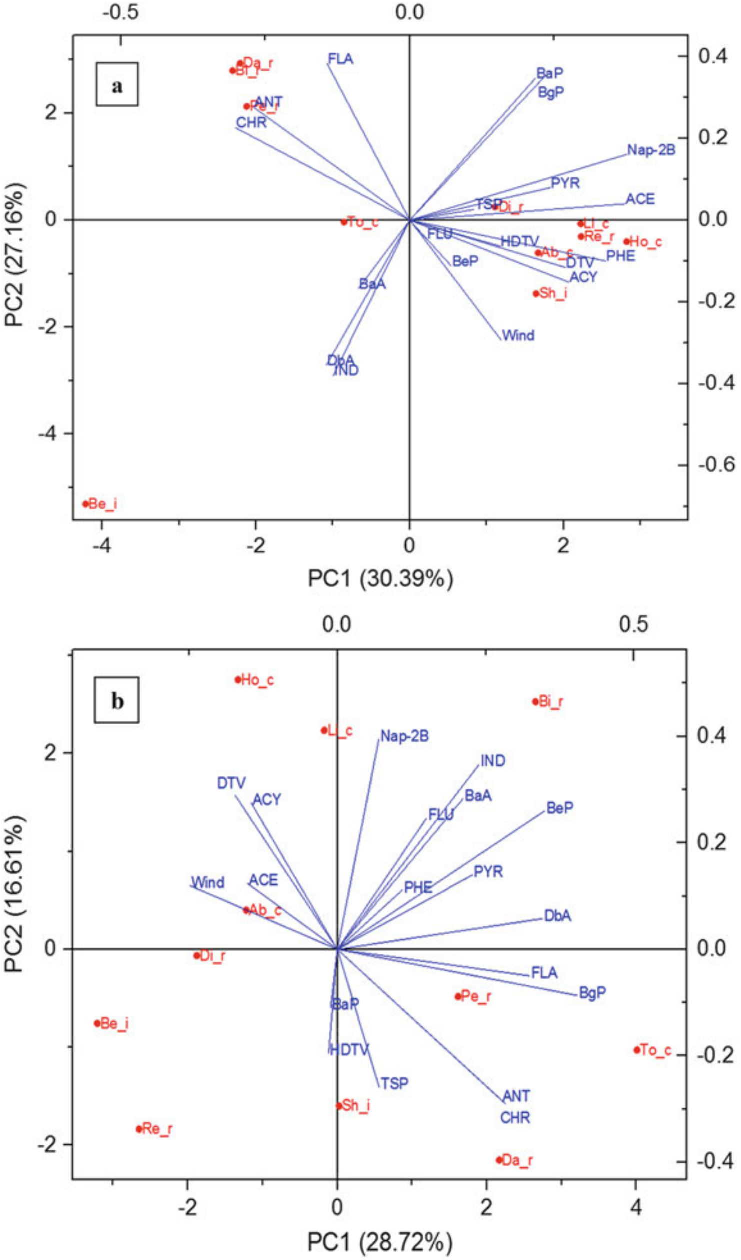

Fig. 3.6 PCA biplots for particulate and gaseous PAH concentrations in the atmosphere during weekdays and weekends (**a**: particulate, weekdays; **b**: particulate, weekends; **c**: gaseous, weekdays; **d**: gaseous, weekends; for data labels refer to Fig. 3.4)

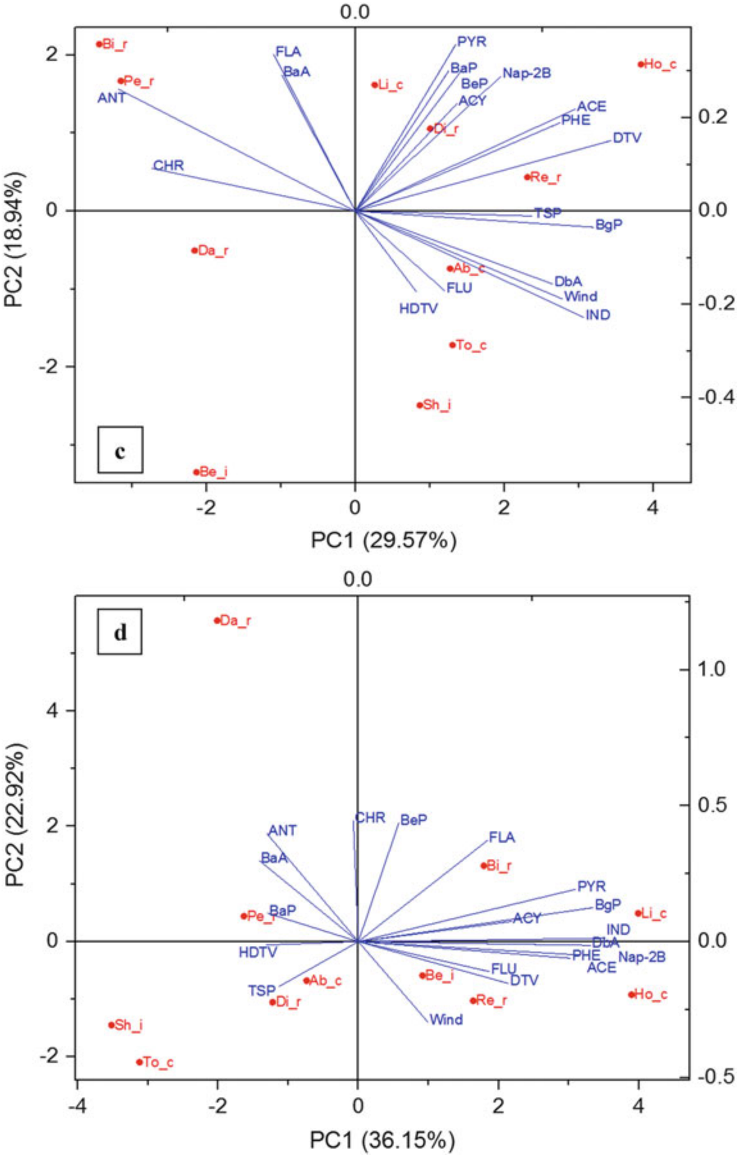

Fig. 3.6 (continued)

anthropogenic activities which generate PAHs during weekends. In this context, background PAHs could prevail at the road sites as traffic related emissions are at a minimum during weekends, which could result in a relatively uniform distribution of atmospheric PAHs.

It was also found that all study sites are relatively scattered in the biplots for both particulate and gaseous PAHs during weekdays and weekends rather than clustered based on land use. This could indicate that land use exerts a lesser influence in the contribution of PAHs to the atmosphere. This further confirms the importance of traffic as a primary source of PAHs in the atmosphere.

3.3 Analysis of Atmospheric Dry and Wet Deposition

3.3.1 Analysis of Total Solids

Figure 3.7 provides a graphical representation of the dry and bulk deposition data for total solids (TS) for Group 1 and 2 sites (see Table 2.2). It is evident that the atmospheric deposition of TS at Group 1 sites is relatively higher than at Group 2 sites, regardless of whether it is dry or bulk deposition. This can be attributed to the fact that Group 1 sites are located in areas with intense anthropogenic activities as discussed in Chap. 2 (see Table 2.1) which would result in a relatively higher generation of particulate pollutants and consequently, higher deposition compared to typical urban roads such as the Group 2 sites.

In terms of dry deposition, the deposited loads of TS generally increased with antecedent dry days. For example, the average dry deposition loads of TS increased from 163.8 mg/m^2 to 706.3 mg/m^2 among the Group 1 sites as the antecedent dry days increased from 3 to 6 days. For Group 2 sites, the corresponding loads increased from 84.4 mg/m^2 to 290.2 mg/m^2 as the antecedent dry days increased from 3 to 7 days. This is because longer antecedent dry days result in a higher availability of TS in the atmosphere, which in turn will contribute to higher dry deposition.

For bulk deposition, the deposited TS loads have a positive relationship with rainfall depth, with higher rainfall depth producing higher bulk deposition of TS for both, Group 1 and 2 sites. For instance, the bulk deposition increased from 512 mg/m^2 to 920 mg/m^2 for Group 1 sites when the rainfall depth increased up to 19 mm.

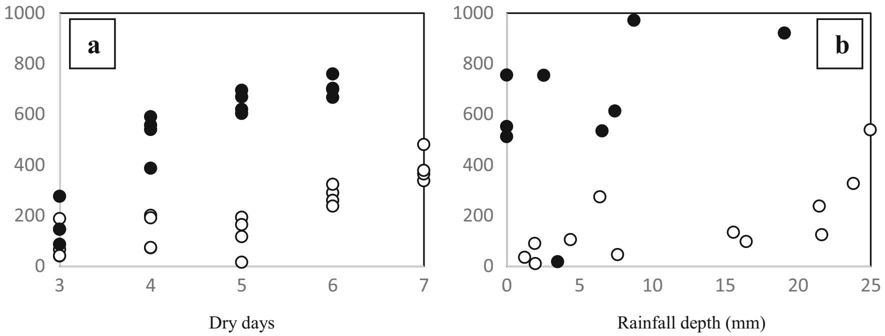

Fig. 3.7 Dry deposition and bulk deposition of total solids (unit: mg/m^2; **a**: dry deposition; **b**: bulk deposition; *closed circle*—Group 1 sites; *open circle*—Group 2 sites)

The corresponding values increased from 6 mg/m^2 to 486 mg/m^2 for Group 2 sites when the rainfall depth increased from 1.2 mm to 25 mm. These observations confirm that bulk atmospheric deposition is strongly related to rainfall depth.

3.3.2 Analysis of Heavy Metals

Figure 3.8 provides a comparison of the deposition rates of heavy metals in dry deposition and bulk deposition. The deposition rates were determined by dividing the heavy metal loads obtained from the sampling by the respective antecedent dry days. It is evident that Zn is the most dominant heavy metal species in both, dry and bulk deposition, followed by Cr while other heavy metals show much lower values. The high loads of Zn and Cr in dry and bulk deposition can be attributed to the increased concentrations of these heavy metals in the atmosphere (Gunawardena et al. 2012).

Furthermore, it is noted that Zn bulk deposition rate is two times higher than its dry deposition. This would mean that scavenging from the atmosphere by rainfall can contribute high loads of heavy metals to road stormwater runoff. Hence, this process can be considered as an important source of heavy metals. However, Cr does not show a significant difference between dry and bulk depositions at most of the study sites. This is attributed to the lower solubility of Cr. As noted by Morselli et al. (2003), the solubility of heavy metals in wet deposition follows the order, Zn > Cd > Cu > Ni > Pb > Cr. In this context, wet deposition can only remove a relatively smaller amount of Cr present in the atmospheric phase. In addition, as found by Samara and Voutsa (2005), the mean mass median aerodynamic diameter (MMMAD) of these heavy metals is in the order of Pb < Cd < Ni < Cu < Cr. Therefore, Cr would be expected to deposit primarily as dry deposition since it has the largest MMMAD value.

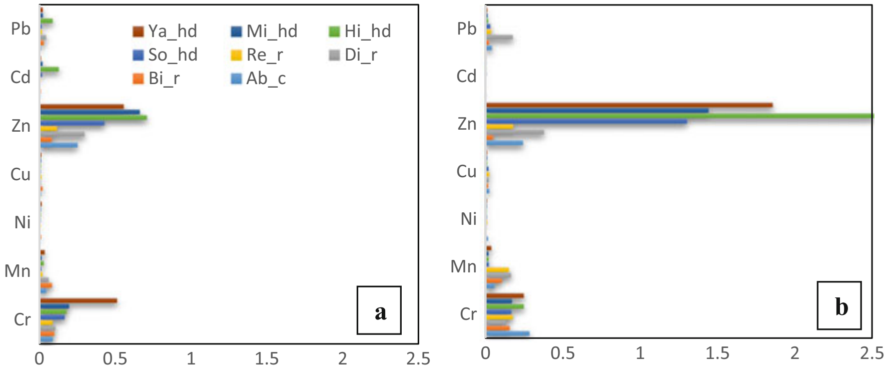

Fig. 3.8 Dry deposition and bulk deposition rates of heavy metals (unit: mg/m^2/day; **a**: dry deposition; **b**: bulk deposition)

PCA was performed to further investigate the relationships between atmospheric deposition and external factors such as traffic and rainfall and was undertaken for dry deposition and bulk (wet) deposition separately. Due to the unavailability of traffic data for Group 1 sites (Highland Park, Yatala, Miami Depot and Southport Library) as explained previously in Sect. 3.2.2, these four sites were excluded from the PCA analysis. The matrix for dry deposition was 20 × 12, the 20 objects being the four road sites (Group 2 sites) with five different antecedent dry day sampling episodes each (see Chap. 2) and the 12 variables were the seven heavy metals, total organic carbon (TOC), total solids (TS), traffic congestion (V/C), antecedent dry days (ADD) and average daily traffic volume (DTV). The matrix for bulk deposition was 12 × 12, the 12 objects being the four road sites (Group 2 sites) with three different antecedent dry day sampling episodes (see Chap. 2) and the 12 variables were the seven heavy metals, total organic carbon (TOC), total solids (TS), rainfall depth (rainfall), antecedent dry days (ADD) and average daily traffic volume (DTV). Figure 3.9 shows the resulting PCA biplots for dry and bulk depositions.

As evident in Fig. 3.9a (dry deposition), TS vector in dry deposition strongly correlates with ADD and Zn. This confirms the strong influence of ADD on atmospheric build-up and consequent dry deposition. Zn could be associated with relatively large particles as dry deposition particles are relatively larger (Gunawardena et al. 2013). Vehicle component wear particles are generally larger than exhaust emission particles (Jandacka et al. 2017). This means that wear of vehicle parts is a major pathway for airborne Zn. It can also be noted that other heavy metals such as Mn, Cd, Ni, Cu and Pb are closely correlated with traffic parameters (DTV and V/C), but do not show a strong correlationship with TS. It can be argued that these heavy metals are primarily associated with the finer airborne particles which do not contribute significantly to the total solids during dry deposition. As noted by Samara and Voutsa (2005), Cd, Mn, Cu, Pb and Ni in the atmospheric phase is less than 2.61 μm in size. This implies that except Zn and Cr, other heavy metals originate primarily from exhaust emissions rather than vehicle component wear.

For bulk deposition (see Fig. 3.9b), Zn and Pb vectors are closely correlated with ADD, but weakly correlated with DTV. This suggests that atmospheric deposition of Zn and Pb depends on the antecedent dry days, and traffic is one of the sources of these two heavy metal species. It is noteworthy that Pb is not correlated with DTV in dry deposition, but has a correlationship with DTV in bulk deposition. This phenomenon suggests that Pb is different to Zn in the atmospheric phase. Pb is primarily present in exhaust emissions, which produce fine particles while Zn is primarily sourced from vehicle component wear as discussed above. However, since the usage of leaded fuel was discontinued more than a decade ago, Pb presence could be due to the re-suspension of already deposited Pb such as in roadside soil. Typically, exhaust particles are relatively fine, and wet deposition is an effective process for removing smaller particles (Fang et al. 2004). As noted by Huston et al. (2009), most heavy metals in the atmosphere are related to particles less than 6 μm size. They also found that rainfall is able to scavenge 2–10 μm size range particles more efficiently.

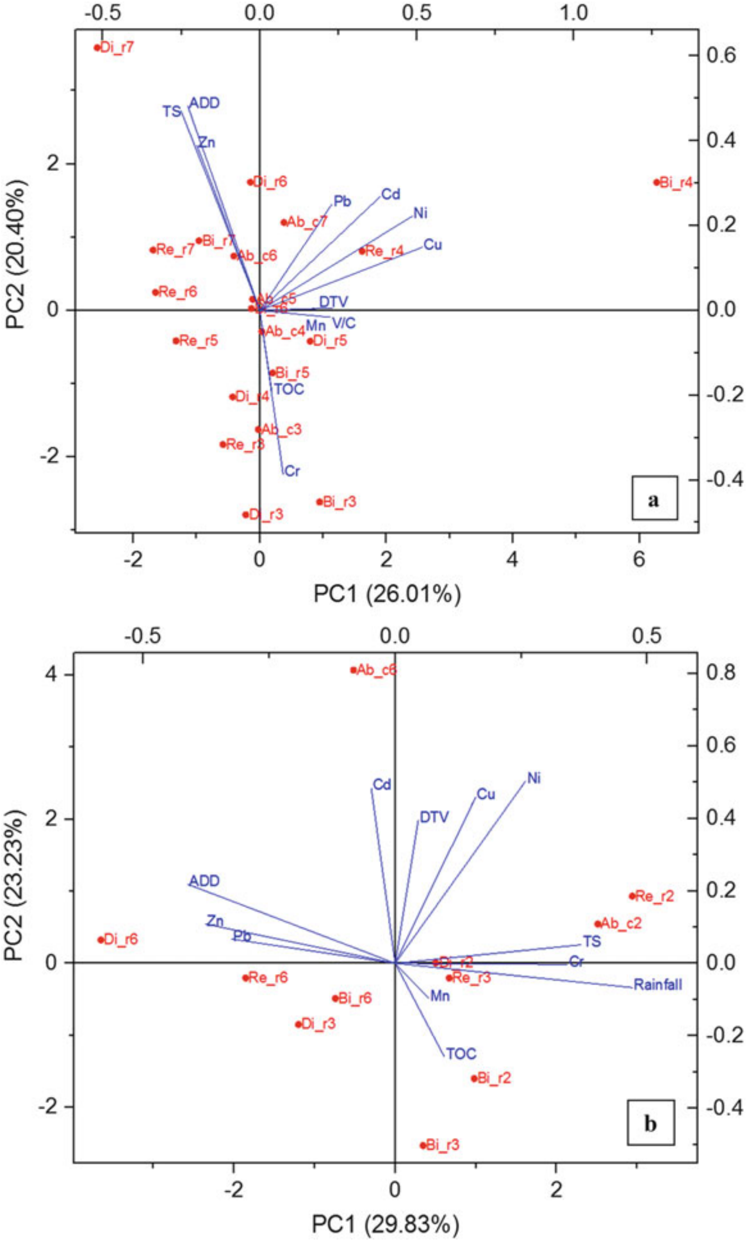

Fig. 3.9 PCA biplots for dry and bulk depositions (**a**: dry deposition; **b**: bulk deposition; for data labels refer to Fig. 3.4)

The correlation between Cd, Cu and Ni and DTV suggests that these metals are generated by exhaust emissions. This can be also supported by their small MMMD values, where Cd, Cu and Ni range between 1.14 and 2.04 μm (Samara and Voutsa 2005). This provides further confirmation of the above conclusion since exhaust emissions primarily generate small particles. Considering that wet scavenging is an efficient process in the removal of relatively small particles, deposition of Cd, Cu and Ni can be considered to be primarily related to bulk deposition. Furthermore, Cr is found to correlate with TS and rainfall depth. This can be attributed to the relatively large MMMD value of Cr (2.9 μm). Wet deposition is responsible for scavenging an appreciable solids load from the atmosphere. This can explain the close correlationship between Cr, TS and rainfall depth.

3.4 Analysis of Road Build-Up

3.4.1 Analysis of Total Solids

The build-up loads of total solids (TS) on road surfaces varied from 0.05 g/m^2 to 1.1 g/m^2 after seven antecedent dry days. Since traffic activities and surrounding land use have been considered as the primary influential factor in road pollutants build-up (Gunawardena et al. 2014), Fig. 3.10 plots the TS build-up loads with average daily traffic volume (DTV) and land use. As evident from Fig. 3.10, TS build-up loads do not show a clear trend with DTV as well as land use. This highlights the complexity of road build-up processes. Other than traffic and

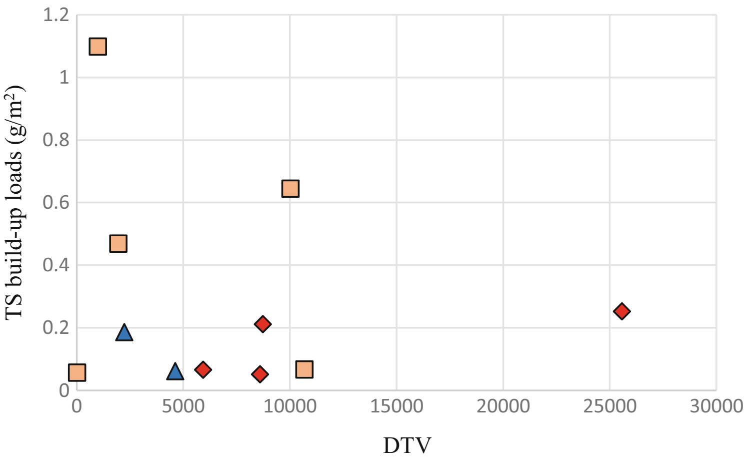

Fig. 3.10 Total solids build-up with average daily traffic volume (*filled square in biege*—residential; *filled diamond in red*—commercial; *filled triangle in blue*—industrial)

Table 3.1 Particle size distribution of TS build-up on road surfaces

		Particle size distribution (volumetric percentages %)				
Land use	Road ID	>300 μm	150–300 μm	75–150 μm	1–75 μm	<1 μm
Industrial	Sh	21.7	13.8	13.7	46.9	3.9
	Be	18.6	15.5	14.6	48.7	2.6
	Mean	20.2	14.7	14.2	47.8	3.3
Residential	Bi	27.6	14.6	10.0	45.7	2.1
	Da	2.8	3.9	8.3	80.0	5.0
	Di	21.4	17.2	24.0	33.7	3.7
	Pe	28.7	18.9	15.9	34.5	2.0
	Re	2.1	3.3	3.4	84.3	6.9
	Mean	16.5	11.6	12.3	55.6	3.9
Commercial	Ho	3.9	5.7	12.9	74.8	2.7
	Li	11.7	10.1	21.1	53.8	3.3
	Ab	2.7	3.3	4.5	85.1	4.4
	To	31.5	14.3	11.8	38.5	3.9
	Mean	12.5	8.3	12.6	63.1	3.6

land use, road build-up is also significantly influenced by other factors such as atmospheric deposition as discussed above.

In this context, an in-depth understanding of road build-up processes and its variability with important influential factors is necessary. For this purpose, each TS build-up sample was divided into five particle size ranges (<1 μm, 1–75 μm, 75–150 μm, 150–300 μm and >300 μm). Table 3.1 gives the particle size distribution for each road site. It can be noted that industrial sites contribute relatively lower volumetric percentage of <1 μm and 1–75 μm particle size fractions, but higher volumetric percentage of 75–150 μm, 150–300 μm and >300 μm. This implies that residential and commercial sites tend to contribute a relatively higher fraction of fine particles to urban road surfaces while industrial areas contribute larger particles as a higher fraction.

3.4.2 Analysis of Heavy Metals

Figure 3.11 compares the build-up load of each heavy metal species. It is evident that Zn is the highest detected heavy metal element (1.07–3.51 mg/m^2), followed by Cu (0.75–2.45 mg/m^2) for almost all the road sites. It is noteworthy that Zn is also the most common heavy metal species in the atmospheric phase and in atmospheric deposition as discussed in Sects. 3.2.2 and 3.3.2. This highlights the appreciable contribution from atmospheric phase to Zn build-up on road surfaces through atmospheric deposition. Cd has the lowest loads on the road surfaces for all the investigated road sites, ranging between 0 and 0.003 mg/m^2. However, Cd generally has a much higher toxicity, compared to other heavy metals. As noted by

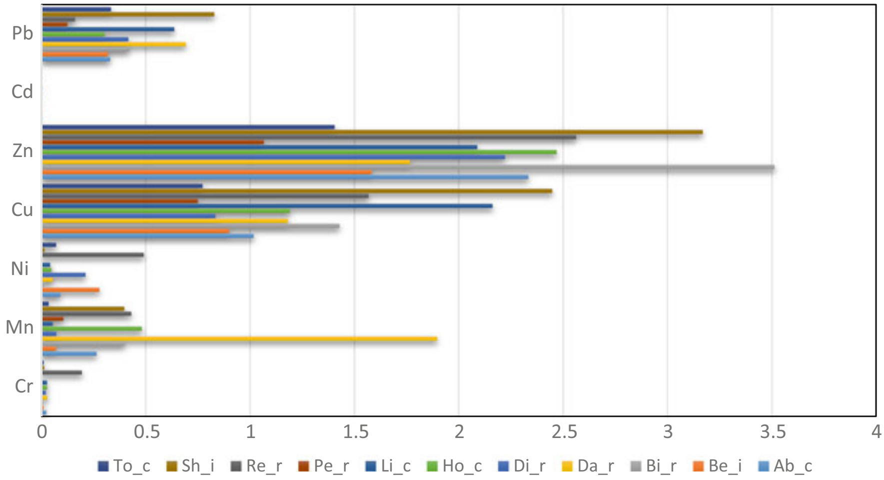

Fig. 3.11 Heavy metals build-up on road surfaces (unit: mg/m^2)

Hakanson (1980), the toxic-response factor (representing the toxicity degree) of heavy metals is in the order of Zn = 1 < Cr = 2 < Cu-Ni = Pb = 5 < Cd = 30. This means that although Cd exists on road surfaces at a relatively much lower level, it could pose a higher risk to the environment and human health when incorporated in stormwater runoff (Liu et al. 2015a, b; Ma et al. 2016).

PCA was undertaken to further investigate the correlation between heavy metals build-up on road surfaces and their influential factors. The selected influential factors were average daily traffic volume (DTV), heavy duty vehicle traffic volume (HDTV), traffic congestion parameter (V/C), total organic carbon (TOC) and total solids (TS). PCA was performed for the five particle size fractions, individually. For each particle size, there were 11 objects representing the 11 road sites and 12 variables including the seven heavy metals (Cr, Mn, Ni, Cu, Zn, Pb and Cd) and the five influential factors noted above. Figure 3.12 shows the resulting PCA biplots.

It can be noted that Zn is closely related to HDTV for all particle size fractions. As previous researchers have pointed out (Mummullage et al. 2016), vehicle component wear contributes a significant amount to Zn build-up on road surfaces. Heavy duty vehicles are expected to have more frequent wear of their components and abrasion with road surfaces due to their weight. Therefore, heavy duty vehicle traffic would be the primary source of Zn build-up on road surfaces. Furthermore, it is evident that V/C vectors have a relatively close correlation with the heavy metal vectors in the case of finer particle size fractions (<1 μm, 1–75 μm and 75–150 μm), but locate far from the heavy metal vectors for larger particle sizes (150–300 μm and >300 μm). These observations suggest that traffic congestion could primarily generate small particles, to which most heavy metals are attached. A similar phenomenon can also be observed for DTV, which has strong correlations with heavy metals for the smaller particle sizes (<1 μm, 1–75 μm, 75–150 μm and 150–300 μm), but not for larger particle (>300 μm). These results mean that higher

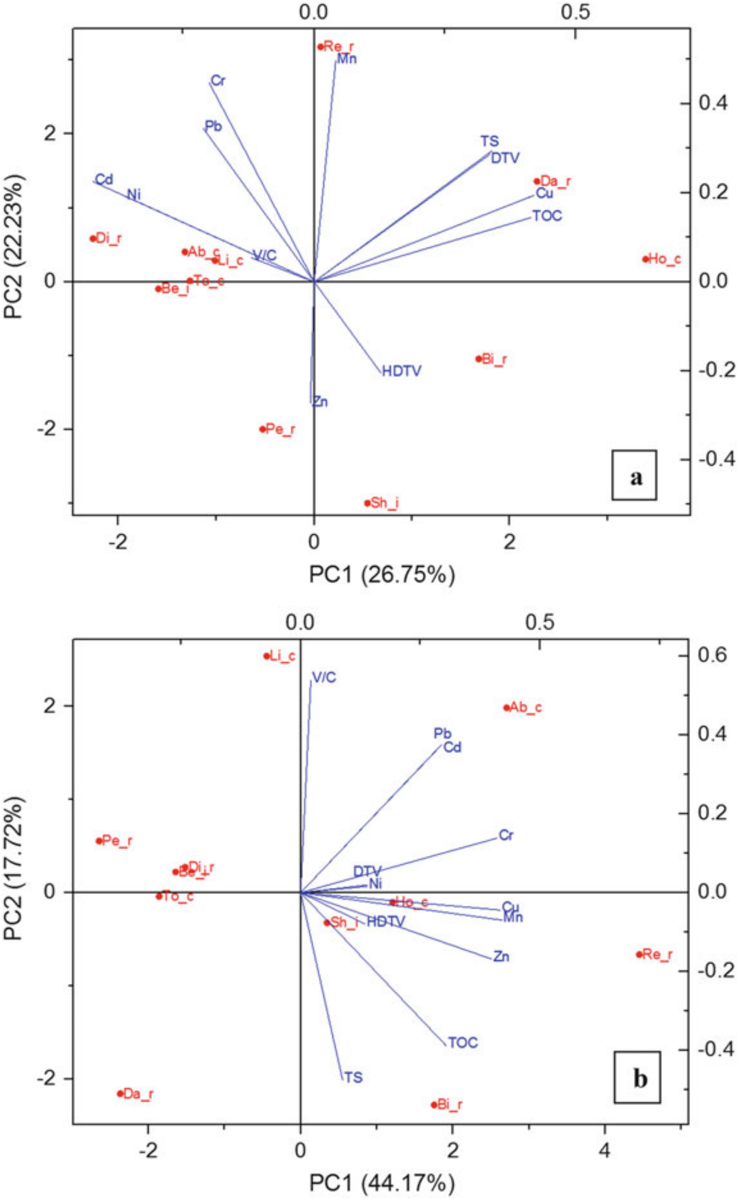

Fig. 3.12 PCA biplots for heavy metals build-up on road surfaces (**a**: <1 μm; **b**: 1–75 μm; **c**: 75–150 μm; **d**: 150–300 μm; **e**: >300 μm; for data labels refer to Fig. 3.4)

traffic volume tends to contribute relatively more small particles to road build-up. This can also be supported by the correlationship between TS and DTV in the PCA biplots. It is evident that TS is closely associated with DTV in the biplots for the small particle sizes (except for 1–75 μm), but has a relatively weak correlation with

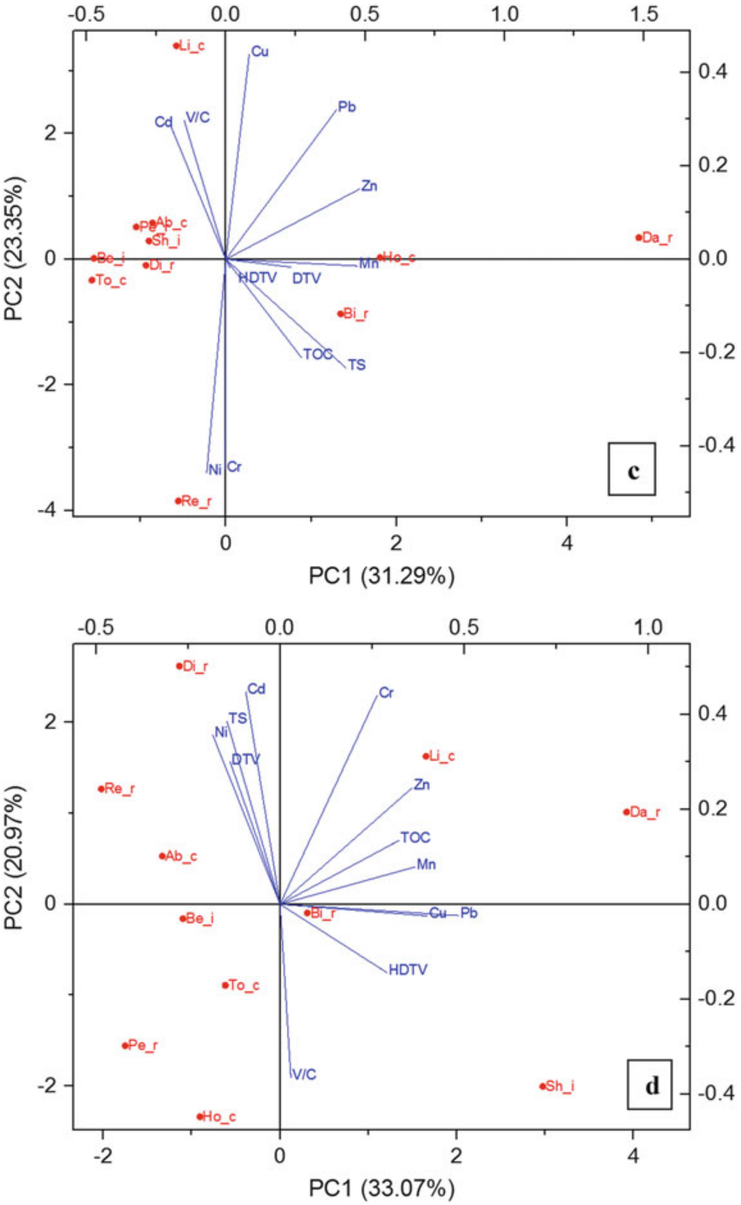

Fig. 3.12 (continued)

DTV in the PCA biplot for >300 μm. In addition, TOC is correlated with one or a number of heavy metals in all particle size fractions. This means that heavy metals build-up on road surfaces might be present as organic complexes, which could

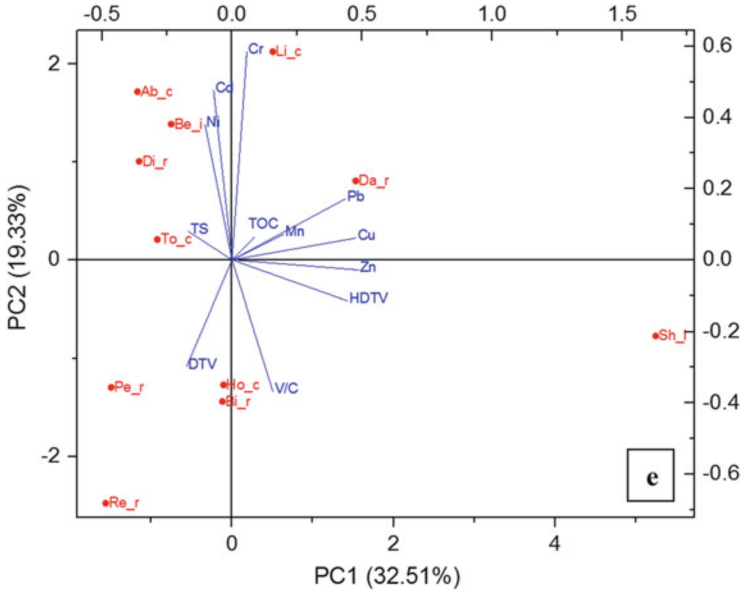

Fig. 3.12 (continued)

influence their solubility and mobility in stormwater runoff (Khokhotva and Waara 2010; Refaey et al. 2014).

Figure 3.12 does not show any grouping of sites based on land use for all the particle size fractions. This means that the influence of land use on heavy metals build-up is secondary to traffic related activities, which can overshadow the impact of non-traffic related activities such as land use.

3.4.3 Analysis of PAHs

Figure 3.13 provides a comparison of 3 ring, 4 ring, 5 ring and 6 ring PAH loads. It is evident that 3-ring PAHs (mean: 118.2 mg/m^2) are detected in the highest loads in the study sites compared to other PAH species (27.5 mg/m^2 for 4-ring, 27.5 mg/m^2 for 5-ring and 17.6 mg/m^2 for 6-ring). Additionally, the data range of 3-ring PAHs is the widest among the four types of PAH species. This highlights the high variability in the spatial distribution of LMW PAH build-up loads across those road sites. These observations are similar to what was discussed in Sect. 3.2.1 in relation to PAHs in the atmosphere. This underlines the strong linkage between atmospheric deposition of PAHs and their build-up on road surfaces.

Figure 3.14 gives the PCA biplots of PAHs build-up for the five particle size fractions. In each biplot, there are 11 objects representing the 11 road sites and 9 variables including the cumulative loads of 3 rings, 4 rings, 5 rings and 6 rings and DTV, HDTV, TS, TOC and V/C. It can be noted that all PAH species are strongly

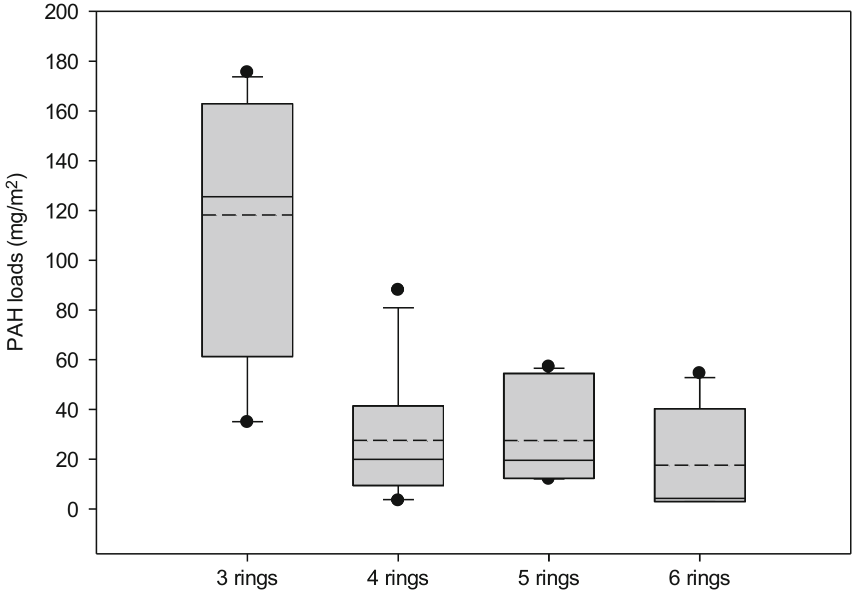

Fig. 3.13 Comparison of PAHs build-up on road surfaces

correlated to HDTV rather than DTV, and this is irrespective of particle sizes, particularly for 5 and 6 rings species. This confirms the importance of heavy duty vehicle traffic as the primary source of PAHs build-up on road surfaces, especially in relation to HMW PAHs. However, V/C does not show a positive correlationship with PAHs, particularly not in the case of 5 and 6 ring species. This means that traffic congestion might contribute a limited LMW PAH load to road build-up, but it does not generate a high HMW PAH load. In addition, TS shows a relatively closer correlationship with PAHs in the particle size of <1 μm compared to the other particle sizes, which confirms that PAHs preferentially tend to adsorb to the finer particles. Furthermore, TOC is weakly correlated to all PAH species for all particle sizes. This implies that complexation with organic matter is not a dominant process in PAHs build-up on road surfaces.

In terms of land use, industrial sites are located in the same direction as the PAH vectors for all particle sizes, while most of the residential and commercial sites are located opposite to PAH vectors. This is attributed to the higher number of heavy duty vehicles traversing through industrial areas when compared to residential and commercial areas. This further confirms the important role played by heavy duty vehicle traffic in influencing PAHs build-up on road surfaces.

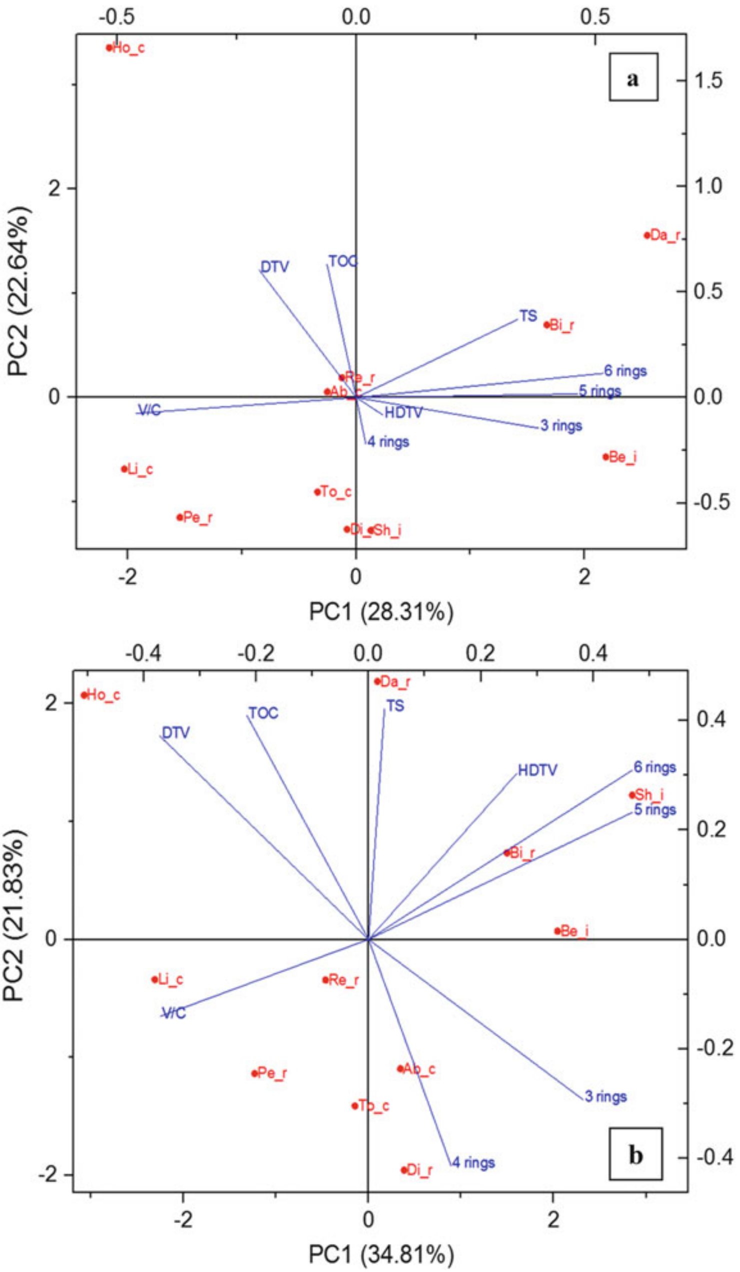

Fig. 3.14 PCA biplots for PAHs build-up on road surfaces (**a**: <1 μm; **b**: 1–75 μm; **c**: 75–150 μm; **d**: 150–300 μm; **e**: >300 μm; for data labels refer to Fig. 3.4)

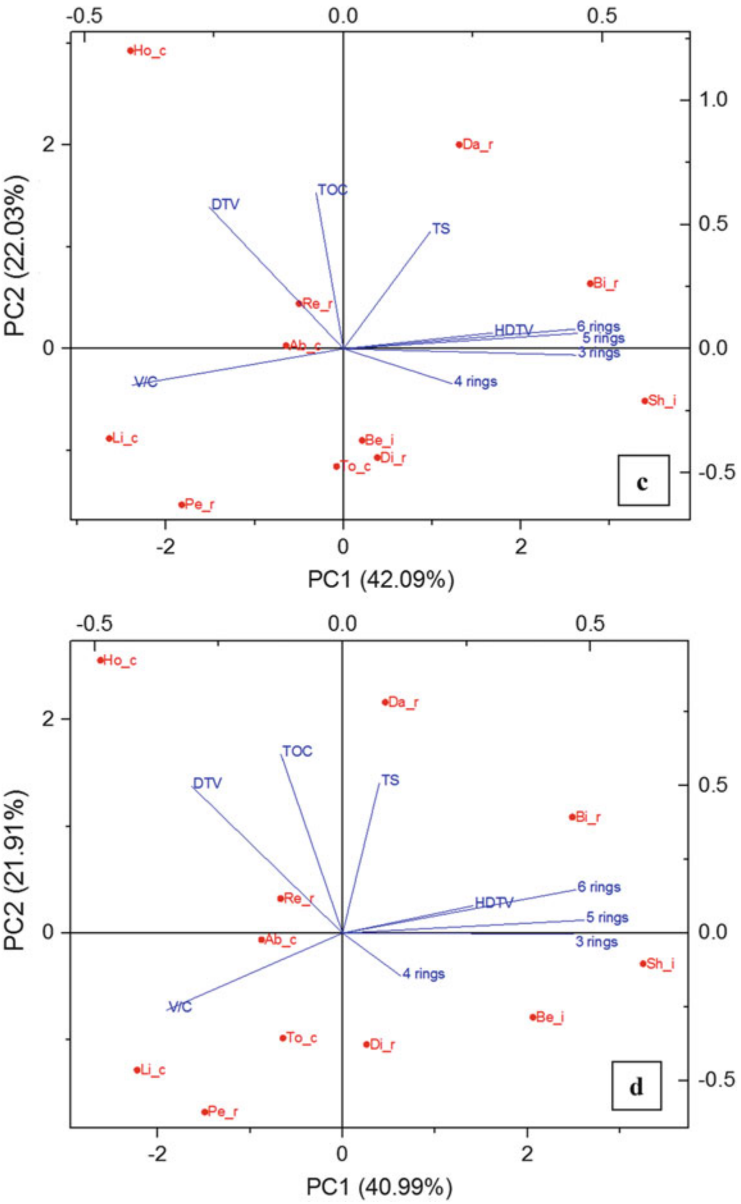

Fig. 3.14 (continued)

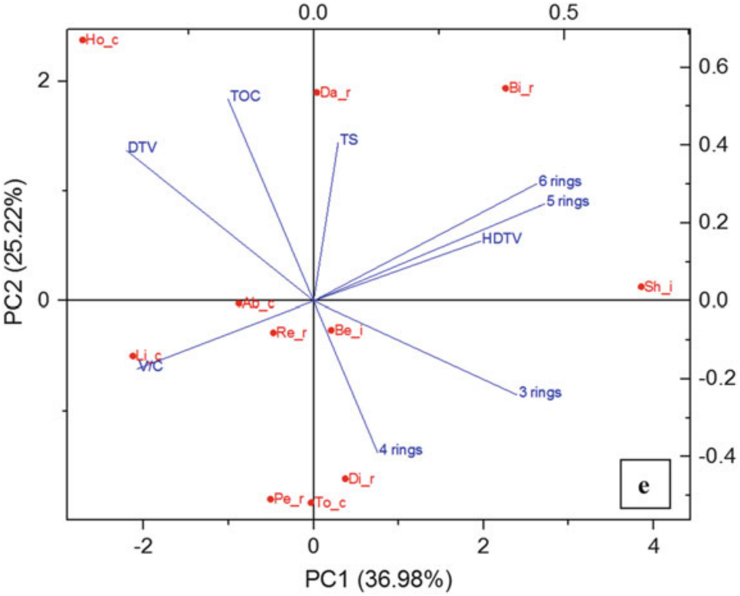

Fig. 3.14 (continued)

3.5 Linking Pollutant Transport Pathways

According to the analysis results discussed in the previous sections, atmospheric build-up, atmospheric deposition and build-up on road surfaces are interlinked. Therefore, the following analysis was undertaken by combining the data in relation to the three pollutant transport pathways.

In the case of heavy metals, data for all three pathways was submitted to PCA, the resulting matrix being 105 × 7. The 105 objects included 11 road build-up samples, 40 dry deposition samples, 24 bulk deposition samples and 30 atmospheric build-up samples while the seven variables were the seven heavy metals (Cr, Mn, Ni, Cu, Zn, Cd and Pb). Figure 3.15 shows the resulting PCA biplot.

It can be noted that there are three clusters representing atmospheric build-up, atmospheric deposition and build-up on road surfaces of heavy metals. However, most of the data points are grouped closely together. This implies that heavy metals in these three phases are interdependent. This confirms that atmospheric pollution can contribute to pollutant build-up on road surfaces through atmospheric deposition. This can also be supported by the outcomes of a number of previous research studies (Sabin et al. 2005; Gunawardena et al. 2013). These researchers have noted that atmospheric deposition makes an important contribution to urban stormwater pollution.

Furthermore, Fig. 3.15 also shows that heavy metals are more related to atmospheric deposition and build-up on road surfaces rather than atmospheric build-up. This implies that higher loads of heavy metals are transported through atmospheric deposition as well as are directly deposited on road surfaces. In addition, Zn and Cr

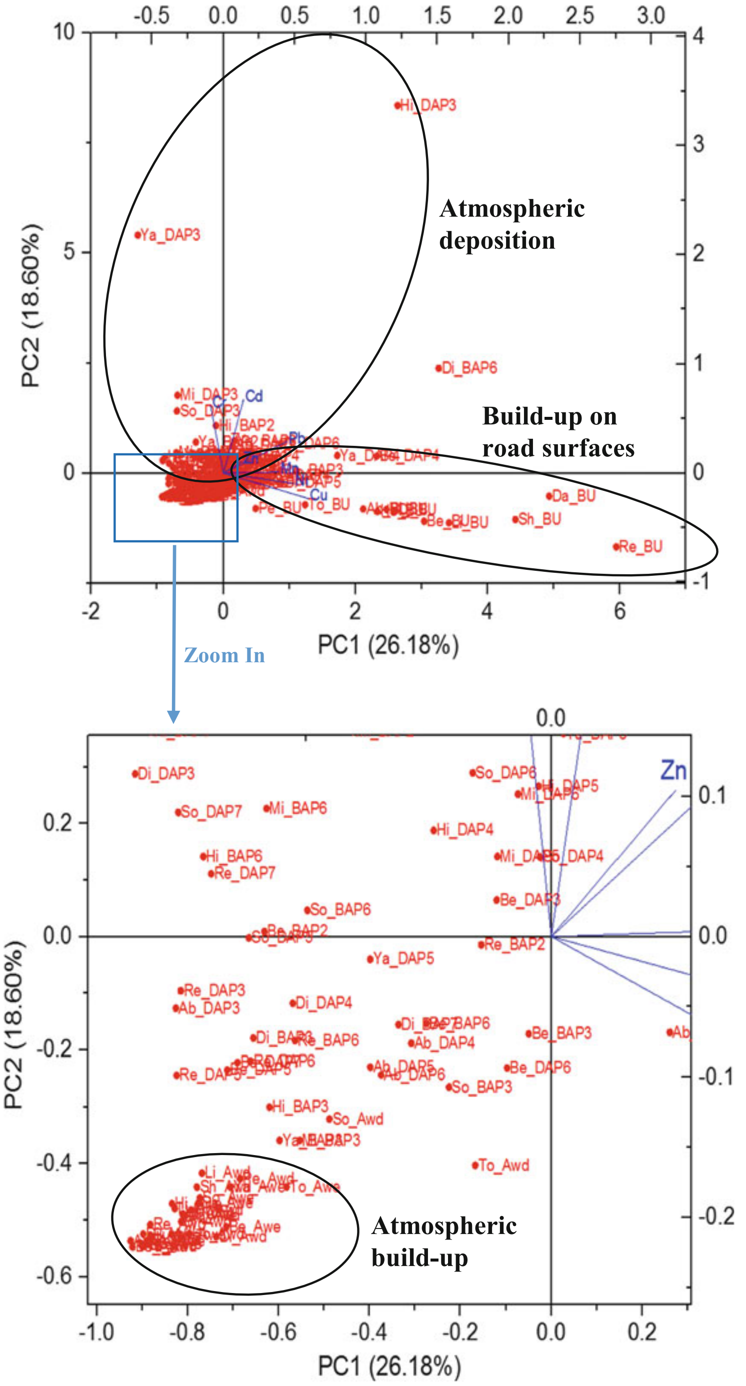

Fig. 3.15 Biplot from combining heavy metal data obtained for the different transport pathways (*BU* build-up on road surfaces, *BAP* bulk atmospheric deposition, *DAP* dry atmospheric deposition, *Awe* atmospheric build-up during weekends, *Awd* atmospheric build-up during weekdays)

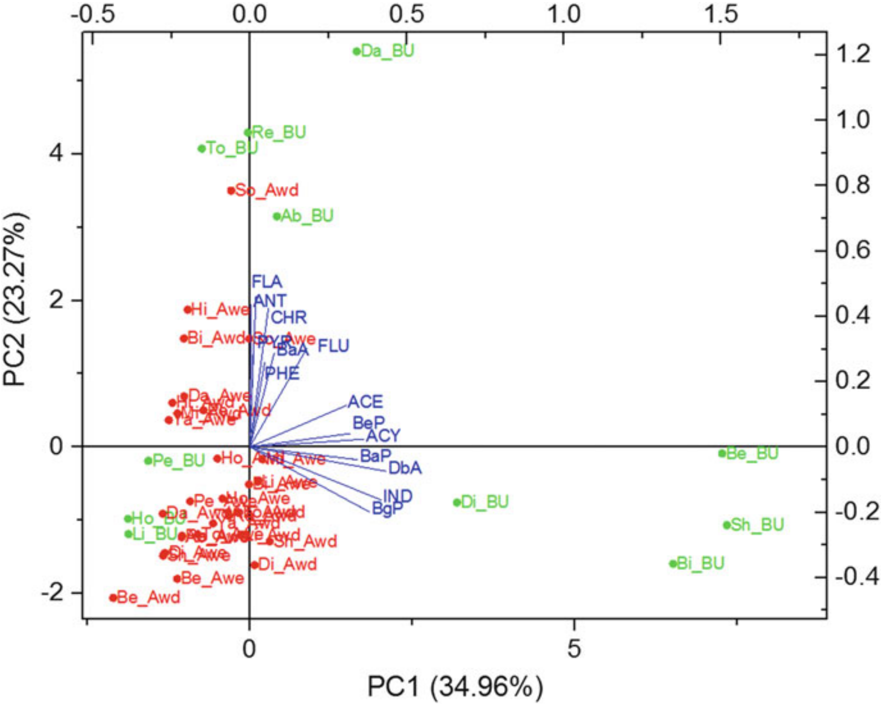

Fig. 3.16 PAHs biplot for linking their transport pathways (*BU* build-up on road surfaces, *Awe* atmospheric build-up during weekends, *Awd* atmospheric build-up during weekdays)

vectors have a similar direction as atmospheric deposition objects, while Cd, Mn, Cu, Ni and Pb vectors tend to point to objects related to build-up on road surfaces. This suggests that atmospheric deposition is the dominant source for Zn and Cr, while road build-up is the dominant source for Cd, Mn, Cu, Ni and Pb.

Figure 3.16 shows the PCA biplot obtained by combining the PAHs data obtained for atmospheric build-up and build-up on road surfaces. It is evident that all PAH vectors point to most of objects representing build-up on road surfaces and are opposite to most of the atmospheric build-up objects. This means that higher loads of PAHs that are directly deposited on road surfaces and PAHs in the atmosphere make only a small contribution to road build-up.

3.6 Conclusions

This chapter discussed three pollutants transport pathways, namely, atmospheric build-up, atmospheric deposition and build-up on road surfaces. In terms of atmospheric build-up, due to higher traffic volume, air pollution during weekdays is more significant than during weekends for particulate matter, heavy metals and

PAHs. This could lead to higher human health risk during weekdays compared to weekends through inhalation. In addition, Zn and Pb were detected as the highest and second highest concentrations in the atmosphere, independent of weekdays and weekends. Zn in the atmosphere is closely related to traffic while Pb is more associated with resuspended soil dust enriched with Pb from past usage of leaded fuel. Therefore, it can be concluded that atmospheric pollution could contribute a significant amount of Zn and Pb to road surface pollutant build-up through atmospheric deposition. Additionally, commercial and industrial land uses were found to contribute higher concentrations of heavy metals to the atmosphere compared to residential areas. This implies that particular attention should be given to commercial and industrial areas in terms of mitigating atmospheric heavy metal pollution. Furthermore, it was found that light molecular weight PAHs with 3–4 rings in the atmospheric phase have a relatively higher concentration and spatial variability than heavy molecular weight PAH species. This is due to the volatile nature of light molecular weight PAHs. Generally, the heavy molecular weight PAHs have a higher toxicity compared to lower molecular weight PAHs.

In the case of atmospheric deposition, it was found that pollutant dry deposition is positively related to antecedent dry days while wet (bulk) deposition is correlated to rainfall depth. Zn and Cr are the most dominant heavy metal species in both, dry and wet deposition. However, Zn was found to be present primarily in wet deposition, while Cr tends to be primarily present in dry deposition. Zn and Cr are more related to vehicle component wear, while Cd, Mn, Cu and Ni are primarily generated by exhaust emissions. Pb could be contributed by the re-suspension of already deposited Pb. These outcomes imply a diversity of contributory sources of heavy metals to atmospheric deposition. Moreover, scavenging by rainfall in the wet deposition process further confirms the importance of atmospheric deposition as a source in stormwater runoff pollution.

In the case of build-up on road surfaces, total solids build-up does not show a clear trend with traffic volume as well as land use. This underlines the complexity of road build-up processes. Other than traffic and land use, road build-up is also significantly influenced by other factors such as atmospheric deposition. Zn has the highest loads in road build-up, followed by Cu. This further confirms the appreciable contribution from atmospheric phase to heavy metals build-up on road surfaces through atmospheric deposition, particularly in the case of Zn, which is also the most common heavy metal species in the atmospheric phase. Heavy duty vehicle traffic is the primary source of heavy metals build-up on road surfaces, whilst land use has a lesser influence on heavy metals build-up. In PAHs build-up, light molecular weight PAH species have a higher load compared to heavy molecular weight species. Again, heavy duty vehicle traffic was found to be closely related to PAHs build-up on road surfaces and industrial land use tends to contribute higher loads of PAHs than commercial and residential areas.

The outcomes of the analysis undertaken by combining the data obtained for all three transport pathways found that higher loads of heavy metals are contributed through atmospheric deposition as well as being directly deposited on road surfaces.

However, it was found that PAHs in the atmosphere make only a limited contribution to road build-up.

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Chapter 4
Predicting Stormwater Quality Resulting from Traffic Generated Pollutants

Abstract Accurate stormwater quality prediction is essential for effective stormwater quality mitigation. The knowledge created in the previous chapters was applied for predicting stormwater quality using mathematical models. This chapter presents a detailed discussion of the outcomes of the modelling study including model selection, input parameter determination and model setup. The model setup procedure consisted of model schematisation, determination of boundary conditions and replication of pollutants build-up and wash-off processes. Eventually, the estimation results using the modelling approach developed are given and a series of predictive equations based on traffic and land use characteristics were developed. These outcomes are expected to contribute to the translation of research outcomes into practical recommendations for model developers, decision-makers and stormwater treatment system designers.

Keywords Mathematical modelling • Stormwater quality estimation • Pollutants build-up • Pollutants wash-off • Predictive equations • Stormwater quality • Stormwater pollutant processes

4.1 Background

Accurate stormwater quality prediction is essential for effective stormwater pollution mitigation. Accuracy strongly relies on the in-depth understanding of pollutant processes and transport pathways. Chap. 3 presents the in-depth knowledge created in relation to atmospheric pollutants build-up, atmospheric pollutant deposition and pollutants build-up on road surfaces. This formed the fundamental platform for developing modelling approaches to accurately estimate stormwater quality. This chapter presents the development of a modelling approach to predict stormwater quality for targeted pollutants (heavy metals and PAHs), incorporating knowledge presented in Chap. 3 into a commonly available modelling tool.

This chapter firstly discusses model selection and approach adopted to determine model input parameters, model setup including model schematisation, determination of boundary conditions and the numerical equations adopted to replicate pollutants build-up and wash-off processes. Outcomes of the modelling approach

J.M.A. Gunawardena et al., *Influence of Traffic and Land Use on Urban Stormwater Quality*, SpringerBriefs in Water Science and Technology,
DOI 10.1007/978-981-10-5302-3_4

are then presented with necessary justifications. Model outcomes and implications discussed are expected to provide practical suggestions and recommendations to model developers, decision-makers and stormwater treatment system designers.

4.2 Model Setup

4.2.1 Model Selection

As stormwater treatment design is commonly based on long-term pollutant characteristics, the modelling approach was formulated to estimate annual pollutant loads (Liu et al. 2016a). However, due to the need for accurate estimation of a range of pollutant types with varied process and pathway characteristics, a state-of-the-art modelling tool capable of simulating pollutant processes on an event-by-event basis was required.

Three stormwater quality models, EPA SWMM (Stormwater Water Management Model), MIKE URBAN and MUSIC (Model for Urban Stormwater Improvement Conceptualization), are commonly used in industry practice in Australia. EPA SWMM is a fully dynamic stormwater and wastewater modelling package developed by the United States Environmental Protection Agency and is a physically based discrete-time simulation model that employs the principles of conservation of mass, energy and momentum (Huber and Dichinson 1988). MIKE URBAN is a Geographic Information System (GIS)-based integrated urban modelling system developed by the Danish Hydraulic Institute (DHI). This model includes a collection system (CS) and water distribution (WD) system, data management, stormwater modelling, wastewater modelling and water distribution network modelling (MIKEURBAN 2008). MUSIC which was developed by the Cooperative Research Centre (CRC) for Catchment Hydrology in Australia, requires long-term continuous rainfall input rather than event-based rainfall data (Lloyd et al. 2002).

Both EPA SWMM and MIKE URBAN were considered suitable for the envisaged modelling as they are capable of simulating pollutants build-up and wash-off processes on an event-by-event basis. However, EPA SWMM has the ability to incorporate user defined pollutant process equations into the modelling structure. Therefore, EPA SWMM was selected as the most appropriate modelling tool for the study. This selection was also supported by the better performance of EPA SWMM in trial simulations, giving consistent output.

4.2.2 Determination of Input Parameters

In typical modelling studies, model calibration and validation play an important role in assessing the accuracy of model outcomes (Henriksen et al. 2003; White and

Chaubey 2005). This is the process of adjusting model input parameters to suit actual field conditions. However, this procedure was not undertaken in this study. Instead, model parameters to suit actual field conditions were determined from the outcomes of the detailed field investigation discussed in Chap. 3. This approach was recommended by Egodawatta (2007). He noted that small-plot pollutant processes can be extrapolated to catchment scale, and this procedure is particularly appropriate for the condition where stormwater quantity and quality data required for calibration and validation are not available for the study areas. In this context, fundamental knowledge generated in Chap. 3 regarding atmospheric build-up, atmospheric deposition and build-up on road surfaces as well as knowledge on pollutants wash-off obtained from previous research studies (Herngren 2005; Egodawatta et al. 2007; Mahbub et al. 2010) were employed to determine the model parameters.

4.2.3 Model Schematisation

Sites investigated in road surface pollutants build-up in Sect. 3.4 were considered as catchments for the modelling exercise. Existing maps and aerial photographs were used to calculate the baseline parameters related to road characteristics such as road width. However, Hope Island road site was removed from the modelling study due to the unavailability of baseline road characteristics. Accordingly, a total of 10 road sites were included in the modelling study.

A 100 m long road section with typical road geometry and drainage characteristics was selected as the schematised model catchment for each road site. The selected model catchment was further divided into two sub-catchments draining to either side of the road (see Fig. 4.1). Road kerb drains were modelled as a triangular open channel section with roughness equivalent to concrete. Relevant geometric data was obtained from maps and aerial photographs provided by the Gold Coast City Council (GCCC).

4.2.4 Boundary Conditions

Stormwater models commonly require two types of boundary conditions, namely, water quantity and water quality. The water quantity is primarily related to rainfall data used in the modelling exercise while rainwater quality was used as the water quality boundary condition, which is associated with wet deposition as discussed in Chap. 3.

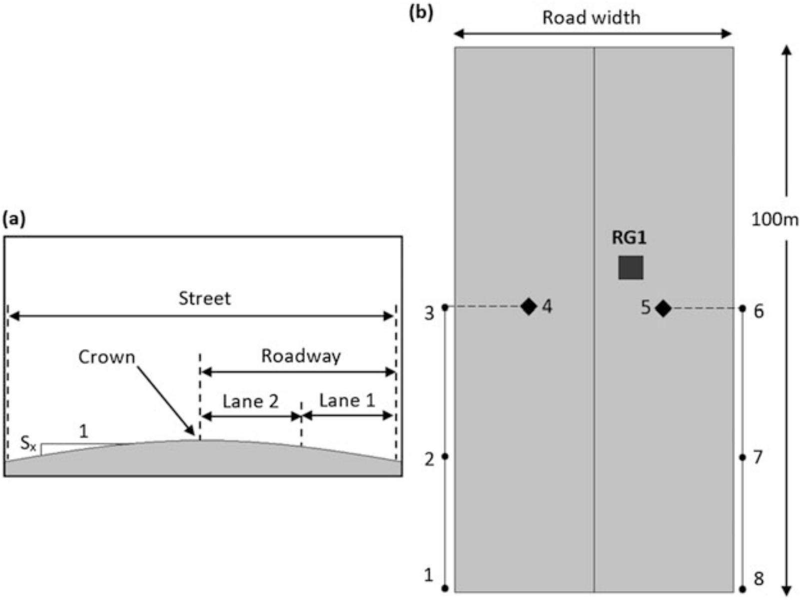

Fig. 4.1 Model schematisation (**a**): road cross section; (**b**): road in model (*RG* raingauge, S_x slope)

4.2.4.1 Rainfall Data

The appropriate selection of rainfall boundary conditions was critical for the accurate estimation of stormwater quality. The rainfall data recorded at the Gold Coast Seaway Station (Bureau of Meteorology station no: 040764) was used as the rainfall boundary condition due to its close proximity to the study sites and the availability of fine resolution rainfall data (6-min rainfall data).

As treatment design is commonly conducted based on an annual pollutant load, representative years should be selected for modelling. After investigating the rainfall data over the period of 2000–2010 (see Fig. 4.2), three representative years were selected. They were the year with minimum annual rainfall depth (2001), the year with average rainfall depth (2004) and the year with the maximum rainfall depth (2010). This was to account for the variability in annual pollutant load due to the variations in annual rainfall characteristics.

4.2.4.2 Wet Deposition

Atmospheric wet deposition was used as one of the water quality boundary conditions in the modelling study. As noted in Sect. 3.3.1, areas with intense anthropogenic activities have a high concentration of pollutants in the atmospheric deposition samples and wet deposition varies with rainfall depth. However, EPA SWMM model is not capable of incorporating variations in rainwater quality with

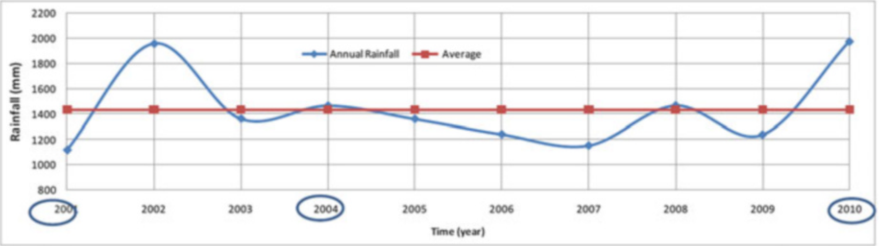

Fig. 4.2 Rainfall data over the period of 2000–2010 at study sites

time. Therefore, average concentrations of solids and heavy metals in wet depositions were used. As PAH concentrations in wet deposition were below the limit of detection, only solids and heavy metals were considered as the quality boundary conditions.

4.2.5 Replication of Pollutants Build-Up and Wash-Off

EPA SWMM model simulates water quantity and quality together by replicating pollutants build-up and wash-off processes on catchment surfaces. For this, appropriate replication equations are needed to be selected according to the pollutants build-up and wash-off characteristics of the given catchment. This section discusses the selection of build-up and wash-off equations as well as the determination of their coefficients.

4.2.5.1 Pollutants Build-Up

Pollutants build-up is a dynamic process and at any given time, the process may undergo change based on the state of deposition and removal characteristics (Liu et al. 2016a, b; Wijesiri et al. 2016). Egodawatta (2007) recommended a power function to replicate pollutants build-up on road surfaces, and his study was undertaken at the same study areas as this study. Consequently, the power equation was selected for the study (as shown in Eq. 4.1). In Eq. (4.1), C_1 is the upper limit of pollutants build-up on a catchment surface. According to the results obtained by Egodawatta (2007), pollutants build-up approaches its maximum possible value after 21 antecedent dry days. C_2 is the build-up rate and is dependent on site-specific parameters such as population density. It was determined based on actual measured build-up values for seven antecedent dry days. C_3 depends only on the road surface type. As all road surfaces are paved with asphalt, C_3 was set as 0.16 to represent a typical asphalt road surface (Egodawatta 2007). All of these coefficients were calculated based on total solids build-up loads since other pollutants such as heavy metals and PAHs can be obtained by determining pollutants–solids

Table 4.1 Coefficients for build-up replication equation

Coefficients	Shipper Drive	Towncenter Drive	Abraham Road	Linfield Road	Beattie Road	Billinghurst Crescent	Peanba Park	Dalley Park Drive	Discovery Drive	Reserve Road
C_1	2.21	0.78	2.52	0.60	0.74	5.60	0.68	13.09	0.80	7.68
C_2	1.36	0.48	1.55	0.37	0.46	3.44	0.42	8.04	1.81	0.49
C_3	0.16									

co-fraction coefficients (representing the percentage of pollutants attached to solids). Table 4.1 gives these coefficients for build-up on each road site.

$$L = \mathrm{Min}\left(C_1, C_2 d^{C_3}\right) \tag{4.1}$$

Where

L—Build-up load (kg/ha)
C_1—Maximum possible build-up load (kg/ha)
C_2—Build-up rate constant (kg/ha/day)
d—antecedent dry days
C_3—Time exponent

4.2.5.2 Pollutants Wash-Off

There are a number of replication methods available for wash-off process simulations including exponential equation, rating curve and event mean concentrations. In this study, wash-off data obtained from Mahbub (2011), which was undertaken at exactly same road sites, was plotted to assess the most suitable mathematical replication equation. The equation format with the least data scatter was selected. As such, it was found that an exponential form of mathematical replication is the most suitable to replicate solids wash-off. The equation format is shown in Eq. (4.2).

$$W = D_1 q^{D_2} L \tag{4.2}$$

Where

W—Wash-off load in units of mass per hour
D_1—Wash-off coefficient
D_2—Wash-off exponent
q—Runoff rate per unit area (mm/h)
L—Pollutants build-up in mass units given in Eq. (4.1)

Wash-off primarily depends on the build-up load (pollutant loads availability prior to rainfall) and rainfall characteristics rather than site-specific characteristics. Therefore, in order to determine the coefficients for the wash-off equation, Eq. (4.2) was expressed as wash-off per unit build-up (W/L), which can be referred to as the wash-off fraction (Egodawatta 2007). W and L are the actual wash-off (obtained from Mahbub 2011) and build-up mass (obtained from this study as discussed in Sect. 3.4) collected at seven antecedent dry days. The wash-off coefficient (D_1) and the wash-off exponent (D_2) were estimated by plotting the wash-off fraction against runoff rate as shown in Fig. 4.3. As shown in Fig. 4.3, the coefficients D_1 and D_2 were determined as 80.409 and -0.875, respectively.

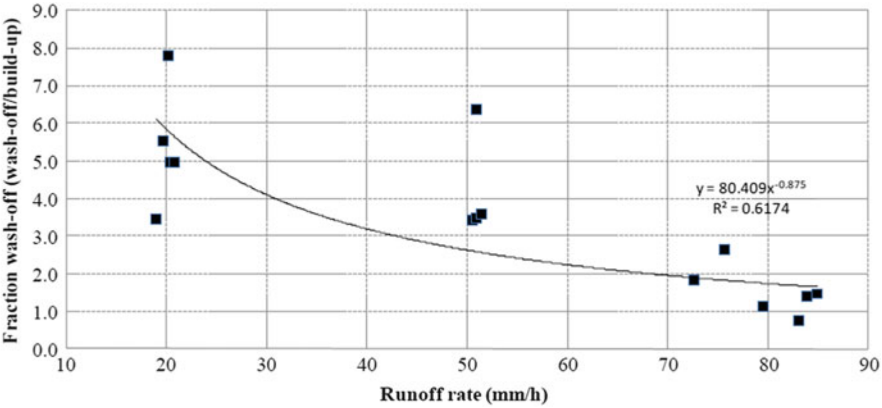

Fig. 4.3 Variation of wash-off fraction with runoff rate for total solids

4.2.5.3 Heavy Metals

As recommended by EPA SWMM, co-fraction wash-off approach was applied to investigate heavy metals co-fractions in the modelling study. In this approach, heavy metals are modelled as a co-fraction of total solids, which was calculated by dividing the heavy metal concentration by the corresponding total solids concentration. In order to determine the co-fraction coefficient for each heavy metal species, variation of co-fractions of heavy metals with rainfall duration was plotted as shown in Fig. 4.4. It can be noted that except for Zn, other heavy metals have consistent co-fractions. Although Zn co-fraction is highly variable, it has a reasonable consistency before 120 min rainfall duration. As rainfall events with duration longer than 120 min is relatively rare, use of co-fraction for Zn was considered appropriate. Accordingly, the resulting heavy metal co-fractions were 0.113, 0.010, 0.001, 0.002, 0.001, 0.008 and 0.004 for Zn, Cu, Mn, Ni, Cr, Cd and Pb, respectively.

4.2.5.4 PAHs

Same as for heavy metals, the co-fraction approach was used for simulating PAH loads. For this purpose, data from Herngren (2005) was used to generate co-fractions for each PAH species. Herngren (2005) undertook his research study in the Gold Coast region, which is the same study area as this study. Therefore, the use of data from Herngren (2005) was considered appropriate. However, only nine PAHs were investigated by Herngren (2005), and hence the modelling was performed for these nine PAHs only. The variation of co-fractions for the nine PAHs with rainfall duration is plotted in Fig. 4.5. It is evident that all PAHs investigated have appreciably consistent co-fractions. Accordingly, the resulting

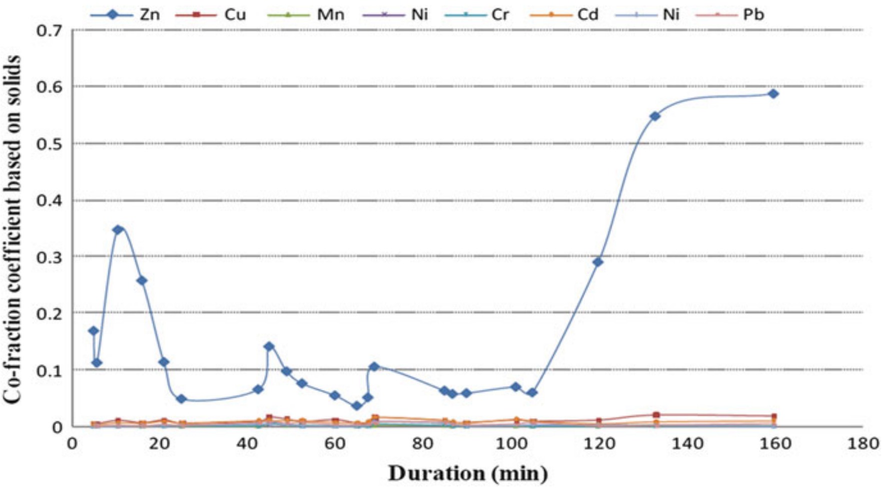

Fig. 4.4 Variation of heavy metal co-fractions with rainfall durations

co-fractions were 0.0018, 0.0012, 0.0019, 0.0009, 0.0027, 0.0027, 0.0024, 0.0014 and 0.0020 for ACE, FLU, PHE, ANT, FLA, PYR, BaA, CHR and BaP.

4.3 Model Results

The modelling was performed for 2001, 2004 and 2010 rainfall events, which are the 3 years with minimum, average and maximum annual rainfall depths. The simulation results were extracted for the ten road sites corresponding to the 3 years. Furthermore, in order to identify the most polluted sites in terms of heavy metal and PAH loads, the modelling results were further analysed using PROMETHEE ranking method. Detailed information on PROMETHEE ranking method can be found in Liu et al. (2015).

In addition, predictive equations were developed based on the modelling results in order to estimate the annual solids loads in stormwater runoff generated by a 100 m long road section. These predictive equations were developed based on traffic and land use characteristics. As heavy metals and PAHs were considered as co-fractions of solids, the predictive equations were developed for solids only.

4.3.1 Heavy Metal and PAH Loads

The simulated heavy metal and PAH annual loads were extracted from the model outputs, and summary of results for heavy metals and PAHs are given in Tables 4.2 and 4.3, respectively. These simulation data were used to undertake PROMETHEE

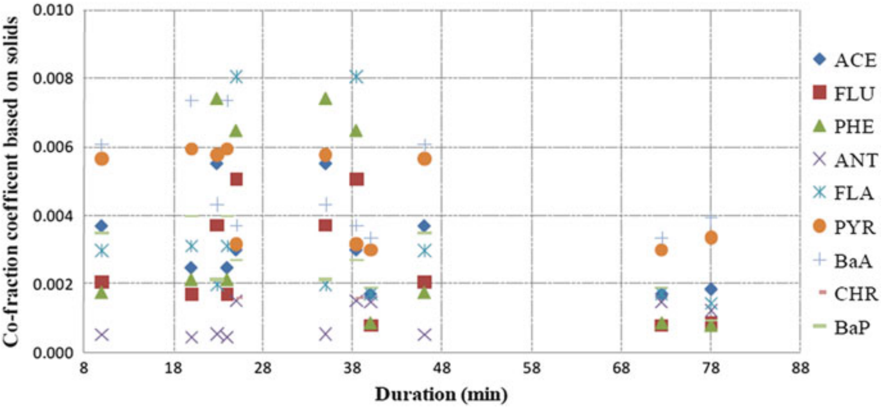

Fig. 4.5 Variation of PAH co-fractions with rainfall durations

analysis. Although the annual heavy metal and PAH loads were predicted for 2001, 2004 and 2010 rainfall events, the PROMETHEE rankings were carried out only for modelling results generated for 2004. This was because the annual rainfall depth in 2004 represents the average rainfall observed during the period of 2001–2010, while the outcomes obtained based on 2001 and 2010 were to understand the limits of variability. Therefore, using modelling results in 2004 gives the most accurate estimation of average annual pollutant loads.

Table 4.4 gives the PROMETHEE ranking results for heavy metals and PAHs, respectively. The five road sites, namely, Da_r, Sh_i, Bi_r, Li_C and Re_r are ranked as the most polluted roads in terms of both heavy metals and PAHs. Most of these roads are within commercial and residential land uses. The results obtained can be attributed to their relatively high traffic volumes. The ranking results can provide useful insights into identifying road areas where stormwater runoff is highly polluted with toxic pollutants such as heavy metals and PAHs and hence need to be provided with appropriate stormwater treatment measures.

4.3.2 Development of Predictive Equations

The purpose of developing predictive equations was to estimate the annual pollutant load generated from roads based on traffic and land use characteristics. This is essential for the implementation of appropriate stormwater treatment strategies.

Multiple liner regression analysis was undertaken to develop the predictive equations to estimate the annual total solids loads based on the model outcomes generated for 2001 (minimum), 2004 (average) and 2010 (maximum) rainfall events. It was assumed that the variability of total solids loads among different sites could be predicted as a linear combination of land use and traffic parameters. Selecting linear regression was because it is the simplest model to investigate the

Table 4.2 Annual total solid and heavy metal loads simulated

Road	Year	Total solids (mg)	Pb (mg)	Cr (mg)	Cd (mg)	Zn (mg)	Mn (mg)	Ni (mg)	Cu (mg)
Ab_c	2001	11,167	31	26	41	699	30	14	59
	2004	13,167	34	33	41	734	39	15	61
	2010	16,707	42	44	47	874	51	18	71
Be_i	2001	10,373	23	30	19	424	36	9	33
	2004	13,317	29	40	21	506	48	11	39
	2010	17,858	39	54	27	665	64	15	51
Bi_r	2001	14,781	47	28	74	1156	32	22	100
	2004	17,983	55	36	85	1346	42	26	115
	2010	19,688	57	44	79	1310	51	25	111
Da_r	2001	33,160	122	45	227	3295	49	59	289
	2004	47,713	176	65	328	4765	69	86	418
	2010	49,116	176	71	321	4713	78	85	412
Di_r	2001	16,404	45	39	60	1017	45	20	74
	2004	20,348	54	51	66	1172	59	23	82
	2010	26,977	71	68	85	1527	79	31	106
Li_c	2001	19,574	52	48	65	1139	56	70	95
	2004	24,794	64	63	75	1356	74	83	111
	2010	30,508	75	82	79	1522	95	93	123
Pe_r	2001	6774	35	19	14	298	23	6	24
	2004	8294	41	25	14	325	29	7	25
	2010	10,568	46	33	14	377	38	9	29
Re_r	2001	19,455	62	44	77	1275	51	25	108
	2004	23,282	77	57	80	1393	66	27	116
	2010	27,531	77	72	79	1466	84	30	120
Sh_i	2001	21,254	46	38	113	1737	44	32	150
	2004	28,252	60	52	149	2295	59	43	198
	2010	28,277	62	60	124	2002	69	38	170
To_c	2001	10,474	12	30	20	436	36	9	34
	2004	13,428	15	41	22	518	48	12	40
	2010	18,000	20	54	28	681	64	15	52

relationship between independent parameters and a dependent variable (Mahbub et al. 2011). In this context, it was assumed that the total solids loads generated by a 100 m road section can be expressed as a linear combination of independent variables as shown in Eq. (4.3).

$$\text{Solid loads} = f(C, I, R, \text{DTV}, V/C, \text{HDTV}) \tag{4.3}$$

Where

C, I, R—Percentages of commercial, industrial and residential areas within 1 km radius from each sampling site, obtained by initially demarcating the area in an

Table 4.3 Annual PAH loads simulated

Road	Year	ACE (mg)	FLU (mg)	PHE (mg)	ANT (mg)	FLA (mg)	PYR (mg)	BaA (mg)	CHR (mg)	BaP (mg)
Ab_c	2001	9.1	6.2	9.7	4.6	13.8	13.8	12.2	7.1	10.1
	2004	9.1	6.0	9.7	4.5	13.7	13.7	12.2	7.0	10.2
	2010	10.4	7.0	11.0	5.1	15.6	15.6	13.9	8.2	11.6
Be_i	2001	4.0	2.7	4.2	2.0	6.3	6.3	5.6	3.1	4.5
	2004	4.6	2.9	4.8	2.2	6.9	6.9	6.2	3.5	5.0
	2010	5.8	3.7	6.2	2.8	8.7	8.7	7.8	4.5	6.5
Bi_r	2001	16.7	11.0	17.6	8.2	24.9	24.9	22.2	12.9	18.5
	2004	19.0	12.7	20.0	9.6	28.6	28.6	25.4	14.9	21.1
	2010	17.6	11.7	18.6	8.9	26.6	26.6	23.6	13.8	19.6
Da_r	2001	50.9	34.0	53.7	25.5	76.4	76.4	67.9	39.5	56.6
	2004	73.7	49.1	77.8	36.9	110.6	110.6	98.2	57.3	81.8
	2010	72.2	48.1	76.1	36.1	108.2	108.2	96.2	56.2	80.1
Di_r	2001	13.4	8.6	14.2	6.5	19.9	19.9	17.8	10.3	14.9
	2004	14.7	9.8	15.6	7.4	22.1	22.1	19.7	11.3	16.5
	2010	19.0	12.6	20.0	9.4	28.6	28.6	25.3	14.7	21.1
Li_c	2001	14.2	9.5	15.0	7.1	21.6	21.6	19.1	11.1	15.8
	2004	16.4	10.9	17.4	8.3	24.9	24.9	22.1	12.8	18.4
	2010	17.5	11.5	18.5	8.7	26.4	26.4	23.5	13.4	19.4
Pe_r	2001	3.0	2.0	3.2	1.5	4.7	4.7	4.1	2.3	3.3
	2004	3.0	1.9	3.2	1.5	4.6	4.6	4.1	2.3	3.3
	2010	3.1	2.0	3.2	1.5	4.7	4.7	4.2	2.4	3.5
Re_r	2001	16.9	11.3	17.9	8.5	25.7	25.7	22.9	13.1	18.9
	2004	17.9	11.8	18.9	8.8	26.7	26.7	23.9	13.8	19.8
	2010	17.6	11.6	18.6	8.7	26.3	26.3	23.4	13.6	19.6
Sh_i	2001	12.5	8.3	13.2	6.3	18.8	18.8	16.7	9.8	13.9
	2004	16.2	10.8	17.1	8.1	24.4	24.4	21.7	12.6	18.1
	2010	17.8	11.8	18.7	8.7	26.5	26.5	23.7	13.8	19.8
To_c	2001	4.1	2.8	4.4	2.1	6.5	6.5	5.9	3.3	4.7
	2004	4.8	3.1	5.0	2.3	7.1	7.1	6.5	3.7	5.3
	2010	6.1	4.0	6.5	2.9	9.1	9.1	8.1	4.7	6.8

aerial photograph from Google Earth and then calculating each land use area fraction using ArcMap.
DTV—total average daily traffic volume used in Chap. 3
HDTV—total average daily heavy duty vehicle traffic volume, refer to data analysis in Chap. 3
V/*C*—traffic congestion parameter, refer to data analysis in Chap. 3

The predictive equations developed are given in Table 4.5. It is important to note that all the equations developed are based on a lower number of data points than what is optimally required to attain 95% confidence (Rubinfeld 1998). Furthermore, these equations are capable of predicting solids loads accurately only within the

Table 4.4 PROMETHEE ranking results

Ranking	Comments	Heavy metals		PAHs	
			Net ϕ		Net ϕ
1	The most polluted site	Da_r	0.7589	Da_r	0.840
2		Sh_i	0.0869	Bi_r	0.016
3		Bi_r	0.0111	Re_r	−0.002
4		Li_c	−0.0612	Li_c	−0.021
5		Re_r	−0.0764	Sh_i	−0.025
6		Di_r	−0.1073	Di_r	−0.047
7		Ab_c	−0.1130	Ab_c	−0.133
8		Pe_r	−0.1486	To_c	−0.199
9		Be_i	−0.1719	Be_i	−0.203
10	The least polluted site	To_c	−0.1786	Pe_r	−0.226

Table 4.5 Stormwater quality estimation equations developed for total solids

Equations	*R*	POT
$\text{Solids(minimum)} = 11{,}204.147 - (0.0700 \times \text{DTV}) + (74.079 \times \text{HDTV}) + (136.582 \times V/C) - (52{,}959.185 \times C) - (7524.183 \times I)$	0.978	0.994
$\text{Solids(average)} = 14{,}540.746 - (0.285 \times \text{DTV}) + (111.716 \times \text{HDTV}) + (745.376 \times V/C) - (83{,}870.577 \times C) - (10{,}027.701 \times I)$	0.986	0.999
$\text{Solids(maximum)} = 16{,}200.682 + (0.137 \times \text{DTV}) + (108.813 \times \text{HDTV}) + (2138.812 \times V/C) - (86{,}809.775 \times C) - (8180.689 \times I)$	0.979	0.995

R regression coefficient, *POT* power of the test

limits of the data set. These limits are DTV, from 29 to 10,639, HDTV from 4 to 1139, *V*/*C* from 0.14 to 1.21, *C* from 0.01 to 0.44 and *I* from 0 to 0.82. Outside these limits, predictions may result in greater variations. However, the prediction accuracy and reliability can be improved by undertaking further investigations and following the same modelling and regression approach for further refinement of the equations. Nevertheless, the outcomes from these equations would be satisfactory for preliminary or feasibility studies.

4.4 Conclusions

This chapter presents a modelling approach by incorporating a series of replication equations into a commonly available model tool, EPA SWMM. The input parameters of the model were determined by the knowledge created in Chap. 3 on atmospheric pollutants build-up, atmospheric pollutant deposition and pollutants build-up on road surfaces, as well as wash-off by referring to past studies.

The modelling results estimated the annual loads of traffic generated pollutants including heavy metals and PAHs in stormwater runoff for each road study site. In addition, these road sites were ranked in terms of annual heavy metal and PAH loads. The ranking can contribute to effective stormwater treatment design based on the identification of the more polluted sites which need to be provided with stormwater treatment systems.

A set of predictive equations for estimating annual total solids loads were developed using traffic and land use related parameters. The equations developed can be used as an urban planning tool not only to estimate solids generation from road sites, but also to identify the required enhancements (such as changes to traffic and land use planning) to improve the resulting stormwater quality. Even though these predictive equations are only applicable within their specified limits, they provide a robust approach to stormwater management. Additionally, it is recommended that the accuracy of the predictive equations can be further improved by including additional sampling sites as part of the further development process.

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Chapter 5
Implications for Engineered Applications and Recommendations for Future Research Directions

Abstract This chapter provides a consolidated summary of the outcomes from the research study undertaken to investigate the influence of traffic and land use on pollutant processes as well as the practical application of the study findings. The chapter also discusses key areas where currently, there are significant knowledge gaps and further investigations are warranted. These include, the assessment of ecological and human health risks posed by stormwater pollutants, the investigation of other traffic related pollutants and the understanding of the adsorption mechanisms of pollutants—solids inherent in the different transport pathways.

Keywords Stormwater pollutant processes • Stormwater quality • Stormwater treatment design • Urban traffic • Land use • Pollutant transport pathways

5.1 Background

This book primarily developed an in-depth understanding of transport pathways for traffic related pollutants, defining linkages between pollutants in the atmospheric and ground phases. The linkages identified can be applied in urban and transport planning in order to ensure that traffic characteristics are managed to achieve environmental sustainability. Heavy metals and PAHs were the targeted pollutants in this study since they are closely linked to vehicular traffic. Additionally, most of these compounds are toxic, which can contribute to adverse human and ecosystem health impacts (Liu et al. 2015; Ma et al. 2016, 2017).

The study confirmed that Zn is the most dominant heavy metal species in both atmospheric and ground phases, while light molecular weight PAHs have higher concentrations and spatial variability. The outcomes also indicate that heavy duty vehicle traffic plays an important role in influencing pollutant generation and accumulation in both, atmospheric and ground phases. These analysis results formed the basis for developing models to predict stormwater quality in an urban environment. The models developed can also be used as a traffic and land use planning tool for safeguarding the urban water environment.

This chapter summarises the key research outcomes obtained from previous chapters and provides practical suggestions for stormwater treatment design. In

J.M.A. Gunawardena et al., *Influence of Traffic and Land Use on Urban Stormwater Quality*, SpringerBriefs in Water Science and Technology,
DOI 10.1007/978-981-10-5302-3_5

addition, knowledge gaps remaining after completion of this study are identified, and recommendations for future research directions are provided.

5.2 Implications for Engineered Applications

5.2.1 Implications Related to Pollutant Transport Pathways

Major analytical outcomes and their potential practical implications related to pollutant transport pathways are outlined below:

- The study found high concentrations of heavy metals and PAHs in the atmospheric phase. Such high concentrations can lead to human health risks. This highlights the requirement for a human health risk assessment framework in relation to road-side atmospheric pollutants.
- Atmospheric pollutant concentrations were high during weekdays compared to weekends. This can be directly attributed to higher traffic volume during weekdays compared to weekends. However, atmospheric pollutants could also be originating from long distance sources with no relationship to traffic and traffic induced re-suspension.
- Compared to other heavy metals, Zn is the most abundant heavy metal species in the atmosphere, atmospheric (dry and wet) deposition and road build-up. Tyre wear, brake pad wear and exhaust emissions are considered as the primary sources of Zn in the urban environment.
- It is noted that the bulk (wet) deposition rate of Zn is two times higher than its dry deposition rate. This means that scavenging from the atmosphere by rainfall can contribute high loads of heavy metals to road stormwater runoff. Hence, wet deposition can be considered as an important source of stormwater pollution. These outcomes also suggest that Zn merits particular attention when treating stormwater runoff from roads.
- Light molecular weight PAHs (3–4 rings) had higher concentrations and spatial variability than heavy molecular weight PAH species (5–6 rings) in both, atmospheric and ground phases. This is due to the volatile nature of light molecular weight PAHs. This underlines the difficulty in treating light molecular weight PAHs in stormwater runoff, compared to heavy molecular weight PAH species.
- Heavy duty vehicle traffic was found to be the primary source of PAHs build-up on road surfaces. In this regard, industrial land use tends to produce higher loads of PAHs compared to commercial and residential areas. This highlights the fact that industrial areas could be critical areas for implementing treatment strategies, particularly for the removal of PAHs from stormwater runoff.
- The analysis of the combined data set collected from the three transport pathways shows that heavy metals in atmospheric phase can contribute to pollutants build-up on road surfaces through deposition. In addition, higher loads of heavy metals are contributed through atmospheric deposition as well as being directly

deposited on road surfaces compared to their atmospheric build-up. However, it was found that higher loads of PAHs are directly deposited on road surfaces, and PAHs in the atmosphere make only a small contribution to road build-up.

5.2.2 Implications Related to Modelling Approach Developed

Major analytical outcomes and their potential practical implications in relation to the development of the modelling approach are outlined below:

- A robust modelling approach was developed by incorporating a series of replication equations into a commonly available modelling tool, EPA SWMM. The approach is capable of estimating the annual loads of traffic related pollutants in stormwater runoff from a given road site.
- Mathematical equations were developed to predict stormwater quality based on traffic and land use characteristics using multiple linear regression. The equations developed can be used not only to estimate solids generation from road sites, but also as an urban planning tool to identify appropriate strategies to improve urban stormwater quality. For example, the equations can be used to identify highly polluted areas as pollutants loads can be predicted based on traffic and land use characteristics.
- The predictive equations developed can also be employed to generate maps using geographical information systems (GIS) to visualise the spatial distribution of stormwater pollution in a given catchment and thereby contribute to the effective implementation of stormwater management strategies.
- It is noteworthy that even though these predictive equations can only be applicable within their specified boundary conditions, they provide a robust approach to stormwater management strategies and would be appropriate for preliminary or feasibility studies. Additionally, it is recommended that the accuracy of the predictive equations should be further improved by including additional data during their development process for other engineered practices.

5.3 Recommendations for Future Research Directions

This research study has contributed new knowledge by establishing the linkages between pollutants in the atmospheric phase and ground surfaces. Additionally, the influence of traffic and land use characteristics on atmospheric build-up, atmospheric deposition and road build-up has been investigated in detail. The application of the fundamental knowledge created was demonstrated through mathematical modelling. However, a number of significant research gaps as discussed below still remain and need to be further investigated.

5.3.1 Assessing Ecological and Human Health Risks Posed by Stormwater Pollutants

This research study investigated heavy metals and PAHs in both, atmospheric and ground phases. The models developed are able to predict annual pollutant loads transported by stormwater runoff, and a set of empirical equations which link stormwater quality and traffic and land use characteristics have been provided. Since a significant number of traffic generated pollutant species are toxic to human and ecosystem health, it is essential to develop approaches to quantitatively assess their ecological and human health risks. As identified in this study, stormwater quality is strongly related to traffic and land use. This highlights the need to establish the linkage between human and ecosystem health risks posed by stormwater pollutants and their influential factors such as traffic and land use. This will provide a clear understanding of the human and ecosystem health risks posed by stormwater pollutants generated by traffic and land use and thereby to improve the effectiveness of urban planning processes to mitigate these risks.

5.3.2 Investigating Other Traffic Related Pollutants

Heavy metals and PAHs are two primary pollutants generated by urban traffic activities. However, traffic can also produce a number of other pollutant species. These pollutants can accumulate on road surfaces either through atmospheric deposition or directly deposit on road surfaces. These pollutants could also have high toxicity and hence can pose ecological and human health risks. Therefore, the transport pathways of these pollutants and their influential factors should be investigated as well. This will provide a comprehensive understanding of traffic related pollutants and their processes and thereby contribute to improved stormwater management.

5.3.3 Understanding Adsorption Mechanisms of Pollutants–Solids Along Different Transport Pathways

Current study results show that traffic related pollutants have a close relationship with solids. For example, Zn was found to be strongly associated with larger particles in dry deposition (see Sect. 3.3.2). Furthermore, solids are seen as an important carrier of other pollutants in stormwater runoff since these pollutants are adsorbed to solids. This was the basis for the modelling approach developed in Chap. 4 using a co-fraction coefficient to simulate heavy metals and PAHs loads in stormwater runoff (see Sect. 4.2.5). However, it has been found that the adsorption mechanisms of pollutants-solids are not necessarily consistent. For instance, Gunawardana et al. (2012) and Gunawardana et al. (2013) investigated solids adsorbing heavy metals in build-up on road surfaces. They found that Cr tends to be attached to solids through cation exchange (Gunawardana et al. 2013), while Zn-solids adsorption is primarily by binding with the oxides of Fe, Al and Mn already present on solids surfaces (Gunawardana et al. 2012). These outcomes highlight the complexity of the relationship between pollutants and solids and thereby underline the need to have an in-depth understanding of adsorption mechanisms of pollutants such as PAHs. The adsorption mechanisms involved in PAHs–solids bonding have not been investigated to the same depth as for heavy metals. Additionally, for different transport pathways, the adsorption mechanisms and their influential factors could be different.

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Appendix: Laboratory Testing Methods

A.1 Heavy Metals Testing

Based on Method 200.8 (USEPA 1994), nitric and hydrochloric acid digestion was carried out to extract total recoverable heavy metals from the collected build-up, atmospheric deposition and air samples. Hot Block digester was used for the digestion. Hot Block digester provides an efficient method for digesting water, wastewater, soil and sludge samples for metals analysis (Environmental Express 2005). This digestion system allows samples to be digested in a small area with minimum heat loss. Samples were digested at 95 °C for 2.5 h without boiling inside a fume cupboard. After allowing samples to reach room temperature, the samples were made up to the original volume. Subsequently, samples were filtered using 0.45-micron syringe filters followed by adding internal standards, including the blanks and certified reference material (CRM).

Detection and determination of heavy metals were carried out by Inductively Coupled Plasma Mass Spectrometer (ICP-MS). ICP-MS was selected after considering its ability to detect heavy metals even at low concentrations (ranging from 0.001 to 0.005 mg/L). Firstly, the instrument was tuned by testing a specially made solution prepared by mixing beryllium, magnesium, cobalt, indium and lead stock solutions in 1% nitric acid to produce a concentration of 100 µg/L of each element. This solution is referred to as a tuning solution. Tuning solution was used to determine acceptable instrument performance prior to calibration and sample analysis. After satisfactory tuning, sample sequence including calibration standards were prepared. Consequently, samples in the liquid matrix were introduced into the machine by pneumatic nebulisation into radio frequency plasma where energy transfer processes cause atomisation and ionisation. The ions were extracted from the plasma through a differentially pumped vacuum interface and separated based on their mass-to-charge ratio by a quadrupole mass spectrometer. The ions transmitted through the quadrupole were detected by an electron multiplier.

J.M.A. Gunawardena et al., *Influence of Traffic and Land Use on Urban Stormwater Quality*, SpringerBriefs in Water Science and Technology,
DOI 10.1007/978-981-10-5302-3

After the sample sequence was tested along with calibration standards, calibration curves were set up ensuring that the residual mean square (R^2) was greater than or equal to 0.98. The concentration of the targeted heavy metals in actual samples were calculated using already established calibration curves. Subsequently, CRM recovery for heavy metals was compared against values given in the standard certificate and was found to be within 85–115%, which was considered acceptable. This was one of the most important quality assurance checks.

A.2 PAHs Testing

PAHs were tested for samples in the atmosphere and build-up on road surfaces. Analysis was carried out as per Method TO-13A and Method 610 (USEPA 1999).

(a) Air sample testing While particulate-bound PAHs were collected using a filter paper, gas phase PAHs were collected using polyurethane foam (PUF) sorbents. PUF sorbents and quartz filter papers were tested separately to determine the gas and particulate phase PAHs in the atmosphere as per TO-13A (USEPA 1999). The initial step was to extract half of the filter paper and PUF sorbent by Soxhlet extraction using 10% diethyl ether in hexane solvent. Before extraction, surrogate standards were added. The extract was concentrated by Kuderna-Danish (K-D) evaporator, followed by sodium sulphate cleanup using column chromatography to remove potential interferences prior to analysis by GC-MS. The sample was further concentrated by N_2 blow-down and then analysed by GC-MS. Prior to testing, internal standards were added to the samples, blanks and CRM.

Method development was to detect all target PAHs with a uniquely identifiable peak in the chromatogram. It was found that temperature programming was one of the most important methods to achieve good separation of PAHs. Additionally, injection volume, flow rate of carrier gas, detection mode and its resolution were changed until optimum separation was achieved. The separation of 16 PAHs was a difficult exercise, as some PAHs have the same molecular weight, but different configurations and almost the same boiling points. However, after a number of trial runs, the test method was developed to the required level of accuracy so that all the target PAH compounds could be separated.

Calibration was carried out with five concentration levels by diluting external standards. As recommended by the GC-MS user manual, standards were tested initially. Then samples were tested using already developed and calibrated test method. Subsequently, sample concentrations were calculated using data analysis software available with the GC-MS. As a part of the quality assurance procedure, CRM recovery for PAHs was compared against values given in the standard certificate and found to be within 85–115% as specified.

(b) Road surface build-up sample testing Road surface build-up samples were tested to determine the PAHs present in the ground phase. Method 610 (USEPA 1999) was adopted to test build-up samples for PAHs. This is the method recommended for the analysis of organic compounds in municipal and industrial wastewaters. The testing procedure was similar to that for air sample testing. However, instead of Soxhlet extraction, liquid–liquid extraction technique was used to extract build-up samples as specified in Method 610 (USEPA 1999). Herngren (2005) found that this is an efficient technique to extract PAHs in the liquid matrix. All the other steps were the same as that employed for the testing of PAHs in air samples.

The extraction of PAHs was done using a 500 mL separatory funnel. As specified, a 100 mL aliquot from each sample was extracted with a 60 mL of extraction solvent. The sample aliquot was mixed with solvent in the separatory funnel for 2 min with periodic venting to release excess pressure. The separatory funnel was then kept for 10 min without disturbing so that the organic layer was separated. Subsequently, the organic layer was separated into a beaker by carefully regulating the bottom valve. The same sample was extracted three times with 60 mL of extraction solvent as described above.

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J.M.A. Gunawardena et al., *Influence of Traffic and Land Use on Urban Stormwater Quality*, SpringerBriefs in Water Science and Technology,
DOI 10.1007/978-981-10-5302-3

Index

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