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Environmental Security

Advanced Water Supply and Wastewater Treatment: A Road to Safer Society and Environment

Edited by
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Advanced Water Supply and Wastewater Treatment: A Road to Safer Society and Environment

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Series C: Environmental Security

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CONTENTS

PREFACE

Growing population and rising standards of living exert stress on water supply and the quality of drinking water. Some of these pressures can be reduced by demand management and water and wastewater reuse. Stable, safe, secure and readily available water supply is one of the key factors, which ensure a good level of the public health, safe and stable society, and improvement of the living standards. Scientific assessments show that about 80% of diseases and one third of the total death toll in the developing countries are caused by the low quality of the drinking water. Other countries are also suffering because of water shortages and insufficient quality of the drinking water. Many rivers in Europe and in other parts of the world are significantly polluted by insufficiently treated or untreated wastewater discharge. This causes low quality of the drinking water in the downstream regions, increased cost of its treatment and production and, also serious impacts on aquatic organisms, including fish populations. Therefore, rational treatment of the wastewater is a very topical issue because this point source of pollution is gaining more and more on importance especially in highly urbanized areas. Reclamation and reuse of various industrial wastewaters and greywater is a promising way for diminishing consequences of the wastewater discharges into the environment.

Water-transmitted diseases can seriously undermine regional security and economic development and even provoke social conflicts. On other hand, many of the water supply problems can be solved, or at least partly mitigated, through relatively inexpensive but still quite technologically effective solutions related to water management/distribution and wastewater treatment (especially in the regions where local population uses mostly septic tanks or cesspools).

Urban water management issues are particularly important in the countries in transition in Central and Eastern Europe. During the last 15 years, political, economical and social changes in the transition countries have influenced almost every element of the public sector, including water services. In the water sector, there has been a continuing expansion of the role of private companies in the management and operation of water and wastewater utilities, but river basin authorities generally remain under the state control. The process of privatization is accelerated by the lack of capital investments in the public sector and issues of economic efficiency. There is an urgent need for exchange of information among various countries on this issue and for identification of best approaches to managing this transition. Thus, this NATO workshop with its focus on both the countries in transition and the traditional NATO countries should facilitate effective exchange of information and strengthening of co-operation among the experts from NATO, Partner and Mediterranean Dialog countries.

NATO Advanced Research Workshops (ARW) are advanced-level meetings, focusing on special subjects of current interest. This ARW on Advanced water supply and wastewater treatment: a road to safer society and environment was held in Lviv under the auspices of the NATO Science for Peace and Security Programme and addressed urban water management problems.

The main purpose of the workshop was to critically assess the existing knowledge on advances in urban water resources management, with respect to diverse conditions in participating countries, and promote close co-operation among scientists with different professional experience from different countries.

The ARW technical program comprised 34 papers on 3 topics, Advanced Water Supply, Advanced Wastewater Treatment, and Case Studies of Water Resource Management. Papers addressed a broad variety of issues corresponding to the ARW topics and ranging from reviews and case studies to scientific papers. The organizers hope that the workshop will contribute to improved water management in the regions addressed and thereby to a better security and quality of life.

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ADVANCED WATER SUPPLY

STRATEGIES FOR ENHANCING SUSTAINABILITY OF URBAN WATER SYSTEMS

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Abstract. Operation of existing urban water systems can be enhanced by implementing sustainability strategies. Two types of such strategies were examined: rainwater harvesting and use, and sustainable wastewater management. The first strategy contributes to reduced imports of source water into urban areas and reduced runoff from urban areas, the second one promotes pollution prevention and recovery of resources, including reclaimed water, energy, and nutrients. Overall, both groups contribute to more sustainable urban water systems requiring fewer resources to provide the water services required and ensuring a better protection of the environment.

Keywords: rainwater harvesting, pollution prevention, recovery of energy and nutrients from wastewater, sustainable urban water systems

1. Introduction

Sustainable development was described by the Brundtland Commission as "development that meets the needs of the present without compromising the ability of future generations to meet their own needs" (Brundtland 1987), and this definition led to the development of other related concepts, such as environmental sustainability, which has become a general goal of current urban water management (Marsalek et al. 2008). When applying the sustainability concept to urban areas, it is helpful to address this issue in the context of the urban water cycle (UWC), which is derived by transposing the hydrological cycle into the urban environment and, in this process, accounting for many

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anthropogenic influences, including those imposed by anthropogenic activities and the water infrastructure. Thus UWC is a conceptual model describing the storage and circulation of water and the associated chemicals and materials in urban areas, where the circulation is facilitated by both natural processes (e.g., evapotranspiration, condensations, precipitation, infiltration, percolation, snowmelt and runoff) and human activities including water import and export, water use, treatment and reuse, with concomitant changes in water quality and transport processes. From a physical point of view, the most sustainable urban water systems are self-reliant systems (Tjallingii 1988), which require the least resources and energy to operate, including the energy expended on resource use, and transport and treatment of urban water. Such systems are expected to create favourable conditions for urban aquatic habitats and their ecosystems, and contribute to preservation of biodiversity (Wagner et al. 2008). Sustainability of the existing urban water systems can be improved by managing the UWC through implementation of sustainability strategies.

Extensive changes in the water cycle of urban areas have been traditionally managed by building urban water infrastructure, which supports water supply, stormwater management and flood protection, wastewater management, and in the case of green infrastructure, also the integrity of urban aquatic habitats (Wagner et al. 2008). Thus, when addressing sustainability strategies, it is insightful to follow the infrastructure system and seek the sustainable approaches supporting specific components of the UWC (Marsalek et al. 2008). This approach has been adopted here, and recognizing the breadth of the issue addressed, the detailed discussion focuses just on two selected strategies concerning: (i) rainwater harvesting and use and (ii) sustainable wastewater management, with implications for advanced water treatment and wastewater management.

2. Rainwater Harvesting and Use (RHU)

Import of water for urban water supply is one of the major water related operations in urban areas, with concomitant impacts on the environment and aquatic habitats. Furthermore, the imported water is largely converted into wastewater and returned back into the environment after some level of treatment, and other impacts are caused by water withdrawal and distribution systems (Marsalek et al. 2008). Thus, all changes of the UWC limiting water import to urban areas contribute to environmental sustainability. One of such measures receiving high attention in recent years is rainwater harvesting and use (RHU).

RHU represented an early form of decentralized water supply and is currently undergoing a great revival as an essential measure of sustainable water management in both rural and urban areas. Among the reasons for this revival, one could name: (a) Growing demands on water supplies while the available sources are generally declining in quantity and quality, (b) recognition of the water-energy nexus, in which transport of water from distant sources requires energy and contributes to increased costs and greenhouse gas releases (further exacerbated by water losses), (c) promotion of sustainability in stormwater management and non-structural flood management which includes runoff (and flood) control and water balance maintenance by rainwater storage and use, (d) needs for good quality water for enhancement of local water resources and support of ecological functions, and (e) needs to cope with water shortages predicted by climate change scenarios for some regions of the world.

The highest level of rainwater use is for potable water supply, after some treatment, with emphasis on disinfection. The next lower level of use is unrestricted urban and recreational uses and agricultural irrigation of food crops. Due to the direct contact with people, this use requires high water quality and includes such applications as landscape irrigation in urban parks and playgrounds; fire protection; toilet flushing; air conditioning; cooling of urban areas by water spraying; unrestricted recreational use – e.g., feed water for lakes and ponds used for swimming and snowmaking; feed water for aquatic habitats; groundwater recharge; agricultural irrigation of food crops grown for human consumption; and, environmental enhancement and groundwater recharge (sometimes practiced as stormwater infiltration in urban areas).

The next lower level is for restricted-access urban use (landscape irrigation – golf courses, highway medians, residential property), restricted recreational use (non-contact – fishing boating), and agricultural irrigation of non-food crops, or food-crops processed before consumption (fodder, seed crops, sod farms, commercial aquaculture). These uses also apply to reuse of “clean” stormwater. Finally, the lowest use is for industrial water supply; requirements on such waters are specific to various industries.

Considering the possible risks involved in rainwater or stormwater reuse for various purposes, there are regulations governing such uses. These regulations specify the reused water quality in term of specific constituents, including microbiological constituents (bacteria, viruses) and chemicals (biodegradable organics, nutrients, heavy metals, residual chlorine, suspended and dissolved solids, emerging contaminants (endocrine disruptors, pharmaceuticals), and sometimes additional parameters serving to assess potential impacts on soils exposed to irrigation by reused water (Asano 1998).

Water reuse regulations and the occurrence of contaminants of concern govern the choices of water to be reused, with preference given to waters that meet the required quality, or can be inexpensively treated to meet it.

Where the reuse water quality does not meet the regulations, it has to be treated by a variety of processes, with emphasis on low-cost passive treatments, including those used in stormwater management (SWM): Bypassing the polluted first flush (this is often sufficient when dealing with rainwater, with suitable roofing materials), settling in stormwater ponds, hydrodynamic solids separation, filtration, disinfection, bioretention, vegetated filter strips, and disinfection (e.g., by chlorination with doses as high as 5–10 mg of chlorine/L, or by UV irradiation).

Rainwater/stormwater reuse systems require storage to balance water demand and availability. This is particularly important for rainwater; when it is readily available (i.e., in wet weather or season), the demands for supplementary water are lower and vice versa. The sizing of storage is important; the overall supply reliability and water saving will increase with the increasing storage, but at the same time, so will the cost. Furthermore, for enhanced reliability of supply, supplemental supplies may have to be incorporated into the supply system (i.e., conventional municipal water supply). Storage facilities are designed in various ways, including small vessels made of clay, covered tanks or cisterns (made of plastic or concrete, sometimes located underground but requiring pumping), or open ponds and reservoirs. The choice of storage structure is very important in terms of overall costs.

Rainwater/stormwater is sometimes stored in open reservoirs, which are cheaper to construct, may have large capacities, but there are losses due to evaporation and leakage, and susceptibility to water quality degradation. Maintenance of water quality in storage is important, often maintaining chlorine residuals is deemed important to prevent growth of bacteria and other micro-organisms and biofilms. Finally, unless the rainwater is collected at the point of use (which is often the case and perhaps the main advantage of rainwater harvesting), it is required to deliver the stored water to the points of use by means of distribution systems. In dual quality water distribution systems, good distinction between various sources of water has to be made, usually by colour coding of distribution pipes.

Institutional feasibility of water reuse depends on local conditions. In some jurisdictions, rainwater use is required in all new developments (e.g., residential housing in some parts of India, irrigation of commercial properties in Phoenix, AZ, USA), but elsewhere, barriers exist. In Canada, the main barriers were identified as the lack of regulations and guidance, including plumbing codes, and economics (Farahbakhsh et al. 2009).

Social impacts and public acceptance are generally good for rainwater/roof runoff and the use on private property. For irrigation of public spaces, some concerns were voiced about micro-organisms in stormwater used for irrigation, because such micro-organisms may be transported by aerosols through the air. Mitigation by irrigating outside of the facility use hours seems adequate.

Besides providing a source of water, RHU is also useful for controlling runoff from urban areas. Thus, when striving for site water balance, rainwater plays an important dual role: as a valuable resource to be utilized beneficially in water supply, and also as a resource that needs to be managed, with respect to flows, volumes and quality, to minimize adverse effects on the environment and the beneficial water uses. This dual role of rainwater/stormwater harvesting and control can be served by shared and integrated facilities, which contributes to the overall cost efficiency of such projects.

Increasing interest in rainwater harvesting and stormwater management is generated by the LEED (The Leadership in Energy and Environmental Design) program certification, which indicates various levels of compliance with the sustainable construction processes established by the US Green Building Council (USGBC, 1998). LEED certified buildings may initially cost more (e.g., paying for the certification process), but over time they have lower operational costs and the productivity of employees in healthier LEED buildings is higher. In practical terms, the LEEDS system provides rating of six major areas of construction and with respect to RHU/SWM, awards points for stormwater management (rate and quantity, treatment), water efficiency (requiring water use reduction), and credits for: water efficient landscaping, innovative wastewater technologies, and water use reduction. Thus, the LEEDS program increases the interest in rainwater harvesting, stormwater management (including site planning), use of rainwater and stormwater in landscape irrigation, water use reduction, reducing heat islands, and prevention of pollution due to construction activities.

The economic feasibility of RHU depends on the availability and price of water, and may not be achievable in regions with abundant inexpensive water. A study conducted in Guelph, Ontario (Canada) (Farahbakhsh et al. 2009) investigated capture of rainwater from a 100 m^2 roof area, storage in a 8 m^3 cistern, and indoor use for toilet flushing and laundry in a household with five persons. This application reduced runoff from the roof area by 89% (65 out of 73 m^3 captured was used) and reduced the municipal water consumption by 31% (65 out of 207 m^3 was covered by rainwater). In the economic assessment, there were no credits given for retrofitted rainwater harvesting, and the cost of each m^3 was about $4.5 (CDN), which was 2–3 times higher than the current cost of municipal drinking water. Similarly, no credits were given for runoff (flood) control arising from providing a potential storage of 65 mm for the roof area. For specific storms events, the actual storage would be smaller, unless operational rules would force drawdown of storage before large rainfalls. It is believed that with more equitable pricing (i.e., getting credits for drinking water savings and runoff control), RHU would be economically feasible even under the current conditions in regions with plentiful water supplies.

3. Sustainable Wastewater Management

The sustainable wastewater management has been investigated by a number of authors who developed recommendations for improving sustainability of wastewater management systems (WWMS). Practical recommendations depend on the overall architecture of WWMS, but essentially, the overall strategy comprises pollution prevention by generating as little wastewater as possible and limiting or preventing its contamination, followed by managing the wastewater as a resource serving to produce: reclaimed water, energy (to meet treatment energy requirements, or even produce surplus energy), and fertilizers. The effectiveness of resource recoveries may be reduced by the presence of persistent pollutants, which limit the use of recovered resources.

3.1. POLLUTION PREVENTION (SOURCE CONTROLS)

The first step towards sustainable wastewater management is minimization of wastewater generation, generally by reducing water consumption and practicing industrial process water recycling. Minimizing wastewater production by reducing water use is important with respect to both the volume of wastewater generated and the energy needed to transport and treat water. There are also concerns about using the highest quality water for all purposes, some which do not require that quality. Both issues are dealt with in the soft path for water approach to urban water management; this concept emphasizes matching the quality of water supplied to the quality required and conserving the highest quality potable water (Brandes and Brooks 2006).

Preventing or limiting wastewater contamination is important particularly in municipalities allowing industrial discharges into municipal sewers; such discharges must be pretreated at source and their quality is controlled by sewer bylaws. For example, Toronto's Sewers Bylaw (City of Toronto 2010), aims to protect water quality by setting strict limits on heavy metals and toxic organic compounds in wastewater discharged to the sanitary and stormwater sewers, and identifying the ways of reducing and/or eliminating pollutants at source. Recognizing that most of such contaminants are hydrophobic, the bylaw helps improve the quality of biosolids (City of Toronto 2010).

3.2. RESOURCE RECOVERY

Resource recovery addresses wastewater reuse, and recovery of energy and nutrients. Four general strategies were recommended by Karrman (2001): separation of nutrient rich waste streams from the rest, recycling of nutrients and efficient use/recovery of energy, prevention of contamination of wastewater flows, and disposal of unavoidable pollution in landfills. Specific strategies are discussed below.

3.2.1. *Wastewater Reclamation and Reuse*

There are two primary drivers for reclaimed wastewater reuse: the need to supplement water supply sources and the need to eliminate wastewater effluent discharge to sensitive receiving waters. The former case is practiced mostly in dry climate, but may offer some economic advantages in other climates as well, e.g., for industrial water supply. Examples of reclaimed wastewater reuse for industrial purposes include concrete production, aggregate washing, equipment washing, cooling towers, stack scrubbing, boiler feed, and process water (excluding food processing). Other examples of reuse include agricultural land irrigation, utilizing both water and nutrient residues (Asano 1998); the NEWater agency in Singapore, which started to replenish 1% of total daily water consumption with reclaimed wastewater (increasing to 2.5% by 2011); and, toilet flushing in high-rise office buildings in Tokyo (Marsalek et al. 2008).

Wastewater reuse for protection of receiving waters is practiced in Florida, where freshwater resources in the form of slow moving rivers and streams have limited assimilative capacity for receiving treated wastewater effluents. In 2000, more than 50% of the state’s total wastewater treatment capacity served for wastewater reclamation and reuse, with reclaimed water use in landscape irrigation, agricultural irrigation, groundwater and wetlands recharge. Planning and implementation of wastewater reuse projects is described in Asano (1998).

3.2.2. *Energy Recovery*

Generally, energy is required to transport and treat water. Therefore, in WWTP optimization, one of the goals is to reduce the energy requirements representing a significant part of treatment costs (25–50%) (Crawford 2010). Good guidance for this process can be found in European Energy Conservation Manuals for WWTPs. Leading examples of such manuals are those from Switzerland and Germany, which have been in use for more than 10 years and produced some remarkable results (BUWAL 1994; North Rhine-Westphalia 1999).

The manuals serve to produce plant energy balances, which are used for optimization of energy use and production. The main energy input is the calorific energy contained in the wastewater organics; the bulk of this energy is removed from the main flow trough primary treatment and captured in the primary sludge. In the sludge processing train, the calorific energy is concentrated by primary and secondary sludge thickening, and fed to the stabilization process, which has the potential to convert solids into methane. Electrical energy is consumed at the plant mostly on aeration blowers, UV disinfection, pumping of influent and other waste streams, and plant lighting.

While anaerobic processes are commonly used to stabilize sludge, anaerobic municipal wastewater treatment with high-rate anaerobic technologies is less well known. It works well in tropical countries, but research is underway how to make it applicable in cooler climates as well. Such research focuses on membrane bioreactors with extended sludge retention times and shorter hydraulic times. This contributes to maintaining slow growing anaerobes in the reactor at high concentrations, enabling high volumetric conversion rates, while the wastewater quickly passes through the reactor. The main advantages of anaerobic treatment are smaller production of sludge and higher output of biogas; both contributing to sustainability.

Application of energy analysis to Swiss WWTPs reduced energy cost at optimized WWTPs on average by 38% (one-third due to improved efficiency, two-thirds due to increased energy production from biogas), and major efficiency increases were realized in the biological stage and by improved energy management. In fact, at present, biogas from WWTPs is the major source of electricity generation from renewable energy sources in Switzerland (Crawford 2010). German results are comparable, indicating average energy savings of 50% (North-Rhine Westphalia 1999). The highest energy savings were achieved at the Strass in Zillertal WWTP in Austria (250,000 PEs in season); after optimization the plant was producing 8,500 kWh/d, and using 7,400 kWh/d (Crawford 2010).

3.2.3. *Nutrient Recovery*

Nutrients in wastewater need to be removed by various treatment processes to avoid their discharges into receiving waters, where they would cause eutrophication. At the same time, such nutrients are needed in agricultural production. Thus, there is interest in recovering nutrients from wastewater and using them as fertilizers.

During the past 20 years, a number of fertilizer products derived from wastewater have been developed, and used as primary sources of N (nitrogen), P (phosphorus) and K (potassium). They differ in their origin and physical form, and include urine (concentrated, or unconcentrated, or biochemically treated), ammonium sulphate, struvite, digester liquid, untreated sludge blackwater, thickened sludge (dry matter in excess of 20%), and compost. Some recovered nutrient products work as well as conventional fertilizers, others may require further processing (Schick et al. 2009).

Phosphorus (P) recovery targets different waste streams and residuals (e.g., process water, sewage sludge, and sewage sludge ash) and uses different technologies (precipitation, crystallization, thermal treatment or wet chemical processes). Some of these technologies are currently fully operational (e.g., struvite formation in fluidized bed reactors), while others are still under development. One of the successful products is struvite, which contains P, N and Mg (magnesium), releases nutrients slowly, which is advantageous for less frequent fertilization, and contains impurities (e.g., caused by heavy metals) at two to three orders of magnitude lower than the commercial phosphate fertilizers (Bhuiyan et al. 2008).

Winker et al. (2009) noted that all these products may contain organic micropollutants found in raw municipal wastewaters (e.g., pharmaceuticals, personal care products), which may have to be controlled by appropriate treatment. Except for urine (Mauer et al. 2006), detailed assessments of micropollutants in sewage-derived fertilizers have not been yet completed.

The other concern in using sewage fertilizers are pathogens, which are found mostly in faeces, but can enter urine as well by cross-contamination. Thus, some forms of pathogen removal need to be applied to both urine and whole sewage fertilizer products. For urine, 6 months storage (without adding fresh urine) was found sufficient, and research on shortening this period is under way (Vinneras et al. 2006). For black matter and sludge/biosolids, thermal treatment (or equivalent) is recommended, e.g., 1 h at 70°C. Thus, new fertilizer products derived from advanced wastewater treatment show a good promise for applications in agriculture, but the associated public health risks need to be assessed and managed, and addressed by further research.

4. Conclusions

Operation of existing urban water systems can be improved by implementing various sustainability strategies. Two of such strategies are particularly promising: rainwater harvesting and sustainable wastewater management. The first strategy reduces imports of source water into urban areas and reduces runoff from urban areas; the second one promotes pollution prevention and recovery of resources from wastewater, including reclaimed water, energy, and nutrients. Overall, both groups contribute to more sustainable urban water systems requiring fewer resources to provide the water services required and ensuring a better protection of the urban environment.

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ENVIRONMENTAL ADVANCES BY WATER SUPPLY IMPACT

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Abstract. The development of the Slovak public water supplies has fallen behind other European countries. Implementation of new policy in this field moved the process from solving the partial problems to a comprehensive approach to protection and use of water regarding their quality and quantity (Act on Waters No.364/2004 Coll). In 2009, over 87.3% of the population was connected to public water systems, which supplied them with drinking water. Paper deals with issues relating to mainly water resources, water quality and protection and the monitoring of the water which are one of main interests in public water supply. The major objective of the Slovak Republic as a member of the European Union includes adopting and implementing EU legislation with respect to the Slovak environment (Directive of the European Parliament and of the Council No. 2000/60/EC). This is a highly demanding task, in particular for those Slovak authorities and organizations responsible for meeting these requirements. The task is especially formidable since, besides resolving all major current problems, they are also expected to outline the future perspectives of Slovak water management.

Keywords: Water supply, water resources, water protection, water management

1. Introduction

The Slovak Republic (territory 49,014 km^2; population 5.4 million) is situated in the temperate climate zone of the Northern hemisphere with regularly alternating seasons. About 38% of the country is forested. Based on measurements of the average annual air temperature, the warmest part of the country is the area of Štúrovo in the south (10.4°C); while the peaks of the High Tatras in the north, in

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particular the Lomnický Peak (–3.7°C), are considered the coldest. The average amount of precipitation is around 760 mm, with the Danubian Lowland being the driest (below 550 mm) and the High Tatras the most humid part of the country (above 2,000 mm).

Since the Slovak Republic is situated on the watershed of the Black Sea (96%) and Baltic Sea (4%), which is the territory where the majority of European rivers rise (excluding the Danube), the regularity of hydrological regime, in particular the high and medium level discharges in the springtime are of great importance.

2. Legislation in the Water Management and International Cooperation

Legislation in 2009 was aimed at meeting the obligations towards the EU related to new European water legislation adopted in 2006–2007 and at introducing common European currency – euro in the Slovak Republic. Standardization for water management sector of the Slovak Republic is conducted in the following technical committees (TC):

TC 1 Water Supply and Sewerage Systems which cooperates with international standardization committees (C150/TC 147, CEN TC164 etc.)

TC 27 Water quality and protection

TC 64 Hydrology and Meteorology

TC 72 Environmental management

International cooperation continued under the intergovernmental agreements, international treaty and international conventions signed in the previous years. International cooperation of the Slovak Republic in water management sector is done through cooperation on transboundary waters. This cooperation is in accordance with the Convention on the Protection and Use of Transboundary Watercourses and International Lakes UNECE (Helsinki Convention), the Convention on the Cooperation in Protection and Sustainable Use of the Danube River and many other agreements or conventions.

The Slovak Hydrometeorology Institute's (SHMI) conducts an assessment of surface water quality of the national river monitoring system based on the results of water analyses (basic physical-chemical parameters, biological parameters, micro-biological parameters, organic and inorganic micro-pollutants and in selected areas also radioactivity parameters) carried out in Slovak Water Management Enterprise (SWME) laboratories (physical-chemical water analyses) and Water Research Institute Bratislava laboratories (biological analyses, analyses of specific organic substances and all analyses of samples from transboundary rivers with Austria, Hungary, Poland and Ukraine).

3. Water Resources

3.1. SURFACE WATER

In the dry periods, the capacity of natural surface water sources amounts approximately 90.3 $m^3 s^{-1}$. When subtracting ecological discharges (minimum discharge needed for supporting and maintaining aquatic life and other functions of a stream), only 36.5 $m^3 s^{-1}$ is available for utilization (excluding the Danube, Morava and Tisa rivers). Water reservoirs across Slovakia allow increasing the discharges in dry periods by 53.8 $m^3 s^{-1}$, thus increasing utilizable discharges to 90.3 $m^3 s^{-1}$.

At present, there are 54 water reservoirs across Slovakia (with the overall capacity exceeding 1 million m^3) with the gross controllable capacity of 1,890 million m^3. The capacity of these reservoirs allows for the interception of about 14% of the annual mean discharge from our country's territory, as well as the increase of low discharges in dry periods by about 55.5 $m^3 s^{-1}$ (above discharge Q_{355} = 80 $m^3 s^{-1}$ [355 day water]). Thus the total increased discharge in rivers initiating within the territory of Slovakia reaches approximately 135.5 $m^3 s^{-1}$ (Q_{355} increased by 69%). Water withdrawal, currently amounting to 39.0 $m^3 s^{-1}$, is equal to about 29% of the discharges during dry periods and to 10% of the mean discharge. The water consumption in the territory of SR varies between 4.8 and 9.0 $m^3 s^{-1}$ and decreases during an average year by 1.5–2.3%. The previously mentioned water reservoirs include 8 reservoirs. Their major purpose is to ensure large-scale drinking water supplies for Northern, Central and Eastern parts of Slovakia. The capacity of these reservoirs is approximately 4.0 $m^3 s^{-1}$.

Surface water supply from surface resources in Slovakia is shown in Table 1 (Ministry of Environment of the Slovak Republic 2008, 2009).

TABLE 1. Surface water supply (WS) in Slovakia (in 1,000 m^3).

Index	Year						
	2002	2003	2004	2005	2006	2007	2008
Surface WS in total of which	672.8	611.3	604.2	510.5	355.9	299.5	295.9
For treatment to drinking water	63.8	63.8	54.3	51.7	52.9	51.0	49.5

3.2. GROUND WATER

Groundwater, as one of important natural resources, represents invaluable, easily available and the most appropriate drinking water resource from quantitative, qualitative and economic viewpoints. Sufficient amount, better quality, low treatment costs and potentially low risk of contamination make groundwater a dominant resource of drinking water (Act on Waters No.364/2004 Coll).

Assessment of relations between potential available groundwater quantity and used groundwater quantity is carried out through the annual water management balance developed by SHMI. Basic evaluation unit of groundwater balance is a hydrogeological region with its subsequent classification into sub-regions.

According to valid hydrogeological regionalization (1995) the territory of Slovakia was divided into 141 hydrogeological regions (Ministry of Environment of the Slovak Republic 2007, 2008).

The total available groundwater amount represents the sum of available resources approved by the Committee for Available Groundwater Quantity Classification and supplies not approved by the Committee which are determined following the volumes documented from hydro-geological observations and surveys.

Total available groundwater resources as of December 31, 2008 (Božíková and Škultétyová 2008):

approved by the "Committee":	45,824.2 l s^{-1}
not approved by the "Committee":	31,255.3 l s^{-1}
total:	77,079.5 l s^{-1}

Usable ground water resources are defined as those ground waters that can be withdrawn from the subsurface by technical means, while keeping the natural balance of the environment. (Ecological limits).

In 2008 the SHMI Water Abstraction Register listed 5,460 resources of Slovakia. Review of groundwater abstraction in Slovakia (2004–2008 according to their selected purpose of use are listed in Table 2 (Klinda et al. 2008).

TABLE 2. Selected use of ground water in Slovakia in l s^{-1}.

Year	Public supply	Food production	Social needs	Total use
2004	9,431.53	322.04	327.02	12,200.85
2005	9,159.87	288.25	279.72	11,867.46
2006	8,836.13	295.62	340.15	11,665.20
2007	8,441.59	383.87	333.44	11,365.96
2008	8,468.8	285.0	271.2	11,122.1

In the assessment of ground water use in Slovakia according to the purpose it can be stated that there was the increase of water consumption in public drinking water supply of the inhabitants and other use. On the contrary, abstractions decreased globally in other sectors.

4. Water Supply

Development Overview – systems in administration of water companies – (WC), local authorities (LA) and other entities is given in Table 3 (SWME 2008, 2009).

TABLE 3. Development overview.

Indicator	Unit	Years					
		2006	2007	2008			
				WC	LA	Other	Total
Length of WS system (without service pipes)	km	26.36	26.90	24.74	1.90	743	27.38
Length of service pipes	km	5.93	6.11	5.39	659	220	6.27

Development of drinking water supply and development of water supply network in administration of water companies, local authorities and other subjects is illustrated in Tables 4 and 5.

TABLE 4. Development of the total number of inhabitants and the number of inhabitants supplied with drinking water [in thousand].

	2005	2006	2007	2008
Total number of inhabitants	5,386.7	5,390.4	5,401.0	5,412.3
Supplied with drinking water from public water supply network	4,594.1	4,653.4	4,653.7	4,670.4
Proportion [%]	85.3	86.3	86.2	86.3

5. Water Quality

5.1. SURFACE WATER QUALITY

The SHMI conducts an assessment of surface water quality of the national river monitoring system based on the results of water analyze (Gov. Regulation No. 296/2005 Coll.):

basic physical-chemical parameters,

biological parameters,

micro-biological parameters,

organic and inorganic micro-pollutants and in selected areas also

radioactivity parameters.

TABLE 5. Development of water supply network in administration of water companies, local authorities and other subjects.

Indicator	Year				
	2006	2007	2008	2009	2010
No of inhabitants supplied from WS network (thousand)	4,653.4	4,653.7	4,670.4	4,696.9	4,723.2
Capacity of water resource (l s^{-1})	33,545.7	32,736.0	33,876.1	33,401.5	33,197.0
Length of water supply networks (km)	26,356.9	26,898.7	27,377.3	27,753.8	28,161.2
Capacity of ground water resources (l s^{-1})	27,713.0	26,904.7	27,128.4	27,715.7	27,566.2
Water produced in water management facilities (million m^3)	334.3	321.6	318.3	317.9	316.9
Of which: water produced from ground water	280.6	271.0	257.8	269.5	269.0

5.2. GROUND WATER QUALITY

The Programme of Water Condition Monitoring for 2008–2010 was prepared and it included the requirements to collect all the information on water condition necessary to be reported to the European Commission in required quality. Monitoring of ground water (GW) chemical condition was classified into basic, operational monitoring and monitoring of protected areas.

Operational monitoring in all ground water bodies assessed as risk because of reaching not good chemical condition. Monitoring network was enlarged by adding 34 piezometric wells in the territory of Žitný ostrov.

The issues of unfavorable oxidation -reduction conditions are becoming essential which is being pointed out by the most frequently exceeded acceptable concentrations of the total Fe, Mn and $NH4^+$. Besides these parameters there was sporadic exceeding in case of Cl^-, SO_2^- and NO_3^-, $CHSK_{Mn}$, soluble substances at 105°C and H_2.

In the objects of operational monitoring, GW has relatively low oxygen content which is also confirmed by the fact that recommended value of the percentage of water saturation by oxygen was reached only in 15% of samples (MoE SR

Resolution No. 221/2005 Coll). Mn and total Fe are the most frequently exceeded parameters which means that unfavorable situation of oxidation -reduction conditions is ongoing. Besides these parameters the exceeded limit values of Cl^- and SO_4^{2-} indicate the impact of anthropogenic pollution on ground water quality.

Land use pattern (agricultural areas) is reflected into increased contents of oxidized and reduced forms of nitrogen in ground water (Ministry of Environment of the Slovak Republic 2008, 2009).

5.3. DRINKING WATER QUALITY

The drinking water quality in public water supplies is assessed on the basis of inspections made by waterworks operators (i.e. the water and sewage works) and it assessed on the basis of the number of determinations of individual water quality parameters exceeding related hygienic limits (Gov. Regulation no. 354/2006 Coll; Stanko 2009).

Public health authorities control ground water quality directly at consumer's place and in case of some defection the water companies should be able to demonstrate where this defection comes from.

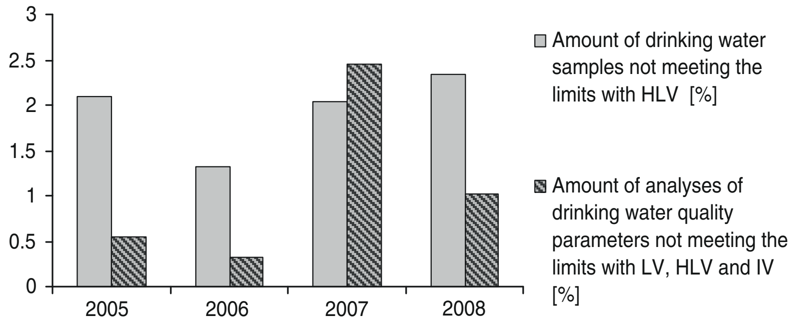
Water quality is assessed on the basis of the number of determinations of individual water quality parameters exceeding related hygienic limits. Government Regulation no. 354/2006 Coll. setting requirements on water intended for human consumption came into effect on June 1, 2006.

In 2008 as many as 11,382 drinking water samples from sampling sites in water distribution network and 287,783 analyses were analyzed. The portion of drinking water analyses meeting hygienic limits reached the value 99.45%. Number of samples meeting the requirements for drinking water quality concerning all parameters reached the value 91.84% in 2008 (see Figure 1).

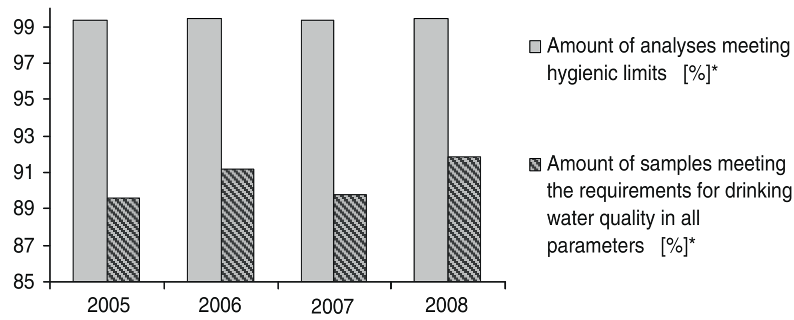
In 2008 the portion of drinking water analyses meeting hygienic limits reached the value 99.45%.

6. Water Resource Protection

Water resource protection should be viewed as an integrated protection of quality and quantity of surface and ground water, including natural curative springs and mineral waters. The major determinant in terms of water resource quality protection is the water pollution source, having either direct or indirect impact on water resources.



IV – indicating values, LV – limit values, HLV – highest limit values, LVRR – limit values of referential risk



* Parameter Free chlorine is not included in the amounts.

Figure 1. The amount of analyses and samples of drinking water quality in %.

Both aspects of water protection (quantitative and qualitative) are subordinated to a territorial water protection system, in particular in such source areas that are considered significant from the perspective of water management. The system consists of three types of protection (Act on Waters No.364/2004 Coll):

general protection;

broader regional; and

special protection.

6.1. PROTECTION OF WATER QUALITY

One of the key roles of water protection in terms of water quality is to resolve the problems relating to sources of pollution. Pollution sources, which have a negative impact on water quality, are broken down into two categories based on the type and severity of their impact:

point sources of pollution (i.e. wastewater discharges from industrial and agricultural facilities and from residences),

non-point sources of pollution.

The currently operated wastewater treatment plants represent a specific problem, because they are overloaded (both hydraulically and from a load point of view) and the wastewater treatment technology does not comply with legal regulation standards any more.

6.2. PROTECTION OF WATER QUANTITY

The major objective of water utilities is to maximize usage of the stored water resource. The Methodology of Establishing Ecological Limits of Ground Water Resource Utilization was developed and applied in the General Protection and Rational Water Utilization. The methodology defines how to establish usable volumes of ground water resources while ensuring sustainable development of the land by defining general ecological limits for the entire watershed – a hydrogeological zone or hydro-geological structure, as well as local ecological limits for particular sources that are being used (springs and wells).

6.3. TERRITORIAL PROTECTION OF WATER RESOURCES

In addition to the protection of water quality and water quantity, a territorial water protection system has also been introduced for the source areas considered significant from the perspective of water management. The system consists of three types of protection:

General protection of water resources pursuant to Act No. 364/2004 Collection on Waters is clearly spelled out for the entire territory of the Slovak Republic. Broader regional water protection is implemented by means of protected water management areas (PWMA, also called “Protected areas of natural water accumulation”).

Special protection with increased severity

7. Conclusions

The water becomes one of the most strategic raw materials. The pollution from natural and antrophogenic activities are two main effects of water pollution and therefore it is necessary to make considerably efforts to protect the environment including water. The fundamental objectives of water management are aimed mainly at providing drinking WS using public WS systems together with wastewater collection and treatment by public sewerage systems to fulfill the commitments towards the EU, at providing water for other economic purposes, preventing and mitigating the consequences of floods and droughts, environmental protection.

The basis of new water policy in the SR was integrated water resources management and protection in hydrological river basins – the so called integrated river basin management. In accordance with requirements of the European Directive the first working version of the Proposal of River Basin Management Plans of the Slovak Republic was developed by the end of 2008.

A significant step in the process of river basin management plans was elaboration of the Overview of Significant Water Management Issues, which serves as a supporting document for further working phase of implementation of the Water Framework Directive.

The development of public WS is done within the Plan of Development of Public Water Supply and Water Sewerage Systems. By implementing this plan by 2015 the number of inhabitants served by the public WS will increase from 86.3% to more than 90%. To ensure the proposed development of public WS it is necessary to build WS from the existing water resources to consumer-sites, water networks in municipalities, accumulation areas for providing continuous drinking water supply and water resources.

8. Acknowledgement

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WATER POLLUTION LEVEL AS A KEY IMPACT ON HUMAN HEALTH. ANALYSIS AND PREDICTION OF HEALTH STATUS AFTER WATER SUPPLY SYSTEM IMPROVEMENT IN CHERNIVTSI CITY

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Abstract. According to the monitoring results of decentralized water supply in Chernivtsi City, pollution maps of city's area have been drawn. Tendencies of change of the most important pollutants have been analyzed. The analysis of death rate, cardiovascular disease, oncological, bronchial asthma frequencies have been studied, along with the ratio of birth defects in relation to potable water quality. A mathematical model of qualitative and quantitative composition of potable water influence on population death rate and oncological disease instances is presented.

Keywords: water pollution, nitrates, nitrites, ammonia, heavy metals, bacteriological pollution, cancer disease forecast, modelling of immune system response on environment pollution, water supply, wells

1. Introduction

Ecological situation and disease rate in Chernivetska Oblast, including Chernivtsi City, causes worries and is produced in considerable degree by high anthropogenic

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influence. Therefore, under present conditions there is a necessity to make a complex study of spatial and dynamic phenomena of ecologically stipulated illnesses, including those caused by centralized and decentralized water supply.

2. Indices: Quality of Life – Quality of Environment

Present national and international policy in health care requires quantitative assessment of the quality of water as one of the main factors of health (Romaniv 2003). Such assessment is worth while to apply to so called "Ecological health", i.e. the health of a person related to the state of environment. a list and recommendations for health indicators (Abrosimova and Ushakov 1998) have been approved in 1995 in Sosnovice, Bulgaria, at an international seminar. The state of environmental indicators World Health Organization (WHO) are divided according to causes as Pressure-State-Response. Today the interaction between the man and environment, taking into account the above mentioned indicators, the EU and WHO analyse according to the model Serdiuk et al. (2003).

The environmental data, European database also include the indicators according to the Health for all Statistical Database (1999), including such indicators:

the number of diseases caused by polluted potable water (by 100,000 people);

percentage of population using water supply systems;

percentage of population using sewage systems.

3. Analysis of Surface Waters in Chernivetska Oblast

In the River Dniester basin average maximum permissible concentrations (MPC) of petroleum products over a number of years of monitoring fluctuated within considerable numbers: from 1 MPCs to 20–28 MPCs (Muha 2008). Average concentrations of petroleum products and phenols were 1–3 MPCs, ammonium nitrogen – 1–9 MPCs, nitrite nitrogen – 1–2 MPCs, copper compounds – 3–12 MPCs, zinc – 1–2 MPCs. Such anthropogenic pressure on water intake confirms ecological pressure on the state of plankton of the Dniester reservoir. The Prut River in Chernivtsi area is an anthropogenic ecological pressure with elements of retrogress (Muha 2008). All this is indicative of high possibility of negative effects for people's health drinking such water.

For surface waters of Chernivtsi Oblast that are used for water supply of the city a high level of pollution by mineral nitrogen compounds is characteristic. These substances are able to get into human body together with potable water causing negative impact on its health.

4. Analysis of Content of Chemical Elements in Subsoil Waters in Chernivtsi

The following typical parameters were selected for the region from controlled substances according to requirements DSanPiN v383 (186/1940) for the analysis of spatial distribution of polluting substances concentrations: general water hardness, mineralization, concentrations of NH_4^+, NO_2^-, NO_3^-, SO_4^{2-}, Cl^-. We shall assess by the concentration of NH_4^+, NO_2^-, NO_3^- the household pollution, whereas by SO_4^{2-} – natural anomalies, Cl^- will be used as an additional parameter for the analysis.

According to NH_4^+, NO_2^-, NO_3^- contents, we can trace excess of MPC in NO_3^- (Figure 1). Sample taking for the analysis was done mostly in areas with no centralized water supply or water sewage system. There were 33 points of water sampling. Therefore such pollution is connected with household and human economic activity.

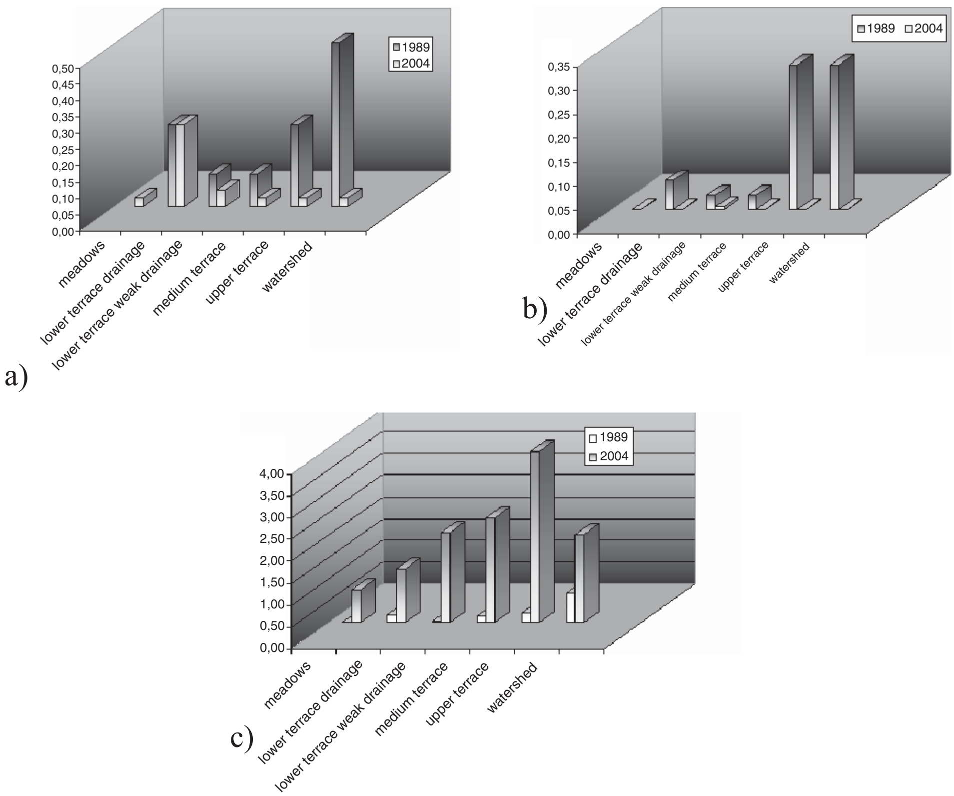


Figure 1. Dynamics of subsoil waters pollution (in MPC) in Chernivtsi by nitrogen compounds (Muha 2008): (a) NH_4^+, (b) NO_2^-, (c) NO_3^-. Values of concentrations are provided in units divisible to excess of MPC.

The exception is the general mineralization index that was increased to 1–1.2 MPC by the year 2004. These processes can be explained by the fact of subsoil water elevation in the city and washing out substances from soils as these are typical components of the soils of the region.

The examination of wells and potable water sources in decentralized water supply in Chernivtsi revealed that about 55% of well are in “satisfactory” state. Sanitary situation in 45% of wells were assessed as “unsatisfactory”. The main reasons for such state were insufficient distance from sources of possible pollution (less than 30 m), residential buildings, absence of cut-off clay well, lids, etc. More than 70% of city wells that have subsoil waters as their source are polluted by nitrogen compounds of biogenic local origin, the end products of which are nitrates. Their average concentration is more than 2 MPCs (Figure 1).

While analyzing the dynamics of pollution from 1998 to 2004, we can see that the dominant pollutant was ammonium and nitrite nitrogen in 1998, whereas in 2004 almost all the nitrogen was in nitrate form. This signifies the aeration of subsoil waters, possibly, due to the decrease of the thickness of aerated layer of soil by raising subsoil waters level, and that such a pollution took place quite long ago.

Raising the subsoil water level and increase in the content of NH_4^+, NO_2^-, NO_3^- in water allows us to suppose that the main reason of such phenomenon is long periodical volumetric escape of waste waters from outdated and considerably damaged sewage system of centralized Chernivtsi drainage system.

4.1. ASSESSMENT OF CHEMICAL ELEMENTS CONTENTS IN THE WATER OF CHERNIVTSI CENTRALISED WATER SUPPLY SYSTEM

Over the many years of municipal water services company monitoring, there were cases of exceeding the content of Pb, Mn and Fe. Content of Mn in the treated potable water of Bila and Rohizna stations, and the concentrations of Mn and Zn at the Popova station was higher 0.4 MPC. Therefore these metals and their concentrations were selected as the key ones while modelling immune system reaction to lengthy use of poor quality potable water.

4.2. NONCONFORMITY OF POTABLE WATER QUALITY

In decentralized sources of water supply (subsoil waters) for Chernivtsi citizens, the concentration of Pb and Zn in water is somewhat higher, and Mn and Fe – lower in comparison with centralized water supply.

Centralized water supply over the period of study (2000–2004) in terms of bacteriological indicators in Chernivetska Oblast 3.6%, (Ukraine – 4.8%) did not meet the sanitary norms, decentralized water supply – 12.0% (Ukraine – 22.7%)(State Committee of Statistics of Ukraine).

In Chernivtsi city the highest nonconformity (for centralized water supply (C) – 9.2%, decentralized water supply (DC) – 42.3%).

TABLE 1. Sanitary nonconformity of potable water quality in Chernivtsi (% of nonconformity according to bacteriological indicators).

Years										Average	
2000		2001		2002		2003		2004			
C	DC	C	DC	C	DC	C	DC	C	DC	C	DC
12.6	51.1	10	72.2	5.6	40.8	8.7	–	8.9	38.2	9.2	42.3

Analysing the correlation of chemical pollution compared to bacteriological, we can see (Figure 2), that the dependency is of exponential character: with the increase of frequency of water nonconformity to quality standards of chemical pollution, the bacteriological pollution increases exponentially. This can happen in a case when along with the chemical pollutants the organic substrate substances can get for micro flora. These microorganisms multiply according to Malthusian law at the starting point, and, thus the dependency of bacterial agents concentration in relation to substratum will be exponential. Such substrata may be urine, carbohydrates, and other organic substances available in household, municipal or farm sewers, for example in Stanko (2009).

5. Chernvtsi City Citizens Quality of Life Analysis

The analysis of frequencies of water quality nonconformity to standards according to chemical and bacteriological pollution proves the weak correlation between these parameters and the bronchial asthma illness rate (Figure 3a, b), and birth defects rate in children (Figure 3c, d).

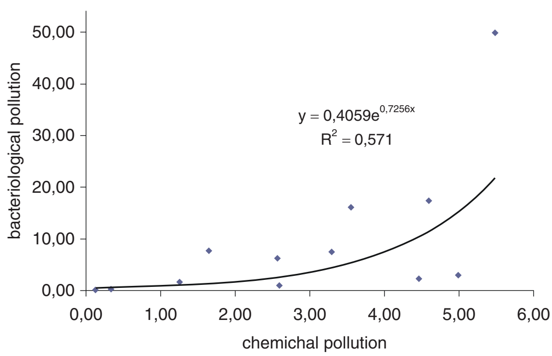
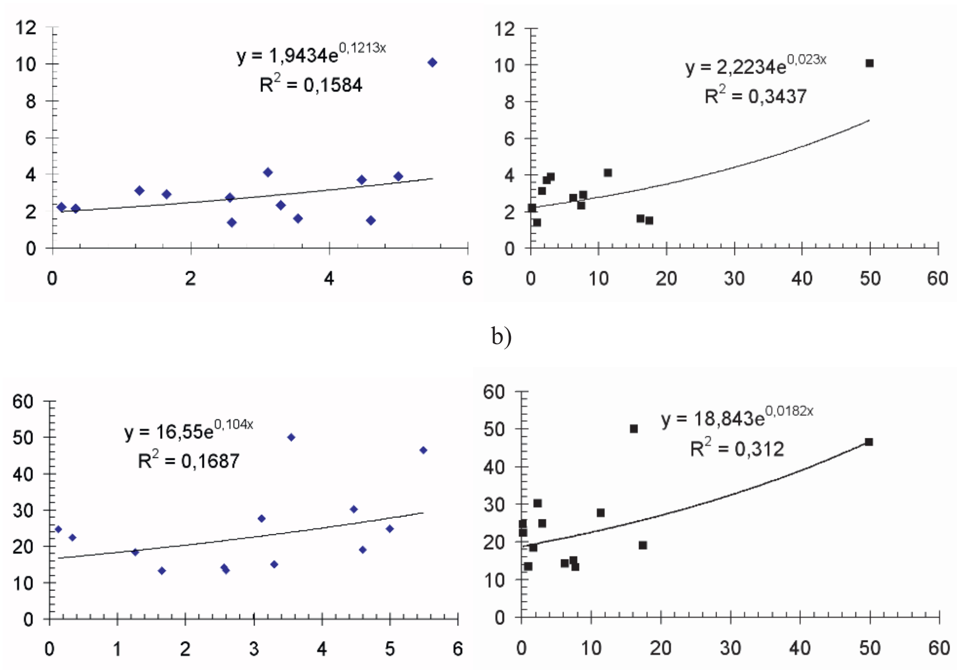


Figure 2. Correlation between nonconformity with the standards of chemical and bacteriological subsoil waters pollution.



a) b)

c) d)

Figure 3. Correlation between water quality nonconformity (y, %) according to chemical (a, c) and bacteriological indicators with diseases (b, d). (a, b) – bronchial asthma, (c, d) – birth defects in children.

Localization of birth defects at place of residence is impossible to establish due to high migration rate in the range of 15–35 years in the city. Nevertheless, such correlation is rational to be connected to the content of nitrogen containing substances of household use, i.e. nitrate concentration, as this indicator in the majority of instances, characterizes the percentage of nonconformities of water quality with the standards. Most reliable such a connection should be expected in the area of decentralized water supply and sewage system absence.

Population death rate unlike bronchial asthma disease and birth defects rates, does not have any clear connection with nonconformity of potable water quality. Thus, we can draw a conclusion that among other factors of environmental indicators, water pollution in Chernivtsi is a factor that stipulates and increases the risk of bronchial asthma development and increase of birth defects in children.

As the main levels of water pollution are in private sector with decentralized water supply and water drain, the above mentioned indicators will be influenced by economical activity of the area, and the dominant pollutants will be nitrates, nitrites, and ammonium ions.

NH_4^+, NO_3^- concentration profiles are shown at Figure 4. NO_2^- distribution is not provided as its content was less than 0.01 MPC. Spatial NH_4^+ distribution analysis enables us to identify ammonia anomaly in E7-F7 squares (Figure 4a). But it is difficult to definitely trace connection of this pollutant with disease and death rates because of small population density in the squares.

Further analysis of disease and death rate maps did not establish correlation with the content of ammonium nitrogen and population health or death rate that lives in the designated area. NO_3^- spatial distribution analysis shows nitrate anomalies in squares A6-B7-8-D7 (we shall show as N I), C7-8-D7-8 (N II), G2-H1-2 (N III), H8-9-10-I8-9 (N IV), J4-5-6-7-8-K4-5-6-7-8 (N V). The most significant is N IV where nitrate pollution level is exceeding MPC more than 9 times. Anomalies N I – N IV are traced at city areas where centralized water supply and sewage system are unavailable, and therefore, citizens use subsoil waters for consumption. Thus, correlation connection of these anomalies with health indicators and death rates may be considered reliable.

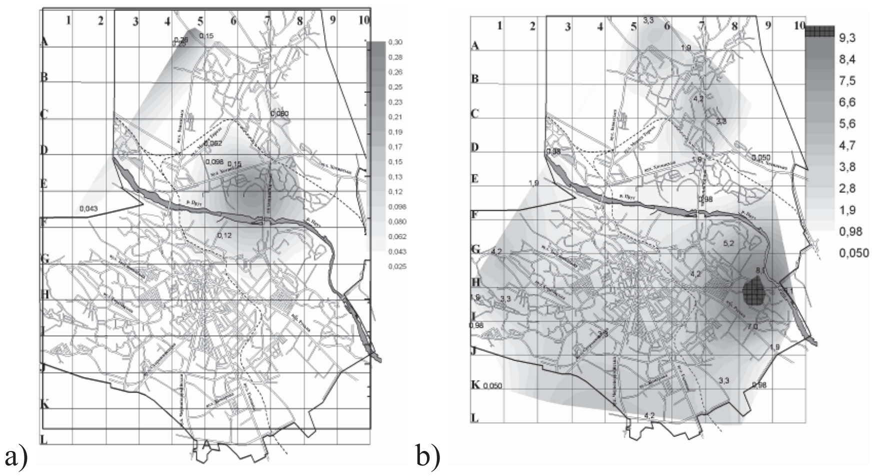


Figure 4. NH_4^+ (a) and NO_3^- (b) concentration distribution of Chernivtsi decentralized water supply. The area of the square is 1,300 × 1,300 m. Values of concentrations are provided in units divisible to excess of MPC. Legend: disease indicator per 1,000 population.

Analysing anomalies locations (as a tracer) and comparing them with the character of oncological pathologies of digestion organs (Figure 5), we see that the areas with high nitrate pollution (Figure 4b) correspond high values for both age groups: 30–59, and over 60 years of age. Analogous situation is seen for oncological pathology (Figure 6).

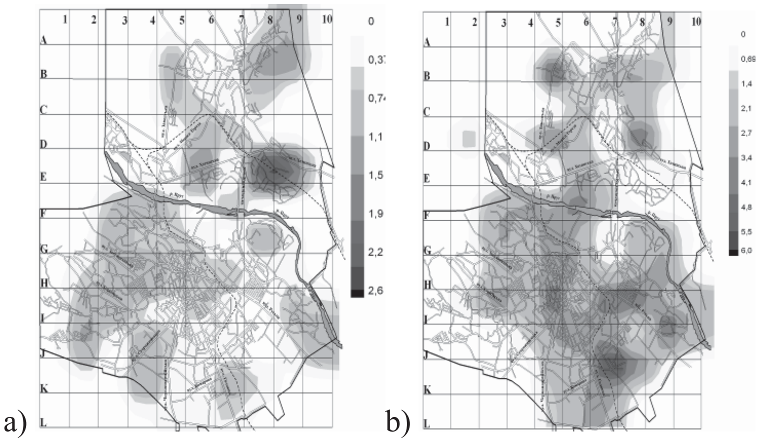


Figure 5. Spatial distribution of oncological pathology of digestion organs and abdominal cavity: (a) age range 30–59, (b) older than 60 years. Diagram was built for the population living not less than 20 years at the same square in Chernivtsi.

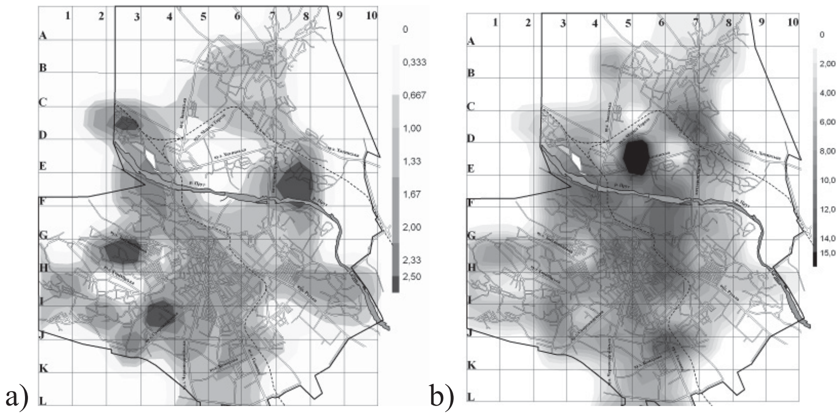


Figure 6. Spatial distribution map for general oncological pathology: (a) age range 30–59, (b) older than 60 years.

Peculiarities of regularities of connection of health – nitrate pollution is weaker dependency for age group over 60 years. Explanation of this effect is hard to have and needs further analysis.

Analysing the location of anomalies and comparing them to the character of population death rate due to cardio-vascular diseases (Figure 7), we can see that weak correlation is traced for only N I – III for age group 30–59 years and for N I, III, age group over 60.

It was established that in the majority of cases subsoil waters of the city have exceeding content of calcium (100–200 mg/l), that is stipulated, mainly,

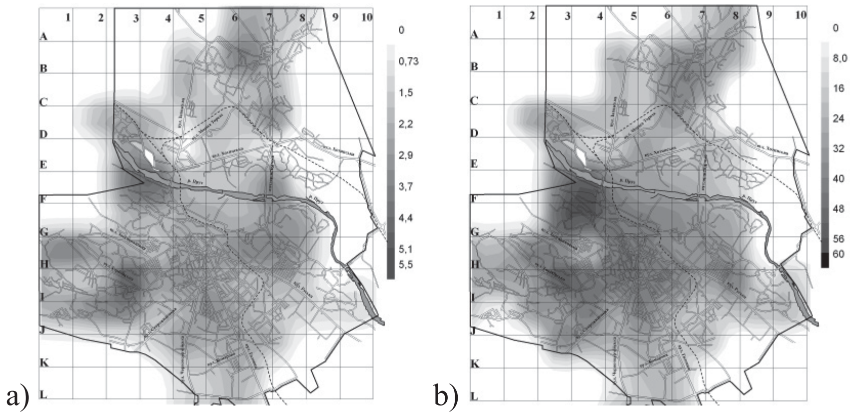


Figure 7. Map of spatial distribution of general death rate due to cardio-vascular diseases.

by the qualities of natural deposits of the region, technogenic pollution and considerable migrational capacity of the element itself. Such state with calcium does not worsen situation of cardiovascular diseases, but, on the other hand, stabilizes the situation. On the whole, freshwater with mineralization up to 1–1.2 g/l for areas N I – IV dominate.

5.1. MODELLING THE INFLUENCE OF WATER POLLUTION ON HEALTH

For model assessment of subsoil waters pollution in Chernivtsi and of negative influence on health of centralized water supply we used our own (made by the author of the article) method of virtual bioindication. The basis of the method became a simple kinetic model of immune system response to antigen that takes into consideration the environmental quality, water quality, and climatic parameters. The scheme of immune system is provided at Figure 8.

We supposed that the main factors of contagious illnesses were the following parameters: concentration of pathogenic antigens that are multiplying – V(t), antibodies concentration – F(t), concentration of lymphoid and haematogenous stem cells – C(t), and their descendants – plasmocytes C'(t), relative characteristic of injured organ – m(t).

The basis for comparison was the model picture of the real system with general pollution 0.4 MPC (nitrates, general mineralization, Pb, Mn, Fe) (Figure 9a). Assessment of potential risk for development of negative for health effects caused by discrepancy in environmental parameters with the standards, and is established by a complex risk functions (Figure 9b). It enables us to assess the risk of oncological illness development that is caused by nitrates, and the products of their metabolism in a body – nitrites, nitrosubstitutes.

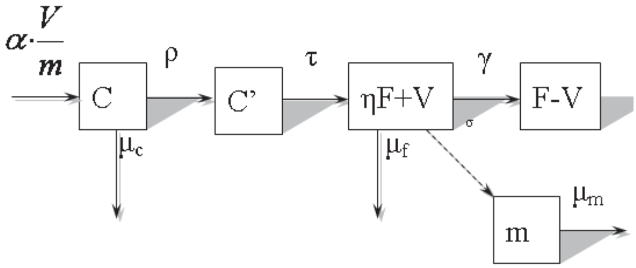


Figure 8. The main factors of contagious illnesses.

5.2. MODELLING RESULTS AND THEIR ANALYSIS

As we see from Figure 9b, in the proposed model immune system reacts slowly to inconsiderable number of pathogenic microorganisms (in time from 0 to 1.25 day). Only mass attack of antigens makes immune system to defend the body (dynamics of C and F curves). To avoid repetition of self infection the organs produce immunocompetent cells quite a long time after the antigens have been destroyed. So, if virtual contagious disease ends by the fifth day, immunocompetent cell production lasts 4 times longer. Immune system needs time for full cycle to cure the body.

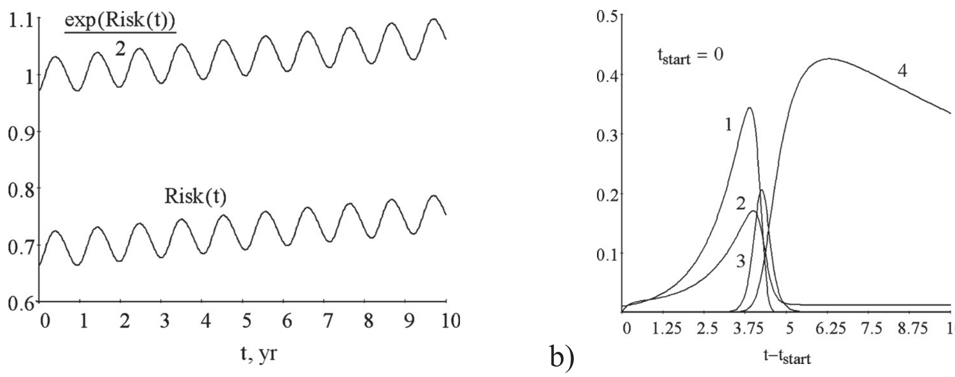


Figure 9. Risk functions (a) and dynamics of the main components of immune system under the conditions of toxin accumulation in a body (b). The length of pollutant influence is 1 year. Level of water pollution is 0.4 MPC. Curves (b): 1 – pathogenic microorganisms V, 2 – degree of organ damage of a body m, 3 – C, 4 – F.

Simultaneous presence of another antigen or its introduction by the moment the full cycle have not been finished causes an effect when the immune system takes a decision to priority treatment. In other words, the immune system will choose to treat more quickly more dangerous disease in the first turn, and only after completion antigen neutralization will start treat the other one and so on. But under unfavourable environment the time to the immune system recovery increases, and intensiveness of C and F component production decreases. As a result the length of treatment increases. Such effect under mixed antigens causes to increase negative consequences for the body or death (in case of complete damage to organs).

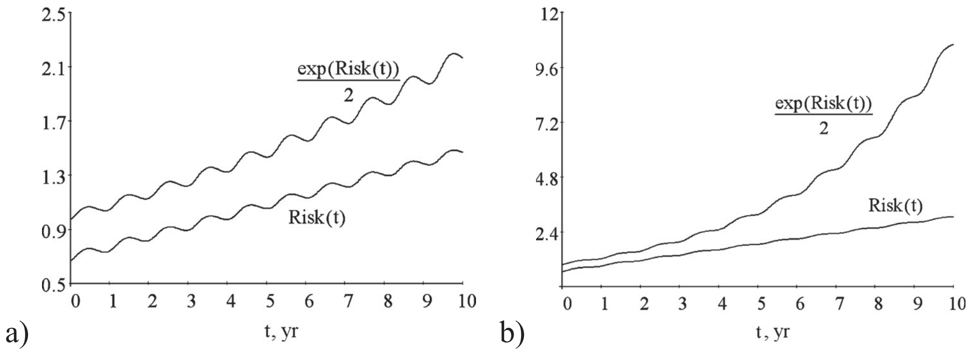


Figure 10. Risk function under conditions of toxin accumulation in a body. The length of pollutant influence is 1 year. Water pollution level: a – 4.5 MPC, b – 13.8 MPC. Curve 1 – linear model of toxins accumulation, 2 – exponential model of toxins accumulation.

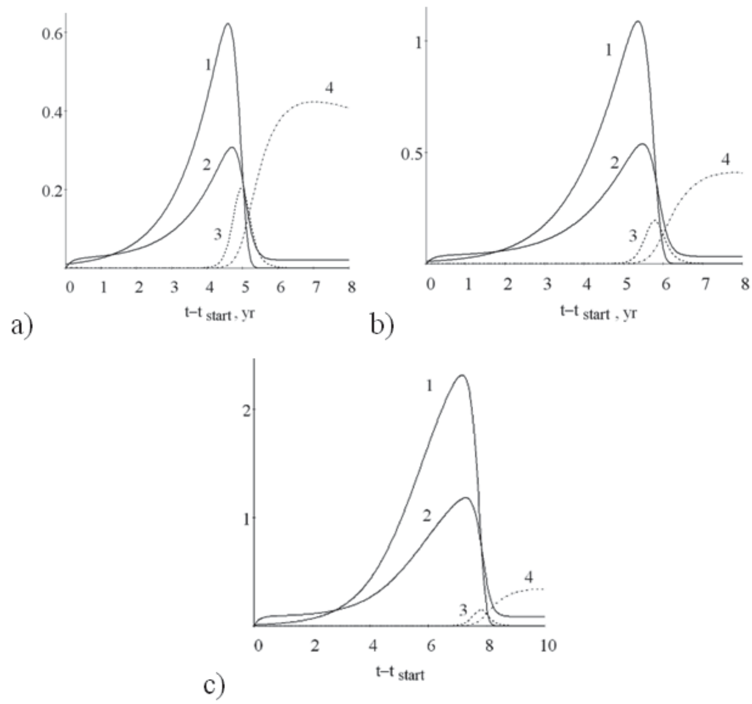


Figure 11. Dynamics of the main components of the immune system under the conditions of toxin accumulation in a body. The length of accumulation of pollutants: (a) 2 years, (b) 4 years, (c) 8 years. Level of water pollution is 13.8 MPCs. The curves: 1 – pathogenic microorganisms V, 2 – degree of organ damage of a body, m, 3 – C, 4 – F.

When the pollution is on the increase up to 4.5–13.8 MPC for water intake in areas of nitrate anomalies N III and N IV, we see that the risk increases with the increase of time when poor quality water is used and toxin or products of their change in a body, and also increases with the increase of pollution level in Figures 9a and 10a, b.

While comparing Figures 9b and 11a–c, we can see that while using water of poorer quality, the disease treatment lasted longer up to 8 days (Figure. 11c) in comparison with cleaner water where the length makes up 4.5, 5.25, 6,25 days (Figure 11a–c). Organ damage and the severity of the effects in case (9b) does not exceed 18% in comparison with 30, 55 and 120% (death at $m > 100\%$) for cases (Figure 11a–c). Disease progress with 18% of organ damage may happen without or with little symptoms – without loss of working capacity, and as a consequence – the absence of losses in production cycle due to temporary disability of an employee.

With the increase of stay under unfavourable conditions (concentrated chemical factor) the number of antigens increases (curve 1), and organ damage is on the increase as well (curve 2), with stable number of immunocompetent cells C and F. These effects lead to complicated contagious disease and considerable loading on body resources, developing of complications.

Pollutants availability in potable water leads to longer time of organ damage with the absence of massive immune system response (the peak of antigens – curve 1 Figures 9b and 11a–c): for instance, for pollutant exposure over 1 year this time span is 4 days, for pollutant exposure 8 years – 7 days. The length of self recovery increases from 5 days (Figure 9b) to 6.4 days (Figure 11b). In the last instance (Figure 11c) the high value of organ damage may be fatal (lethal case).

Thus, bioindicative virtual model demonstrates dangerous effect of toxins accumulation in a body and manifestation of this effect in some time 2–8 years and more. Such peculiarity is characteristic also for oncological diseases; latent period is about 30 years from the onset of this factor influence.

As a result of modelling, a forecast maps of general death rate have been drawn, the risk of oncological pathology development as a result of use of polluted subsoil waters by nitrates, Pb, Mn, Fe, Cu.

Comparing Figures 5, 6 with 12, we can see that the model gives adequate results of population health quality depending on the level of subsoil waters pollution that are used for domestic needs, including food.

The verification of the suggested model for the River Prut and Dniester water quality data (Moraru 2006) shows that mutagenic effect should be expected for risk values higher than 2.8 (the ratio of maximum pollution level for this paper is 2.5 MPC) where organ damage value is $m = 0.27$ for the Prut river. For risk value 3.71 (ratio of maximum pollution value is 4.6 MPC) where organ damage value is m = 0.383 for the Dniester river. We have to mention that the model takes into account only inorganic pollution, and the rest of the components are not taken into account, but such a possibility is feasible for the model.

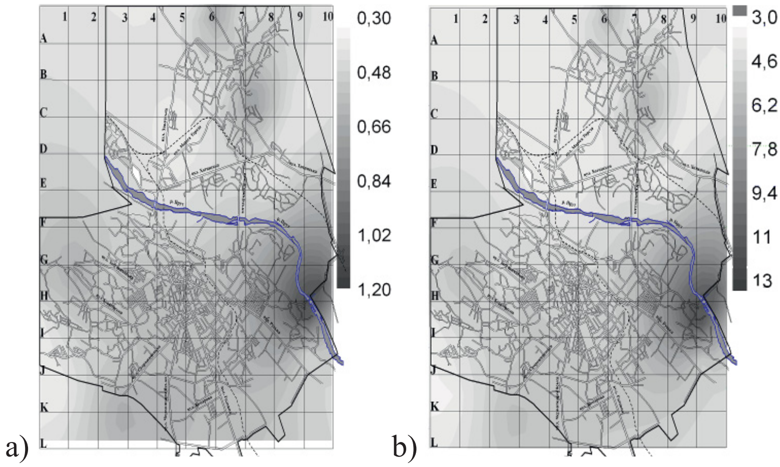


Figure 12. Forecast maps of oncological pathology risk (a), and general death rate (b).

The provided in Moraru (2006) analysis proves that in general qualitative and quantitative composition of river water is dangerous for use as potable water in centralized water supply. It is connected with chemical type pollution that creates favourable conditions for bacteriological pollution which is proven by our analysis (Figure 2). Likewise the outcome that the ecological state of the rivers causes the mutagenic activity of water demonstrating real state of water pollution and causes of oncological diseases.

Therefore to provide water supply of safe quality for lengthy consumption it is necessary to use the methods of water treatment enabling to treat the water with pollution level (aggregate value) <1.0 MPC. And thus the best water intake in such situation for Chernivtsi is artesian wells.

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EXAMPLES OF RECONSTRUCTION AND EXTENSION OF GROUP WATER SUPPLY SYSTEMS IN THE CZECH REPUBLIC

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Abstract. The paper provides two examples of extension and reconstruction of group water supply network in The Czech Republic. Both projects represent solution to problems with provision of potable water in adequate quantity and quality. The first project aimed to construct new water infrastructure and reconstruct existing infrastructure within the Dyje river basin (namely Břeclavsko region). Within the project, extension of the existing main water supply network was implemented due to a bad quality of local water resources. The second project proposed reconstruction of the existing water main supply system due to a poor raw water quality of the source, obsolete treatment technology and unsatisfactory technical condition of the main water supply system in the Třebíčsko region.

Keywords: water supply, construction, reconstruction, Břeclavsko region, Třebíčsko region

1. Introduction

Currently more than 92% of inhabitants in The Czech Republic are supplied with drinking water from water supply systems. Most of the water supply infrastructure in The Czech Republic was built in the 1960s to the 1980s (Látal and Hlaváč 2010). This paper aims to present two examples of the projects that were designed and implemented in The Czech Republic. The first project presented in this paper was designed to supply thirteen municipalities of the Břeclavsko region with drinking water of adequate quality. The second project

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of this paper is an example of reconstruction of main water supply system in the Třebíčsko region. The main water refers in this context to the water supply systems at a district level.

2. Břeclavsko – Reconstruction and Construction of the Water Infrastructure within the Dyje River Basin

The project of reconstruction and construction of the water infrastructure in the Břeclavsko region is located in the southeast of the Czech Republic (see Figure 1). It deals with water supply and sewerage of the Břeclavsko region (AQUA PROCON 2008). The project follows the Strategy of The Cohesion Fund and Government Decree 125/2004. The overall objectives of the project are to:

Reconstruct the existing wastewater treatment plants to comply with EC Directive 91/271/EEC on Urban Waste Water Treatment (UWWT Directive) and EC Directive 86/278/EEC (Sewage Sludge Directive)
Reconstruct and construct sewerage network.

Reconstruct and construct water treatment plants and related water mains to achieve compliance with EC Directive 98/83/EEC on the Quality of Water Intended for Human Consumption (Drinking Water Directive)

Due to its complexity the whole project has been divided to ten subprojects (see TABLE 1).

TABLE 1. Overview of ten subprojects within reconstruction and construction of water infrastructure in the Břeclavsko Region (based upon AQUA PROCON 2008).

Number and basic description of subprojects	
1	Břeclav – WWTP 50,543 PE and sewerage 6.3 km reconstruction and completion
2	Mikulov – WWTP 24,850 PE and sewerage 2.2 km reconstruction and completion
3	Hustopeče – WWTP 9,900 PE and sewerage 6.4 km reconstruction and completion
4	Velké Pavlovice – WWTP 5,400 PE and sewerage 2.3 km reconstruction and completion
5	Valtice – WWTP 9,700 PE and sewerage 3.0 km reconstruction and completion
6	Podivín – WWTP 3,500 PE and sewerage 1.3 km reconstruction and completion
7	Kobylí – new WWTP 2,420 PE and sewerage 8.3 km construction
8	Lednice – WWTP 12,000 PE and sewerage 7.3 km reconstruction and completion
9	Pohořelice – WWTP 9,900 PE and sewerage 5.4 km reconstruction and completion
10	Břeclavsko – water supply
– WTP 140 l/s upgrading and reconstruction	
– new main water supply system 13.5 km construction	

Subprojects 1–9 dealt with reconstruction and construction of WWTPs and sewerage network in the region. Except for one location (WWTP Kobylí) all wastewater treatment plants in the region have been upgraded and sewage network was reconstructed and extended. The last subproject dealt with drinking water supply of 13 municipalities in the vicinity of the town Mikulov, the Břeclavsko Region.

Figure 1. Reconstruction and construction of water infrastructure in the Břeclavsko Region – location of the subprojects.

2.1. WATER SUPPLY IN BŘECLAVSKO REGION AND MAIN REASONS FOR IMPLEMENTATION OF THE SUBPROJECT

The following part will discuss subproject number 10 – extension of main water supply system and reconstruction water treatment plant Lednice. In total thirteen municipalities to the southwest of Mikulov were supplied with water from local sources (see Figure 2). It was not possible to further exploit these sources due to high level of contamination (mainly nitrates and sulfates) resulting from intensive agricultural production. In the region there was only one water treatment plant (WTP) in Lednice that supplied water in adequate quality and quantity. The plant treats water from underground sources with increased content of iron and manganese. It was built in the beginning of 1960s and was further reconstructed in the first half of the 1970s. The purpose of the latter reconstruction was to increase capacity of the plant to 100 l/s. However, the capacity of the WTP was not sufficient to connect 13 municipalities in the project area. Furthermore the technological equipment was obsolete and at the end of its operability. The building parts of the plant were in a bad technical condition.

2.2. BASIC DESCRIPTION OF THE PROPOSED SOLUTION

As it was mentioned earlier, the aim of this subproject was to provide inhabitants and other water users in the region with water of adequate quantity and quality. A new delivery system was constructed and connected 13 municipalities of the region to the WTP Lednice. The project proposed construction of these structures: (1) pumping station Mušlov, (2) pressure main pipeline from pumping station Mušlov to water tank Březí, (3) water tank with pumping station Březí, and (4) pumping station Novosedly.

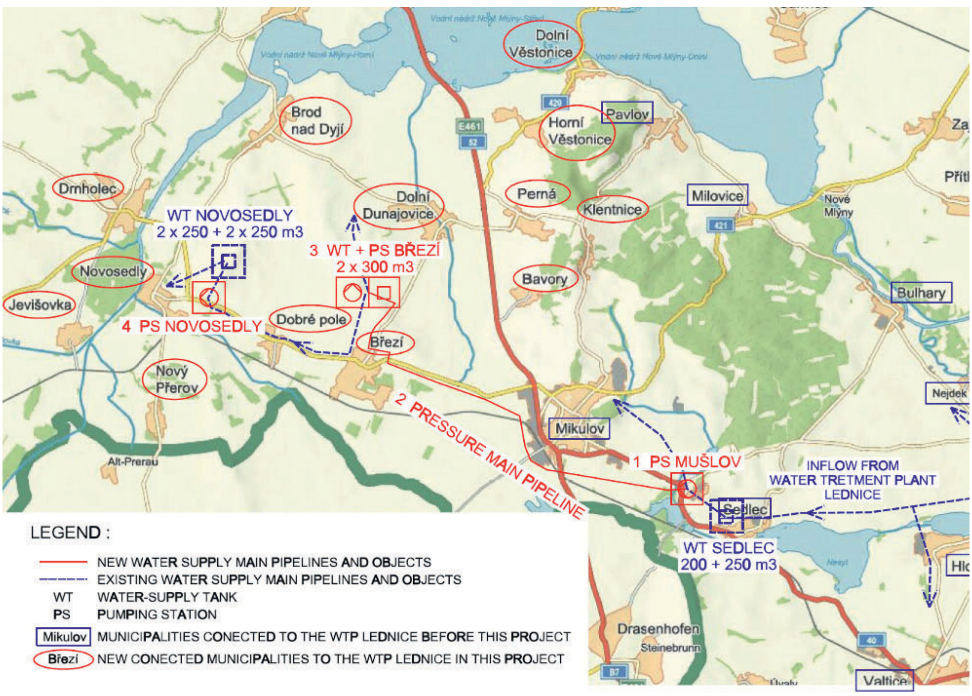

Figure 2. Newly connected municipalities to the WTP Lednice.

New pumping station Mušlov was constructed instead of the previous one (Figure 6). In the station two pumping units were installed. One supplies water through the existing network to the town Mikulov and the second unit pumps water to the newly-built main pressure pipeline to the water tank Březí. The new WT Březí was placed instead of the previous tank. The capacity of the tank was increased from 250 to 2 × 300 m^3. A disinfection system Cl_2 was installed in this tank to ensure water disinfection (Figure 7). From this tank water is transported by gravity through the existing network to municipalities Březí, Dobré Pole and to the new pumping station Novosedly (Figure 8). One pumping unit was installed to the water tank Březí to pump water is through the existing pipeline to the existing water tank Dolní Dunajovice. Investment costs for the new water supply infrastructure were €3.9 million.

As the last step of the project design, overall reconstruction of WTP Lednice was proposed to ensure provision of drinking water that complied with present legislation. Capacity of the WTP was increased to 140 l/s. Capacity of storage tanks was more than doubled from one tank of 650 m^3 to two tanks of 750 m^3. Old technological equipment was replaced and technology of water treatment was changed (Figure 3, 4 and 5). Investment costs of reconstruction reached €2.4 million.

Figure 3. Reconstruction of WTP Lednice – main building before (on the left) and after (on the right).

Figure 4. Reconstruction of WTP Lednice – accumulation tank before and after the reconstruction.

Figure 5. Reconstruction of WTP Lednice – pipelines and equipments before and after.

Figure 6. PS Mušlov – traditional architecture of the wine region – pump. station as a wine-cellar.

Figure 7. WT Březí – traditional architecture of the wine region – water tank as a wine-cellar.

Figure 8. PS Novosedly – traditional architecture of the wine region.

3. Třebíčsko – Ensuring the Drinking Water Quality within the Water System of Southwest Moravia

This chapter would like to present a project with the overall objective to reconstruct the existing main water supply system in the Třebíčsko region. The project area is located in the southeast part of the Czech Republic (see Figure 9). The aim of the project was to improve quality of water supply in the region to comply with present Czech and European legislation. Main reasons for project implementation were (1) poor raw water quality of the source – water reservoir Vranov in a range of parameters like AOX, phenols, (2) obsolete treatment technology and unsatisfactory technical condition of the building parts of the water treatment plant Štítary, (3) poor technical condition of water supply network like pipelines, armatures, pumps and other equipment. Water mains were made of black steel and at the time most of them was at the end of its operability. Parts of water mains from black steel caused secondary pollution of transported water.

The project proposed reconstruction of water treatment plant Štítary and reconstruction of three water mains and related structures. These mains deliver water from different sources (WTP Štítary, WTP Mostiště and water source Heraltice) to the district town of Třebíč and other municipalities in the region (AQUA PROCON 2009). As the entire project is extensive, it has been divided into four subprojects (see Figure 9).

TABLE 2. Overview of four subprojects located in the Třebíčsko Region (based upon AQUA PROCON 2009).

Subproject	Proposed measures	Investment costs
1. Reconstruction of WTP Štítary	Reconstruction of the plant and water treatment technology Increase of capacity to 200 l/s	€5.9 million
2. Reconstruction of water main Častohostice – Třebíč	New water mains in length 10.1 km Reconstruction of 2 pumping stations and 3 water tanks	€5.4 million
3. Reconstruction of water main Ovčírna – Třebíč	New water mains in length 7.6 km Cementation of internal surface of pipelines – 0.6 km Reconstruction of 1 pumping station and 2 water tanks Construction of 2 armature shafts	€3.5 million
4. Reconstruction of water main Heraltice – Třebíč	New water mains in length 11.2 km Cementation of internal surface of pipelines – 1.3 km Reconstruction of 2 water tanks	€2.5 million

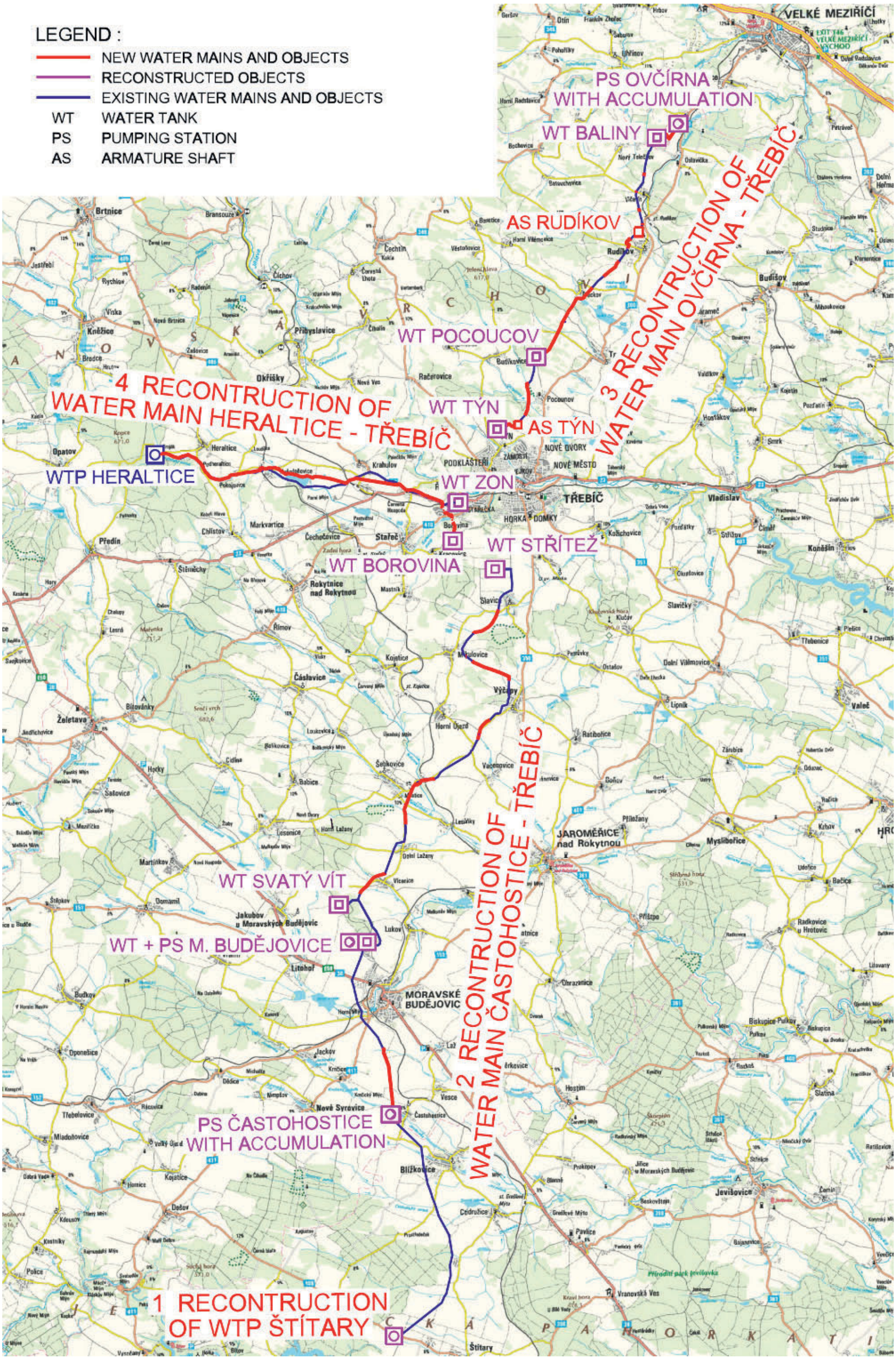

Figure 9. Location of four subprojects in the Třebíčsko region.

The first subproject proposed an entire reconstruction of the water treatment plant Štítary. The plant treats water from water reservoir Vranov. The reservoir is intensively used for recreation and worsening water quality in the reservoir was one of the reasons for implementation of this subproject. The aim was to modernize treatment technology and to increase capacity of the plant to 200 l/s due to planned connection of other consumption areas. Water treatment technology was reconstructed. New equipment in flocculation and sedimentation tanks and in open sand filter, new chemical management, and new disinfection equipment were installed. Furthermore, water treatment technology was completed with filtration on GAU filters.

Treated water from WTP Štítary is distributed to the main water system. Due to a poor technical state of the water main from Častohostice to Třebíč, old part of the water mains from black steel was replaced by new pipelines from ductile iron in the length of 10.1 km. It was necessary to reconstruct two pumping stations (Častohostice and Moravské Budějovice) and three water tanks (Moravské Budějovice, Svatý Vít and Střítež). New stainless steel pipelines and technological equipment were installed in the pumping stations and water tanks (Figure 10).

The town of Třebíč is not only supplied with potable water from water reservoir Vranov but also from water treatment plant Mostiště located to the north and water source Heraltice located to the west of Třebíč. Because the technical state of these water mains was also poor, reconstruction of the two main water systems was implemented. Firstly, the project proposed reconstruction of water network from pumping station Ovčírna to Třebíč in the length of 7.6 km. Secondly, water main from the source Heraltice to the water tank Borovina in the vicinity of Třebíč was reconstructed in the length of 11.2 km. In the water network all parts from black steel were replaced with new pipelines from ductile iron. Cement lining of internal surfaces was applied in the total length of 1.8 km in pipes from black steel that were in a good state. All water tanks and pumping stations were reconstructed and new technological equipment was installed (Figure 11).

Capacities of different water mains are designed to ensure water supply in to approximately 100–110 l/s in case of impair or failure of one of the mains. This capacity will cover usual water consumption of the area supplied. Key points of the network were equipped with monitoring devices to control water quality from a dispatching center in Třebíč.

Figure 10. WT Borovina – before (on the left), after (on the right).

Figure 11. PS Častohostice – old horizontal pumping units (on the left) needed larger space than new vertical pumping units space (on the right). A pumping unit contains three pumps. Each pump is equiped with a frenquency converter for smooth power regulation.

4. Conclusions

Reconstruction and extension of water supply network is a key challenge to ensure provision of potable water in adequate quality and quantity and a prerequisite to fulfill commitments towards European directives and national legislation. The two examples shown in this paper illustrated complexity of behind consideration of each project implemented on the regional level.

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NOM REMOVAL FROM FRESHWATER SUPPLIES BY ADVANCED SEPARATION TECHNOLOGY

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Abstract. Natural Organic Matter (NOM) present in drinking water supplies is not known to have any direct effects on human health; however, its reactivity with dissolved and particulate species significantly impacts on water quality and treatment needs. It is known nowadays that NOM can be removed by a variety of methods, including molecular sieving through nanofiltration membranes, coagulation with subsequent floc separation, oxidation followed by biofiltration and sorption processes including chemisorption (ion exchange), and physical adsorption (activated carbon). Evolution of water-related directives and more restrictive standards for drinking water, however, constitute the requirements for investigating new, more efficient and cost-effective treatment processes. The paper contains an overview on the state-of-the-art methods for NOM removal from supply waters, then describes a new technology, developed and patented by the research center of Veolia Environment, which effectiveness has been tested and validated on the supply water source of a plant located in Brittany (France).

Keywords: Natural Organic Matter (NOM), coagulation, nanofiltration, adsorption, oxidation, clariflocculation

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1. Introduction

Surface water bodies contain diverse types of aquatic Natural Organic Matter (NOM), produced by a variety of sources. NOM can be microbially derived (autochthonous), resulting from processes such as leachate and extracellular release of algae and bacteria, and terrestrially derived (allochthonous), originating from decomposition and leaching of plant and soil organic matter. NOM is therefore a complex heterogeneous mixture of organic compounds, consisting of aromatic, aliphatic, phenolic, and quinonic structures with varying molecular sizes and properties. The complexity and heterogeneity of aquatic NOM have made its structural and functional characterization extremely difficult (Swietlik and Sikorska, 2005). One common approach for its characterization is to divide the mixture into the hydrophilic and hydrophobic fractions. The hydrophilic fraction includes, e.g. carboxylic acids, carbohydrates and proteins, while the hydrophobic fraction includes humic substances (HS) (Crouè et al. 2000). HS is a term referring to a broad class of interrelated compounds, including, for example, humic and fulvic acids. Compositions of HS vary from source to source with respect to, e.g. solubility and reactivity (Aiken et al. 1985; McCreary and Snoeyink 1980). NOM classification is represented in Figure 1 (Leenheer and Crouè 2003).

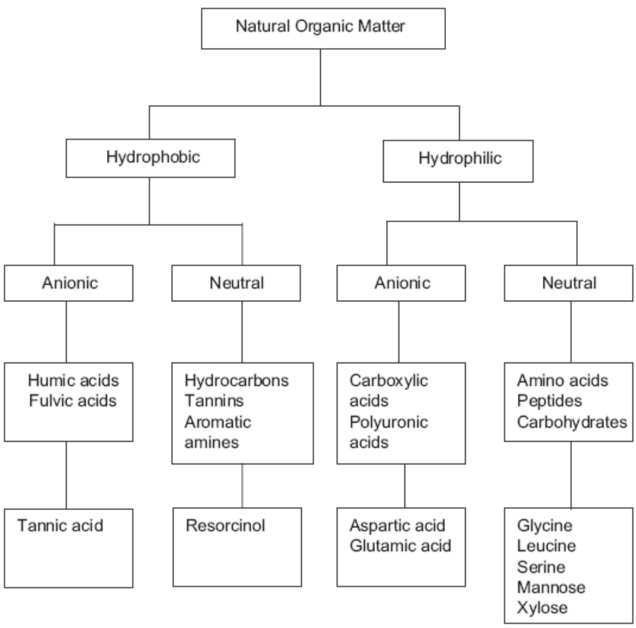


Figure 1. NOM classification.

Regardless of the source, NOM should be removed from drinking water for a number of reasons, including that it may: affect organolectic properties of water (color, taste and odor); react with disinfectants used in water treatment, thus reducing their disinfection power, producing undesirable disinfection by-products (DBPs) of various kinds, and influencing disinfectant demand; affect process design, operation and maintenance; affect stability and removal of inorganic particles; control coagulation conditions and coagulation performance, also influencing coagulants dosage demand; affect corrosion processes; affect biostability and biological regrowth in distribution systems; form complexes with, and increases mobility of, chemical substances found in nature; foul membranes; reduce adsorption capacity of granular or powdered activated carbon (GAC/PAC) by pore blocking; compete with taste and odor compounds for adsorption sites in GAC/PAC (Eikebrokk et al. 2006).

In drinking water treatment, NOM can be removed through a variety of mechanisms, including: coagulation, GAC adsorption, membrane filtration, and biological degradation. NOM may also be partially transformed through oxidation during an advanced oxidation process. Individual methods will be analyzed in the following section.

1.1. STATE-OF-THE-ART TECHNOLOGIES FOR NOM REMOVAL

1.1.1. *Coagulation*

Coagulation is probably the most commonly used method for NOM removal. The conventional process incorporates several physicochemical processes including rapid mixing, slow mixing (flocculation), sedimentation, filtration, and disinfection. Coagulation reactions take place almost instantaneously in the rapid mix stage of the water treatment process and continue until the water is filtered. The effectiveness of coagulation affects the efficiency of the subsequent sedimentation and filtration processes.

Effective coagulation is achieved through addition of charged (or other destabilizing) species into the water source. This process may be accomplished using coagulants, the two most commonly used in practice being: hydrolyzing metal ions Al_3^+ and Fe_3^+, typically supplied as aluminum sulfate ($Al_2(SO_4)_3{\cdot}14H_2O$), and ferric chloride ($FeCl_3{\cdot}6H_2O$). Aluminum sulfate, commonly referred to as alum, is the most widely used coagulant in water treatment processes.

NOM removal in this case is due to several mechanisms which include double layer compression, charge neutralization, sweep coagulation, and inter-particle bridging (Check 2005). Several factors influence the efficiency and effectiveness of coagulation by metal salts. These factors include, but are not limited to, coagulant dose, pH, alkalinity, temperature, and ions present in solution.

Ambient pH is critical in maximizing NOM removal effectiveness. Although maximum adsorption of both humic and fulvic acids occurs under acidic conditions, studies have shown that adsorption is the key mechanism involved in their removal over the entire pH range (Dempsey 1984). NOM removal by mineral adsorption occurs primarily due to Van der Walls forces or polarization arising from the rearrangement of macromolecules. Through this mechanism, polar moments in two adjacent molecules will cause a net attractive force. Hydrophobic humic molecules, the most easily removed by coagulation, are strongly influenced by physical absorption (Matilainen et al. 2002). However, there is a general consensus that higher molecular weight NOM compounds are more easily removed than their low molecular weight counterparts.

1.1.2. *Activated Carbon Filtration*

The adsorption behaviour of NOM is particularly difficult to understand due to its heterogeneous nature (Newcombe 1999). Studies showed that NOM adsorption is controlled predominantly by the relationship between its molecular size distribution and the pore size distribution of the carbon (Newcombe et al. 2002, Maitilanen et al., 2006). The lifetime of GAC filters can be expanded by reactivation, however, thermal carbon reactivation can lead to an enlargement of the macropores because of burn-off effects, increasing the removal of the high molecular weight NOM and decreasing that of low molecular weight (Boere 1992).

Direct AC adsorption is in general not recommended since the sorption capacity is quickly reduced by pore blocking caused by the large humic substance molecules. Coagulation prior to GAC filtration can remove particles that might clog the filter. Pre-coagulation also removes NOM, which reduces the loading on the GAC filters (Jacangelo et al. 1995).

GAC adsorption can be applied following water preoxidation by ClO_2; this may lead to the formation of organic by-products due to interactions between GAC, NOM and ClO_2. It has been observed (Swietlik et al. 2004) that ClO_2 may cause a break-up of the larger molecules, and alter the molecular size distribution of NOM towards smaller molecules. On the contrary, oxidation with small doses of ClO_2 can increase the molar masses of some NOM molecules. It was demonstrated that even a small dose of ClO_2 may significantly influence the adsorptivity of NOM onto GAC: indeed after ClO_2 oxidation, GAC adsorption of high molecular weight NOM was higher than that of unoxidized NOM (Swietlik et al. 2002).

1.1.3. *Membrane Filtration*

Nanofiltration (NF) technology has proved to be a successful alternative process for drinking water treatment, due to its superior removal of disinfection by-product precursors, minimal use of chemicals, reduction in sludge production, and potential for use in compact systems. The cost of this process is at the moment higher than those of coagulation and GAC adsorption (Table 1); however the rate of decrease in costs of this particular technology over the past years has been greater than that associated to other treatments.

NOM can be effectively removed by NF, and to a less extent, by tight-UF membranes through a combination of diffusion, convection, and electrostatic repulsion mechanisms. The dominant transport mechanisms of NOM through NF depends on the operating conditions as well as the size of solutes and pores.

The typical pore size of these membranes is 1–5 nm, operated at the pressure of 4–8 bar (Ødegaard et al. 2000).

TABLE 1. Qualitative summary of selected aspects of some technologies used for NOM removal (Jacangelo et al. 1995).

Treatment process	NOM removal efficiency	Process complexity	Process cost
Coagulation	Fair good	Low-medium	Low-medium
GAC adsorption	Very good	Medium-high	Medium
Nanofiltration	Excellent	Medium	Medium-high

A typical flow diagram of a membrane filtration plant is shown in Figure 2: raw water passes through a pre-treatment unit, normally a micro-sieve with openings of about 50 μm. After this, pressure is raised up to the operating pressure of the membrane unit by a circulation pump. Cross flow filtration takes place in the membrane unit resulting in a clean water stream (permeate) that has passed through the membrane and a dirty water stream (concentrate) that flows through a reduction valve, bringing its pressure back to atmospheric.

Since the reduction of calcium and bicarbonate concentrations through the membrane is about 15–30%, an alkaline filter (calcium carbonate) can be included in order to increase these levels.

The NF process is often adopted when NOM content/color is high (>30 mg/l) and turbidity low (<1 NTU). The most typical problems are those connected to capacity loss caused by membrane fouling. In most cases, this is due to excessive design flow, relatively to the characteristics of the water treated (high particle concentration and high NOM-content).

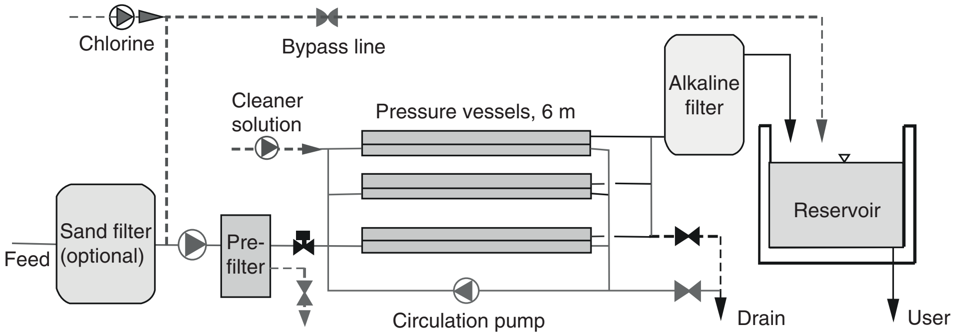


Figure 2. Typical flow diagram of a nanofiltration process.

Studies carried out in Norway (Ødegaard et al. 2010) showed that the criteria for success in operating NF-plant for NOM-removal consist of the use of low flux (<20 l/m^2h) combined with low recovery (<70%), use of cellulose acetate membranes (to avoid adsorption fouling) and adoption of proper cleaning procedures (daily with a diluted solution, combined with a more comprehensive chemical cleaning once or twice a year).

1.1.4. *Advanced Oxidation Processes*

An alternative group of technologies that can be used to remove NOM and minimize the formation of DBPs, is that of the Advanced Oxidation Processes (AOPs) (Chin and Berubè, 2005). AOPs are defined as near-ambient temperature processes that involve the generation of highly reactive radical intermediates, especially hydroxyl radicals. These radical are extremely reactive and capable of oxidizing some of the NOM present in raw waters. The most common process to generate ·OH is through the use of combined catalytic oxidant such as ozone-ultraviolet (O_3-UV) and hydrogen peroxide ultraviolet (H_2O_2-UV). Although all 3 of the above processes can produce OH, the O_3-UV process provides the maximum yield of ·OH per oxidant input (Gottschalk et al. 2000).

1.2. AN ALTERNATIVE ADVANCED SEPARATION TECHNOLOGY FOR NOM REMOVAL

Ballasted flocculation is a physical-chemical separation process that employs a high density additive (usually sand) to promote the formation of a heavier floc, which then settles more rapidly than in the traditional flocculation process.

In this instance, a patented version of the ballasted flocculation technology Actiflo-Turbo®, developed by Veolia Eau, was modified by means of activated carbon (PAC) injection into the pre-contact chamber, in order to verify its NOM removal capacity in a practical situation.

The system, denominated Actiflo®Carb (Figure 3), is equipped with a pre-contact tank where the incoming raw water flow is quickly mixed to the PAC (both fresh and recirculated), allowing NOM adsorption (contact time about 4 min). The subsequent additions of coagulants in a second smaller chamber at slow stirring speed, and then of polymers and Actisand® (a patented, "calibrated" type of sand) in a third flocculation basin, allow the quick generation of heavy flocs that are subsequently subjected to ballasted flocculation and sedimentation within a fourth basin equipped with tube settlers. The settled "sludge", consisting of spent PAC and Actisand®, is then recirculated to a hydrocyclone where the two components are separated and recovered, to be reused in the process.

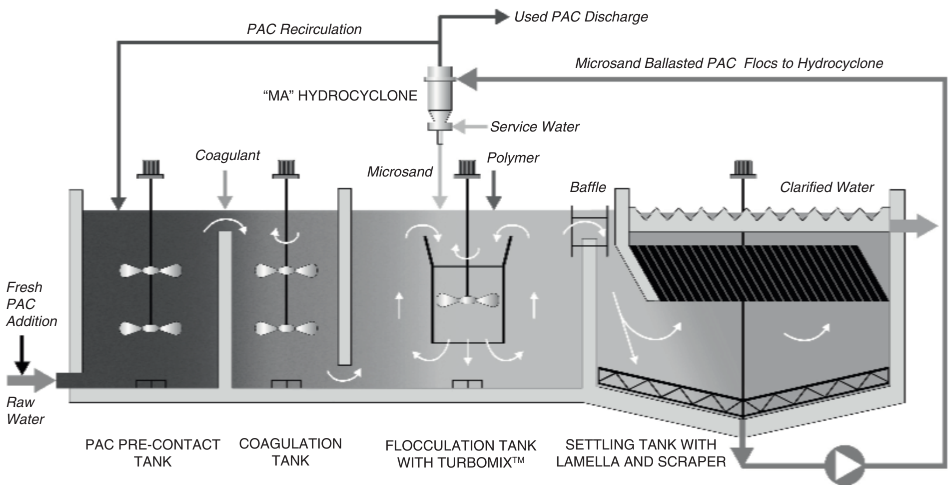


Figure 3. Actiflo®Carb process flowsheet.

An Actiflo®Carb pilot plant (Figure 4), with the capacity of 50 m^3/h was installed at a water treatment plant in Brittany (France), where supply water from the local lake, rich in NOM contents, is currently treated to drinking water standards. The pilot was positioned off-line after the existing flotation tank and substituted the existing oxidation/sand filtration/oxidation/GAC process train in treating part of the water, in order to verify whether these units could be substituted more efficiently and economically.

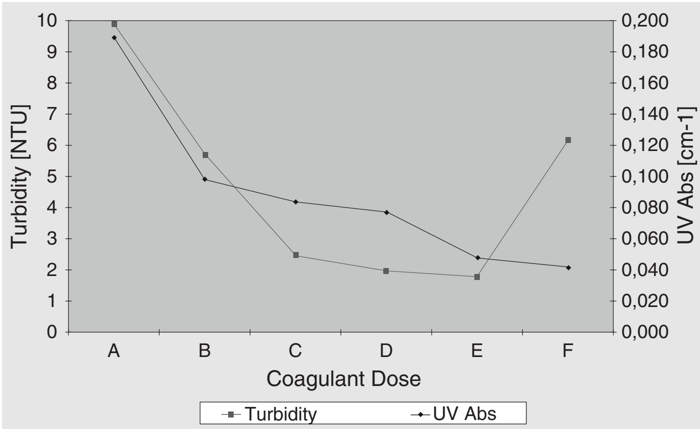
Figure 4. The Pilot plant.

2. Preliminary tests

In order to optimize the performance of the Actiflo®Carb plant, jar tests were carried out to determine the ideal type and best dosage of reagents that should have been be added during the process. The tests also allowed to determine the sequence with which reactives ($FeCl_3$, aluminum, polymers and PAC) should have been added; other variables included operational pH, Actisand® composition (selected granulometry) and contact times in the basins. In the case of PAC, one additional parameter was the ratio between new and recirculated PAC. A large number of possible combinations among these factors were investigated.

2.1. RESULTS

Some of the results are illustrated in the following figures. Some of the specific values/types of reactants have been withdrawn due to industrial product development reasons, and described as “Dose AB, etc.” or “Microsand A, B, etc.”. Figure 5 shows the optimal dosages for the coagulant agent $FeCl_3$, which affects turbidity measured as UV adsorbance. Figure 6 shows the variation of turbidity and absorbance with varying selections and dosages of Actisand®.



Figures 5. Optimal dosages for the coagulant.

Figure 7 shows the effect of the organic coagulant polymer dose on turbidity and UV absorbance, while Figure 8 shows the influence of PAC contact time on effluent turbidity and UV absorbance.

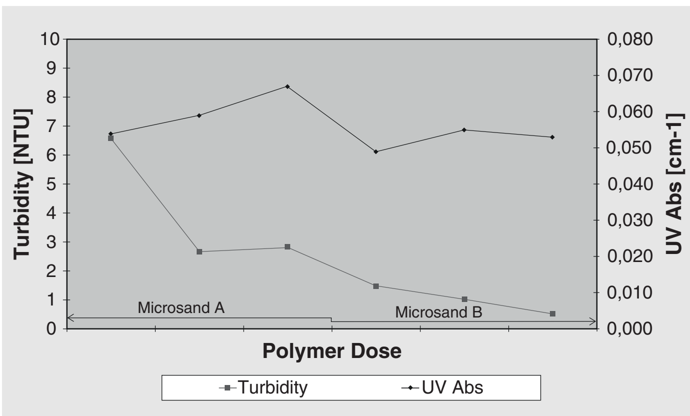


Figure 6. Variation of turbidity and absorbance with varying types and dosages of Actisand®.

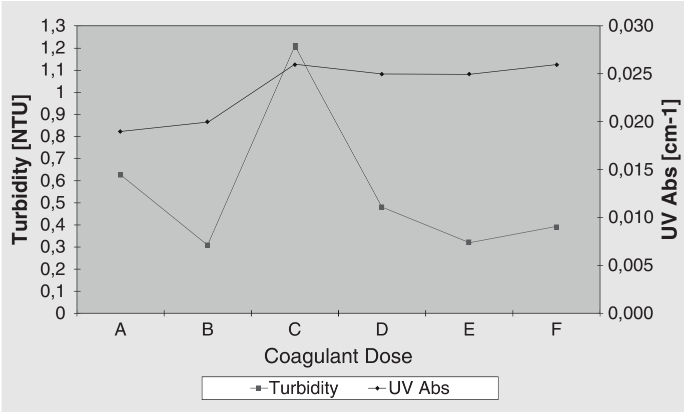


Figure 7. Effect of the organic coagulant polymer on turbidity and UV absorbance.

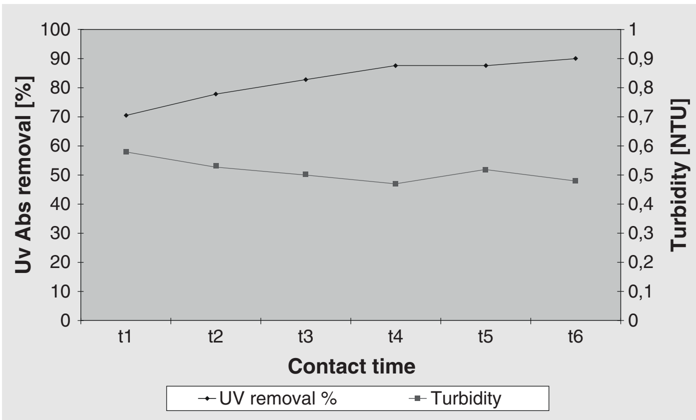


Figure 8. Influence of PAC contact time on effluent turbidity and UV absorbance.

NOM removal was determined in terms of COD and turbidity removal efficiencies using a UV turbidimeter, which was preventively cross-calibrated and proven to carry very high correlation with traditional measurements methods. The results obtained show that COD removal is somehow proportional to PAC dosages (Figure 9), optimal PAC dosages lie generally below 25 mg/l, as higher feed rates do not achieve a correspondingly higher COD removal.

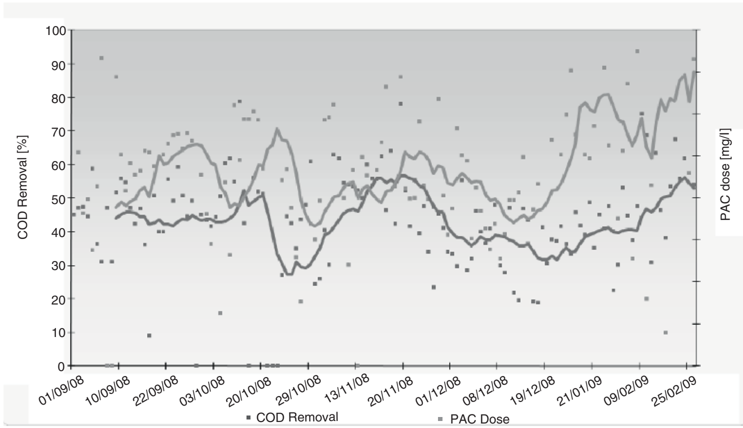


Figure 9. Relationship between PAC dosage and COD removal.

Turbidity is an important control parameter representing the correct operation of the flocculation process (Figure 10). As particles with diameter between 1 and 10 µm (mostly colloidal) do not settle well by gravitational forces alone, they constitute the primary turbidity cause in the raw water. Surface properties, not mass, is the factor that keeps them in stable suspension, therefore consistent floc formation is a key requirement to achieve their removal. An optimal identification of reagent types and dosages allowed to obtain consistent values of effluent turbidity well below 0.5 NTU even with influent values >4 NTU.

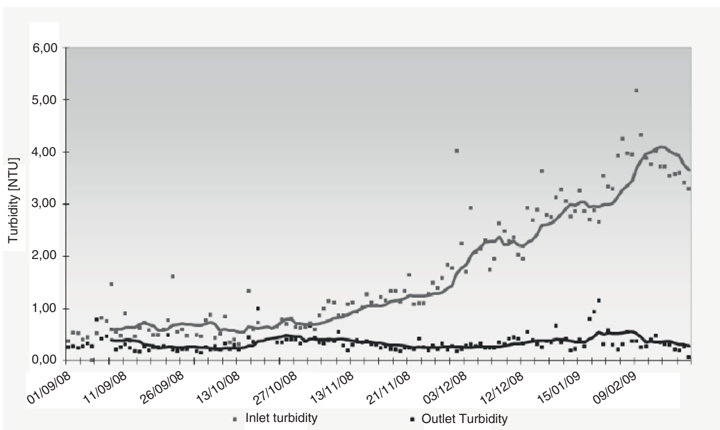


Figure 10. Influent and effluent turbidity during the study.

3. Conclusions

The use of PAC to enhance drinking water treatment processes can nowadays be considered an almost standard procedure. This study presents an innovative application where AC is added to the patented reactor Actiflo-Turbo®. This unit is a clari-flocculator whose special performance is based on patented design and on the use of a special "calibrated" type of sand that allows rapid homogeneous floc formation and their very fast settling. Actiflo®Carb thus combines the benefits of ballasted clarification and of the adsorption capabilities of carbon. This unit, located downstream of a existing pretreatment, allowed significant additional removals of organic matter (as COD, >50%) and turbidity (from 50% to 90%) compared with more traditional methods. The key to the success of this process is its correct setup with the identification of optimal types and dosages of reagents. Based on the results of the tests conducted it is foreseeable that this new technology could be used for removal of other hard-to-tackle pollutants potentially contained in freshwater supplies.

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ADVANCED WASTEWATER TREATMENT

THE INFLUENCE OF SEASONALITY ON THE ECONOMIC EFFICIENCY OF WASTEWATER TREATMENT PLANTS

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Abstract. Many tourist areas are often characterized with seasonal water demand. The influence of seasonality on water management is more intensive in the context of water scarcity. Thus the use of so-called non-conventional water resources in these areas becomes a key aspect. In this sense, efficient performance, both in technical and cost terms, favors water reuse possibilities and, therefore, increases the supply of non-conventional resources. In tourist areas, seasonality is a determining factor in the efficiency of wastewater treatment plants (WWTPs) as these are operating at full capacity only during the summer season while the rest of the year they have under-utilization problems. Using the Free Disposal Hull (FDH) methodology, this paper analyzes the efficiency differences between those WWTPs located in tourist areas with strong seasonality, in relation to those located in non-tourist areas. Moreover, the efficiency of WWTPs with extended aeration technology has been determined, as well as the efficiency of plants with activated sludge processing.

Keywords: Seasonal water demand, Economic efficiency, Wastewater treatment plants, Free Disposal Hull (FDH) methodology, Extended Aeration Technology

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1. Introduction

Water reuse presents the major advantage of providing an alternative low-cost resource that can serve to limit water shortages, better preserve natural resources, and contribute to integrated water management systems (Lazarova et al. 2007). This is the reason for the recognition of the growing importance of water reuse in many regional areas such as coastal zones, which are subjected to harsh conditions of water stress.

At the same time, water scarcity increases in coastal zones which are often characterized by high population density and intense tourism and economic development, which translates into an intense seasonal water demand (Salgot and Tapias 2004). Therefore, the use of non-conventional water sources becomes a key aspect. Accordingly, water reuse in tourist zones has some specific characteristics compared to other areas, including large seasonal flow variations, the need for efficient onsite wastewater management, and higher treatment requirements to minimize the potential health risks (Borboudaki et al. 2005).

Despite the benefits of water reuse, any given analysis of its potential in a particular region requires an extensive knowledge of the wastewater treatment process from both a technical and cost point of view (Hernandez and Sala 2009). Although the collection of performance indicators associated with the processes of wastewater treatment is not a widespread procedure in the literature, the usefulness of this indicator has been demonstrated. According to Hernández and Sala (2009), efficient performance of wastewater treatment plants (WWTPs), favors water reuse possibilities.

Despite the undeniable applicability of efficiency indices in the field of water reuse, this methodology needs to be adapted to the specific area of study. Thus, in the case of seasonal tourist areas this is certainly a factor in determining the efficiency of processes as it assumes that a WWTP is operating at full capacity only during the summer months and suffers problems of underuse the rest of the year (Muñoz and Caus 2005). The population fluctuations imply significant variations in the flow of wastewater to be treated and in the pollutant load of same.

With the aim of contributing to a better understanding of the influence of seasonality on the treatment processes and the real options for the reuse of reclaimed water, in this paper we want to analyze the efficiency of a group of WWTPs using the methodology known as Free Disposal Hull (FDH). For this reason, we have carried out an empirical study on two samples of WWTPs operating in the Region of Valencia (on the Mediterranean coast of Spain) and studied the differential behavior between those located in tourist areas with a strong seasonality, with respect to those that do not exhibit seasonality. This analysis is applied to two different types of treatment. On the one hand, we determine the efficiency of those plants whose technology is extended aeration (EA) and, on the other hand, those plants whose process is activated sludge (AS). Thus, after applying the FDH methodology, information is provided on which of the two technologies is more affected by seasonality.

2. Methodology

2.1. DETERMINATION OF SEASONALITY

The main objective of this study is to evaluate the influence of seasonality on the efficiency of WWTPs. For this reason it is necessary to determine which plants do and do not show seasonality. The influence of seasonal factors can be determined based on two criteria: volume of wastewater treated and eliminated pollutant load expressed as population equivalent (PE). Since the municipalities served by the analyzed WWTPs do not have separate sewerage networks, during rain events these WWTPs receive a large amount of storm water together with wastewater. It is considered that the appropriate parameter to determine the seasonality of the plant is PE.

Having defined the criterion of seasonality and knowing the monthly data processed by each of the analyzed plants, those WWTPs that show seasonality have been identified. In the absence of contributions in the literature on this area, the identification criterion for seasonal behavior has been considered as being where the average number of PE treated during the months of July and August is higher by 15% compared to the annual average.

2.2. EFFICIENCY

From an economic point of view, the term efficiency is associated with a rational use of available resources, that is to say, it is used to describe a production process that uses in an optimal way all the factors of production according to the existing technology. Farrell (1957) became the pioneer in the study of frontier functions used as references for obtaining efficiency measures for each farm. At its most fundamental, a DMU (Decision Making Unit) is considered efficient if it is located on the efficient frontier. On the other hand, a DMU is considered inefficient when situated under the frontier. Data Envelopment Analysis (DEA) and FDH are two alternative techniques available for coming up with an approximation of the efficient frontier. These two mathematical programming techniques permit the measuring of the relative distance from where an individual DMU is found to the estimated frontier and, therefore, also produce measurements of the relative inefficiency of the cited DMU compared to the remaining units. Introduced by Charnes et al. (1978), DEA has been widely used because it can be applied in a wide variety of situations and has also undergone a number of theoretical extensions that have increased its flexibility and applicability. For a description of this method, see Hernández and Sala (2009).

As a continuation of the DEA methodology, the FDH technique was proposed in the work of Deprins et al. (1984) and since then its use has been spreading in different types of applications (Tulkens 1993; Tulkens and Vanden Eeckaut 1995; among others). A comparative study of these two approaches can provide information about the complexities of measuring productive efficiency (Grosskopf 1996; Simar and Wilson 2000). DEA and FDH, as two deterministic nonparametric methods, do not assume any particular functional form of the frontier. Instead, they consider that the best technology in practice is the frontier of a set of production possibilities constructed as the envelope of the observations. The basic motivation for using the FDH methodology in this work, is to ensure that efficiency measurements calculated for a reference boundary are only constituted of actual production units.

According to the model FDH, given $K = 1,2,...,k,...,K$ production units or WWTPs, each one of which uses a vector of inputs $x^k = (x_1^k, x_2^k, ..., x_N^k)$ (Nx1) to generate a vector of outputs $y^k = (y_1^k, y_2^k, ..., y_M^k)$ (Mx1), where λ is a vector of variable intensity (K × 1). The measure of efficiency θ is obtained by solving for each unit k' the following integer linear programming problem:

$$\begin{aligned}
& E_I(y^{k'}, x^{k'}) = Min\ \theta \\
& s.a \\
& \sum_{k=1}^{K} \lambda_k y_{km} \geq y_{k'm} \quad m = 1,...,M \\
& \sum_{k=1}^{K} \lambda_k x_{kn} \leq \theta x_{k'n} \quad n = 1,...,N \\
& \sum_{k=1}^{K} \lambda_k = 1,\ k = 1,...,K \\
& \lambda_k \geq 0,\ k = 1,...,K \\
& \lambda \in \{0,1\}
\end{aligned} \tag{1}$$

The measure of efficiency $E_I(y^{k'}, x^{k'}) = \theta$ is bounded between 0 and 1. Specifically, it is considered that a unit of production is efficient if θ = 1, while it is inefficient if $0 \leq \theta < 1$. The difference between the index θ and the value 1 is the potential reduction in inputs to obtain the same outputs.

Once the efficiency indexes have been obtained, we aim to assess the possible relationships between this efficiency measurement for each WWTP and the seasonality. In order to achieve this, a second stage analysis is undertaken. From among the few options the literature provides, we use the Mann-Whitney Test (the non parametric equivalent of the Variance Analysis of one factor) as the most suited to our objective. This entails ascertaining whether or not there are significant differences in the mean values obtained in the efficiency index between the two groups in which the sample of plants have been divided, in terms of the seasonality.

Also, using these results as a basis (which could verify the more efficient operations in non-seasonality plants compared to plants affected by seasonality), we want to calculate to what extent seasonality plants could reduce their input costs if, given their vector of output, they operate with the same efficiency as the group of non-seasonality plants. To do this we use the following expression:

$$ICR = \left(E_I^{n5} - E_I^{5}\right)C_{mean}^{5} \tag{2}$$

where,

ICR: Input Cost Reduction,

E_I^{ns} : refers to the mean value of efficiency for the non-seasonality plants,

E_I^{s} : symbolizes the same indicator, but for the seasonality plants, and

C_{mean}^{s} : represents the average cost of inputs for the seasonality plants.

Through the application of this methodology, it is possible to obtain a better understanding and to quantify the influence of seasonality on the efficiency of WWTPs and, consequently, the options for water reuse. The empirical application presented is based on a sample of plants using two different types of technology: extended aeration (EA) and activated sludge (AS). For each type of treatment, the plants have been divided into two groups according to the influence of seasonality. A detailed description of the sample used is available in the following section.

3. Sample Data Description

The data used in this empirical application correspond to 76 WWTPs located in the Region of Valencia (Spain). The total sample of plants has been divided into two groups depending on the applied technology. The treatment capacity of plants with EA technology is between 10,000 and 75,000 PE, whereas for AS it is from 30,000 to 150,000 PE. We have tried to find some consistency in the ability of plants to avoid the effects of this variable on efficiency levels. The AS process is used by 32 plants of which 14 are affected by seasonality (according to the criteria above), while 44 plants carried out the treatment process using the EA technology with 20 plants showing seasonality effects.

For both technologies, it is thought that as a consequence of the treatment process, four outputs are generated: suspended solids (SS) (y_1), organic matter measured as chemical oxygen demand (COD) (y_2), nitrogen (N) (y_3) and phosphorus (P) (y_4). The inputs necessary to carry out the process are: energy cost (x_1), labor cost (x_2), reagent (x_3), maintenance cost (x_4), waste management cost (x_5) and other costs (x_6). These variables are described in Table 1. Statistical information has been supplied for the year 2008 by the Regional Wastewater Treatment Authority (EPSAR).

TABLE 1. Sample description.

			AS Treatment		EA Treatment	
			Without seasonality	With seasonality	Without seasonality	With seasonality
Number of WWTPs			18	14	24	20
PE			58,639	45,789	21,364	17,603
Variable						
Output (kg/year)	SS	y_1	1,150,957	940,527	206,662	314,302
	COD	y_2	3,945,548	1,769,063	330,994	641,874
	N	y_3	134,716	81,328	13,526	28,218
	P	y_4	34,696	16,998	2,057	6,045
Inputs (€/year)	Energy	x_1	245,826	272,995	130,688	112,193
	Labor	x_2	368,049	488,910	185,027	164,437
	Reagent	x_3	79,762	60,206	35,247	31,304
	Maint.	x_4	94,256	136,218	38,279	38,315
	Waste	x_5	207,898	99,299	50,240	50,936
	Other	x_6	45,522	72,099	32,687	26,422

4. Results

Following the methodology previously raised, efficiency scores have been obtained for each of the sample plants according to the type of treatment used. Calculations have been performed using the software GAMS-CPLEX. Here are the results obtained for both of the groups of seasonal and non-seasonal plants in the two technologies studied.

4.1. EXTENDED AERATION (EA)

To determine if seasonality influences the efficiency of WWTPs operating under EA, the mathematical model (1) has been solved for a sample of 44 plants. The results appear in Table 2. It is noted that all WWTPs of this group show a highly efficient performance. Those plants not affected by seasonal factors operate with greater efficiency. In fact, 75% of non-seasonal plants operate at a maximum level of efficiency compared to 55% of plants at maximum efficiency in the group of plants with seasonality. The result obtained in the Mann-Whitney Test confirms that the differences in the efficiency levels between both groups are significant.

TABLE 2. Efficiency of WWTPs with extended aeration technology.

	With seasonality	Without seasonality
Total number	20	24
Efficient units	11	18
% Efficient units	55.0%	75.0%
Efficiency index (Average)	0.8680	0.9220
Mann–Whitney Test	0.049	

To further explain this differential behavior between the two groups of WWTPs, ratios of cost per PE, based on average values, have been calculated. As shown in Table 3, the plants affected by seasonality show a higher cost per PE treated. Globally, the costs of operation and maintenance of these plants are 9% higher, on average, compared to the non-seasonal group of plants. All cost items are higher with the exception of other.

TABLE 3. Cost of operation of WWTPs with EA technology, expressed in €/PE.

	PE	Energy	Staff	Reag.	Mainte.	Waste	Other	Total
(1) Without seasonality	21,364	6.117	8.661	1.65	1.792	2.352	1.53	22.101
(2) With seasonality	17,604	6.373	9.341	1.778	2.177	2.893	1.501	24.063
(2)/(1)%	0.82	1.04	1.08	1.08	1.21	1.23	0.98	1.09

Given that the average level of efficiency for non-seasonal plants is 0.9220 and for seasonal plants it is 0.8680, and knowing that the average cost per plant for the latter group is €433,501 per year, it is observed that if these seasonal plants operated with the same level of efficiency as the non-seasonal plants, they could save 5.41% of their overall costs, on average.

4.2. ACTIVATED SLUDGE (AS)

As with the EA technology, to obtain the efficiencies of the WWTPs, we have solved the mathematical model (1) for a sample of 32 plants. As seen in Table 4, there is a noticeable difference in efficiency between plants affected by seasonality and non-seasonality. In fact, the former have an average efficiency of 0.761 compared to 0.894 for the latter. Furthermore, in the first group only 28.6% of the plants are efficient while in the non-seasonal group, this percentage stands at 72.2%. It is important to note that the Mann-Whitney test confirms that there are significant differences in terms of efficiency.

TABLE 4. Efficiency of WWTPs with activated sludge technology.

	With seasonality	Without seasonality
Total number	14	18
Efficient units	4	13
% Efficient units	28.6%	72.2%
Efficiency index (average)	0.7610	0.8940
Mann–Whitney test	0.011	

Table 5 shows that plants under the influence of seasonality have a higher cost per PE treated. Overall, this group of plants has a 39% higher ratio compared with non-seasonal plants, on average.

TABLE 5. Cost of operation of WWTPs with AS technology, expressed in €/PE.

	PE	Energy	Staff	Reag.	Mainte.	Waste	Other	Total
(1) Without seasonality	58,639	4.192	6.277	1.36	1.607	3.545	0.776	17.758
(2) With seasonality	45,789	5.962	10.678	1.315	2.975	2.169	1.575	24.673
(2)/(1)%	0.78	1.42	1.70	0.97	1.85	0.61	2.03	1.39

We calculate the cost of seasonality for plants located in tourist areas. Knowing that the average level of efficiency of non-seasonal plants is 0.894 and for seasonal it is 0.761, and that the average cost per plant for the latter group is €810,210 per year, then it is clear that if these plants behaved with the same efficiency, this could save a non-seasonal plant 13.27% of its costs, based on average values. This result would symbolize the negative economic impact that seasonality has on these plants.

Having established the relevance of the seasonal factor in the efficient behavior of WWTPs and their direct impact on the increased costs of operation, we now search for solutions. Accordingly, it is important to note that the two technologies studied belong to the so-called biological treatments and, therefore, are characterized by high inertia, meaning they have a low adaptability to sudden or transitory overload conditions.

There is no doubt about the importance of the design phase of a WWTP, although it would be necessary to study each individual WWTP to determine the most appropriate solution in each case, a feature common to all of them is modularity. In cases where the plant has several parallel treatment lines, operations are more efficient since the operating equipment of the plant is adapted to the actual flow being treated.

One partial solution in situations of punctual seasonality would be physico-chemical treatments as these types of treatments have a rapid response time to changes in the wastewater. However, this type of process has higher costs than biological treatment due to the consumption of chemical reagents. One option is a treatment regimen based on a conventional biological system for the permanent population and a complementary physicochemical system for the seasonal peaks.

5. Conclusions

The presence of seasonality implies that during much of the year the communities that are served by WWTPs remain almost empty, while over holiday periods there is a high occupancy level.

Using the PE variable as a criterion to determine the seasonality of the plants and through the implementation of the FDH methodology for a sample of 76 WWTPs, we have found that plants affected by seasonality are less efficient in terms of cost than those plants that do not exhibit seasonal behavior.

The efficiency analysis has been conducted for two types of treatment: EA and AS. While the results show that for both technologies, non-seasonal plants are more efficient than the seasonal ones, the truth is that this factor has a greater effect on those plants using AS technology.

To this effect, after analyzing the ratios of cost per PE, it is noted that in the case of EA the costs of seasonal plant operation are, on average, 9% higher than for non-seasonal plants, while for AS technology this figure rises to 39%. Another result that is certainly significant is that if seasonal plants were to operate with the same efficiency as unseasonal ones, they could save, on average, 5.41% of their costs in the case of EA and 13.27% for the AS process.

Ultimately, the application of the FDH methodology to the sample of studied WWTPs leads us to conclude that seasonality is certainly a determinative factor in explaining the inefficiencies in terms of cost in the treatment processes.

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PERSPECTIVES OF DECENTRALIZED WASTEWATER TREATMENT FOR RURAL AREAS

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Abstract. The paper deals with some processes and procedures in preparation and implementation of storm water management and treatment from small sized communities. In such communities, decentralized way of storm water management and waste water drainage and treatment can be considered. However, it is important that the communities have objective information at their disposal, as well as materials and data to compare possible solution variants in linkage to the aims and requirements of individual communities, to possibilities and ways of providing financial resources. The communities must consider whether and up to what amount, as the case may be, they shall impose a financial burden on property owners, i.e. the inhabitants in the community.

Keywords: sewerage systems, storm water management, decentralized sanitation, MBR

1. Introduction

There are growing concerns about long-term environmental protection. Not only the financial reasons, but also the concerns about securing continuous use of water and protection of the aquatic ecosystem raise doubts about the suitability of the existing method of draining urbanized areas. In principle, such a drainage method is called for that would ensure protection of mankind against the environment but also the protection of environment against mankind. The existing wastewater collection methods allows for the penetration of harmful substances into sewerage and the present wastewater treatment cannot prevent from the penetration of these substances into water courses and partly

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into groundwater. All these facts result even in challenging the municipal drainage based on combined sewerage. This situation is exacerbated by industrial wastewater, crafts, hospitals and industrial plants. The non-conformities when checking discharged wastewater support the behavior of the polluters who in many cases discharge other substance in other quantities than as officially permitted. Finding an acceptable compromise between these contradictory objectives is the basis of the future solution to urban areas drainage (Krejcí et al. 2002). The paper deals with the prospects of the sustainable water management in urban areas. A number of examples from abroad indicate possible ways of addressing these issues.

2. Wastewater Management

Wastewater management is one of the essential functions of the society. The produced pollution originally returned into the environment, where it decomposed and was integrated into the mass cycle. This situation lasted until the end of the 19th century when public water supply and sewage systems started being developed. At the beginning of the 20th century, wastewater disposal changed from recycling to discharging into recipients. The subsequent degradation of the sources of water resulted in environmental protection in the second half of the 20th century (Bodík et al. 2007).

The increasing comfort of living, recreational and tourist activities in rural and tourist areas are conditioned by the solution to wastewater disposal. However, the conditions of wastewater collection and drainage in the countryside are much more diverse and sensitive than in cities. Non-critical transfer of municipal equipment and technologies to rural conditions causes a number of operational and, in particular, economic problems. However, similar problems may be caused by uncritical and insufficient professional application of alternative technologies (Stanko 2009a).

Once the agglomerations above 2,000 people equivalent, which are more or less publicly funded, are handled, the core of the wastewater disposal will shift to localities that will have a very little or no hope of obtaining assistance from public funds.

It is already obvious that the current trend of wastewater collection and treatment cannot be implemented in these localities for financial reasons. Therefore, it will be necessary to look for new water treatment technologies and methods. This will entail the necessity to modify the existing legislation and technical standards (Mahríková 2007).

Wastewater management is discussed more and more often now than its disposal. Wastewater is not understood as waste but as a resource, a raw material. A number of examples from abroad show that this trend can be implemented. However, the actual environmental impacts will still be discussed and the opinion will never be unanimous.

3. Sewage Water Collection Technology

In principle, two approaches are possible. A centralized solution is based on a systematic sewerage draining wastewater to a single treatment facility. The sewerage may be combined and separate. The separate sewerage drains sewage water and rainwater through a single pipe profile. It must be designed to handle great rainwater flows which are seldom and one-time. The separate sewerage consists of two pipe systems. The sanitary sewage made of pipes of significantly smaller profiles than in the case of combined sewerage, drains sewage water. Rain water sewerage drains rainwater. Its design may be simpler than in the case of the combined sewerage. It may drain only a part of the sewerage zone, always the shortest to the watercourse, then it may be more shallow (Stanko 2009b).

The combined sewerage causes considerable problems in small municipalities in terms of wastewater treatment. Rainwater must be overflow to the water course upstream the wastewater treatment plant. This causes significant pollution of the water course – if no storm water tank retaining water to be treated at the wastewater treatment plant later is provided. It may be quite difficult to construct and keep overflow chambers on a small scale to ensure their reliable operation. Very often they either discharge even dry weather flows to the water courses or, on the contrary, they cause flooding of the wastewater treatment plant by rainwater flows. The smaller the locality, the greater the oscillation of the flow rates and the more sensitive and demanding the rain water overflows (Stanko 2008a).

Alternative sewerage is recommended in certain conditions that are defined as complex for classic gravity sewerage. These complex conditions are especially in municipalities with scarce building density, water resources protection zones, flat areas with the necessity to drain wastewater from low-laid areas, rocky sub base, high groundwater levels, shifting sand, complicated built-up areas hindering building work and obstacles, such as water courses, service networks etc.

3.1. VACUUM SEWERAGE

Vacuum sewerage is based on the principle of generating permanent vacuum in the pipes generated in a vacuum station, i.e. a vacuum tank, by vacuum pumps. The system consists of vacuum sewerage pipes, transfer shafts with valves and connection of the pipes and the vacuum station. The vacuum pipe connects the transfer shaft with the vacuum station. Standard profiles are DN 80–150 mm. The total route of one branch may reach up to 3,000 m. The transfer shaft is used to connect the individual structures to the vacuum pipes. It collects wastewater flowing from the structure in a standard sewerage system. The vacuum station consists of a vacuum storage tank and vacuum pumps generating vacuum in the pipes (0.2–0.8 Bar). Wastewater is conveyed from the storage tank to a superior sewerage system by a submersible pump, or directly to the WWTP. The advantage is that the wastewater cannot leak from the pipes, the flow velocity prevents from the settlement of solid particles in the pipes, low construction costs and the wastewater is transported under aerobic conditions. The disadvantage is the risk of the valve clogging and higher consumption of electricity.

3.2. PRESSURE SEWERAGE

Pressure sewerage is suited for flat areas with a greater distance between drained buildings. The system consists of a pressurized system and pump sumps. The pressurized system installed at a frost-free depth copying the ground level. The most frequent pipe diameters are in a range of DN 40–150. The system may discharge into a WWTP or gravity sewerage. It is vital that the pipes are designed with a minimum sewage water speed of 0.7–0.9 m/s in order to ensure self-cleaning of the pressure pipes. Sanitary sewage is discharged by gravity into pump pits (collection shafts). The advantage is a small scope of excavation work – the pipes are installed at a frost-free depth (0.9–1.2 m), independence of the ground slope, it can also be pumped uphill, no infiltration water, self-cleaning effect – the pipes do not have to be cleaned – the system is maintenance-free, the capital expenditure is on average 40–50% lower than in the case of the gravity sewerage.

The disadvantage is the dependence on the supplies of electricity, use only for the drainage of sanitary sewage (separate sewerage) and the operation of the pump sumps requires regular maintenance.

3.3. PNEUMATIC SEWERAGE

Wastewater from a locality flows into a collection shaft in a pneumatic pumping station. From this shaft the water flows by gravity into pressure vessels. Once the vessel is filled up, the inlet automatically closes and compressors push the volume of the vessel by pressurized air into a small-diameter delivery pipe leading to the WWTP. The delivery pipe can overcome long distances at great gradients without hydraulic shocks as the sewage in the pipes is abundantly aerated (air pillow). The advantage is that it is possible to convey a strongly polluted medium without getting in contact with the rotary equipment even over long distances, minimum maintenance demands and the pipes copy the ground level and must be installed at a frost-free depth (approx. 1.2 m). The disadvantage is the dependence on the supplies of electricity and the use for sewage water only (separate sewerage).

3.4. SMALL-PROFILE SEWERAGE

A small-profile system conveys water pre-treated in septic tanks from buildings by gravity using pipes with a diameter of 65–150 (200) mm. The treatment processes start in the sump working as a septic tank. The condition for the small-profile sewerage is a very low concentration of suspended solids larger than colloids at the outlet of the septic tanks as there is a risk of clogging the small profiles in critical points. The small-profile sewerage needs gravity flow of pre-treated sanitary sewage. The septic tank works with a practically stable level, the volume of the water section will be adjusted according to the recommended retention time. The small-profile sewerage is suitable for municipalities outside flatlands with more scattered housing development. The pre-treated sanitary sewage is handled by infiltrating into ground water, reed wastewater treatment plant and mechanical – biological treatment plant. The advantage lies in the savings in terms of capital expenditure on the pipes. The system conveys pre-treated water; it is assumed that there is a minimum of solid impurities, less infiltration water, given the smaller size of the jacket and smaller perimeter of the sealing, lower burst rate caused by static overloading; the static parameters profiles worsen with the size and capex savings. The disadvantage is the operation of the septic tanks with respect to sludge removal (it is a matter of responsibility and regular checks), grants and funding – a larger share of investments in a private farm compared to classic sewerage.

4. Stormwater Management

Stormwater runoff from urbanized areas plays one of the crucial roles in the field of urban drainage. During intensive rain events, the stormwater runoff exceeds by far other types of wastewater and has a major impact on the design and sizing of a number of structures in the urban drainage system. The stormwater runoff from urbanized areas also contains significant share of polluting substances, which affect the sewer system, wastewater treatment plant and the receiving body of water, but they also affect potential use of stormwater and its infiltration (Hlavínek et al. 2008).

At present, there are a number of reasons for restricting the stormwater runoff from the individual buildings. The most important include:

Possibility of using stormwater as service water in households for purposes that do not require quality drinking water,
Reduced flow-rate in the sewerage during rain events and support of the function of the technical system, particularly the combined sewerage,
Reduced hydraulic load and mass load at the WWTP during rain,
Reduced hydraulic (mechanical) impacts on organisms in small water streams,
Reduced BOB pollution cause by combined system overflows during rain,
Support of the renewal of groundwater etc.

4.1. USE OF STORMWATER

What we encountered most often in practice are solutions using stormwater for irrigating green areas, either manually or automatically using a time-controlled automat or based on the measured soil moisture content. The retained water is also used as service water for washing, mainly in those areas where the groundwater is hard or contains a higher share of iron, manganese. It is also used for toilette flushing (the capacity of the cistern supplying WC and laundering should correspond to a one-month water consumption), for washing machines, dishwashers, for cleaning purposes, as operating water for crafts and industries, etc.

The level of stormwater pollution is generally defined as follows:

Slightly polluted – stormwater runoff from residential areas (streets, cycle tracks, pavements, green areas, etc.),

Normally polluted – water from residential-industrial, villages, parking lots and roads,

Strongly polluted – water from motorways, national busy roads, uncovered warehouses and transit warehouses storing harmful poisonous substances.

The stormwater pollution thus very strongly depends on the local marginal conditions. Stormwater runoff from the streets should infiltrate only through a revived soil layer of after pre-treatment.

4.2. STORMWATER RETENTION

At present, there is a trend of an enlargement of built-up areas in urbanized catchment areas and resulting increase in the volume and peaks of stormwater runoff. Each urbanized area causes changes in the character of direct stormwater runoff and it is desirable to identity a potential suitable solution to the runoff conditions in the urban area in the form of stormwater retention. The problem of large drained areas may be addressed by retention – water storage and its controlled discharge to the receiving body of water. The retention tanks replace the natural retention characteristics of the landscape, protection against floods, stormwater runoffs and the tanks also retain flushes. However, their protective function prevails. Other tanks fulfill this task as a secondary task.

The group of protective retention tanks includes:

Dry retention tanks (retaining flood-level flow-rates, reducing critical flood flows and they get empty once the flood wave passes),

Retention tanks with a clearly defined protective space (transforming the flood wave and once it passes, the protective space is emptied in a controlled way down to the level of defined storage space),

Erosion control tanks (retention of sediments),

Stormwater tanks (ensuring retention, short-time water storage, treatment and use of water from rain precipitation),

Infiltration irrigation basins (short-term retention of surplus incoming water, its partial use for irrigation),

Intermittent basins (designed to balance out the shock discharge waves in distant profiles with a controlled flow-rate).

4.3. DECENTRALISED RETENTION OF STORMWATER

Decentralized retention is stormwater retention in individual houses. The runoff is restricted using equipment for runoff control (throttling lines, vortex regulators and filtration beds).

Equipment used for stormwater retention, without integrated infiltration into the subsoil is divided as follows:

Pool with biotope,

Retention on terraces, horizontal and slanted roofs,

Stormwater retention tanks,

Retention in parking lots and industrial premises,

Retention channel,

Filtration pit,

Plastic honeycomb blocks,

Infiltration with retention space,

Retention equipment combined with pipe infiltration.

4.4. STORMWATER INFILTRATION

With respect to various options, we distinguish between: direct infiltration, infiltration with over ground water retention, infiltration with underground water retention, and combinations. This also includes designs of storm-water tanks, intended for the use of stormwater before infiltration. In a number of European countries the infiltration of unpolluted or little polluted stormwater runoff is supported also by administrative and legislative instruments. A principal question which is still very much questioned is the definition of "unpolluted" or "little polluted" stormwater runoff.

The marginal conditions for infiltration are the following:

Stormwater runoff pollution,

Requirements for groundwater protection,

Requirements for soil protection,

Method of infiltration (type of structure).

The systems for stormwater runoff infiltration can be distinguished according to the following criteria:

Central or decentralized,

collection ability (storage),

demands on surface areas,

type and distribution of hydraulic load.

The main technical principles for infiltration are the following:

areal infiltration,

broad-base terrace infiltration,

combination of broad-base terraces and trenches (multi-component infiltration element),

trench and pipe infiltration,

shaft infiltration,

infiltration tanks,

multi-component system.

Runoffs from hardstanding areas are divided with respect to the concentration of mass loading and potential impacts on the underground water into three categories related to the intentional infiltration:

harmless (wholesome),

tolerable,

intolerable.

Harmless stormwater runoff may be infiltrated through the non-saturated zone without pre-treatment. However, these runoffs are not mass unloaded. Nevertheless, the concentrations are considered to be so low that it is not necessary to be afraid of the harmful pollution of underground water or deterioration of its quality.

Tolerable stormwater runoffs may be infiltrated after adequate pre-treatment, while using treatment processes in the infiltration system. Infiltration through grasses surfaces may be sufficient in dependence on the characteristics of the catchment area and retention time of the infiltration space.

Intolerable stormwater runoffs should only be infiltrated after adequate pre-treatment or to be discharged to the sewerage.

The stormwater infiltration is enabled by the infiltration system. At first sight, it is usually a simple civil structure. However, practical examples show that the proper functioning of these structures conditions by a suitable design and careful execution is not possible without special knowledge and experience. What is also important is the professional maintenance of these structures.

5. Wastewater Treatment

The principles of conceptual solutions in the future include the principle of not transferring the solutions to problems to other localities, and not burdening other entities with the solutions (preference given to local and immediate solutions without burdening the inhabitants who are not responsible for the problem caused), preventing from long-term mitigation of the damage to water resources and land fund, promoting the inclusion of civilizing activities into the natural water and food cycles and use less raw materials and energies for identical or even larger operations (Mahríková 2009).

The modern trends of wastewater management are built upon the thorough separation of pollution at the source. A person produces approx. 500 l of urine a year (yellow water), 50 l of faeces (black water and 50,000 l of other water (grey water). The specific conceptions of DESAR systems make use of dividing wastewater from households into black, yellow and grey water.

The partial DESAR concepts include household wastewater collection and its transport to a central wastewater treatment plant through a separate system. An improved option is the collection of urine using no-mix toilets and storage in individual households. The urine is emptied and discharged at night through the existing sewerage and treated separately at the wastewater treatment plant. Other wastewater from households is collected and treated conventionally. Surface run-off is discharged locally and separately into soil (Stanko et al. 2008b).

The full DESAR concepts include a small-size closed water and material cycle, with the minimum inputs and outputs from one of the defined systems. Such concepts make sense mainly in rural areas where nutrients can easily be utilized by local agricultural facilities, the volume of rainwater per person is significant and the pipes for long distances are very costly. Treatment, renewal, and recycling of water and nutrients based on decentralized technologies must be further developed and tested. In the past, highly sophisticated scenarios were designed for future decentralized drainage, approaching extensive decentralization by separating all kinds of domestic water and installing individual pipe systems. Extensive applications in demonstration projects will show whether these comprehensive concepts can be considered to be feasible (Lens et al. 2001).

6. Membrane Treatment Technologies

Given the growing demands for the quality treated water, in particular where the treated water is reused, it is necessary to search for progressive treatment technologies which will be able to produce good quality service water. One of the most promising technologies that are used in the world even for wastewater treatment to be reused as drinking water is the membrane treatment technology.

The membrane processes are understood as processes the treatment effect of which is based on various permeability of the individual particles through a membrane. When applying the membrane technologies in the wastewater treatment process it concerns mainly the separation of suspended solids, i.e. biomass from the wastewater environment

Activation processes with membrane sludge separation can be divided according to the operating method and load as follows:

1. Medium- and high-loaded activation process with high sludge concentration and regular excess sludge withdrawal.
2. Low-loaded activation process with high sludge concentration and occasional excess sludge withdrawal.

Type 2 is used mainly at WWTP 's with minimum requirements for attendance, i.e. packed and small-size wastewater treatment plants. These WWTP's keep a maximum volume of sludge in the activation tank at 10–15 g/l and sludge withdrawal is minimized. There is also a requirement that membrane regeneration should be as little as possible and, if possible, by flushing only without chemical regeneration.

7. Conclusions

The conception discussed above is feasible. At present, there is a number of examples that have been implemented along the lines of this conception and have been used in practice. Checking the efficiency of the implemented measures and the observance of achieving the defined targets is an integral part of the integrated solution. A thorough check of the implemented solutions is also a precondition for further methodological development of the urban drainage integrated solutions and a major step to ensure sustainable development.

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COMBINED SEWER NETWORK IN HILLY REGION: FIELD SURVEY AND POLLUTANT OVERFLOW OPTIMIZATION

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Abstract. Combined sewer networks in hilly regions present unusual and unexplored issues due to the high flow velocity which characterizes sloped systems. This work aims to present the results of a field survey carried out at the experimental combined sewer urban drainage system of Volterra (Tuscany, Italy, total surface 146 ha, maximum slope 14%). Field data have been used to calibrate the numerical model based on the network geometry and on the rainfall events of 2007 and 2008. A simple characterization of the pollutant and the analysis of their correlation with the total suspended solids have been carried out. Finally, the optimization of new designed overflow structures has been carried out based on the analysis of the pollutant features and on the evaluation of the pollutant loads delivered in the water body.

Keywords: combined sewer networks, field survey, pollutant, overflow structures

1. Introduction

Combined sewer networks in hilly regions often present unusual features which, if not correctly assessed, would lead to unpredictable network behavior (network surcharges, non-optimal overflow derivation, etc.). In hilly regions, the sewer pipes have large slopes and economical reasons or bad design practice do not always consent to account for it. Hence, when a strong run-off occurs over the ground surface, high quantity of sediments and pollutants can enter the sewer

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network. The water pollution is a function of several parameters. The contribution of each source of contaminant in urban areas was analyzed in previous studies (Gobel et al. 2007). Accordingly, the pollutants accumulation on the ground in urban areas is a complex phenomenon depending on: (1) extension and population density of the area; (2) use of land; (3) the typology of sewer network; and (4) the usual weather conditions occurring in the area. Moreover, another peculiarity characterizes this type of sewer network, i.e. high velocity flow (>2 m/s) which generally leads to a high erosion of the pipe surface and high quantity of sediments carried by the sewer network. The main impact in terms of pollutant comes from the sediment deposited into the sewer and re-suspended by the flood (Stanko and Mahríková 2009; Ahyerre et al. 2001). A correct survey of the combined network and a design of all the structures involved in the transport process has to be developed.

In the present paper, an analysis of combined sewage networks was done in the urban area of Volterra, Tuscany, Italy. A numerical model was applied based on field data in order to foresee both the qualitative and hydraulic aspects which characterize the urban drainage system.

2. Study Area and Data Collection

The experimental catchment basin of the city of Volterra (N43°24′07″ E10°51′34″, Tuscany, Italy) consisted of 11 sub-basins. The total urban area is 146 ha and is characterized by the presence of two treatment plants, located both in the north and south part of the town. Three of these sub-basins were monitored for two years (2007 and 2008). Namely, two sub-basins discharging in the north treatment plant (named Docciola and Macello, see Figure 1a) and one discharging in the south treatment plant (Borgo Santo Stefano, see Figure 1b). The sub-basin Docciola has a total surface of 21.65 ha, of which 55% are un-pervious, an average altitude of 510 m and a total difference in height of 60 m. In this sub-basin a combined sewer network is present. The conduits are both rectangular and circular in shape. Rectangular conduits vary between 600 × 400 mm and 900 ×6 00 mm, whereas circular conduits vary between 200 and 1,000 mm.

The sub-basin Macello has a total surface of 10.08 ha (almost 75% impervious), an average altitude of 510 m and a total difference in height of 71 m. This sub-basin is high densely inhabited and it represents one of the oldest part of the town, as it is part of the medieval center. It is served by a combined sewer network made of both rectangular (range between 300 × 400 and 700 × 2,000 mm) and circular conduits (range between 200 and 500 mm).

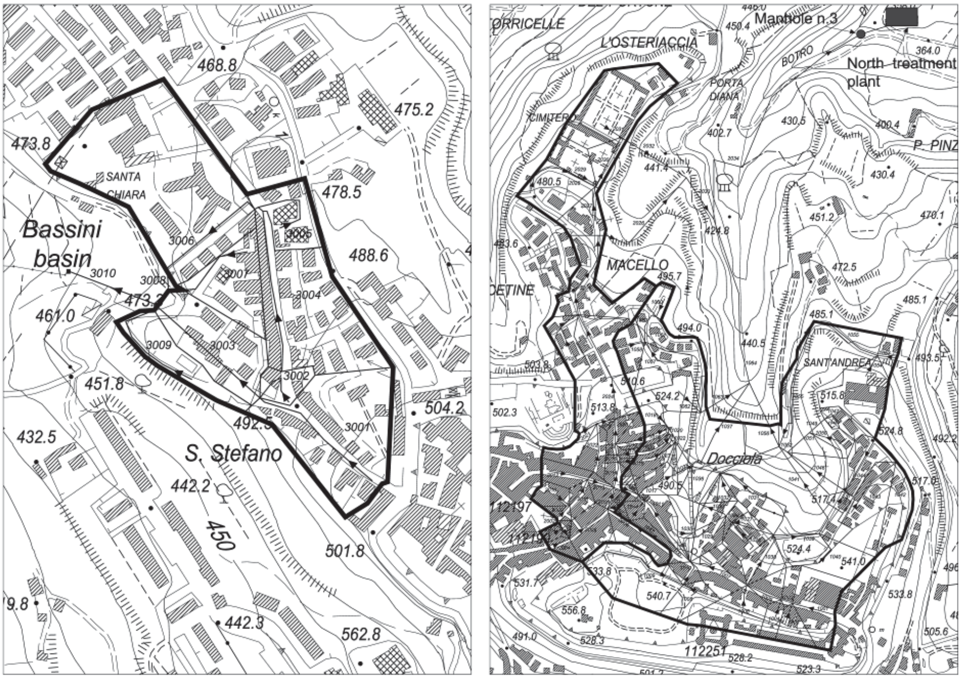

Figure 1. Plan of the sub-basins (a) Borgo Santo Stefano and (b) Docciola and Macello with the indication of the monitored manhole and accumulation basin: (•) manhole (⟶) network elements, (▬) total sub-catchment area, (—) sub-catchment area relative to each element.

Both previous sub-basins merge into one circular conduit whose diameter is 500 mm and flows in the north treatment plant. This last conduit presents several hydraulic problems as it is characterized by an extremely small diameter and a very large slope (>10%). Moreover it is located in a not stable area with high slopes, thus it is subjected to frequent breaks (Figure 2a). Along this main conduit several manholes are present, some of which are subject to frequent over flows. In order to prevent a surcharge of the treatment plant, in the downstream manhole a conduit was located at a certain level from the bottom discharging directly in an adjacent water body. This structure was analyzed in a previous study (Carnacina et al. 2008) and both the hydraulic and quality parameters were monitored. Moreover a numerical simulation of both the flow characteristics and water quality characterizing this structure was developed. The sub-basin Borgo Santo Stefano has a total surface of 7.17 ha (almost 75% impervious), an average altitude of 480 m and a total difference in height of 48 m. It is served by a combined sewer network, whose conduits are all circular and diameters range between 300 and 500 mm. At the downstream end of the sub-basin a small detention structure is present. In the structure the water is discharged in the south treatment plant by a 500 mm conduit located at 0.38 m from the bottom of the basin. The excess flow is discharged into the hydrographic network by means of a trapezoidal weir located at 0.63 m from the detention basin bottom. This structure was carefully monitored for all the two years, as frequently the flow was discharged in the adjacent water body. The detention basin was modeled in laboratory and it was observed that its functioning is not adequate. A numerical model was used to reproduce both the hydraulic and the water quality characteristics in correspondence of the structure. Water quality data were also collected by means of an automatic pollutant monitoring system located both at the monitored manhole and at the detention basin (Figure 2b).

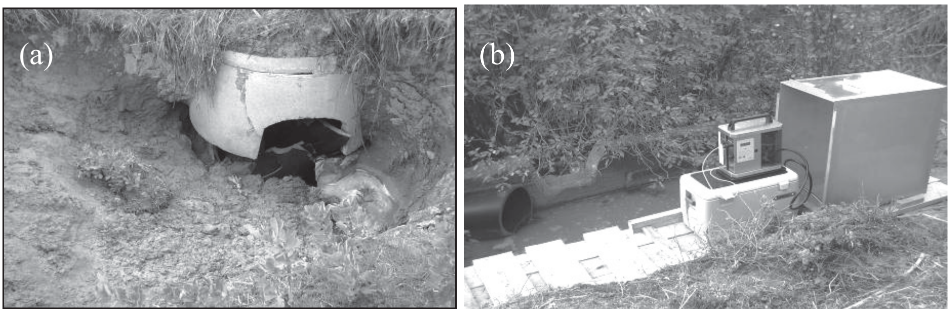

Figure 2. (a) network break due to slope instability and (b) pollutant monitoring system located at the detention basin.

The following water physical and quality parameters have been measured: pH; electric conductibility (µS/cm); BOD_5 (mg/l); COD (mg/l); TSS (mg/l). In Figure 3 an example of a typical survey output is showed.

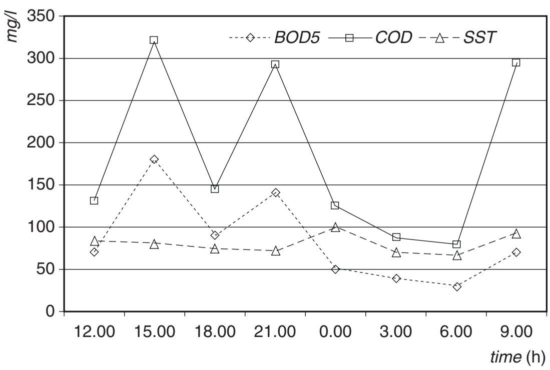

Figure 3. Example of a survey output measured at accumulation basin (30-31/10/2007).

3. Pollutant Analysis, Numerical Model Calibration and Optimization

According to (Bullock et al. 1996; Barco et al. 2003), the correlation between TSS, COD and BOD_5 is generally linear. However, the regional changes, climate, soil nature, build-up, run-off features and the characteristics of local production, may lead to different analytical correlations.

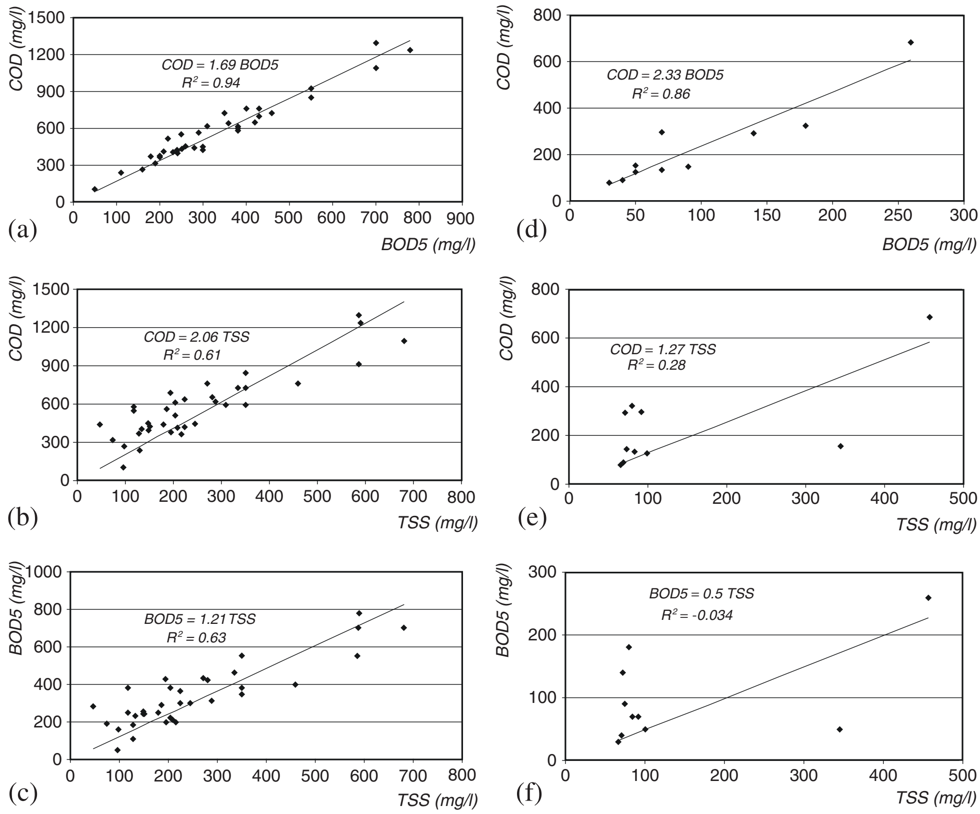

Figure 4. Correlation between COD, BOD_5 and TSS in the detention basin for both (a), (b), and (c) dry period and (d), (e) and (f) wet period.

Hence, in order to improve the design efficiency, the study of the local correlation between TSS, which in general can be easily determined by simple field survey systems (Ahyerre et al. 2001), and either COD or BOD_5 has to be performed. According to Figure 4, two different correlations can be assumed during drought and wet period between the measured parameters. During dry weather periods (Figure 4a–c) data show the best correlations between COD and BOD_5, whilst COD/TSS and BOD_5/TSS assumed lower R2 values. The same occurs during wet period. A good BOD_5/COD correlation can be observed.

Respect to the dry period, the presence of COD increases, i.e. the ratio COD/BOD_5 is higher. Correlations between COD/TSS and BOD_5/TSS can be hardly established. This occurrence is mainly due to the fact that in the detention basin a re-suspension of solids deposited during the dry periods takes place. Thus, the quality characteristics of the water in the detention basin are deeply influenced. Similar considerations can be done also for the monitored manhole (Figure 5a–c). Both the monitored points show similar correlations during the dry weather period.

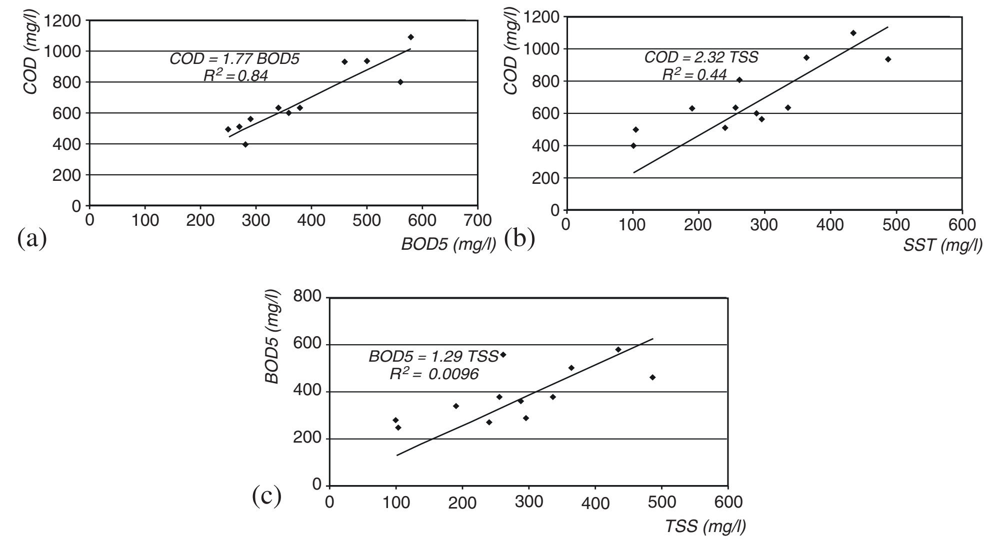

Figure 5. (a, b, c) Correlation between pollutants for monitored manhole in drought period.

The hydraulic sewer network has been modeled by means of the Bentley SewerGEMS® V8 XM software. The calibration has been based on the data relative to eight different years (from 2001 to 2008). Figure 6 reports the hydrographs relative to 2 years (2007–2008) in which also the water quality was surveyed.

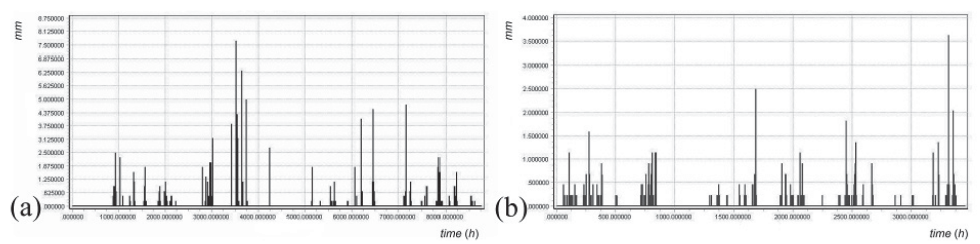

Figure 6. Rainfall events for (a) year 2007 and (b) year 2008.

Moreover, the calibration has also been based on the results given by physical models of both the monitored manhole and the detention basin which were built in the laboratory. Figure 7a shows the computed discharge at the detention basin inlet and the relative rainfall event intensity.

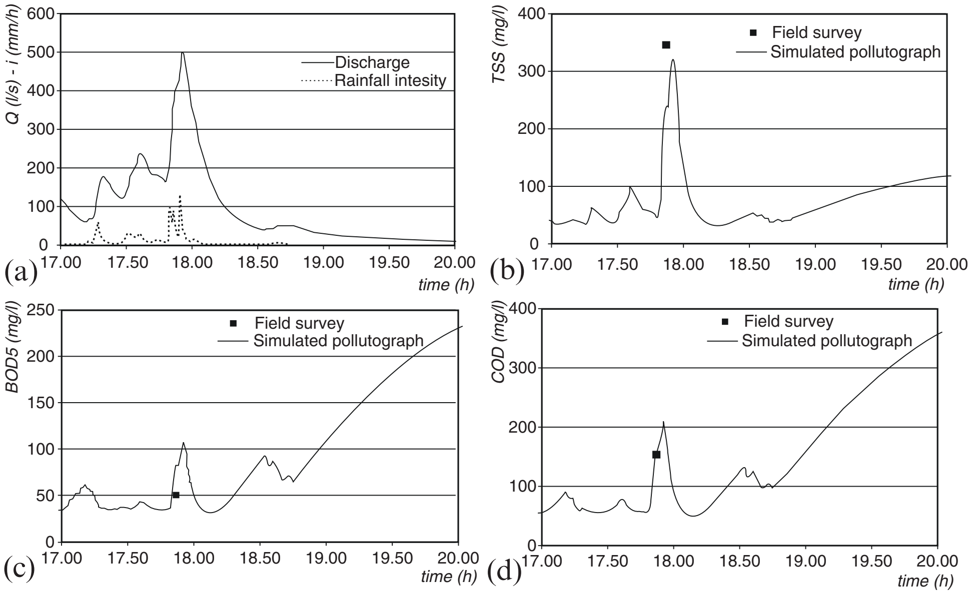

Figure 7. (a) Computed discharge at the detention basin inlet; (b), (c) and (d) comparison between simulated and measured values of TSS, BOD_5 and COD respectively for the rainfall event of 26/10/2007.

In Figure 7b–d, a comparison between the numerical model outputs and the field data is proposed. It can be observed an overall good agreement between the measured and modeled pollutant loads. Hence, after the calibration, it has been possible to evaluate by means of the numerical model, the total pollutant loads for each monitored year. Figures 8–9 show the pollutographs (TSS and COD) relative to the years 2007 and 2008 for both the detention basin and the monitored manhole. According to the numerical results, high concentration of TSS and COD are discharged directly into the hydrographic net, which can further contribute to the reduction of the biological characteristics and the quality of the receiver water bodies.

Based on the model calibration and simulations, a network optimization has been proposed. The actual discharge conveyed into the treatment plant is much bigger than that relative to the dry-season periods, due to the high velocity which occurs into the networks. This may leads to high volume to be stored into the treatment plant, whit evident problems in terms of depuration management and efficiency. However, during heavy rainfall event, it has been possible to measure pollutant peaks: i.e. TSS = 2,146 mg/l and of COD = 3,572 mg/l due to the transported sediment eroded by the high velocity flow which occurred inside the networks systems. Hence, a high volume of pollutants are delivered into the hydrograph network. The network optimization aims to increase the network efficiency in terms of volume of water conveyed into the treatment plant, of pollutant mass and of discharge frequency into the hydrograph network. Hence, the actual detention basin can be replaced by a first flush detention basin which has been studied and designed, as shown in Figure 10.

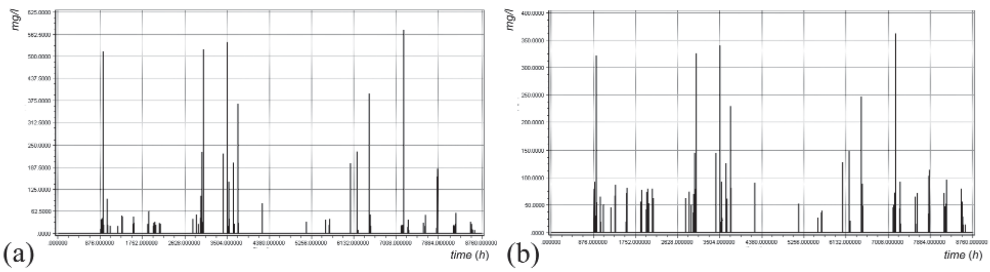

Figure 8. Simulated outlet weir pollutograph at the detention basin (year 2007): (a) TSS and (b) COD.

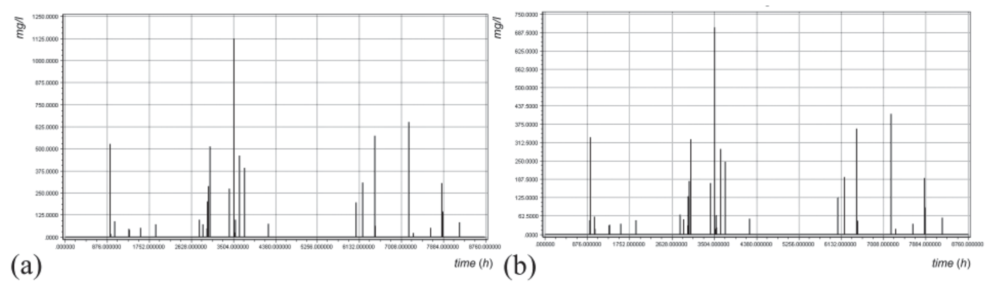

Figure 9. Simulated outlet pollutograph at the monitored manhole (year 2007): (a) TSS and (b) COD.

The new system consisted of a by-pass (jump bottom outlet of 325 cm^2 area) linked with both the first-flush detention basin and the treatment plant. The bottom outlet conveyed directly in the treatment plant both the dry-season discharges and first-flush discharges up to 3Qn = 10.5 l/s, where Qn = average sewer discharge. Q greater than the maximum capacity of the bottom outlet are stored in the first flush detention basin. The detention basin is linked to the hydrograph network by means of a weir located at 4.85 m from the bottom. The basin allows for both an intermittent and a continuous flush into the treatment plant by means of a regulated gate. The intermittent functioning occurs when the gate is kept completely closed up to when the first flush detention basin is full and then it is opened.

The volume efficiency εv, mass removal efficiency εm, and discharge frequency efficiency εf, are defined as (NCHRP-565 2006):

$$\varepsilon_v = \frac{\sum_{i=1}^{N} V_{i\,in}}{\sum_{i=1}^{N} V_{i\,tot}} = 1 - \frac{\sum_{i=1}^{N} V_{i\,sc}}{\sum_{i=1}^{N} V_{i\,tot}}; \quad \varepsilon_m = \frac{\sum_{i=1}^{N} M_{i\,in}}{\sum_{i=1}^{N} M_{i\,tot}} = 1 - \frac{\sum_{i=1}^{N} M_{i\,sc}}{\sum_{i=1}^{N} M_{i\,tot}}; \quad \varepsilon_f = \frac{N_{in}}{N} = 1 - \frac{N_{sc}}{N} \tag{1}$$

where $V(M)_{in}$ = volume of water (mass of pollutants) conveyed into the first flush detention basin of the single rainfall event (i.e. event i), $V(M)_{tot}$ = total volume (mass of pollutants) for the same event; $V(M)_{sc}$ = volume (mass of pollutants) discharged into the hydrograph network; N_{in} = total number of rainfall event completely intercepted by the basin; N_{sc} = total number of events partially discharged into the hydrographic net; N = total number of rainfall events considered.

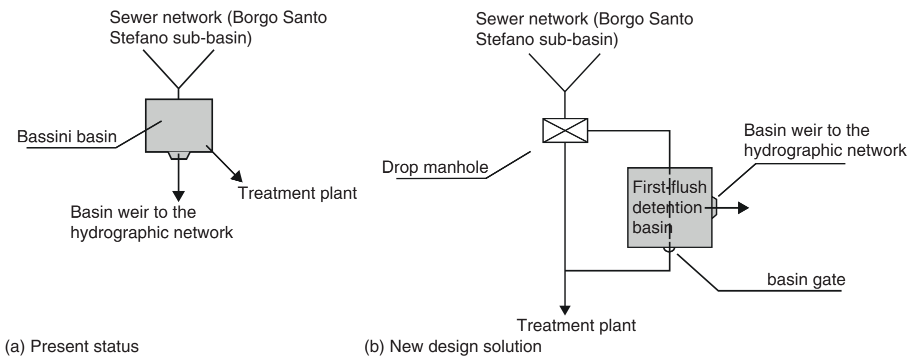

Figure 10. (a) Network present status, (b) first flush detention basin sketch new design.

Hence, several different first flush detention basin specific volumes DSV have been considered, were DSV = DV/Aimp, DV = first flush detention basin volume (m^3), and Aimp = total impervious area discharging in the first flush detention basin (ha). Efficiencies for different DSV and both intermittent and continuous discharge patterns are listed in Table 1.

TABLE 1. Average efficiencies evaluated for 6 years of simulation periods and for different first flush basin specific volumes.

	Intermittent discharge DSV (m^3/haimp)			Continues discharge DSV (m^3/haimp)		
	15	25	50	15	25	50
ε_v (%)	15	19	30	33	37	46
ε_m TSS (%)	5	8	14	11	14	22
ε_m COD (%)	14	17	24	24	27	34
ε_f (%)	30	34	43	33	37	46

Accordingly, the efficiency increases as DSV increases (higher detention volume). Moreover, a comparison between intermittent and continuous cases shows a higher performance both in terms of volume and mass of pollutant for the continuous case, while the frequency efficiency showed slight differences. However, for DSV = 25 m^3/ha_{imp} and for the intermittent functioning, the maximum discharge conveyed to the treatment plant is Qmax = 37 l/s = 10Qn which is lower if compared with Qmax = 55 l/s = 16Qn relative to the continuous functioning case. Thus the last functioning case is less suitable for treatment reasons.

4. Conclusion

The combined sewer network of the Volterra experimental catchment basin has been analyzed. Pollutants data have been collected and a correlation between TSS, COD, and BOD_5 has been obtained. By means of a field survey and physical models it has been possible to correctly calibrate the quantitative and qualitative numerical model to assess the total annual loads of pollutant discharged by the combined sewer network. Results from the numerical model have shown a low performance of both the monitored manhole and the detention basin in terms of pollutant discharged into the hydrographic network. Hence, based on the efficiency in reduction of discharged water volume, pollutant mass removal and reduction of discharge frequency, new solutions have been proposed to improve the pollutant removal performance.

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SOLAR WATER PURIFICATION AT HOUSEHOLD LEVEL

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Abstract. Some low-cost alternatives for water purification by solar energy are analyzed, mainly those feasible in rural communities. These alternatives were divided into thermal and photochemical processes and the advantages and limitations of each method are presented. Results of the efficiency of the purification processes using a flat solar collector, as well as polyethylene bags and containers and glass flasks directly exposed to the sun, are presented. The evaluation of a prototype showed that the process is useful even on cloudy days since it depends more on the quantity of total radiation than on direct radiation only. Experimental results show that the water from kitchen and bathroom can be treated by solar energy and its chemical oxygen demand reduces up to considerable limit that it can be recycled for gardening or for toilet flushing purpose. By employing catalyst recovery and reuse, the operation and maintenance cost reduces considerably.

Keywords: water disinfection, water detoxification, solar energy, photochemical processes, solar flat reactor, polyethylene bag, TiO_2

1. Introduction

In recent years, it has been found that solar purification is one of the promising methods for the disinfection and detoxification of the water. Solar purification process uses sunlight as the primary energy input required in reactions that break down contaminant molecules in water. Furthermore the combination of light and catalysts has proven very effective for water purification (Goswami 1997).

World Health Organization Standards for water per capita is 135 l/ capita/day. Out of that, drinking – 03 l, cooking – 04 l, bathing – 20 l, washing clothes – 25 l,

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washing utensils – 20 l, toilet flushing – 40 l, gardening – 23 l. Quite a large portion of the water (63 l) is used for last two purposes and the quality of water for that can be type B (inferior to type A i.e., for drinking and cooking) (Márquez-Bravo 2007).

Waste water from bathrooms, kitchen and rain water can be collected in settling tank where primary treatment of water will be done and then it is taken to second tank in which powder (catalyst) is mixed into it and pumped to solar flat plate reactor. After solar detoxification, the water is stored in the storage tank and recycled for toilet flushing and gardening. So the waste water from kitchen, bathroom can be recycled for toilet flushing and gardening after passing from solar experimental set-up (Inamdar and Singh 2008).

The aim of the paper is to develop a method which takes care of energy saving and water saving together. Solar photo catalytic purification will be investigated through laboratory experiments as an alternative to conventional secondary treatment. To the best of our knowledge the application of solar purification at household level in sites at latitude more than 45° has not yet been investigated. In conventional treatment methods, lot of energy is wasted and also they generate harmful byproducts. In stead of these methods solar purification method is used because – (a) It carries eco-friendly operation, (b) It does not create any harmful byproducts, (c) It is energy efficient method as it uses solar energy .

2. Thermal Purification Processes

High temperatures have a marked effect on all types of microorganisms. At high temperatures, vegetative cells die due to protein denaturalization and hydrolysis of other components. In water, bacteria die between 40 and 100°C; while algae, protozoa, and fungi die between 40 and 60°C. Spores require extreme heat conditions to be destroyed: 120°C in wet heat (steam) for 20 min or 170°C in dry heat for 90 min (Caslake et al 2004).

2.1. BOILING AND PASTEURIZATION

Boiling is one of the most effective and accessible methods for water disinfection. Pasteurization is a complementary treatment, based on the time/temperature relation to destroy pathogenic germs that may be present in the water. This process destroys coli forms and other non thermo-resistant bacteria. However, susceptibility to heat is conditioned also by other factors such as the concentration of cells, their physiological condition, and others (Rose et al. 2006).

It has been observed that heating water at above 62.8°C for 30 min or 71.7°C for 15 s is sufficient to remove water-borne bacteria, rotaviruses and enter viruses from contaminated water. In addition, cysts of Giardia lamblia that are usually resistant to chlorination, are inactivated easily at 56°C during 10 min, while the thermal death point of Entamoeba histolytica cysts has been set at 50°C (Gelover et al. 2006).

2.1.1. *Using Solar Heaters*

Boiling and pasteurization can be carried out with solar heaters. The operation principle of these systems is known as convector circuit or passive solar heating, where solar radiation heat is absorbed by the black pipes, increasing water temperature inside the connector and consequently reducing water density. Under these conditions, the cold water column in the return pipe to the collector is no longer balanced by the lower-density hot water column and, by gravity, the former falls and displaces the latter toward the tank. This natural circulation known as "thermo siphon" continues as long as there is sufficient heat to increase the water temperature and the resulting push force can overcome the pressure drop in the system.

When a solar heater is used for disinfection, efficiency depends directly on the temperature reached for pasteurization. Among the experimental data, it was also observed that in 99% of the cases, coliform removal is total for effluent temperatures of 55°C. However, for safety reasons, it is desirable to leave a margin and establish 60°C as the minimum disinfection temperature. On sunny days it is possible to reach a maximum temperature of 70°C, while during cloudy days, the maximum temperature is 55°C.

2.1.2. *Using Solar Stoves*

A solar stove consists of a couple of boxes that may be made of cardboard, one inside the other, used to trap sun heat and use it, in this case, to heat water. The principle is to use the heat from the sun by radiation trapping it inside the small box and preventing it from escaping by covering the box with a transparent glass pane. This heat is transferred by conduction through metal pots to the water contained in the pots. It is desirable to use a reflector to direct solar rays toward the box, maintaining the heat.

Free space between the two boxes is filled with an insulating material that may be balls of newspaper, rubber foam, etc. The inside of the small box is coated with reflecting material such as aluminum foil. At the bottom of this box, a black color sheet is placed. It is also advisable that metal pots be painted black or smoked to absorb more heat. Metal pots should be used preferably. Clay pots are not so recommendable because this material is insulating but also preserves the heat more. If there is sunshine for more than 6 h, they can be used without problems.

Through the use of solar stoves, it is possible to disinfect water in dark glass containers in 1 or 2 h. Coliform bacteria are inactivated at temperatures above 60°C, while in solar stoves; water can reach temperatures as high as 90°C.

We carried out some preliminary tests for 20 days. A cardboard box lined both inside and outside, with aluminum foil and a glass cover of 3 mm was used. A thin aluminum pot painted in dull black was placed inside the box. The pot contained 10 l of water contaminated with one liter of the effluent that passes through the facilities. The exposure period was 5 h. The average temperature reached by the water during the testing period was 55.6°C, with a maximum of 60.5°C and a minimum of 50°C, while the average outside temperature was 25°C. In all the analyses, the removal of total coliforms and faecal bacteria was 99.9%.

2.1.3. *Using Solar Stills*

In the simplest solar stills, the solar collector consists of a black horizontal tray containing the water to be distilled, which is called the distillant. The black surface of the tray absorbs solar radiation, producing heat that is immediately transmitted to the water. As the sun rises on the horizon during the morning, the distillant is warmed, reaching its highest temperature shortly after noon, and then it cools down as the sun sets.

To prevent undesirable loss of heat, it is necessary to insulate the bottom of the pan thermally. A well-insulated still should not be hot on the lower part. The heating of the distillant increases its steam pressure. This steam pressure is far higher than that of the mineral salts. Upon heating a solution, water evaporates while salts are retained in the pan, achieving an efficient separation. To facilitate evaporation, the evaporator should have a large area compared with the volume of distillant that it contains.

Once the water, free of salts, is converted into steam, it must be returned to its liquid phase on a clean surface and then extracted from the still. This takes place in the condenser, which is usually a glass cover or some other transparent material placed above the evaporator at the right distance and slope.

In a solar still, the tray or collector can be made of several different materials resistant to water and to a temperature of 80°C. Collector-evaporators have been built with iron sheets, plastic strengthened with fiberglass, masonry, wood, Ferro cement, etc. The material most used for condensers is glass or some plastics such as acrylic, polyethylene, polyvinyl and polyester, although the latter tend to degrade faster by solar radiation and become opaque with time.

On sunny days the common box-type still produces between three and five liters daily of distillate per each square meter. This means a reduction in the depth of the distillant from 0.3 to 0.5 cm/day, thus, feeding can be performed once a day. This form of discrete or batch operation is practical when feeding is performed manually, as proposed for a rural family system.

3. Photochemical Purification Processes

The bactericide effect of sunlight has been known for a long time. At first, it was thought that this effect was due to the exclusive action of UV rays, afterwards, it was verified that it is determined by the combination of several wavelengths of the spectrum. Recently, numerous studies (Fisher et al. 2008) have been carried out to determine the conditions under which solar disinfection is possible. Results show that, mainly in tropical areas (preferably between 0 and 35° latitude), where solar radiation reaches a certain level (>500 W/m^2), it is possible to disinfect small volumes of water contained in translucent glass or plastic containers. Disinfection can be assumed to be safe and 100% inactivation is obtained when accumulated solar radiation exceeds 4,000 W-hs/m^2 during exposure time, which is generally after 5 or 6 h. Experimental studies have determined that the time required for total removal of certain microorganisms varies between 15 min and 8 h.

It was found that the dose of solar radiation required to inactivate E. coli, the bacteriophage f2, and a rotavirus was approximately 555 W-h/m^2 measured in the range of 350–450 nm of wavelength, or the equivalent of 5 h around noon at 35° latitude. Likewise, the encephalomyocarditis virus was twice as resistant to solar radiation.

Several preliminary experiments were conducted to evaluate the effectiveness of this method in total and faecal coliform removal at 45° latitude. In these experiments, different water volumes were exposed in containers of different materials (polyethylene bags, glass bottles and plastic demijohns) for 5 h. Every hour, a sample was taken and the result of each sample was compared with the initial population of bacteria, to obtain the removal percentage. The results of these experiments showed that total coliform removal is more efficient in polyethylene bags and 99% removal is achieved in 4 h of exposure. Therefore, it is assumed that by using this material, removal is quicker, and in a way this is regardless of the volume. It was also observed that when using plastic demijohns, disinfection was slower and that 6 h were required to achieve 99% removal. Finally, glass bottles showed the lowest efficiency; for a 2-l volume, 4–6 h were required to achieve total disinfection.

These preliminary results were the basis to consider this procedure as adequate for rural communities. The method is extremely simple and economic.

However, there are still many doubts regarding the process in sites with latitude more than 45°. The main doubts were: what solar radiation conditions make disinfection possible; what should be the turbidity limit; and what level of bacteria concentration is possible to inactivate by applying this process.

4. Combined Process of Solar Purification

We proposed a device consisting of water feed deposit, a thermo siphon and a condenser. It is useful in areas where the temperature is not high enough for condensation to occur; in such cases, the thermo siphon heats the water before it passes to the condenser. The thermo siphon is a sealed wooden cabinet, with two transparent glass sheets measuring 80 × 80 cm with a 2 cm separation between them. The collector has 15 copper tubes, 1.5 cm in diameter, connected to two heads, 2.5 cm in diameter: a lower inlet head and a higher outlet one. The structure is supported on a laminated tray painted dull black. The thermo siphon is connected to the condenser by means of a copper pipe 1.5 cm in diameter, and it has a stopcock to regulate the flow to one drop per second. The condenser is a wooden hermetically sealed cabinet. In the front, it has a transparent glass sheet, 80 × 60 cm. Water from the thermo siphon is collected in a laminated tray in the lower part of the condenser, where it evaporates when the temperature rises. The distillate is collected in a tray measuring 60 × 15 cm with an orifice in one end that drains to the collection deposit. When the stopcock opens, the water flows to the thermo siphon and on to the condenser tray. Then, the stopcock is closed and it is necessary to wait for the temperature inside the collector to rise up to approximately 70°C. Then the water from the thermo siphon flows up to the condenser tray.

4.1. EXPERIMENTAL

The waste water from kitchen to be treated was stored in a tank in which a catalyst TiO_2 powder is mixed in desired proportion of 0.1%. The titanium dioxide powder was specified as having 80/20 anatase/rutile composition, primary particle size~ 30 nm and surface area 50 m^2g^{-1}. Readings were taken at different retention time from 1 to 12 h. A flow meter was used to record the system flow rate. The fluid was pumped into the reactor where it formed a thin layer of water so that the fluid comes in contact with the solar radiation and it is continuously recycled.

After every 1 h some sample was taken out for taking readings. Chemical oxygen demand was measured by reflux method titrating against solution.

Photo-catalyze reactions have been successfully modeled with a Langmuir equation. Reaction rate was 0.1. From the first order kinetics, the required residence time can be calculated by using mentioned equation. The residence time needed depends on the desired final degradation of the effluent. Reactor design is done on the basis of residence time required for desired degradation of effluent and the type of reactor.

TiO2 (1 g/l) was used to repetitively degrade different solutions of same concentration effluent. After one use (UV irradiation for 6 h) the solution was filtered and the catalyst rinsed with water. Then the so-used catalyst was employed to degrade a new solution having same concentration for 6 h. The process was repeated for some times.

Domestic waste water of initial COD 870 mg/l was taken for the experimental study and it was exposed under solar radiation on experimental set up at reactor angle of 30° and constant discharge of 60 l/h so as to get thin layer of water.

It was observed that after every hour COD got reduced and in 12 h of solar exposure time, it got reduced from 870 mg/l up to 220 mg/l. As observed, there is a substantial decrease of the COD of the solution, which continuously decreases with time. COD is decreased to 50% in 4 h, while at the end of the experiment more than 85% of the COD is removed.

Catalyst reuse can be done after each run. It depends upon the amount of catalyst recovered because the catalyst may be poisoned by contaminants or be washed away in the discharge water. This will reduce catalyst life and require additional catalyst for each run (Zhang et al. 2001). The results show that after every use 8–10 % catalyst was lost. Degradation percentage also decreased marginally up to 4 uses and after that degradation was quite noticeable.

4.2. COST OF COMBINED SOLAR PURIFICATION

The following are the variables that have an important bearing on the cost of the solar purification process: rate constant, desired destruction level and reactor design (Goswami et al. 1997). Capital cost including reactor, storage and settling tank, piping, fittings, pumps, blowers, controls, installation etc. Operational and maintenance cost including catalyst, pre and post treatment, energy, maintenance.

Capital cost was assumed as €1,150 and operation and maintenance cost as €600 per annum for the treatment of 200 l waste water per day. The cost of reactors and tanks in capital cost and catalyst cost in operating cost are the dominant components of overall solar purification process. Among the operation and maintenance cost, catalyst cost is the highest one. This cost can be minimized if catalyst recovery and re-use is done.

5. Conclusions

All solar purification processes mentioned can be implemented in rural areas with latitude more than 45° during summer. The final recommendation will depend on the geographical location, water quality and habits and preferences of the population. It is recommended that further research be carried out on the efficiency of other solar disinfection methods, in order to offer the population more alternatives.

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APPLICATION OF MEMBRANE AND MEMBRANE-LIKE TECHNOLOGIES FOR STATE-OF-THE-ART WASTEWATER TREATMENT

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Abstract. Membrane Bioreactors (MBR's) are at the present time considered a key technology in wastewater treatment, either as a final process, or considering further additional options of water reuse, which is an emerging issue in many water-scarcity areas throughout the world. MBR technology has proved to provide reuse-quality water, and offers the unique capability to allow such upgradings while minimizing both the needs of available space and of building additional structures in an existing plant. In this paper, typical MBR projects, representing large- to small-scale applications, examples of plant upgrading, hybrid concepts, and different flow concepts, as well as examples of membrane-like applications, are illustrated.

Keywords: MBRs, WWTPs, wastewater, upgrading, nutrients, energy, BCR

1. Introduction

Membrane Bioreactor (MBR) technology is the combination of traditional activated sludge treatment with sludge separation by micro- or ultra-filtration membranes (pore size of typically 10 nm to 0.5 µm), to produce a particle-free effluent. The latter step replaces the clarification basins traditionally used in the activated sludge process to achieve suspended solids separation by gravity. The barrier offered by the membrane system, in addition to solids separation, provides some degree of disinfection of the treated effluent, and also enables process operation at higher sludge concentrations (typically up to 20 g/L versus

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2–6 g/L commonly achieved with conventional systems), and therefore allows substantial reduction of necessary footprints and volumes of facilities.

MBR's are, at the present time, considered a key technology in wastewater treatment, either as a final process, or considering further additional options of water reuse, which is an emerging issue in many water-scarcity areas throughout the world.

MBR-technology applications in the field of municipal wastewater treatment started over 20 years ago, when submerged membrane packs were first experimented in Japan by Yamamoto in the 1980s. Since then, MBR technology has become one of the most versatile environmental technologies, finding application in wastewater treatment, water treatment, water desalination, groundwater remediation, water reuse, and virtually any other existing or imaginable water-related process, in Europe (Figure 1), as well as worldwide. The first full-scale applications were seen during the early and mid-1990s, initially in small units, serving individual buildings, and, later on, in small municipal facilities. As of today, submerged MBR technology can easily be found as the core element in wastewater treatment plants of any size, municipal and industrial.

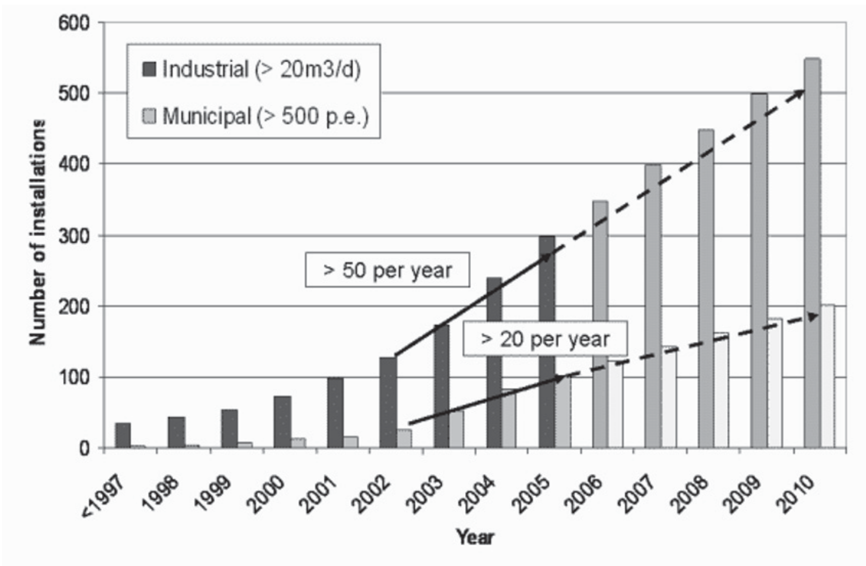

Figure 1. Industrial and Municipal MBR plants in Europe (Lesjean and Huisjes 2007).

If adoption of MBR's was initially limited because of the higher costs and uncertainty over the life of the membranes, the situation has changed over the past ten years. Firstly, membrane costs have decreased significantly, and steel and concrete costs have escalated, economically favouring smaller MBR-based systems with a steady trend that makes these plants more and more competitive with the conventional technologies, such as CAS (Conventional Activated Sludge), in particular where the peculiar MBR advantages (small footprint and volumes) can play the difference. Secondly, there is nowadays more certainty on the process life of membranes so that replacement costs can be planned and quantified with greater certainty.

In this paper, a few typical MBR projects, representing large- to small-scale applications, examples of plant upgrading, hybrid concepts, and different flow concepts, as well as examples of membrane-like applications are illustrated.

One of the major drawbacks of submerged MBR technology today is still represented by the energy required for the conduction of the process. Some examples of solutions introduced to minimize energy demand are also discussed.

An example of membrane-like technology is also illustrated, consisting of a patented bioreactor (BCR® – Biomass Concentrator Reactor) that can perform much like an MBR in many situations, avoiding some of the drawback (mainly energy requirements) of the former.

2. MBR Applications in Large WWTPs

Nowadays MBR's are being designed for plants as large as 120,000 m^3/d average flow. While many issues are the same regardless of size, the design of a large scale MBR facility has increasing complexity due to the complications of solids treatment, flow variation, and end-of-the-line reliability issues.

Currently, one of the largest operating MBR installations in the United States is the Broad Run Water Reclamation Facility, a new 42,000 m^3/d plant located in the Dulles Area Watershed, upstream of a drinking water supply in the Potomac River basin (Fleischer et al. 2009). The facility, using a membrane bioreactor (MBR), followed by granular activated carbon (GAC) treatment, and ultraviolet (UV) disinfection, is designed to meet very stringent discharge standards, including total nitrogen (TN) ≤ 4 mg/L, total phosphorus (TP) ≤ 0.1 mg/L, and COD ≤ 10 mg/L. The MBR is operated in a five-stage Bardenpho configuration, and modified to save energy by recycling the highly-oxygenated return activated sludge of the MBR to the first aerobic stage. Alum is introduced in the MBR basin for phosphorus removal. The facility also incorporates a fully automated plant-wide control system to optimize treatment efficiency, and energy and chemicals consumption.

Through optimization of recycle streams (anoxic and nitrified recycles and RAS), aeration control, and the removal of soluble organic nitrogen in the activated carbon treatment, the plant is able to meet an average effluent TN concentration of less than 2.5 mg/L without supplemental carbon addition, and meets the 0.1 mg/L TP permit limit through the single-point alum addition directly in to the MBR .

2.1. PROCESS OPTIMIZATION IN LARGE WWTPS

The Ulu Pandan MBR Plant (Singapore) is a retrofitted MBR demonstration plant that supplies users 23,000 m^3/day of industrial water, from an influent that is 90% domestic and 10% industrial wastewater. Figure 2 shows the schematic diagram of plant. Two aeration tanks in the old Water Reclamation Plant were each converted to anoxic and aeration zones (40% and 60% of volume, respectively). The mixed liquor in the bioreactor was designed to be in the range of 6,000–10,000 mg/L.

The membrane tank was divided into five membrane trains, each fitted with five membrane cassettes, with a total area available for filtration of 37,920 m^2. Solids in the membrane filtration compartments were designed to be as high as 12,000 mg/L. The reinforced ultrafiltration membranes were immersed directly into the mixed liquor; the MBR system performance was controlled and monitored on-line by a SCADA system.

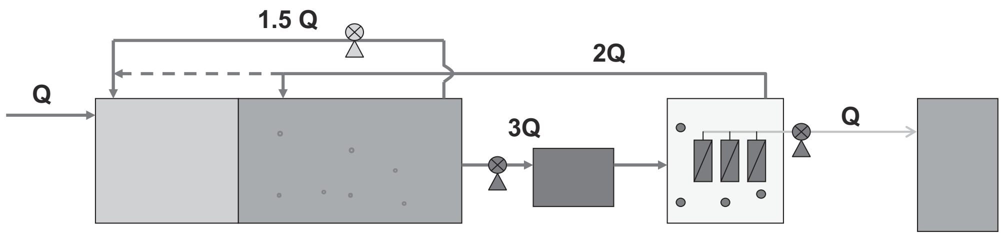

Figure 2. Schematics of the Ulu Padan MBR plant (Tao et al. 2009).

The plant optimization (Tao et al. 2009) consisted of reducing overall energy consumption without compromising product quality and quantity. Baseline studies were first carried out to identify the major energy-intensive components; then, a comprehensive system optimization was carried out, including the operating parameters SRT, MLSS concentration and recirculation, process aeration and membrane scouring rate.

Through pilot studies, energy consumption was initially reduced from 1.3 KWh/m^3 to less than 0.7 KWh/m^3. As blowers and mixed liquor transfer pumps are the major energy consuming equipment in these facilities, variable frequency devices were installed; thus achieving a reduced energy consumption as low as 0.59 KWh/m^3 at design conditions (10,000 mg/L MLSS). As sludge retention time (SRT) and MLSS level in the bioreactor are linked together, both can be controlled by daily wasting excess sludge from the system. By reducing MLSS level to around 6,000 mg/L from about 10,000 mg/L at initial start-up, the average specific energy consumption was further reduced to 0.549 KWh/m^3.

Two mixed liquor recirculation options were available at the Ulu Pandan Plant: option 1 was to recirculate mixed liquor (ML) (2Q) from the membrane tanks directly to the inlet of the anoxic tanks; option 2 was to recirculate ML (2Q) from the membrane tanks to the inlet of the aeration tanks, and recirculate ML (1.5Q) from the end of the aeration tanks to the inlet of the anoxic tanks. The second option allows to utilize the residual oxygen in the ML and reduce its possible impact on denitrification efficiency. However, requirements of total nitrogen removal were not very stringent, and the saving of process aeration through such recirculation was not obvious. Option 1 was therefore adopted: this reduced energy requirements as the additional 1.5Q recirculation was eliminated, and energy consumption was reduced to 0.535 KWh/m^3.

Oxygen sensors were initially installed in the aeration tanks to monitor and control oxygen levels, with setting point at 1.5 mg/L DO. This value, however, tuned out to be in excess of process requirements, and the incorporation of online ammonia -nitrogen and TOC meters, allowed further reduction of process aeration without compromising process performance. In the end, process aeration could be reduced to 60% of the design value, with no obvious impact on MBR effluent. This led to an energy consumption further reduced to 0.475 KWh/m^3.

Initially, a 10s ON/OFF cyclic membrane air scouring was incorporated in the design of the filtration system, already helping to save 50% on membrane cleansing energy. More than 30 months of continuous operation suggested that membrane aeration rate could be further reduced, allowing to save an additional 40% of these requirements, and dropping plant energy consumption to around 0.4 KWh/m^3, while maintaining discharge standards. The optimization thus led to overall energy savings equal to 2.52 MW-hours per year.

3. Small-Scale Application of MBR Technology

MBR technology can also be applied at the very small scale (household), replacing low-level technologies such as Imhoff tanks and maintaining BOD_5 removal efficiencies greater than 99%. Matulova and Hlavinek (2009) evaluated the performance of a three-tank-in-series (each with a volume of 0.58 m^3), single-household wastewater treatment plant with submerged membrane module (household MBR plant) serving a four-people family house, and comparing the response of MBR and CAS systems to different conditions during real operation, such as long periods of zero influent/load, or the presence of large amounts of concentrated wastewater, extreme winter temperatures (below 5–6°C), and high pH values.

The MBR setup showed an important advantage compared to a CAS process with secondary clarifier, as the membrane prevented the leak of biomass from the biological system (particularly at a low hydraulic loads typical of a household WWTP design). The MBR showed in this respect advantages over conventional processes, however, such superior effluent quality is not always requested, especially at really small-scale applications, and the combination of higher investment, operational costs, and a higher degree of process complexity also brings negative implications on the applicability of this technology. Capital and operational costs analysis of the system, compared with conventional single household WWTP and cesspit (Imhoff tank) systems shows that at this scale, capital and operational costs of household MBR's significantly exceed those of conventional household WWTP.

Bodik et al. (2009) studied the behaviour of a commercial, domestic WWTP with immersed membrane module over the long term. The domestic WWTP with total working volume of 1,450–1,500 L was installed at the municipal WWTP Devínska Nová Ves, near Bratislava (ca. 30,000 PE). The tested plant consisted of primary settling with volume of 730 L, and a biological AS reactor with volume of 720–770 L (Figure 3). Raw wastewater, after passing through the fine screens of the municipal WWTP, was pumped into the pilot at the rate of 450–700 L/d. Suspended solids were then settled and accumulated at the bottom of the settling volume. This wastewater then entered the biological AS reactor equipped with immersed membrane modules and two fine-bubble aerators. The air flow rate was 60 L/min. Long term operation of the activated sludge tank without excess sludge wasting was possible due to an effective pre-treatment phase (high HRT in the pre-sedimentation tank). Problems were encountered with membrane fouling that could not be removed or suppressed by air scouring or other physical means (such as backflushing of the membrane by reversing the flow of water through it to dislodge the fouling layer), but demanded chemical cleaning. Notwithstanding these shortcomings, this study confirmed the possibility of long-term operation of domestic WWTP with immersed membrane modules.

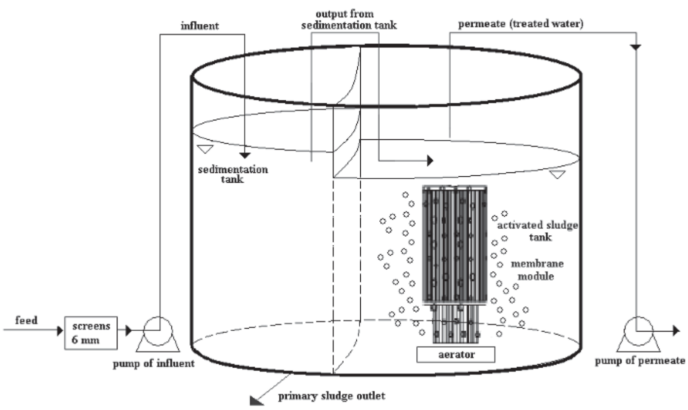

Figure 3. Commercial domestic WWTP with immersed membrane module.

4. Small-Scale Application of MBR Technology

As pressure on existing plants and/or treatment requirements will raise, upgrading of existing WWTP's will become a greater challenge than the construction of entirely new plants, as facilities do exist already, and space for new construction/expansion will be at a premium. MBR technology has already been considered as an alternative for WWTP's upgrade, and is indeed one of the most suitable ones: retrofitting of existing activated sludge plants with the conventional technology would demand substantial increase of both the activated sludge volume and (even more) of clarification surface.

This technology has already been proven to provide reuse-quality water and offers the unique capability to allow upgradings while minimizing the need of building additional tanks or use more space on site. New MBR technologies using external, tubular membranes arranged into membrane "skids" can greatly simplify plant upgrading and retrofitting by placing the membranes outside of the bioreactor, rather than immersing them in the mixed liquor. The flexibility offered by an external membrane design makes MBR upgrades practical for any suspended-growth treatment plant, regardless of bioreactor configurations or tank dimensions. In addition, operating costs of the innovative external membrane system is less than the immersed one due to the inclusion of a patented airlift that internally air scours and cleans the tubular membranes as they operate. As a result, significantly less scour air is required than with immersed systems, and the overall operating cost of the MBR system is reduced (LeBrun and Morgan 2008).

4.1. UPGRADING TO HIGHER EFFLUENT STANDARDS

In addition to drastically reduce volume/surface requirements in retrofitted plants, MBR technology could also be considered where specific effluent criteria, such as higher removal of suspended solids or absence of pathogens, have to be met, such as when discharging into small creeks, bathing waters or sensitive areas. One such example has been reported by Frechen et al. (2009) at the WWTP of Bergheim-Glessen (Germany), where MBR technology was used to meet advanced requirements caused by the discharge of wastewater in to a sensitive wetland.

Upgrading occurred at the existing location, using already existing facilities and nearly doubling WWTP capacity from 5,000 to 9,000 P.E. by introducing MBR technology. Mechanical pre-treatment was completely renewed, consisting of screening, aerated grit-chamber and grease-trap, and sieving (mesh 0.75 mm). The existing oxidation ditch was used as activated sludge volume, followed by membrane modules installed in four separate filtration chambers.

The operating parameters of the upgraded facility, shown in Figure 4, are: SRT about 25 d, MLSS conc. 8 kg/m³, maximum inflow HRT = 6 h.

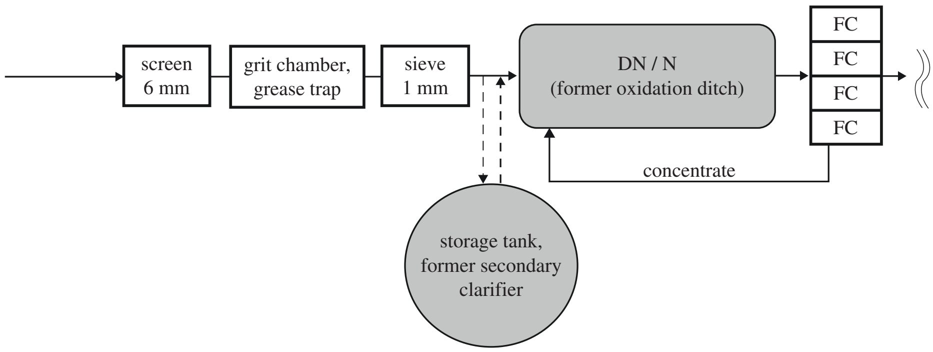

Figure 4. Upgraded scheme of Bergheim-Glessen WWTP (Frechen et al. 2009).

It should be remembered that secondary clarification is one of the “bottlenecks” of a traditional WWTP (Capodaglio, 1994) and that clarification failure (due to poor sludge settling characteristics and/or excess hydraulic loads on the clarifier) may lead to temporary or permanent failure of the entire process, depending on the degree of solids loss. Older plants, which drainage basin has substantially expanded during the service years are especially subject to this problem. Replacement of traditional clarifiers with membrane filters can be a way to avoid clarification poor performance caused by chronic hydraulic overload, thus upgrading and increasing plant capacity.

5. New Plant Layouts Made Possible

The small footprint required by MBR plants allows fully enclosed installation in buildings designed to blend in with the surrounding environment, thus making possible to address issues of landscape integration, amenity, and not last, odour or noise abatement, for example in tourism-dedicated areas or in the vicinity of protected areas.

For the replacement of the Johns Creek Water Pollution Control Plant, the Fulton County Commissioner Office designed a novel-type 60,000 m^3/d facility integrated in a 20 ha environmental campus that includes a park open to the public, 15 ha of nature trails, and an 800 m^2 educational facility that will be used to educate schoolchildren about the impact of water quality on the environment. At the heart of the below-ground water reclamation facility is the innovative use of membrane bioreactor technology, allowing the footprint of the JCEC facility to be much smaller than that of a standard facility. The JCEC facility sits on four acres; the building is designed to mimic the architecture of a historic mill. All the equipment is housed indoors, with silencers and sound enclosures installed around most of it, and an odor control system among the most advanced (Figure 5).

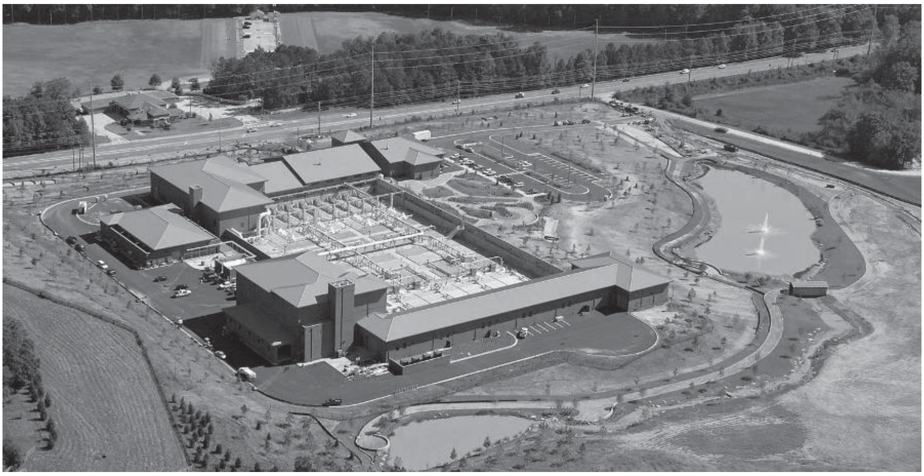

Figure 5. The JCEC 60,000 m^3/d WWTP.

6. Nutrient Removal with MBR's

Biological processes in MBR systems are no different from those in traditional AS systems with settling tanks, therefore process design principles are the same. Nutrient removal MBR plants are seeing more widespread application, as the solids-free effluent they can provide is particularly desirable in situations where very low effluent total phosphorus (TP) concentrations must be achieved: such solids-free effluent in fact allows plants to meet limits of less than 0.1 mgP/L (Dold et al. 2009).

Liu et al. (2009) report about the City of Siloam Springs, (AK, USA) which WWTP must meet an effluent TP limit of 0.025 mg P/L. Achieving these limits implies reaching very low soluble P levels, and essentially, a solids-free effluent: both conditions could be met with a pilot MBR plant with limited chemical addition. Process configuration in this case was a UCT-type nitrification-denitrification system with a membrane tank replacing the settler. Unique feature of the system was a small contact tank (10 min HRT) for chemical (alum) addition, located between the main aerobic reactor and membrane tank (PVDF hollow fibre membranes with normal pore size of 0.04 mm and maximum pore size 0.1 mm. Table 1 shows the design and operating parameters of the process.

TABLE 1. Design and operating parameters for the Siloam Springs pilot (Liu et al. 2009).

Reactors	Volume (L)	Operation	Values (units)
Anaerobic (AN)	1,816.8	Flow rate	21,802 (L/d)
Anoxic (ANO)	3,633.6	SRT	51 (d)
Aerobic (AE)	4,542	Dissolved oxygen (DO)	2 in AE and 7 in MOS (mg O/L)
Alum contact tank	378.5	Alum dosing	17.5 mg/L influent flow
Membrane tank (MOS)	265.7	Temperature	Approximately 20°C

The pilot plant was operated for about one year. Measured COD values during this time indicated that COD removal was very good, with an average effluent COD of 12.7 mg/L; measured effluent NH_3-N concentrations showed that the system nitrified completely, with an average NH_3-N of 0.61 mg/L (influent TKN 24–55 mg/L). Measured effluent TP show that the system exhibited biological P removal with varying efficiency before chemical addition was introduced. With chemical addition, the effluent average TP was 0.024 mgP/L.

The test results indicated that an MBR process was able to achieve extremely low TP permit limits, and that chemical addition did not affect other biological activities, i.e. COD removal, nitrification and denitrification.

It can therefore be concluded that MBR processes can successfully operate nutrient removal under tight requirements; however, due to the characteristics of these systems, special consideration ought to be given to some aspects of plant design and operation. These include:

1. solids: in traditional nitrification-denitrification processes, MLSS concentration is approximately uniform in the different zones, while in membrane processes MLSS concentration can differ substantially depending on recycle flows arrangements, resulting in sludge distribution between anaerobic, anoxic and aerobic zones different from those expected. Also, in traditional systems with settling tanks, MLSS concentration does not change significantly in the short term, while in MBR systems MLSS concentration can show substantial hourly variations due to time-varying inflow. Hence, also mass fraction distributions can change with time, complicating the problem of sizing zones for optimal nutrient removal performance;
2. dissolved oxygen: MBR systems typically operate with high DO concentrations (6–8 mg/L) in the membrane tank. If recycle flow from this zone is directed to anoxic sections upstream, high DO (and possibly, nitrates) will reduce overall nutrient removal efficiency. Recycle arrangements must take this into account.

7. Operational Problems

Perhaps the major obstacle to a wider acceptance of MBR's in practical applications consists of the problems associated to membrane fouling, leading to a gradual decline in permeate flux, and shortening the longevity of membrane modules. Many strategies have been proposed to minimize these effects, such as: preparation of antifouling membranes, pretreatment of feed suspension, careful control of operating conditions, appropriate membrane fabrication and modification. Among the most efficient strategies, which can save at least 10% of the operating cost, is optimization of cleaning operations (Wang et al. 2009).

Literature (Nyström and Mänttäri, 2009; Moreau et al., 2009; Pattanayak et al., 2009) shows that fouling is a complex processes, and cleaning efficiency is largely governed by membrane fouling mechanism, cleaning mode, pollutants species, washing conditions (detergent species, temperature, volume, and concentration, pH, cleaning time, backwashing mode, backwashing cycle and transmembrane pressure) and so on. De La Torre et al. (2009) performed an intensive monitoring campaign on four MBR plants, investigating fifteen operational parameters on a weekly basis in the attempt to determine the most significant indicator for membrane fouling. Their study demonstrated that there is no single universal fouling indicator, but that explanations must be searched in the combination of several parameters.

Statistical multivariable analysis identified the following parameters as likely indicators of fouling: transparent exopolymer particles (TEPs) and bTEP (bound TEP) (TEP represents a new parameter recently introduced especially for the investigation of MBR fouling), temperature (since it influences nitrification and the flocculation state of the biomass – floc sizes and release of extracellular polymeric substances), and nitrate concentration.

An interesting result was that classical parameters for filterability and settleability taken from conventional AS practice, still commonly used for evaluation of sludge filterability in MBRs, like time-to-filter, capillary suction time and diluted SVI did not show strong relationships with sludge critical flow.

8. Membrane-Like Technology

Capodaglio and Callegari (2009) applied a membrane-like-technology biological reactor to achieve biological removal of MBTE (a compound that can be biologically treated only at high MLSS concentration) from groundwater. The first difference between this reactor (called BCR®, Bio-Concentrator Reactor) and traditional MBR's lies in the material and characteristics of the media filter. In this case, the filter consists of an ultra-high-molecular-weight polyethylene sheet (UHMWPE), 4 mm thick, modeled in a corrugated cylindrical shape, with pore size averaging 20 μm (Figure 6). Another significant difference is that the

BCR® is more competitive with mainstream conventional MBR's, as these must use pressure or vacuum pumps to produce the transmembrane pressure to allow water permeation, while the former relies on gravity flux alone to operate, under very limited head (max. 5 cm of water); the limited operational pressure on the filter also limits fouling and allows a longer operational duration of the filtration medium. Finally, the specific shape of the filter medium allows for on-line filter backwash, thus allowing semi-continuous process operation and minimum downtime due to maintenance.

Limited testing on urban wastewater have shown interesting initial results. Pending confirmation, it is thought that the BCR can have a role in treatment of urban wastewaters, with benefits similar to those of MBR processes, where a high degree of effluent filtration (or disinfection) is not required.

Figure 6. Interior view of the BCR.

9. Conclusions

MBR technology has become a successful alternative to the conventional approaches for treating domestic and industrial wastewaters. This process produces effluent with excellent quality that can be reused for different applications. The advantages associated with MBR's, such as small footprint, flexible design, and possibility of automated operation caused an exponential increase in the application of this technology in the last two decades.

MBR technology is ideally suited for traditional AS plant capacity/ efficiency upgrades as it requires minimal expansion in terms of new structures. It is fully applicable in the case of nutrient removal requirements and can be adapted to existing processes significantly increasing nutrient removal efficiencies. Optimization of plant energetic performance is possible by carefully considering and reassessing all internal requirements.

The technology, by virtue of its minimalistic volumetric requirements can also allow new WWTP development standards to allow reduced environmental and visual impact and better landscape integration.

MBR-like technology has also been studied and initial evaluations are promising. These technologies are similar in concept to membrane filtration, but operate at larger mesh values (typically 5–20 μm) so that disinfection is not assured; on the other side, they are much more economical to run than MBRs, especially as far as energy requirements are concerned. They are also less subject to fouling and can be cleaned by simple backwashing.

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Sitology

MBR Network – www.mbr-network.eu

TYPE OF SEWER SYSTEM – TECHNICAL AND ENVIRONMENTAL ADVANCES AND ARRANGEMENTS

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Abstract. The last time changed the view on water and waste water infrastructure. The goal is to reach not only the new sewer system, new water supply built, but the very important becomes the rehabilitation and reconstruction. The present state, only 59.4% (Figure 1) connected people on public sewer system, make press for designing remain percentage connected, base on EU promise fulfilling. The decision, which type of sewer system built makes press on investments and for their decreasing to find a new solution for the water management solve as complex. The experiences with the operating combined and separated sewer system involve the questions concerning technical, economical and environmental aspects. Only the general problem comprehension will give us the proper answer for decision. The advances and effect arrangements of various sewer types give us the right direction.

Keywords: water supply, sewage, advances, combined, separated sewer system

1. Introduction

The experiences of the Slovak sewer system operation could define the advances comparable the past approach. The extensive sewer system built in last 15 years was orientated to build the separated sewer system. The combined sewer system became expensive and concerning the arrangements didn't fulfill the extensive requirements for the general covering of the sewer system in Slovakia. The newest

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information about public sewer system covering, show us, that only build the domestic waste water sewer system can fulfill the EU promised to dewater municipalities more than 2,000 and less than 10,000 inhabitants till year 2015 and municipalities with agglomeration more than 10,000 inhabitants till 2010. It is the Slovakia's obligation. The failure of this obligation will be affected by the penalty.

Comparable EU countries, the Slovakia is lag behind the inhabitants connection on public sewer system. In 2008 it was only 59.4%. The highly-developed EU countries such as Germany, France, Finland, Spanish, Netherland and Austria it represent 84.4%.

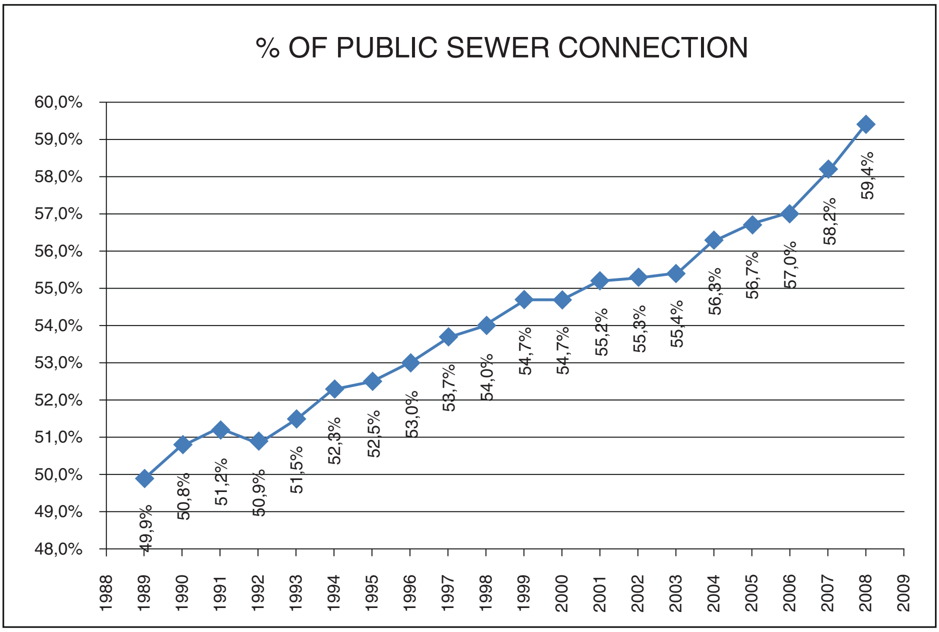

Figure 1. Slovakia public sewer connection advance in last 20 years.

The Slovakia plan is to eliminate this adverse state till 2030, but with the EU grants supporting. Fulfilling the EU promise will be beneficial influence on water course purity.

The quality of treated waste waters outflow from WWTP fulfills the limits on 90%. It means that Slovakia must reach to advance in technological WWTP equipment and switch to more modern revitalization methods. The Ministry of Environment of Slovakia estimates the investment costs on €30 milliard. This is the draft estimate, because real audit of water management sector was not done to this time.

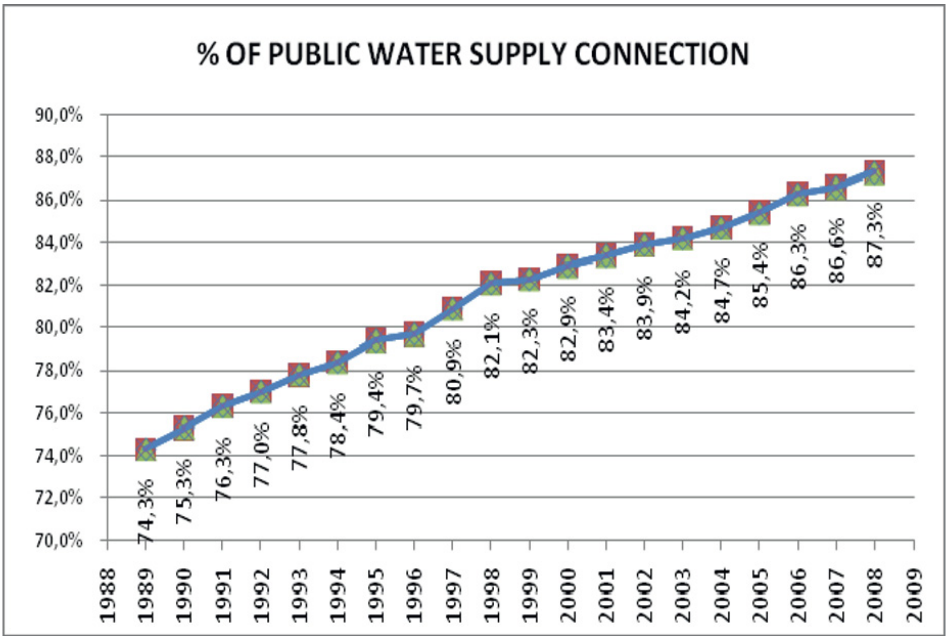

Figure 2. Slovakia public water supply advance in last 20 years.

2. Water Price Influence

The opinion about water price is very serious problem. The water companies need huge money for fulfilling the EU promises concerning waste water collection and treatment. This promise was done by Ministry of Environment of Slovakia, so the responsibility of water companies is disputable. For the fulfilling the promises, the water companies make the press on the Regulatory Office for Network Industries, which every year provide the decree about water price. The analysis of water price background setup the water price on level, which is tolerable for costumers and can reflectance the water companies' operational costs. It doesn't respect the fast investments into water sector. The results of discussion about the water price show: (A) from one side, negative effect of the low individual water connection through household connection and decreasing water demand. Together with this fact, it makes the press to decrease waste water price. It concern mainly in not high developed regions of Slovakia. (B) On the other hand, not enough sources for the new build up send the Slovakia into the ungrudging situation. The indebtedness of water companies, don't allow to loan drawdown. This situation asked us about the inadequate EU promises and make press on the government to initialize the negotiation process about the EU promises compliance. In "Conception of water management policy in the Slovak Republic in 2005" approved by NR SR (national council of Slovakia, Slovakia plans perspective percentage of connection to year 2015 approximately 75%. The 56% of exploitable water supply (Figure 2) are located on the west part of Slovakia, east part dispose only 17%, the rest 27% are on the middle part.

The permanent decrease of water demand causes by the agricultural and industrial production decreasing too. The water demand decreased in 36% in last ten years. The largest volume of water consumption was the water supply waters that decrease about 32%. The irrigation decrease about 60%, the food industry about 46% and other industry about 65%.

The water demand is about 115 l/cap/day, comparable year 1990 it was 200 l/cap/day. The decreasing of water consumption is in the relation with the low purchasing power. Comparable Hungary – 135 l/cap/day, Poland 124 l/cap/day it is the low consumption (Ghawi and Kriš 2009). Only Czech countries have 107 l/cap/day. The present sate in EU countries, with 160 to 170 l/cap/day Slovakia wants to reach till years 2020–2030.

3. The Legislative

The base document, which has influence on water management is the Water framework Directive about Waters No. 2000/60/EC, with define the legislative framework of European water policy. The most important document is the directive No. 91/271/EEC concerning urban waste water treatment, and their collection, treatment and discharging, from the 21 May 1991. Present Slovak legislative is in accordance with the No. 91/271/EEC. The transformation is into the Act No. 364/2004 about waters and changed by the Slovak national council No. 372/1990 about delinquency called "Water Law" and Government Decree Act 296/2005, which determine the requirements for qualitative and quantitative limits of surface and others waters, the pollution limits of waste waters (Mahríková 2009). The problematic concerning public water supply and waste water system is defined by the Act No. 442/2002 about public water supply and sewage, complemented by the Act No. 276/2001 on Regulation in Network Industries and on Amendments and Additions to Some Acts. In the 2003 was the whole Slovak region announced as sensitive region by the Slovak government Act No. 249/2003, which constitute the sensitive and vulnerable regions. The Slovak water legislative, connected to EU water legislative direction concerning water supply and waste water are directed to the environmental protection, with the aim to protect the water supply through the water management, ensure the access to the health water.

4. Separated Sewer System

This is the basic inhabitants living municipality requirement. The main role of the separated sewer system is dewatering the domestic waste water from residences to waste water treatment plant – WWTP through the sewer system. The people, who live in their residences, are not very often informed, which sewer system dewaters their waste water to WWTP. This illiteracy cause the problems with storm water dewater, mainly in residence areas, where the people connect their roofs and pavement areas to the sewer system in some cases, which is designated only for the domestic waste waters. People assert, that they pay the waste waters, so they have accrue dewater the roofs and pavement areas from their residence. This misunderstanding cause the problem mainly with the capacity and energy consumption of separated pumping stations, and consequently in WWTP. The role of water companies is to inform about the function and sewer system type, directed to residences. The Slovakia standard for determining the domestic waste water amount uses the follow design formula (1):

$$Q_{dwf} = I_{no} \cdot q_{wwp} \cdot k_h \tag{1}$$

where:

Qdwf – amount of domestic waste water s; Ino – number of inhabitants connected to the actual computed point; kh – maximum hourly coefficient, which depends on the inhabitants number Ino.

This (1) computes only the amount of domestic wastewaters, but this is determined for the sewer pipe diameter design. The pipe profile design depends on the computed amount of waste water Qd-dwf, and this value is twice Qdwf (2)

$$Q_{d-dwf} = 2 \cdot Q_{dwf} \tag{2}$$

The multiplication factor 2 show, that the pipe profile will be fill on half capacity. The rest capacity represents the reserve, which is exploiting for the annual sewer cleaning under sewer operation.

5. Combined Sewer System

The goal of the CSS – combined sewer system is dewater together domestic waste waters and storm waters. This sewage type is very old; it was built in the history in many big towns, such as Paris, London, New York and others.

What is the advantage? The historical principle was to provide the self cleaning service for sediments of dry weather flow without equipment exploitation.

The waste waters were drain directly to recipient, with only the dewatering interest. The idea about the waste water treating was not interested.

New era showed us, that the non-treated waters cause the various problems in the recipients. The huge recipients, such as big rivers, have the self cleaning ability concerning waste water s. But the population density increasing, together with living standard, causes the enormous amount of pollution increasing. Many rivers lose the self cleaning ability. It was the one reason for waste water treatment plant (WWTP) building.

The combined sewer system, dewatering the waters to the waste water treatment plants, causes the non-uniformity flow to the WWTP. That means, in dry periods the pollution goes directly to the WWTP. In wet period, the municipal waste waters are mixed with the storm waters. And this is the problem, because the WWTP is designed only for the municipality waste water treating and some polluted parts of storm water, mean first flush. The other storm waters needs to separate and send directly to the recipient, because the WWTP capacity and the technology process doesn't allow treat all waste water from the watershed.

This storm water separation is executed through the combined sewer overflow – CSO structure, which is designed for the specific amount of storm waters separation.

The Slovak big cities uses the combined sewer system for dewater the storm and municipality waste waters (Šerek et al. 1986).

The basic principle, how to determine the amount of storm and municipality waste waters is based on basic rational formula.

$$Q_{sw} = S\ .\ \mathrm{q}_{sw}.\psi \tag{3}$$

where:

Q_{sw} – amount of storm water; qsw – specific rainfall capacity (similar on specific storm/rainfall intensity) (l.ha-1s-1) (6); ψ – runoff coefficient (range 0–1).

Specific rainfall intensity qsw represented by capacity-duration-frequency – CDF curves are determined for 68 rain stations in Slovakia (Urcikán and Imriška 1986), which measure the rainfall intensity. The CDF curves are used mainly for periodicity/frequency 0.5 or 1.0, depends on locality size (Šamaj and Valovič 1973). The elaboration of rainfall intensity produces the block rains, through the CDF curves. This block rains, depends on storm duration is used for determining the storm water flow (McCuen 2007). Formula (3) determines only the storm waters amount. For total design flow determining for combined sewer system, we use the follow formula (4)

$$Q_{d-css} = Q_{sw} + Q_{dwf} + Q_b \tag{4}$$

where:

Q_{dwf} – represents dry weather flow – municipal waste water; Q_b – ballast waters. The amount of Q_{dwf} is neglected under the condition, when the Qdwf is less than 10% of Q_{sw}, The ballast water Q_b is included, because the sewer system is very often untightness.

The formula (4) shows, that in dry weather period, only amount of municipal waste water flows into the sewer system. This flow must be drain into the WWTP.

In the wet weather, when the storm start, the specific amount of waste waters are dewater to the WWTP and rest to the recipient through the CSO structure. The determination, which part will be dewatering to the WWTP is not easy for determining, because this determination influences the WWTP pollution and capacity loading or recipient pollution. The CSO structure is the very risk factor on CSS, concerning environment protection and cleaning process optimization. Slovakia uses two ways for the waste water flow determination: (a) method of the dilution ratio and (b) method of the boundary rain.

The dilution ratio n method defines as the ration between domestic waste water and storm water. Usually this ratio represents 1–4 or 1–8 in last time. The more dilution mean, that the larger waste water flow will be dewater into the WWTP for treating, and it means the greater recipient protection against pollution.

Determine the WWTP flow by using the Boundary rain method is base on watershed size and this is defined by formula (5)

$$Q_{boundary} = S.\psi \cdot q_b \tag{5}$$

where:

q_b – represents the specific capacity of boundary storm, range <from 10 to 25 l/s/ha>. This value depends on self-cleaning recipient ability. Generally the larger recipient, with the more self-cleaning ability, uses the smaller specific boundary rainfall capacity and vice-versa.

6. The System for Design

The many Slovak sewer system were designed and recalculated by the SeWaCAD – computational software system, which can design and recalculate existing sewer systems, combined and separated, by the rational formula. This system is a user friendly and with huge computer capacity. The goal of this system is to design the longitudinal profiles of sewer pipes, which is useful for build the sewers. The system works very dynamic, and the hydro-technical computation is directly transferred into the graphical representation. This software offers to solve the separated and combined sewer system. Because the combined sewer system design is more complicated when the domestic waste water sewer system; system contains the rainfall tool (Figure 3) with the rainfall database from 68 Slovak rainfall stations.

$$q_{sw} = \frac{K}{t^a + B} \tag{6}$$

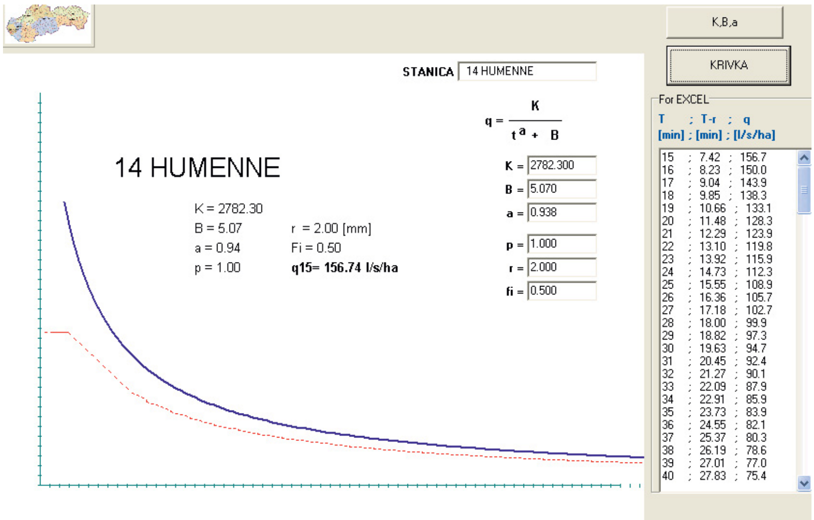

Figure 3. The capture of screen represents the rainfall curve for the rainfall station Humenne, the curve is computed by SeWaCAD software.

The formula (6) shows the basic principle of the qsw designation, where the K, B, a represent the parameters which represents the specific rainfall station, where the measurement data were elaborated. t – represents the time of the rainfall duration.

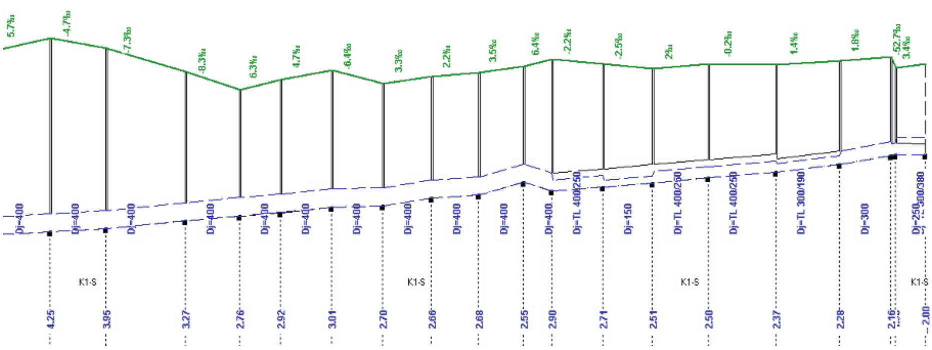

Figure 4. The longitudinal profiles for the sewer system design – example of the existing sewer system.

The Figures 4 and 5 show the existing sewer system (Stanko and Sirák 2009) and indicate the overload of this part of the sewer pipes. The color lines shows the percentage of overload of the combined sewer system (Figure 5), and the number in brackets shows the value of existing diameter and the other the design diameter of the sewer pipe (Mahríková 2008).

The design of the longitudinal profiles represents very hard work for designers; because it needs to be careful in the same time with the hydro-technical and graphical computes. Only the repeat computation could bring the requirement results. The system SeWaCAD allows designing not only the hydro-technical computes, but containing the slope generator, which can design the slopes for the designed pipes. Base on slope design, there is possibility of diameter change and vice-versa.

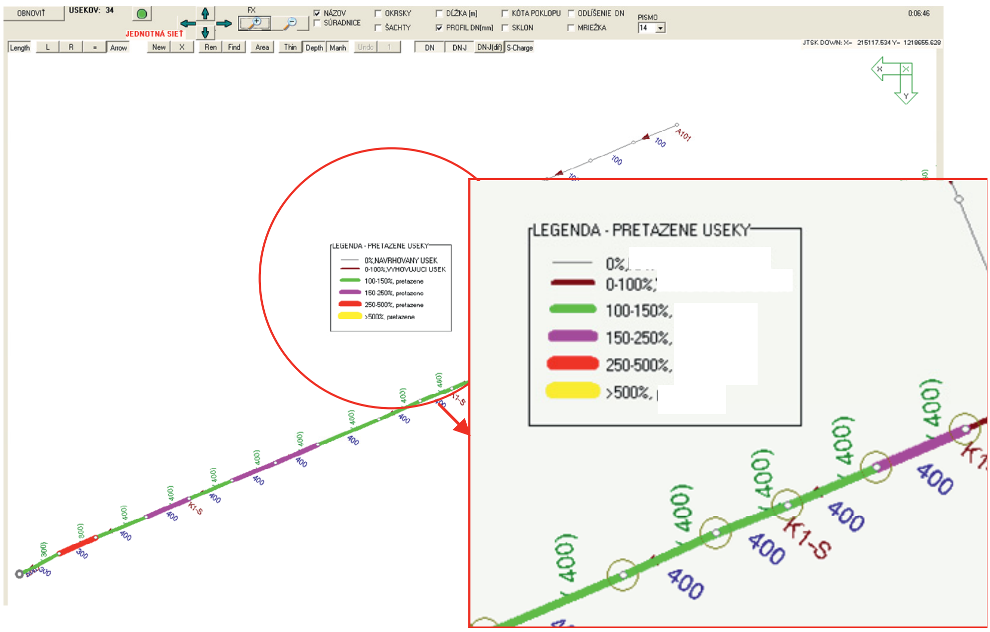

Figure 5. Example of sewer system overloading.

The recommendation for minimal profile of public sewer system is 250 mm diameter. In the past it was 300 mm in diameter for the sewer pipes design. Concerning the minimal slope computation the 250 mm has the worse influence on excavation depth and over-charge the investment costs. But on the other hand, the operational conditions are improved by using the new design conditions.

7. Conclusions

The improvement on the present Slovak situation concerning public sewer connection, which now represents about 59.4% (Figure 1) is complex process, which depends on technical, financial and legislative conditions, together with EU fulfilling processes in the water management. The chose for new sewer built up must consider all conditions. The paper presents the actual situation in Slovakia, which makes a high press for building the new sewers; briefly describe the technical software for the sewer system optimizing. The designing system must by effective and fast. We have to take occurrence on CSO too, than we plan to build the combined sewer system, because the environment pollution is in risk.

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OZONATION OF TERTIARY TREATED WASTEWATER – A SOLUTION FOR MICRO POLLUTANT REMOVAL?

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Abstract. The design criteria for wastewater treatment plants (WWTP) and the sludge retention time, respectively, have a significant impact on micropollutant removal. The upgrade of an Austrian municipal WWTP to nitrogen removal (best available technology, BAT) resulted in increased elimination of most of the analyzed micropollutants. Substances, such as bisphenol-A, 17α-ethinylestradiol and the antibiotics erythromycin and roxithromycin were only removed after the upgrade of the WWTP. Nevertheless, the BAT was not sufficient to completely eliminate these compounds. Thus, a pilot scale ozonation plant was installed for additional treatment of the effluent. The application of 0.6 g O_3 g DOC-1 increased the removal of most of the micropollutants, especially for compounds that were not degraded in the previous biological process, as for example carbamazepine and diclofenac. These results indicated that the ozonation of WWTP effluent is a promising technology to further decrease emissions of micropollutants from the treatment process. Additionally to the assessment of the removal potential for micropollutants, the technology was evaluated for the disinfection potential in regard to bacterial standard hygienic parameters and model viruses and the impact on acute and genotoxic activities. Furthermore the endocrine potential was investigated.

Keywords: wastewater treatment, micropollutants, ozonation

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1. Introduction

In recent years the occurrence of endocrine disrupting compounds (EDCs), pharmaceuticals, personal care products (PPCPs) as well as industrial and agrochemicals in the aquatic environment increasingly is reported by various authors (Daugthon and Ternes 1999; Kolpin et al. 2002). The application of BAT in wastewater treatment at the present level does not provide complete elimination of all micropollutants and subsequently, residues of the above mentioned substances enter the aquatic ecosystem through the emission of even treated wastewater. This poses new challenges for wastewater treatment. Since most of the micropollutants are of anthropogenic origin even tertiary treated wastewater is considered to be one of the major point sources (Ternes 1998; Kümmerer 2001; Heberer 2002a; Clara et al. 2004a) for the release into the environment. The removal potential for organic micropollutants during biological wastewater treatment meanwhile extensively is documented in literature both for conventional activated sludge treatment plants (CAS) and in membrane bioreactors (MBR), e.g. by Clara et al. (2004b, 2005a) and Joss et al. (2005). According to their studies no significant difference was observed between CAS and MBR when a critical solids retention time (SRT) necessary for nitrification (SRT >10 days at 10°C) was exceeded and the suspended solids concentration in the effluent was low for the CAS plants. Even though the concentrations of micropollutants are in the range of ng L-1, adverse effects on water organisms cannot be excluded, especially if the potential effect of EDCs on aquatic life is considered (Halling-Sørensen et al. 1998; Sumpter 1998; Arcem 2003; Sumpter 2008; Kümmerer 2009). Public awareness and the intensification of the urban water cycle, following increasing indirect reuse of surface waters as a drinking water resource, are two other reasons for the current research focus on the occurrence of micropollutants in the aquatic environment. Persistent compounds have been tracked from wastewater to drinking water (Heberer 2002b; Benotti et al. 2009).

Several technologies for further micropollutant removal such as ozonation (Huber et al. 2005), advanced oxidation (Huber et al. 2003), activated carbon (Westerhoff et al. 2005) and filtration (Poseidon 2004) have been investigated for their ability to further remove PPCPs and EDCs from wastewater.

Out of those technologies, the application of ozone proved to be a promising and suitable technology for the removal of micropollutants in laboratory, pilot and full scale experiments (Ternes et al. 2003; Poseidon 2004; Bahr et al. 2005; Huber et al. 2005; Bahr et al. 2007; Esplugas et al. 2007; Nakada et al. 2007; Hollender et al. 2009).

The application of Ozone in waste water not really is a new approach, but its application till now is rather limited to industrial applications and disinfection purpose, whereas the targeted application for micropollutant removal in municipal plants is a rather new application. This is the reason, why design criteria and operational experience are missing till now despite intensive research done on international level.

Expectations and treatment goals for the application of ozone in municipal wastewater treatment can be summarized as

Removal of organic micropollutants

Removal of color (humic substances)

Disinfection

Diminishing ecotoxicological effects

This should be reached by

Robust process technology

Easy operation and maintainance

Cost efficient methodology

Without the production of relevant oxidation byproducts

Especially the cost and byproduct aspects are referred to as limitations for a wider application. Indeed new studies (e.g. Schaar et al. 2010; Hollender 2009) show, that both aspects nowadays are no “killing arguments” against the application of ozonation in municipal wastewater treatment any more.

In this paper general aspects of the application of the ozonation process as well as results from a 1 kg h^{-1} ozonation pilot for the additional treatment of tertiary treated wastewater after full nitrification and denitrification are presented. This study supports design criteria that were investigated in recent scientific work. Values for ozone dosage and contact time as main design parameters as well as the requirement of an extensive tertiary treatment (e.g. low loaded activated sludge system with full nitrification/denitrification) now can be considered as assured.

2. Basics of Ozonation

Ozone consists of three oxygen atoms and is a reactive gas. It is a powerful oxidizing agent and forms hydroxyl radicals in contact with water. While ozone itself only oxidizes certain substances, the hydroxyl radicals attack a wide range of substances. Ozonation thus leads to the breakdown of various complex compounds. During this process, not only pollutants but also microorganisms are destroyed; for this reason, ozone is frequently used as a disinfectant.

Ozone is a very powerful oxidizing agent (E0 = 2.07 V) that can react selectively with a wide range of substances containing multiple bonds (such as

C=C, C=N, N=N, etc.) – and therefore aromatic structures (Figure 1), but not with singly bonded functionality such as C–C, C–O, O–H at high rates.

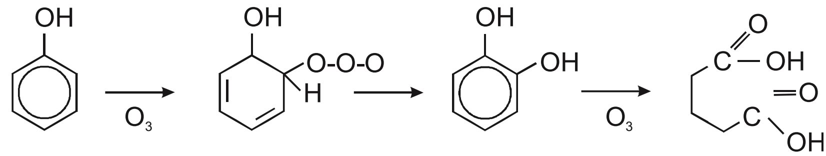

Figure 1. Cleavage of an aromatic ring structure by ozone attack.

Dissolved in water, ozone remains as O_3, reacts with electron dense chemical structures or it can decompose by complex mechanisms (Figure 2) producing the free hydroxyle radicals (OH•) that is even a stronger oxidizing agent then the molecular ozone. Whereas ozone is rather selective in regard to the targeted structures, the hydroxyle radical reacts comparable unselective.

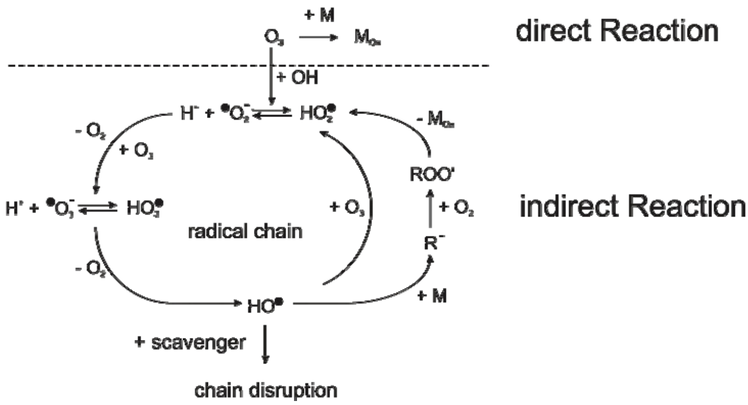

Figure 2. Chemistry of direct and indirect ozone reactions (adopted from Stählin 1985).

All oxidation reactions occur simultaneously, but depending on the matrix, presence of promotors for hydroxyle radical formation, scavenges and the nature of predominant residual substances in the previously biologically treated wastewater one or the other reaction predominates. Main water chemistry as water hardness (HCO_3^-), humic acids or orthophosphate can act as scavengers. In a watermatrix with a high scavenger content – as wastewater is – the indirect ozone reaction via hydroxyle radicals therefore is less efficient compared to the direct ozone reaction.

Due to the nature of substances addressed in the micropollutant discussion – most of them show aromatic ring structures – and the indirect ozone reaction on the one hand not avoidable in the wastewater matrix and on the other hand inhibited by scavengers, wastewater oxidation can be performed with molecular ozone only without initial consideration of AOP (Advanced oxidation process).

Both, direct and indirect ozone reaction can be considered as second order reaction:

$$d[S]/dt = k\,[S]\,[O_3]$$

k = reaction constant (velocity constant)
S = substance concentration
O_3 = ozone concentration

Reaction velocities of hydroxyle radicals are in the range of 108 and 1,010 L mol^{-1} s^{-1} and therefore faster compared to ozone reaction constants that are between 1 and 103 L mol^{-1} s^{-1}. The chemical structure of the target substances is responsible for the value of the reaction constant. Half life time additionally depends from the ozone dosage applied (Figure 3).

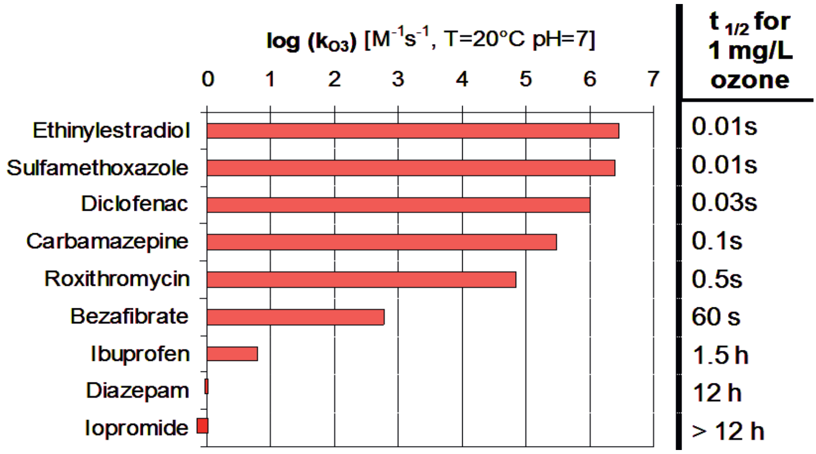

Figure 3. Examples for reaction constants of substances with ozone (Huber 2003).

Another conclusion that can be drawn from the Figure is that certain substances, as the x-ray contrast media Iopromide showing very low reaction constants will not be destroyed in reasonable time during the postozonation in municipal wastewater treatment. As the contact time in municipal systems is in the range of minutes, substances with log k_{O3} <2 L mol^{-1} s^{-1} will show no or no significant removal. Alone from those principal and theoretical considerations a complete mineralization or at least destruction of mother substances cannot be expected by ozonation of even tertiary treated wastewater. Only comparable high and therefore expensive ozone concentrations and the induction of high hydroxyle radical formation by addition of H_2O_2 or UV that can somehow surpass scavenger termination would lead to additional removal.

3. Technical Realization of Ozonation

Ozone usually is produced via the corona-discharge (Figure 4) method. The connection between the oxygen molecules is broken up and oxygen radicals are produced, that connect with the oxygen molecule to O_3. The residual heat has to be removed by a cooling system.

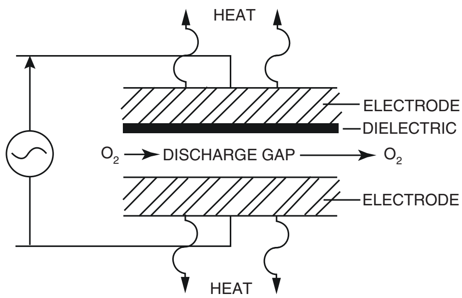

Figure 4. Basic principle of an ozone generator (www.lenntech.com).

For the feed inlet usually pure oxygen is used. The oxygen can be produced on site by PSA (pressure swing absorption) based on the filtration of ambient air or be supplied in a pressurized tank as industrial liquid oxygen (LOX).

The produced ozone gas can be dissolved in water by different means. Venturi injection and diffusers are the most common techniques. A venturi injects the ozone gas in the water via a vacuum. The advantages of a venturi are the compact installation, possible high yield (up to 90%) and high material robustness. The introduction via diffusers is comparable with the introduction of oxygen for the activated sludge process. The biggest problem with diffusers is the choice of ozone resistant but flexible materials (e.g. Silicone).

Depending on the injection system, the positioning of the injection system and the chosen reactor configuration (plug flow or full mixed reactor) the implementation of a static mixer can be of advantage.

Not all ozone reacts with target substances. Due to overdosage ozone can escape to the gaseous phase and therefore is lost for the oxidation process. In order to avoid environmental and human exposure to that excess ozone a closed system with destruction of the excess ozone in the gas phase is required. The catalytic destruction of ozone is the most used process where the ozone containing gas is sucked into the destruction unit, heated to avoid moisture that would destroy the catalyst and decomposed to O_2.

In Figure 5 the fate of ozone in an oxidation application is summarized.

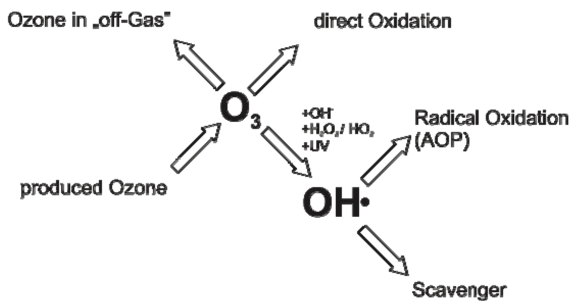

Figure 5. Fate of Ozone in matrix solutions.

4. Ozonation of Tertiary Treated Wastewater

The ozonation pilot plant is situated at the location of a two-stage activated sludge plant in Austria being upgraded from a high loaded WWTP with carbon removal only, to a low loaded, nutrient removing WWTP in 2005. 80% of the incoming wastewater is collected by a combined sewer system and 20% by a separate sewer system. Solids retention time normalized to 10°C (SRT10°C), hydraulic retention time (HRT) and the food to microorganism ratio (F/M) for conventional wastewater parameters are listed in Table 1. In Table 2 typical effluent concentrations for carbon, nitrogen and phosphorus are given.

TABLE 1. Characteristics of the investigated WWTP.

$SRT_{10°C}$ (d)	HRT (h)	F/M (g COD $gTSS^{-1}d^{-1}$)*
17*	22	0.15–0.2

* in the 2nd treatment stage

TABLE 2. Typical effluent characteristics at the WWTP.

COD (mg L^{-1})	TOC (mg L^{-1})	BOD (mg L^{-1})	TN (mg L^{-1})	NH_4-N (mg L^{-1})	NO_3-N (mg L^{-1})	TP (mg L^{-1})
34	8	4	9.8	0.6	6.9	0.9

4.1. PILOT PLANT SETUP

The pilot plant includes an ozone generator (Wedeco, type SOM 7) with a production capacity of 1,000 g h^{-1} and a 2,670 m^3 storage tank for liquid oxygen for the feed gas supply (Messer Austria). A schematic diagram of the pilot plant is given in Figure 6. The reactor unit consisted of two cylindrical reactors with a working volume of 5 m^3 each at a filling level of 1.6 m. Feeding with previously tertiary treated wastewater was constant and done by abstracting effluent from the effluent channel via pump. Tracer experiments with uranine and oxygen transfer tests proved that each reactor was a completely mixed system. The two reactors were operated in series with the first reactor (R1) in downflow, counter current mode. Ozone was dosed to R1 via two fine bubble plate diffusers (Aquaconsult Anlagenbau). The diffuser plates were made of silicone and polyurethane, respectively, in order to test the stability of the material during ozonation. No ozone was supplied to the second reactor (R2) which acted as a reaction unit operated in upflow mode.

Ozone concentrations in the feed gas (O_3in) and in the off gas of the first reactor (O_3out) were continuously monitored by ozone analyzers (BMT 964). O_3 in the offgas of R1 was catalytically destroyed in a residual ozone destruction unit, ROD (Wedeco, type COD 28). The dissolved ozone concentration was measured alternately in the effluent of both reactors (R1 out, R2 out) with an amperometric ozone probe (Orbisphere Model 31330.15). Both the pH (WTW, 340 i) and the spectral absorption coefficients from 200 to 750 nm (s::can spectro::lyser™) were measured in the influent and in the effluent of the pilot plant.

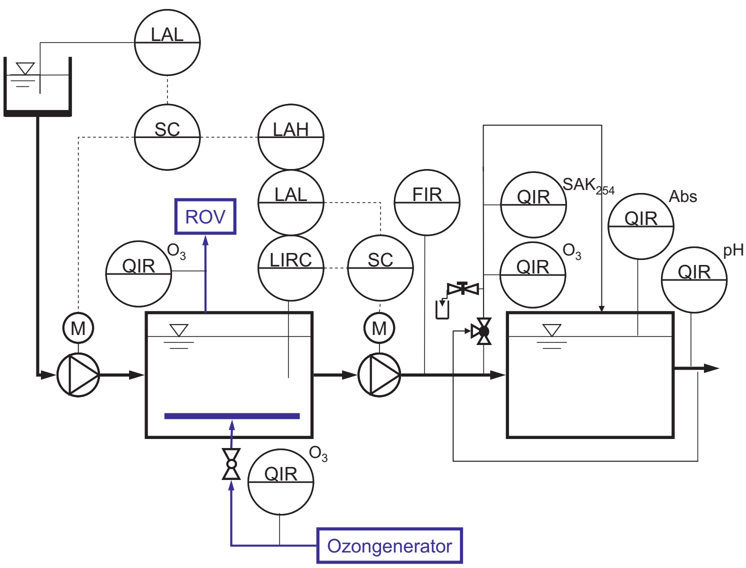

Figure 6. flow scheme of the pilot plant

FIR	flow indication registration
LAH	level alarm high
LAL	level alarm low
LIRC	level indication registration control
QIR	quality indication registration
ROV	residual ozone destruction unit
SC	frequency control.

4.2. OPERATION PARAMETERS

4.2.1. *Contact Time*

The pilot plant was operated with two reactors in series (see above). Mean total retention time was app. 2 × 10 min. Up to mean dry flow conditions oxidation reactions were finished after the first tank resulting in no residual ozone in the effluent of the first reactor. Under storm water conditions with lower DOC contents in the effluent of the full scale plant connected upwards, residual ozone concentrations of app. 1 mg L^{-1} could be measured in the effluent of reactor 1 but no in the effluent of reactor 2.

4.2.2. *Ozone Concentration*

Ozone was dosed to the first reactor (R1) at a gas flow rate of 2.5 m^3 h^{-1}. Relevant parameters for three intensive measuring campaigns (MC) such as the temperature (T), the transferred ozone dose (O_3), the liquid ozone concentrations in the two reactors (O_3 R1, O_3 R2), the DOC_0 in the influent to the pilot plant (effluent of the low loaded WWTP) and the specific ozone consumption (zspec, transferred ozone dose normalized to DOC_0) are given in Table 3.

TABLE 3. Relevant parameters for the ozonation during three sampling campaigns.

	DOC_0 (mg L^{-1})	O_3 (mg L^{-1})	zspec (g O_3 g DOC_0^{-1})	O_3 R1 (mg L^{-1})	O_3 R2 (mg L^{-1})	T (°C)	pH
MC 1	7	7.5	0.9	0.9	0.0	19.0	6.7
MC 2	7.4	5	0.6	0.7	0.2	17.1	6.8
MC 3	5.8	4.6	0.6	0.1	0.0	20.8	6.8

In order to make literature data comparable it makes sense to relate applied ozone concentrations to the initial DOC in the inflow of the ozonation step as the DOC represents a sum parameter for matrix substances targeted by ozone. Due to the low effluent concentrations in the μg L^{-1} range, the target substances themselves are only a small fraction of the DOC and therefore outcompeted by the matrix. Due to that fact stating ozone concentrations alone would not allow to compare reaction kinetics and degradation of substances on microgram level.

The ozone concentrations tested were in the range of 5–7.5 mg L^{-1} resulting in specific dosage of zspec = 0.6–0.9. A specific ozone dose of 0.7 g O_3/g DOC_0 is suggested for design and routine operation. Hollender et al. (2009) compare the effect of different specific ozone doses on the removal efficiency for micropollutants and suggests similar settings.

TABLE 4. Analyzed compounds, CAS number, limit of detection (LOD) and quantification (LOQ) and the EQS as annual average (aa) and maximum allowable concentration (mac) for inland surface waters.

Substance	Abbr.	CAS No.	LOD (ng L^{-1})	LOQ (ng L^{-1})	EQS (ng L^{-1})
17α-ethinylestradiol	EE2	57-63-6	0.4	0.7	
Estrone	E1	53-16-7	0.8	1.5	
Bisphenol-A	BPA	80-05-7	8	15	1,600*
Nonylphenol	NP	25154-52-3	10	20	300^{aa}/$2{,}000^{mac+}$
Nonylphenol monoethoxylate	NP1EO	104-35-8	30	60	
Nonylphenoldiethoxylate	NP2EO	20427-84-3	20	40	
Octylphenol	OP	1806-26-4	45	90	100^{aa}/n.a.+
Bezafibrate	BZF	41859-67-0	10	20	
Carbamazepine	CBZ	298-46-4	0.5	1	
Diazepam	DZP	439-14-5	1	2	
Diclofenac	DCF	15307-86-5	10	20	
Erythromycin	ERY	114-07-8	10	20	
Ibuprofen	IBP	15687-27-1	10	20	
Iopromide	IPM	73334-07-3	10	20	
Roxithromycin	ROX	80214-83-1	5	10	
Sulfamethoxazole	SMX	723-46-6	5	10	
Trimethoprim	TMP	738-70-5	10	20	
Galaxolide	HHCB	1222-05-5	20	40	
Tonalide	AHTN	1506-02-1	20	40	
Ethylenediaminetetra-acetic acid	EDTA	60-00-4	500	1,000	50,000*
Nitrilotriacetic acid	NTA	139-13-9	500	1,000	50,000*
Diethylenetriamine-pentaacetic acid	DTPA	14047-41-7	2,500	5,000	
1,3-propylenediamine-tetraacetic acid	1,3-PDTA	1939-36-2	500	1,000	
Diuron	DIU	330-54-1	1.5	2.9	
Di-n-butyltin	DBT	1002-53-5	0.1	0.2	10*
Tri-n-butyltin	TBT	56573-85-4	0.1	0.2	0.2^{aa}/1.5^{mac+}
Tetra-n-butyltin	n.a.	1461-25-2	0.1	0.2	
Di-n-phenyltin	DPT	1135-99-5	0.1	0.2	
Tri-n-phenyltin	TPT	668-34-8	0.1	0.2	

* national EQS, annual average (BGBl. II 96, 2006)

+ EU Water Framework Directive (DIRECTIVE 2008/105/EC)

5. Results for Micropollutants

Substances summarized in Table 4 were analyzed for their removal during ozonation and in the previous biological wastewater treatment. In Schaar et al. (2010) a detailed review and comparison between results from the high loaded and the low loaded plant is given.

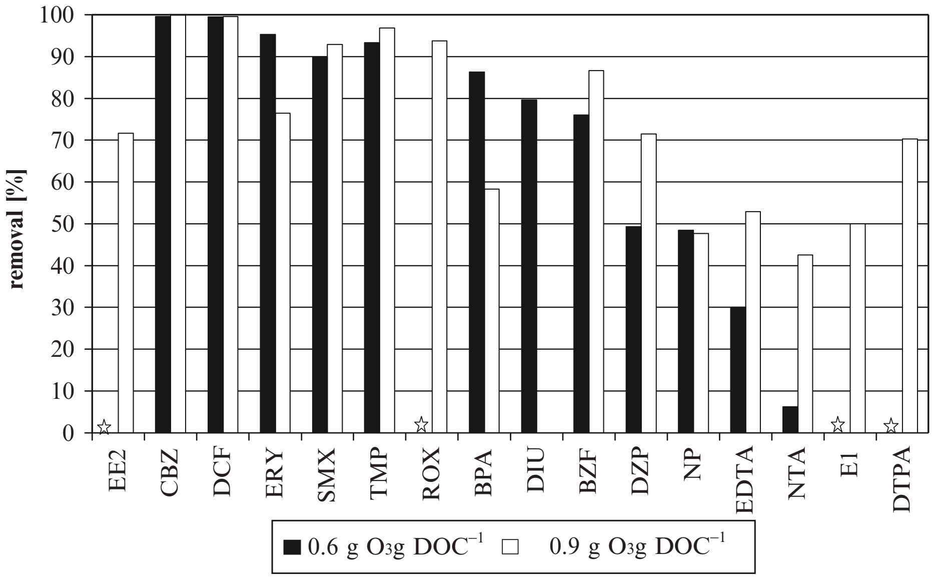

Figure 7. Removal of selected micropollutants in an ozonation pilot plant at a specific ozone consumption of 0.6 and 0.9 g O_3 g DOC_{0-1} (for substances labeled with an asterisk the influent concentration to the pilot plant was below LOD, respectively and no removal could be calculated).

Data in Figure 7 represent elimination in the ozonation pilot applying different ozone dosage zspec as percent difference between the inflow to the plant and the effluent of reactor 2. Depending from the inflow conditions (=efficiency of the upstream biological step) it occurred that no removal could be calculated because of concentrations below LOD already was observed there. LODs for the substances investigated can be found in Table 4.

Six classes of micropollutants were distinguished, the classes representing different degrees of micropollutant removal in the biological treatment step and in the low loaded plant with the subsequent (Joss et al. 2006) ozonation step (Table 2). Class I represents PPCPs whose removal in the biological treatment step, both under high and low loading, exceeded 90%. Class II comprises PPCPs whose removals were equal (±10%), but less than 90% under high and low loading. Class III groups the micropollutants that were better removed under low loading conditions. Class IV micropollutants were only eliminated in the low loaded WWTP. The fifth class comprises the two pharmaceuticals CBZ and DCF that were not removed during biological treatment, but were removed during the subsequent ozonation step. Finally, class VI micropollutants are those whose removal was considerably increased during the subsequent ozonation. Representatives of the various classes are listed in Table 5 (Schaar 2010).

TABLE 5. Categorization of micropollutants according to the degree of their removal by biological treatment and subsequent ozonation. Abbreviations see table 4

	Characterized by	Representatives
Class I	>90% removal under high loading	DBT, TBT, NTA
Class II	Equal removal (±10%) under high and low loading; <90% removal	ATHN, HHCB, TMP, SMX
Class III	Higher removal under low loading	IBP, BZF, E1, EDTA, OP, NP
Class IV	Removal under low loading only	ERY, ROX, EE2, BPA, NP1EO, NP2EO
Class V	No removal in high and low loaded WWTP, but good removal during ozonation	CBZ, DCF
Class VI	Considerable increase in removal during subsequent ozonation	ERY, SMX, TMP

5.1. RESULTS FOR DISINFECTION

The limits for Escherichia coli and the Intestinal enterococci regulated in the European bathing water directive (DIRECTIVE 2006/7/EC) were met in the effluent of the ozonation pilot plant whereas HPC was not decreased significantly. This is due to the effect that ozone does not penetrate microflocks present in the effluent of the upstream biological step but only kills the bacteria at the outside layer of the flock whereas the bacteria situated in the center of the flock are not effected.

5.2. RESULTS FOR ECOTOXICOLOGY

Standardized ecotoxicity tests were applied to assess the toxicity of the tertiary treated wastewater before and after ozonation at two specific ozone consumptions TABLE) for green algae (DIN EN ISO 8692), daphnids (DIN EN ISO 6341), and fish eggs (DIN 38415-6). Endocrine effects were tested using the OECD 21-day Fish Assay (OECD 2009). Immunoreactive substances were measured using enzyme immunoassays considering both unconjugated estrogenic (E-Assay) and androgenic (T-Assay) activity (Palme and Möstl 1994).

None of the ecotoxicity tests revealed acute toxicity in the WWTP effluent before and after the ozonation step. Hence, ozonation did not increase the aquatic ecotoxicity.

The results of the enzyme immunoassays indicated a decrease of endocrine binding activity in the ozonated effluent depending on the specific ozone consumption (Table 6). The concentration of the immunoreactive steroids decreased by a factor of more than hundred and sixty to seventy, respectively, which was mainly attributed to the decrease in estrogens. The androgenes only declined by factors ranging from two to ten. Taken together, the results of the enzyme immunoassays clearly indicated a dominance of estrogenic activity in the effluent of the WWTP, while androgenic activity dominated in the effluent of the ozonation pilot plant.

TABLE 6. Estrogenic (E-Assay) and androgenic (T-Assay) activity in the effluent before and after the ozonation step during three sampling campaigns at 0.6 and 0.9 g O_3/g DOC.

	E-Assay [ng/L]			T-Assay [ng/L]		
	0.9g O_3/g DOC	0.6g O_3/g DOC		0.9g O_3/g DOC	0.6g O_3/g DOC	
effluent WWTP	37.9	17.7	13.6	10.0	3.0	2.2
effluent ozonation plant	0.2	0.3	0.2	1.0	1.4	0.9

5.3. RESULTS FOR MUTAGENITY

Three different standardized mutagenity tests were investigated:

The Salmonella/microsome assay is based on the detection of the induction of back mutations in different strains of Salmonella typhimurium which lead to histidine auxotrophy (Maron and Ames 1984). The samples were tested with three strains, namely TA98, TA100 and TA102 and the experiments were carried out as plate incorporation assays as described by Maron and Ames (1984), in presence and absence of metabolic activation mix.

The SCGE – comet assay was carried out with primary rat liver cells. The impact of the samples on DNA migration was tested in single cell gel electrophoresis assay (SCGE, also known as "comet assay"). This technique is based on the detection of DNA migration in an electric field (Singh et al. 1988).

The Allium cepa micronucleus (MN) is based on detection of clastogenic and aneugenic effect via formation of micronuclei in meristematic cells. In the present study the most widespread protocol of MN tests by Ma et al. (1995) was applied.

Results of the Salmonella/microsome assay – Ames test for unconcentrated samples show that all samples are devoid of mutagenic activity in the Salmonella/microsome assay. With concentrated samples however, mutagenic effects were found in the effluent of the WWTP. The mutagenic effects were decreased by

39% after ozonation of the samples in strain TA98 without metabolic activation, while no effect was seen in the base-substitution strain (TA100). Results of the SCGE assays indicate significant induction of DNA migration for the effluent of the WWTP and for the effluent of the ozonation reactor, compared to the control. The effluent of the pilot plant showed a lower extent of DNA damage compared to the untreated effluent and the effluent of the ozonation reactor. In the MN test exposure to the investigated samples caused not increase of the MN frequencies. This indicates that the ozonation of tertiary wastewater does not cause MN induction in Allium cepa roots.

5.4. COSTS

A reasonable cost estimation based on the operation of the pilot plant actually is restricted to the operational costs of about 1.2 €Cent m^{-3} corresponding to about 80 €Cent PE^{-1} a^{-1}.

6. Acknowledgement

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COMPARISON OF TWO TREATMENTS FOR THE REMOVAL OF ORGANIC MICRO-POLLUTANTS: CONVENTIONAL ACTIVATED SLUDGE (CAS) FOLLOWED BY ULTRAFILTRATION (UF) VS. MEMBRANE BIOREACTOR (MBR)

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Abstract. The potential of MBR systems to remove organic micro-pollutants was investigated at different scales, operational conditions, and locations. MBR effluent quality was compared with that of a conventional activated sludge (CAS) plant, followed by ultrafiltration (UF), operated and tested in parallel. A MBR pilot plant in Israel was operated for over a year at an MLSS range of 2.8–10.6 g/L. The MBR achieved removal rates comparable to those of a CAS-UF plant at the Tel-Aviv WWTP for macrolide antibiotics such as roxythromycin, clarithromycin and erythromycin and slightly higher removal rates than the CAS-UF for sulfonamides. A laboratory scale MBR unit in Berlin – at an MLSS of 6–9 g/L – showed better removal rates for macrolide antibiotics, trimethoprim and 5-tolyltriazole compared to the CAS process of the Berlin WWTP Ruhleben at

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identical raw wastewater quality. Sulfamethoxazole and 4-tolyltriazole were removed slightly better in the CAS while the benzotriazole removal was more significant. In pilot MBR tests at an MLSS of 12 g/L in Aachen, Germany, operating flux significantly affected the resulting membrane fouling rate, but the removal rate of dissolved organic matter and of bisphenol-A was not affected.

Keywords: antibiotics; organic micro-pollutants; membrane bioreactor; municipal wastewater; ultrafiltration

1. Introduction

Effluent quality of biological wastewater treatment processes are of importance, when recycling of wastewater is targeted. Especially remaining concentrations and fates of trace organic pollutants are of particular interest and considered to be one basis for risk analysis in irrigation or potable reuse. The present study's objectives are to compare at the pilot-scale level, the fate and the efficiency of removal of micro-pollutants in municipal wastewater treated by coupling biological treatment and various membrane technologies.

Coupling the conventional activated sludge (CAS) process with ultrafiltration (UF) provides particle free and physically disinfected effluent quality at a comparable level to that achieved by the novel membrane based approach of membrane bioreactor systems (MBR). The potentials of both processes to remove trace organics were investigated in parallel in Israel and Germany at different operational scales.

Previous studies have mentioned the sludge retention time (SRT) as a key parameter for the removal of micro-pollutants in conventional activated sludge (CAS) treatment and in membrane bioreactor systems (Clara et al. 2004; Kloepfer et al. 2004; Lesjean et al. 2005; Cirja et al. 2008). In general, it is concluded that a higher SRT enhances the removal of trace organics (possibly due to biological adaptation by specific microorganisms), but in cases with increased SRT and biomass, the selective adsorption of trace organic compounds may also be favourable. At current state there is a lack of comparative studies related to the fate of micro-pollutants in activated sludge treatment technologies for CAS and MBR at different scales.

In this research, the Ben Gurion University (BGU) and Mekorot – the Israeli Water Company set up and operated a pilot scale MBR unit in parallel to a CAS-UF pilot-plant already in operation at the Shafdan Sewage treatment plant (STP), south to Tel-Aviv. Analytical methods and measurement capacities are provided by TU Berlin and after knowledge exchange, certain compounds were analyzed by BGU in parallel. RWTH Aachen investigated interactions of membrane flux operation conditions vs. removal of bulk organic compounds and trace organic removal in a pilot scale MBR (puron membranes). To derive CAS-UF vs. MBR results at different scale and with German wastewater, smaller scale MBR laboratory unit (non woven textile flat sheet membrane) was set up and operated in parallel to the STP Berlin Ruhleben.

2. Materials and Methods

2.1. SYSTEM I (TEL-AVIV/ISRAEL)

A large UF/RO pilot plant (45 m^3/h) desalinating the Shafdan secondary effluent, was used in this project. The UF system is based on the ZeeWeed-1000 immersed hollow-fiber membrane. It contains a feed tank with 24 membrane modules with a total membrane area of 1,000 m^2 (Figure 1). The secondary effluent is vacuum-filtered; every 50 min filtration cycle ends up with a 1 min BW (Back-wash) by a reverse flow direction, with additional air scouring. The filtrate is stored in a tank before serving as feed to the RO membranes. Throughout most of the experiment time period, the UF capacity was stable at 45 m^3/hr.

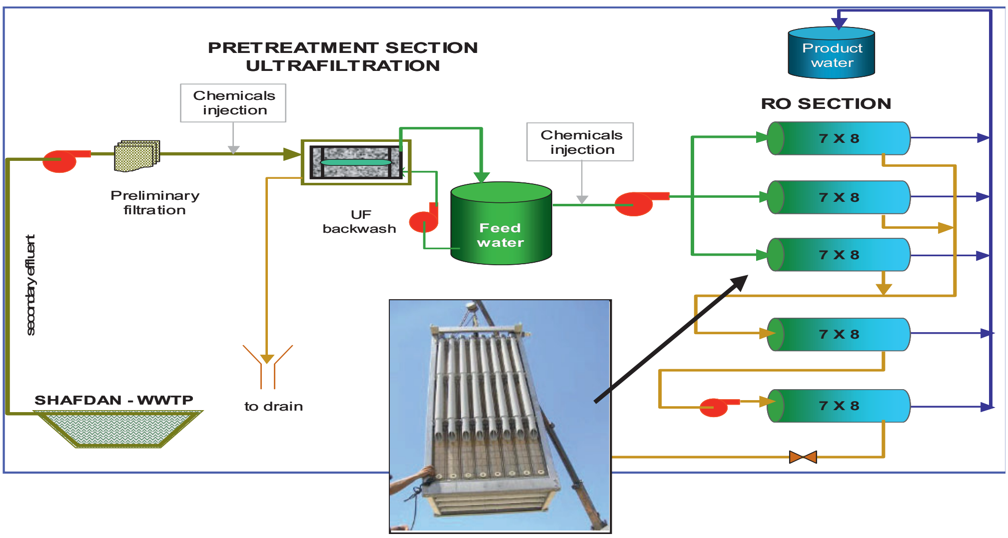

Figure 1. A schematic diagram of the CAS-UF/RO pilot plant and UF filtration cassette.

The MBR system has been fed with the same raw sewage as the CAS/UF. The system contains a bioreactor which is divided into three areas (40 L anaerobic zone, 80 L anoxic zone and 120 L aerobic zone) and a 110 L membrane tank (Figure 2). It is automatically operated with a varying flux of 15–20 lmh. It was first operated with one ZW-500 hollow fiber membrane, with an area of 1 m^2 and 100,000 dalton MWCO (Molecular Wight Cut Off). An additional 1 m^2 of membrane has been added to increase the flux. Operational parameters (filtration duration, BW duration, pH and flux) are changed for optimization of the system. In addition to twice a week tests of BOD, COD, TSS, VSS, MLSS, NH_4^+, NO_3^-, PO_4^{3-}, composite samples for micro-pollutant determination were collected and sent on regular basis to the research partners (TUB), and also been tested at BGU.

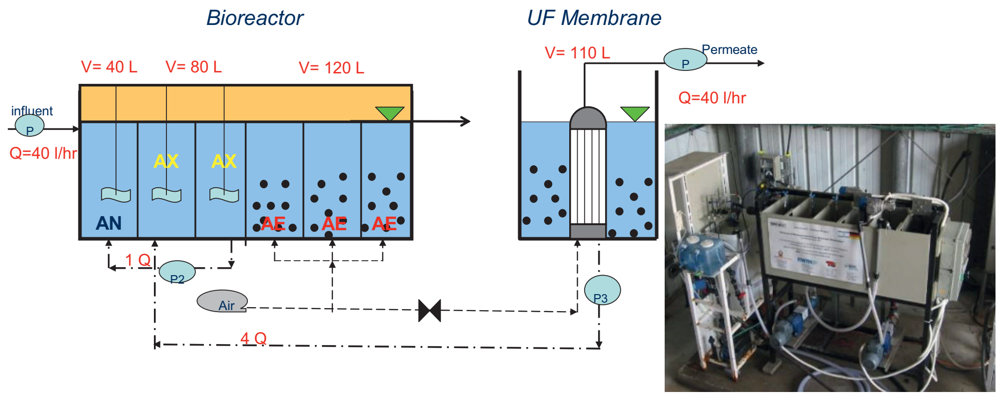

Figure 2. Process overview of Membrane Bio Reactor (MBR) and picture.

2.2. SYSTEM II (BERLIN/GERMANY)

Lab scale MBR trials: In addition to the MBR pilot plant in Shafdan, a MBR laboratory plant was designed, set up and operated at TU Berlin. The MBR system was assembled from September to October 2007 and started operation in Nov. 2007 with raw sewage (after sedimentation, 1.1 mm filtration) from the WSTP Berlin Ruhleben (240.000 m^3/d). The small-scale MBR plant (Figure 3) consists of three chambers at different redox conditions with a total operational volume of 1.5 L (anaerobic 250 ml, anoxic 500 ml, aerobic 750 ml); it operates at the comparable hydraulic retention time as the CAS system (15 h vs. 24 WSTP Ruhleben).

A non-woven membrane flat sheet pillow is submerged in the aerobic reactor (A = 100 cm^2, pore size = 10 µm). The filtration cycle consist of 10 min filtration, 2 min backwash/relaxation. Average mixed liqueur suspended solids (MLSS) was 7–8 g/L. In addition to the organic analysis program standard parameter like COD, TP, PO_4-P, TN, NO_2-N, NO_3-N were measured.

Lab scale CAS/UF trials: Flat sheet UF filtrations of the CAS permeate were conducted in parallel to the MBR tests in order to compare its efficiency regarding the micro-pollutants removal.

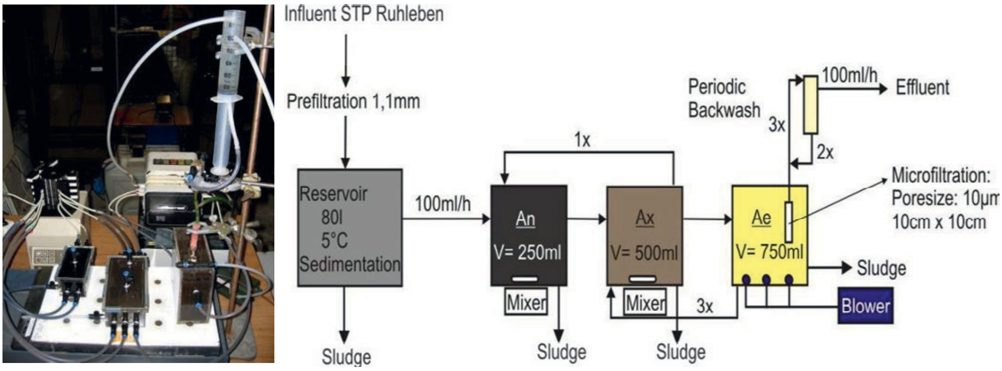

Figure 3. Picture and set up of lab MBR plant.

2.3. SYSTEM III (AACHEN/GERMANY)

A pilot MBR is operated at the municipal wastewater treatment plant (WWTP) Aachen-Eilendorf in Germany. Primary effluent of the conventional activated sludge WWTP is used as influent for the pilot MBR. The pilot plant with a total biological reactor volume of 0.63 m^3 divided into a pre-denitrification reactor (0.2 m^3) followed by a nitrification reactor (0.2 m^3) was configured to test three submerged capillary hollow fibre modules in parallel. Three permeate extraction pumps allow a simultaneous operation with different operational conditions for each membrane module (Figure 4). Each membrane bundle (membrane material: PES; nominal pore size: 0.05 µm; PURON®, Koch Membrane Systems GmbH, Germany) provided a total membrane area of 1.7 m^2.

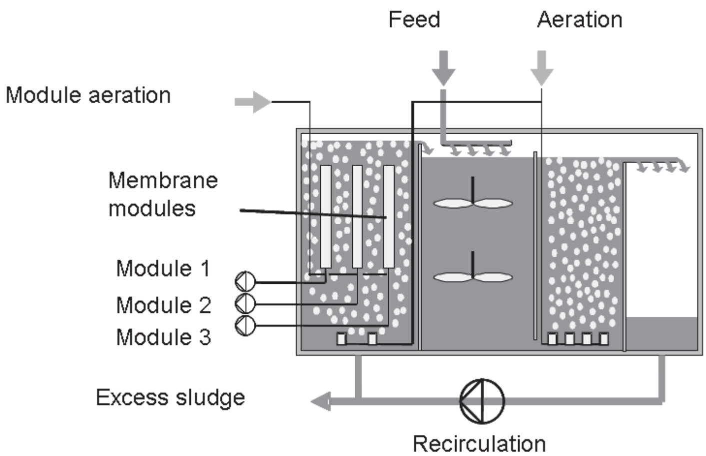

Figure 4. Flow scheme of the pilot-scale submerged MBR.

Frequent wastewater analysis of quality parameters such as COD (chemical oxygen demand) of feed and permeate as well as mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) of the activated sludge were carried out to monitor the performance of the pilot plant. The raw wastewater composition was typical for German conditions. Except for inevitable variations, the general MBR performance was stable within the defined criteria: average SRT = 30.2 d, MLSS = 12.7 ± 4.8 g/L, F/M ratio = 0.055 ± 0.069 kgBOD/(kgMLSS/d). Activated sludge samples were taken from the membrane tank and permeate samples were taken from each membrane module. The samples were cooled during transport and storage (T = 4°C). The activated sludge was centrifuged for 30 min at 4,350 rpm (~4,400 g) and subsequently filtered through a paper filter (black ribbon). To compare membrane filtration performance of the three modules online data of the pilot MBR were used (Table 1). Permeate flux J_P, transmembrane pressure difference *TMP* and effluent temperature *T* were recorded.

TABLE 1. Key operational parameters of CAS-UF and MBR systems investigated.

	Parameter \ Plant	I	II	III
UF	Capacity [m^3/h]	45	Lab filtration	–
CAS	HRT [h]	14–16	24	20
	MLSS [g/L]	2–3	2–5	3
	SRT [d]	2–4	9–15	2–3
MBR	HRT [h]	9–12	15	10
	MLSS [g/L]	2.8–11	6–9	8–12
	SRT [d]	>40	>70	30
	Capacity [m^3/h]	0.04	1*10–4	0.1
	Aerobic tank (L)	120	0.75	300
	Anoxic tank (L)	80	0.5	300
	Anaerobic tank (L)	40	0.25	–

I – Tel-Aviv, Israel, II – Berlin, Germany, and III – Aachen-Eilendorf, Germany

2.3.1. *Analytical Procedures*

In addition to standard tests for nutrients and organic compounds, organic micro-pollutants were concentrated by SPE (solid phase extraction) procedure and analyzed by LC-MS-MS (liquid chromatography-mass spectrometry) both in Germany and in Israel, according to the protocol which is described by Asmin et al. (2006). The micro-pollutants included macrolide antibiotics such as erithromycin (ERY), roxithromycin (ROX), clarithromycin (CLA), trimethoprim

(TMP), and sulfonamides such as sulfamethoxazole (SMX) and sulfamethazine (SMZ). Erythromycin was analyzed as its degradation product with loss of one water molecule since it is unstable under acidic conditions (pH <7) and was formed to anhydroerythromycin (ERY-H2O) through the analytical procedure. benzotriazole (BTri), 4-tolyltriazole (4-TT) and 5-tolyltriazole (5-TT) were analyzed according to the method described by Weiss et al. (2005). Bisphenol-A (BPA) was tested and analyzed by RWTH Aachen University with an adapted LC-MS method according to Rodriguez-Mozaz et al. (2004).

3. Results and Discussion

The COD and NH_4 removal rates were comparable (and sometimes even better) for all three MBR devices. As for nitrite, nitrate and phosphorus, the MBR had achieved lower removal rates compared to CAS treatment, due to periods of unstable operation conditions (Table 2).

TABLE 2. Concentrations and removal efficiency of COD and nutrients in System I (Tel Aviv), System II (Berlin) and System III (Aachen).

	System I			System II		
Parameter	MBR effluent	MBR removal	CAS removal	MBR effluent	MBR removal	CAS removal
	[mg/l]	[%]	[%]	[mg/l]	[%]	[%]
COD	20.7 ± 4.5	98	97	26.5 ± 5.1	94	91
TKN	30.9 ± 5.2	48	96	31.4 ± 9.5	56	79
NH_4-N	0.1 ± 0.05	>99	93	0.01 ± 0.03	>99	>99
NO_3-N	13.0 ± 8.5	–	–	25.3 ± 6.7	54	84
NO_2-N	0.7 ± 0.3	–	–	n.a.	–	–
TP	7.2 ± 3.4	44	90	5.0 ± 0.9	39	96
PO_4-P	6.3 ± 6.0	11	86	4.8 ± 1.1	<1	96
	System III					
COD	14.5 ± 3.7	93	95			
TKN	n.a.	n.a.	n.a.			
NH_4-N	0.05 ± 0.17	>99	>99			
NO_3-N	8.3 ± 3.31	–	–			
NO_2-N	n.a.	n.a.	n.a.			
TP	1.36 ± 0.72	35	98			
PO_4-P	n.a.	n.a.	n.a.			

n.a. – not available

3.1. RESULTS FOR SYSTEM I (TEL-AVIV/ISRAEL)

In Figure 5, two trends of removals for two kinds of polar micro pollutants are reflected. For macrolides antibiotics, the average concentration is lower in the CAS-UF permeate compared to MBR effluent (even if the min./max. range bars overlap). For the concentration of the sulfonamides, the situation is reverse and lower in the MBR permeate. This can be explained by the SRT of the two pilots (2.8 days in the CAS compared to >40 days in the MBR). Higher SRTs allows the enrichment of slowly growing bacteria and consequently, the establishment of more diverse physiological capacities (Kreuzinger 2007). Ternes and Joss (2006) claims that Log Kow >3 of micro pollutants can indicate a high bio-accumulation potential in CAS treatment, sometimes as a primary stage for biodegradation. Log Kow of CLA, ERY and ROX are 2.75–3.16. Log Kow of TMP, SMZ and SMX are a lot lower: 0.89–0.91 and therefore removed in relatively low rates in the CAS.

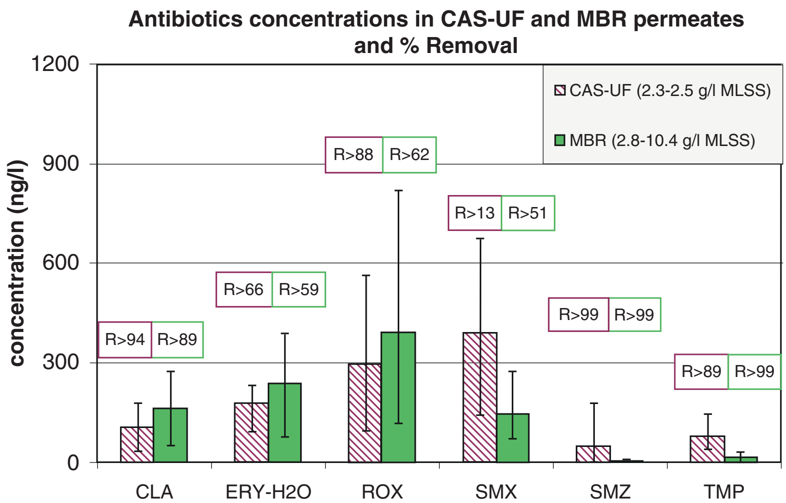

Figure 5. Average antibiotics concentrations after CAS-UF and MBR treatments, n = 12, monthly sampling, May 2008–Feb. 2009.

Clara et al. (2004) stated that the far and most important difference between the MBR and the CAS-UF is the SRT, which can affect the removal of the micro pollutants by biodegradation and adsorption to suspended solids. An assumption was made that the relatively high polarity and hydrophilic nature of the sulfonamides and trimethoprim favors their adsorption to sludge and biodegradation in high MLSS concentrations, due to the typical sludge structure that is formed. Therefore, the increase in MLSS is a lot less significant to the macrolides removal, as opposed to the significance for sulfonamides removal.

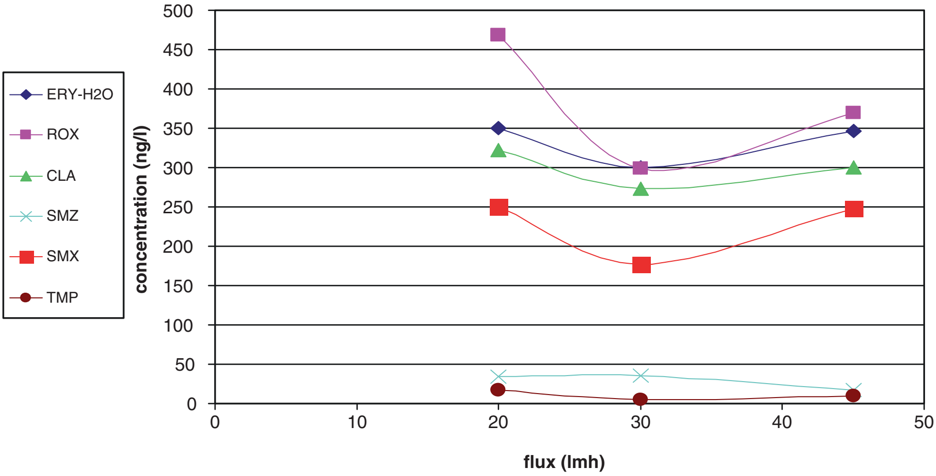

Figure 6. Antibiotics concentrations vs. flux in the CAS/UF (n = 12).

Another experiment that included changes in flux, was carried out in the UF after CAS, in order to determine the effect of flux on the removal of antibiotics (Figure 6). Weber et al. (2004) claimed that an increase in pressure for achieving higher fluxes might cause a reduction of micro-pollutants removal. Despite some differences in the antibiotic concentrations after the UF filtration in 20, 30 and 45 lmh, no certain trend was seen regarding the affect of flux change on the micro-pollutant removal. Nevertheless, those experiments have shown, as opposed to the common knowledge, that the UF contribution to the removal of micro pollutants is not negligible as was claimed by Radjenovic et al. (2007), since the UF membrane pore size is 100 times bigger than the micro pollutants molecules sizes. The addition of UF after CAS improved the removal of ROX, CLA, SMX and TMP by up to 28%. It is explained by additional adsorption, to the suspended matter which is accruing in the membrane tank and to the biofilm which is being formed on the membrane surface.

3.2. RESULTS FOR SYSTEM II (BERLIN/GERMANY)

In Figure 7 the concentration of selected antibiotics are given for raw water and MBR lab scale effluent. In general removal rates for investigated macrolides and sulfonamides are >90%, with the exception sulfonmethoxazole, which is known to be a persistent compound (its average removal is around 38%, with a large standard deviation). Sulfamethazine was completely removed from an initial raw water concentration <100 ng/L (not shown).

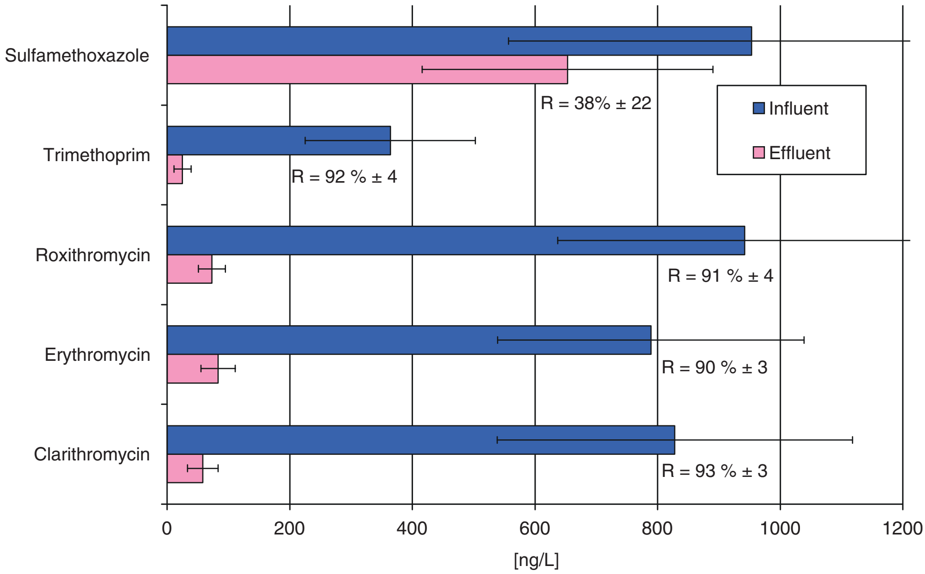

Figure 7. Average concentration and standard deviation of sulfonamide and macrolide antibiotics in sewage and lab scale MBR effluents and resulting removal rates (n = 6).

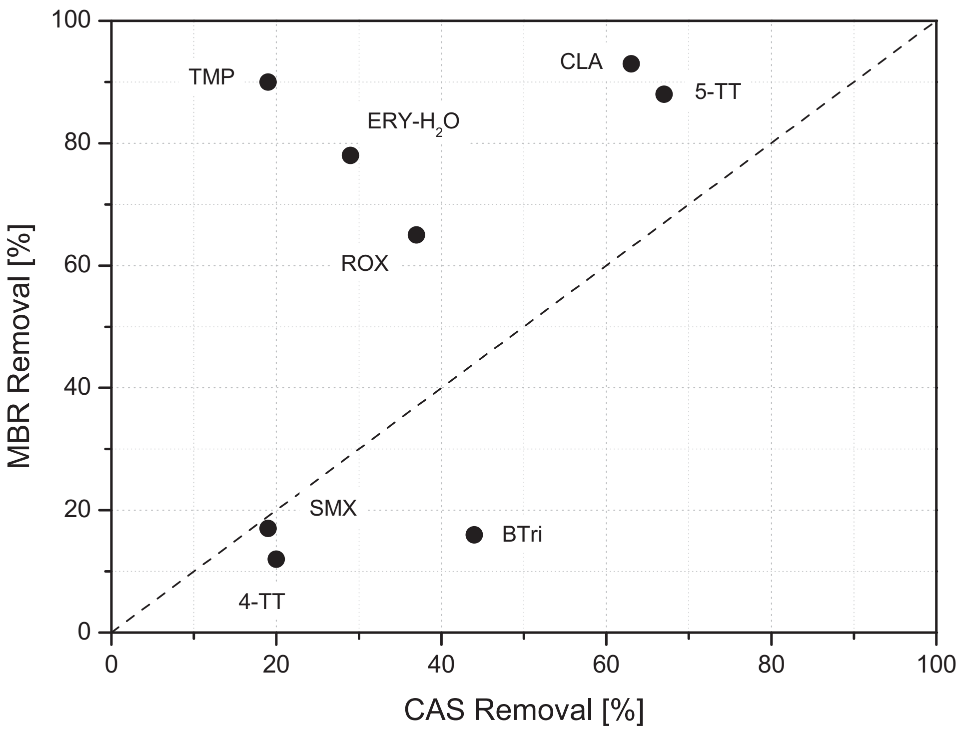

Figure 8. Comparison of the relative removal rates of trace pollutants in system II (n = 12).

Figure 8 demonstrates that in system II, for most of the investigated compounds (especially antibiotics except SMX), the lab scale MBR system performed better than the CAS process. In particular for TMP, a real improvement of the MBR is shown. This is not the case for BTri and 4-TT. As a result of 12 parallel sampling campaigns, the conclusion is that the lab-scale MBR under given operation conditions removed macrolides better, for SMX and 4-TT removal rates are quite close and only for BTri, CAS Ruhleben has significant advantages. The antibiotics removal differences between system I and II can be explained by varying pilot sizes, sewage composition, operation conditions, pH and temperature.

3.3. RESULTS FOR SYSTEM III (AACHEN/GERMANY)

Flux is mentioned as a control parameter in membrane filtration affecting the permeate quantity, quality and membrane fouling rate. Additional data regarding the flux influence on micro-pollutants can assist in controlling their removal rates. A higher flux which is obtained by higher filtration intensity is expected to increase the fouling rate on the membrane surface (for the same filtration regime), due to higher colloid loadings to the membrane surface (critical flux phenomena) and overall increase in particles concentration inside the membrane tank. The results from system III (Figure 9) indicated that the applied operation conditions resulted in a significant difference of the fouling rates. The module with the highest gross flux (module 2) showed the highest fouling rate (1.2·1, 011 1/m/d) which was almost an order of magnitude higher compared to the lowest fouling rate of module 3 (2.4·1,010 1/m/d). The fouling rate of module 1 (7.2·1,010 1/m/d) was between module 2 and 3. These results clearly indicate the adverse effect of instantaneous permeate flux on the fouling behaviour. Backwash proved to be slightly more efficient than relaxation periods.

The micro-pollutants are significantly smaller than the membrane pore size, and therefore should not be blocked resulting in an increase of their concentration in the permeate with the increase of flux, as stated by Radjenovic et al. (2007). Experiments in MBR III (system III) showed that removal of BPA in a relatively low fouling rate was 44% and three- to five-fold increase in the fouling rate did not affect the removal of BPA in a constant trend (first a decrease to 33% and then an increase to 56%). As displayed in Figure 10, in most samples BPA concentrations of the permeate were lower than in the supernatant indicating an interaction of BPA with the membrane and/or the fouling layer. It is known from literature that BPA can be adsorbed to the membrane (Salehi, 2008). In the light of the above mentioned weak correlation between BPA removal and fouling rate, the cake layer conditions appear to influence the removal of BPA. Similar results regarding the unclear affect of flux on the removal of antibiotics were obtained in system I, indicating that flux cannot serve as a control parameter for the removal of micro-pollutants. Furthermore it can be concluded that MBR fouling plays only a minor role in removal of organic micro-pollutants while other factors such as SRT, HRT and properties of the micro-pollutants prevail.

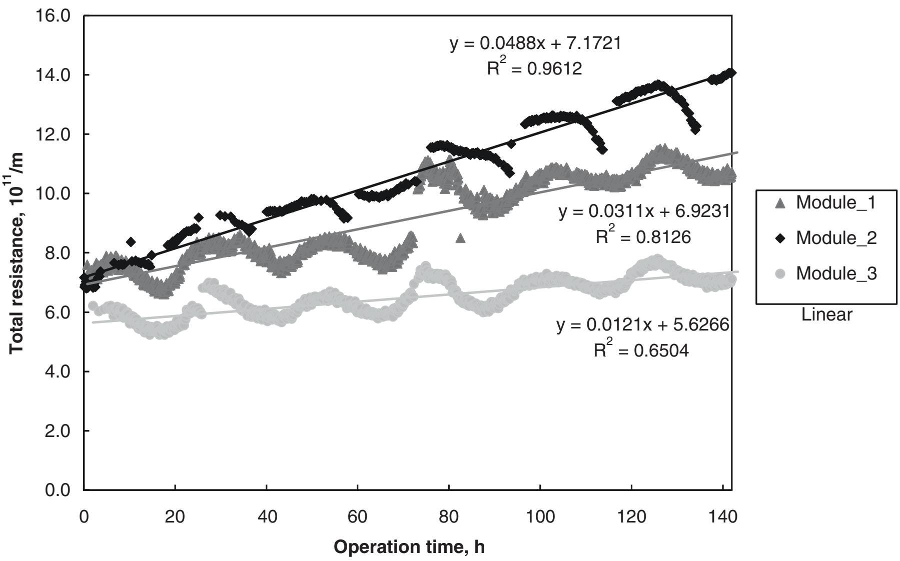

Figure 9. Total resistance (temperature corrected) and fouling rates during the study.

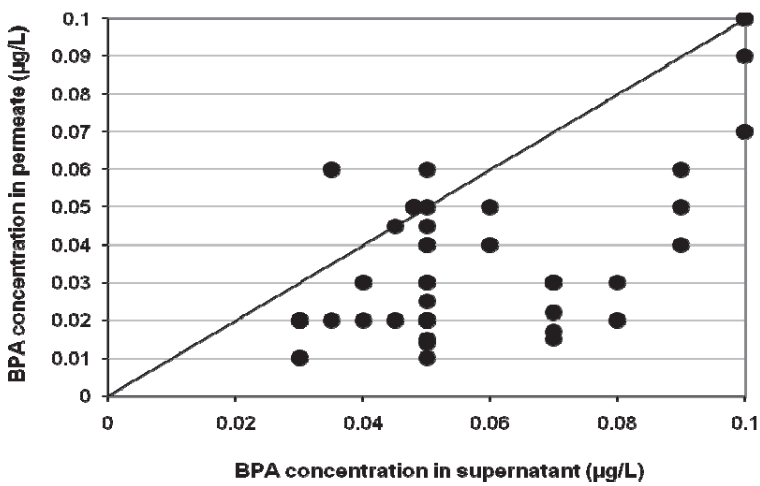

Figure 10. Effect of membrane separation on BPA removal in MBR III.

4. Conclusions

Three MBR pilot plants were operated for over a year, in three different locations: Tel Aviv (Israel), Berlin and Aachen (Germany). These plants differed in size and in some operational conditions and were tested in parallel with CAS and CAS-UF pilots in terms of micro-pollutants removal. After reaching stable operation conditions, all three MBR devices achieved similar and sometimes even better removal rates of organic and nitrogen compounds in comparison to CAS. Noticeable differences in sewage composition, operation conditions, pH and temperature of the three systems, have led to some differences in the evaluated MBR relative efficiency. While projecting a dominant removal in the TUB system, the MBR was more efficient only for the sulfonamides in the BGU system relatively to the CAS/UF. Nevertheless, BGU and Aachen systems had proven that flux has no clear trend regarding its affect on OMPs removal. Specific conclusions obtained can be summarized as follows:

4.1. SYSTEM I

The two pilot plants are operating in parallel successfully over a period of twelve months on the same raw water influent at the STP Shafdan. Capacities of both systems differ by a factor of 1,000: CAS-UF (45 m^3/h) and MBR (40 l/h).

The MBRs showed a significant advantage in sulfonamide and TMP removal due to high SRT and MLSS concentration, which allows the enrichment of slowly growing bacteria and consequently, the establishment of more diverse biodegradation capabilities.

The high MLSS concentration increased the adsorption and biodegradation capabilities and therefore improved the sulfonamide removal by 30%.

The advantage due to high SRT and MLSS concentration was less significant for macrolides removal, and in some cases the CAS and CAS-UF were even more efficient.

Additional UF filtration after CAS had increased the antibiotics removal by up to 28%, probably due to adsorption to particulate materials and their removal on the UF membrane surface, rather than biodegradation.

4.2. SYSTEM II

A small scale lab MBR systems (2.5 l/d) was designed and put into operation with identical hydraulic retention time and redox conditions as the large scale CAS process in Berlin Ruhleben (240.000 m^3/d) but twice as high MLSS concentration (7–8 g/L).

The small lab MBR operated stable over a period of 10 months, effluent quality for COD and NH4 are comparable or lower than the of the CAS process. Denitrification was partially established (<50% TN removal), biological phosphorous removal could not established due difficulties with excess slugde withdrawal

For trace organic compounds the lab scale MBR system was able to substantially remove most of the antibiotics and 5-TT (>78%), partial removal was achieved for SMX, BTri and 4-TT (12–17%).

Preliminary comparison of CAS and MBR effluent quality related to trace organic compounds reveal lower concentration in MBR permeate for most of the investigated compounds at same raw water inlet qualities.

4.3. SYSTEM III

Three identical hollow fibre membrane modules (PURON®, Germany) were operated in parallel in a pilot-scale MBR .

BPA concentrations in the permeate were lower than in the supernatant suggesting an interaction of BPA with the sludge organic residual and the membrane and/or the fouling layer.

Instantaneous flux significantly affected the resulting fouling rate.

Flux and fouling rate changes in the MBR system had varying effects on micro-pollutant removal efficiency; no clear correlation could be tracked.

Similarly, the membrane retention of BPA (33–56%) varying at different fouling rates shows possible interactions with bulk organic matter.

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SLUDGE TANKS OPERATION IN SMALL AND MIDDLE-SIZED WASTE WATER TREATMENT PLANTS

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Abstract. Sludge treatment in the small and middle-sized WWTPs represents a separate unit in waste water treatment. In the past years this issue did not receive proper care due to missing legislation. After Slovakia entered the EU, our country has been following the EU requirements, which have been implemented into Slovak legislation. On January 1, 2004 Act No. 188/2003 Coll. on application of treatment sludge and drain sediments into the soil came into force. It established requirements on thickened and dewatered sludge before its utilization in agriculture. The improving of building of new small and middle-sized WWTP to the year 2015 will also improve the production of treated sludge. Therefore the question of sludge solution is of high importance. We expect growing number of WWTP with sludge treatment in open sludge tanks. In our research work we have applied the description of processes which are in process in sludge tanks. We monitored operation of open sludge tanks on two WWTPs directly in the sludge objects and on models, where we simulated several treatment conditions. The objective of our work is to create requested treatment condition in sludge tank; so that the process of sludge thickening and stabilization has sufficient efficiency and treated sludge can be used according to valid Slovak legislation in other procedures.

Keywords: sludge treatment, small and middle urban areas, legislation in Slovakia, operation of sludge tanks, disposal of sludge

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1. Introduction

In the world as well as in our country large point sources of pollution are first to be cleaned and inspected. In Slovakia, Act No.364 on Water came into legal force in 2004. This Act is in compliance with European Council Directive 91/271/EEC of 1991 on management of urban waste water in order to avoid harmful impacts on the environment. The EU Member States are obliged to ensure all sites beyond 2000 PE (depending on the size of the urban area) to divert waste water and its subsequent purification.

Out of the total number of 2,881 villages in Slovakia more than a half of those do not have public sewage with waste water treatment plant.

Development of public sewerage lags behind the development of public water supply in Slovakia. In 2008, 3,196.6 thousand of inhabitants, i.e. 59.06% of the total population, were connected to the public sewerage system. The most unfavourable situation is in small towns.

Built waste water treatment capacities in many cases do not comply with current legislation, raising demand for their reconstruction in order to achieve higher efficiency of cleaning (Rajczyková and Kolektív 2001; Ministerstvo životného prostredia 2008b).

At present there are about 200 sewage treatment plants in Slovakia, which are under the management of water companies that provide treatment of canalised waste water from medium and small urbanized units.

That type of sludge treatment and disposal of wastewater treatment plants represent a separate unit for sewage treatment. In the past, this issue was not given sufficient attention, which was mainly due to the lack of legislation. New Act no. 188/2003 Coll. on application of treated sludge and drain sediments into the soil, entered into legal force, changing the overall view of sludge as waste.

Currently valid classification system of sludge based on strict distinction between raw and stabilized sludge provided smooth operation for operators of the WWTP with aerobic or anaerobic sludge stabilization. This current status is put to an end by amendments to legislation on waste management and will need to be updated.

2. Waste Water Sludge Production and Disposal in Slovakia

There is a great disproportion between connection to water supply system and connection to sewage system in Slovakia. More than 86.3% of population is connected to public water supply system, but only 57.5% of Slovak population is connected to public sewage system. You can find some districts where is the

connection lower than 30%. We have to solve this problem in the near future. There is coming great amount of finances for building a new sewage system in Slovakia. But at first we have to find the general idea how to build this system with the view of technical and economical relations. Quantitative production of sludge from urban waste water treatment as well as the issue of their contamination has been continuously monitored in Slovakia since 1998. Basic principles, together with the monitoring, have been derived from the concepts of management of sludge from municipal wastewater treatment plants. Controlled land application of sludge was stipulated as the principal method of handling sludge. This process has not only been selected for being relatively the cheapest way for the final disposal of sludge, but is assumed to be the most acceptable option in the Slovak conditions, as well (Šumná et al. 2008).
Two methods of controlled application of sludge into soil are used:

Direct application of sludge into soil as of the Act no.188/2003 Coll. on application of waste water sludge into soil

Application as of the Act no. 136/2000 Coll. in wording of Act no.555/2004 Coll. on fertilizers, for example, as compost or soil-growing medium. In this case the product is subject to certification.

Overview of sludge production from urban wastewater treatment for wastewater treatment plant and carried out handling them in the time period of 2001–2007, as shown in Table 1.

TABLE 1. Amount of sludge applied to the soil from the year 2001 to 2007 (Ministerstvo životného prostredia 2008a).

Year	Sludge production solids	From its Soil application		Temporary storage		Storage on the landfill	
	t/year	t/year	%	t/year	%	t/year	%
2001	53,350	37,855	71.0	8,493	15.9	7,002	13.1
2002	51,270	41,960	81.8	4,870	9.5	4,440	8.7
2003	54,340	39,330	72.4	6,900	12.7	8,110	14.9
2004	53,110	42,530	80.1	5,860	11.0	4,720	8.9
2005	56,360	39,120	69.4	8,710	15.5	8,530	15.1
2006	54,780	39,405	71.9	6,130	11.2	9,245	16.9
2007	55,305	42,315	76.5	9,400	17.0	3,590	6.5

In the context of increasing requirements for wastewater treatment – the implementation of Council Directive 91/271 EEC on Urban Waste Water, the increase of sludge production by about 20–40% is to be expected in the near future. It is mainly the addition of sludge from small sewage treatment plants without significant involvement of industrial waste water, so a certain degree of contamination of sludge can be expected, which corresponds to the requirements of the process, limiting its application to the soil (Ministerstvo životného prostredia 2008a).

3. Sludge Tanks in Communal WWTP

Municipal wastewater treatment plants from rural settlements significantly affect local water management conditions. They are currently receiving much attention both in Slovakia and abroad. In Slovakia, they dispose of about 15% of the total pollution. They are mostly located further away from rivers or in areas of greater interest, water recreation or water demands (Ministerstvo životného prostredia 2008b).

Technological line of the mentioned WWTPs is simpler as in the case of large plants. Primary sedimentation is left out in the process of mechanical cleaning. Biological treatment is often dealt with by long-term activation with aerobic sludge stabilization. This type of activation is characterized by long periods of time flowing (24–48 h) and a high sludge age (20–50 days). Volume load and load sludge load are very low; resulting in constant under-nourishment of sludge, which therefore gradually dies and decomposes. There is not enough excess sludge, furthermore it is largely aerobically stabilized; it does not need to be further processed anaerobically, which would be very demanding and non-economic for small sources of waste water.

4. Design and Operation of Sludge Tanks

The sludge tank is designed for continuous operation in order to thicken and stabilize excess sludge. Tank capacity is calculated according to the produced amount of aerobically stabilized sludge per day. Capacity of sludge tanks is calculated in order to enable storage of sludge for a period of 150 days. The parameters that must be considered in the capacity dimensions are: the average daily flow into the WWTP, number of equivalent population connected, type of pollution and its concentration according to BOD_5. It is recommended for the sludge tanks to be monolithic. Prefabricated steel tanks are also used; however, they cause undesirable heat loss. The ground plan of the object is circular or rectangular. Mixing of sludge in the tanks is provided by blending devices which help to improve the sediment and thickening ability of sludge. Quality of the dehydration process in the tanks is a function of sludge properties. The temperature of sludge and the way it is mixed influences it to a large extent. Balanced temperature in a given unit of time is necessary to ensure faultless operation of sludge tanks (STN 75 6402 1999).

Proper handling and operation of sludge tanks plays an important role in wastewater treatment. Its contents should be periodically refilled by surplus sludge, surplus sludge water should be released by spillway facilities and sludge tanks filled with concentrated and stabilized sludge should be emptied as necessary. The question of proper operation of the sludge tanks was studied at the Department of Health and Environmental Engineering, the Civil Engineering Faculty at the STU in Bratislava. It was done in the form of research model, as well as research carried out directly in the tank.

5. Model Device

Due to the closer monitoring of processes in sludge tanks we created a model facility, which helped us to simulate different conditions in the tanks and their influence on sludge thickening and stabilization. The experimental device consisted of three models, which were used to simulate real conditions of sludge thickening and stabilization processes in the sludge tank. Dimensions and capacity of the model device were designed in order for the thickening zone to proportionally match the real height of this area in the sludge tanks for wastewater treatment. Conditions for sludge thickening and stabilization were created in each model.

In the first model, the sludge was aerated by pressurized air. Air was supplied to the model by a compressor with adjustable intensity aeration. The choice of the effort was important so that the process of sedimentation and thickening was not disturbed. Length of aeration during the day in terms of quality of sludge thickening was also being altered.

In the second model, we used a mixing stirrer bar driven by an electro motor that was connected through a voltage transformer to the power source. While mixing, we worked with adjustable mixing intensity. It varied from 6 to 10 revolutions per minute.

In the third model sludge was left to settle freely without any mixing.

We simulated a process of filling and discharge of wastewater treatment plant in the model device. Given that the dehydration and stabilization processes of sludge depend on the sludge temperature, which is in open sludge tanks influenced by air temperature, we divided our research into two parts, in order to observe:

- Summer operation
- Winter operation

Along with the research model, control research was conducted in the sludge tank object. Timing of measurements corresponded with one operational cycle of sludge tank.

The priority of the measurements was to evaluate and compare the results for the following parameters measured in the experimental facilities and sludge tanks:

- volume of solids in concentrated sludge
- amount of organic matters
- BOD_5 in sludge water
- dewatering (LCST device; Mahríková Ivana 2009)

The aim of the research was to design the optimum operation of open sludge tanks, in such manner that the sludge, as a residual product resulting from treatment of waste water after treatment in sludge operation reached properties of sludge suitable for further use. We tried to achieve:

- minimal sludge volume
- highest ratio of sludge solids
- stabile amount of organic solids
- dewatering sludge properties suitable for mechanical sludge dewatering

To achieve these objectives, we selected two wastewater treatment plants. These were wastewater treatment plants serving up to 20.000 PE inhabitants, connected to the sewage treatment plants. After completing the measurements and evaluation of research on the model device, we could conclude that by proper operation of these objects optimal properties of concentrated sludge could be obtained; and such sludge is prepared for further use. For each wastewater treatment plant it is necessary to create a separate proposal for optimal operation of sludge management, depending on the quantity and quality of sludge, the size of the facility, weather conditions and possibilities for further processing or use of concentrated sludge.

The research results will help us to create a guide for operators of sludge tanks and other facilities connected with them. It is essential for operators to follow a few basic conditions for optimal operation of sludge tanks.

For the homogenisation of sludge and creating optimal conditions for sludge thickening – slow mixing by mechanical stirrer driven by an electric motor with adjustable intensity; optimal speed of the stirrer in tank circuit is 3–4 m/min. Mixing with higher intensity could disrupt the process of dehydration and sedimentation in the tank.

To achieve the highest possible degree of aerobic sludge stabilization, while mixing the sludge in the tanks – compressive aeration with adjustable intensity is needed. For smaller tanks it is sufficient to install aerators in the bottom of the tanks. For larger tanks aeration is ensured by aerating elements fixed to the bottom and sides of the tank. Volume intensity of aeration needed to achieve aerobic sludge stabilization is recommended to be 1–2 $m^3/m^3.h$.

The time of retaining sludge in the sludge tank needed to complete the process of dehydration and aerobic sludge stabilization in the summer – is at least 35 days. STN 75 64 01 specifies the minimum time for retaining in case of an accident, to be 30 days. The optimal period for storing the sludge in sludge tanks, according to STN 75 64 01, is 150 days. With long-term decline in temperatures below +6°C, it is advised to extend the retention time in tanks.

In observing the time of filtered sucking on the LCST device, this parameter for sludge with good drainage properties ranged from 300 to 480 s. Thus, such treated sludge is suitable for further processing and use in agriculture.

6. Conclusions

Given the anticipated construction of new wastewater treatment plants in the small and medium-sized metropolitan areas, and to that related increased sludge production, the question of tackling wastewater treatment plant sludge is highly important. For small sources of pollution it is not profitable to build sludge treatments with anaerobic decomposition of sludge in septic tanks. For these sites, in terms of both economic and ecological point of view, it is more appropriate to use aerobic treatment of sludge in open tanks as sludge tanks. We assume that the number of treatment plants that use sludge tanks for storage and treatment of sludge shall increase significantly in the near future.

Our research may help in designing and constructing sludge management facilities at newly built wastewater treatment plants, but especially when they are introduced into service. Proper operation of processes in the sludge tanks improves the quality of sludge, minimizes its volume and provides an opportunity for its further use. It therefore significantly reduces the costs of operating sewage treatment plant itself. In the times of global crisis this fact is actually a great asset.

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USE OF NATURAL MATERIALS FOR WASTEWATER TREATMENT & IMPROVEMENT OF WATER QUALITY

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Abstract. In the present work the results of purposeful researches are submitted in the field solutions and waste water of application natural zeolites, tuff and agricultural by-products as sorbents for removal of ammonia and organic substances from water. The abundance and availability of zeolites, tuff and agricultural by-products/the by-products include soft lignocellulosics such as apricot and peach seeds, also mentioned seeds based activated carbon/make them good candidates as sorbents for waste water treatment. Technological stability of zeolites as sorbents is determined by such characteristics as mineral – their low cost, their availability, chemical composition, sorption ability, mechanical and physical properties, and then filtering properties. Adsorption by agricultural by products is preferred because of its have low sensitivity to flow fluctuations and exhibits greater flexibility. In other case activated carbons also is preferred because of its large surface areas resulting in higher separation efficiency by activated carbons. The advantages of agricultural by-products in comparison with other sorbents are their low cost, availability of extraction, operational flexibility and control.

Keywords: natural zeolites, mordenite, clinoptilolite, agricultural by-products, ligno-cellulosics such as apricot, peach, apples seeds based activated carbon adsorption, adsorbent, wastewater treatment, ammonia, organic pollutants

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1. Introduction

Armenian water resources generally originate within its own territory and add about 7.8 km^3 annually, which includes 4.7 km^3 of surface water and 3.1 km^3 of groundwater. There are more than 300 rivers over 10 km in length and 9,500 small drains up to 10 km long. About 30 small rivers and drains empty into Lake Sevan, adding about 700 million m^3/year to the lake, with only the Razdan River draining from it. It should be note, that mentioned water resources have many ecological problems – they content more organic pollutants, metals and ammonia.

The problem of removal of hydrocarbons and ammonium from water resources an urgent task. Many manufacturing processes form organic pollutants (benzene, toluene, ethylbenzene, xylenes, phenol, aniline and their derivatives), which are toxic substances. Organic toxic substances are the main sources of anthropogenic pollution and come from agriculture (stock-breeding, farming, mineral fertilizers, poisonous chemicals), industry and household sewage waste water. Organic compounds can be major pollution problem in soil and groundwater. Their presence in water can create a hazard to public health and the environment of organic pollutants.

At this time the amount of dissolved organic matter in Lake Sevan catchment basin has increased up to 3 mg/l; the content of chlorides and sulfates has increased several fold; the concentration of nitrogen nitrate and ammonia forms have increased ten-fold; the total mineralization has grown from 130 to 190 mg/l. The rivers are most polluted Lake Sevan with ammonia and heavy metals. All rivers are high in iron compounds (70–140 mkg/l) and low in manganese content (7–18 mkg/l). Noticeable changes took place in the concentration of mineral nitrogen which is the consequence of mineral fertilizers and stock-breeding development.

2. Improvement of Water Quality

One of important and nowadays technology for waste water treatment is sorption process.

In this paper for a sorption process the use of natural zeolite and tufas was proposed. The increasing demand for ion-exchange materials to solve ecological problems stimulated the intensive study of natural and modified zeolites because they are considered to be cheap modified sorbents (Breck 1974; Collela 1999). The technological stability of zeolites as sorbents is determined by such characteristics as mineral and chemical composition, sorption ability, mechanical and physical properties, and then filtering properties (Breck 1974).

Natural zeolites are used in the following fields of waste water cleaning (Collela 1999):

1. removal and recovery of NH_4,
2. removal and storage of radionuclides,
3. removal and storage of heavy metals,
4. removal and treatment of organic compounds.

The application of the Armenian natural zeolites in the processes of water preparation has been scientifically approved according to the all-round evaluation of mechanical, physical, physical-chemical, and technological properties of developed zeolites. The chemical stability and mechanical strength of natural Armenian zeolites such as Mordenite and Clinopilolite meet the requirements of filtering materials (Torosyan et al. 2002).

The abundance and availability of agricultural by-products/the by-products include soft lignocellulosics such as apricot, peach, apples seeds based activated carbon/make them good candidates as precursors for activated carbons (Ahmedna et al. 2000).

Adsorption by agricultural by products is preferred because of its have low sensitivity to flow fluctuations and exhibits greater flexibility. In other case activated carbons also is preferred because of its large surface areas resulting in higher separation efficiency by activated carbons. Activated carbon is also used in water treatment plants for the removal of odors and tastes. Agricultural by products and activated carbons from them, on the other hand, can be made a renewable resource. Preliminary studies on cost estimation have shown that agricultural by-products can be manufactured for as $0.03 per kg and agricultural byproduct based activated carbons – $0.14 per kg.

In the present study we use some fruits/apricot, peach/seeds and based on them activated carbon. The advantages of agricultural by-products in comparison with other sorbents are their low cost, availability of extraction, operational flexibility and control. The effectiveness of agricultural by-products made activated carbon for the removal of organics by adsorption also is enhanced by its large surface area.

3. The Using Zeolites and Tuff in Present Research

Volcanic tuff and zeolites (zeolite-tuff also) occur in nature in specific kinds of rocks. Volcanic tuff are widespread in Shirak region, specially in Artik. Zeolite rich rocks are widespread in Northern part of Armenia, occurring in very extended geological formations. The zeolite types are exclusively clinopilolite – in Idjevan (Northern-East of Armenia) and mordenite in Shirak (Northern-West of Armenia). Taking advantage of their high zeolite content, high cation exchange capacity and selectivity, many agricultural applications of Armenian zeolites have been proposed recently. Some of Armenian natural zeolites were categorized from the point of view of chemical composition, type of structure and chemical, thermal and radiation resistance.

These natural zeolites produced in Armenia and volcanic tuff residues were employed for this study.

4. The Using Agricultural By-Product in Present Research

The abundance and availability of agricultural by-products/the by-products include soft lignocellulosics such as apricot, peach, apples seeds based activated carbon/make them good candidates as precursors for activated carbons. It has been rare literature on the use of agricultural by-product based activated carbon for wastewater treatment processes.

The samples used in this study consisted of:

(A) Four experimental carbons, namely

1. Peach seeds breaking
2. Peach seeds based activated carbon
3. Apricot seeds breaking
4. Apricot seeds based acid-activated

(B) One commercial carbons, namely Carbonsorb-AB

This carbon was selected as a control for this experiment as they have found to possess the desirable physical and chemical characteristics and was extensively used in wastewater treatment plants and rivers.

5. Result and Discussion

The ammonium in water and wastewater can be toxic to the aquatic life and should be removed to prevent environmental pollution. Several processes are currently used for the removal of ammonium from aqueous solutions. Ion exchange with natural zeolites is among the methods most commonly employed.

Zeolites (also zeolite tuff and volcanic tuff) are materials known for they ability to remove ammonia preferably from waste water (Lahav and Green 1998; ECWATECH-2000). One of the aims of this work is to investigate ion exchange of ammonium $(NH_4)^+$ with zeolites obtained from the abovementioned deposits in Armenia. The ion exchange capacity of natural zeolites, especially from Armenian deposits, offers the possibility for their application to the purification of ammonia-contaminated water. At our opinion volcanic tuff also can practical application as residues from construction tuff.

At first the ability of mordenite to purify waste water is compared to normal river gravel. The tested zeolite was superior to gravel in the oxidation of ammonium ions through nitrite ions into nitrate ions. The decrease in the amount of ammonium ions resulted not only in exchange with Ca_2^+ mainly in the zeolites, but also microbial oxidation on the surface of the zeolites. Thus, a long-term decrease in the amount of ammonium ions may be possible. This observation suggests that mordenite seems to promote purification with the help of microbial oxidation, with frequent exchange between Ca_2^+ and NH_4^+ at the zeolite surface.

Higher ammonia sorption (Table 1) is evident in clinoptilolite treated by ethanolamine (5) and ammonium salt – Catamine AB clinoptilolite (6).

TABLE 1. The adsorption of NH_3 [g] on the zeolites/10 g/.

N	Zeolite	1 day	3 day	5 day	7 day	10 day
1.	Tuff	0.24	0.41	0.57	0.62.	0.71
2.	Mordenite	0.38	0.51	0.62	0.70	0.76
3.	Mordenite Treated by 0.5N $CaCI_2$	0.86	1.02	1.15	1.22	1.38
4.	Mordenite Treated by 1N $CaCI_2$	1.14	1.71	2.13	2.46	2.98
5.	Clinoptilolite modified by ethanolamine	2.08	2.37	2.51	2.95	–
6.	Clinoptilolite modified by Catamine-AB	1.86	2.16	2.49	2.97	2.98

Adsorption from wastewater with organic pollutants involves concentration of the solute on the surface. Here, it has been had adsorption and desorption process together which will attain an equilibrium state. We used Dubinin-Radushkevich and Freundlich models for description of the adsorption data on zeolite, for agricultural by-products and activated carbon is convenient to use Langmuir isoterms theory.

It has been shown that Armenian modified zeolites, specially them modified analogs can be used as good sorbents for organic compounds sorption from waste water.

In the present work the results of purposeful researches are submitted in the field solutions and waste water of application natural zeolites and modified analogs as sorbents for removal of organic substances from water.

Polluted by hydrocarbons water passes through a column filled with adsorbents. Hydrocarbons are taken from water, remaining in limits of adsorption column. The cleared water leaves a column for direct use or further treatment.

The higher adsorptivity shows natural clinoptilolite modified by mono-ethanolamine – about 100% extraction of phenol from 0.015M solutions, and also rather high sorption activity of benzene, toluene, xylene from water solutions/from 50 up to 70% /. The quantitative adsorption takes place in case of the H-form natural mordenite .

The linear dependence between concentration of phenol in a water solution and appropriate molar refraction is preset at 20°C. The measurements were carried out in concentration limits from 0.05 up to 0.3 mol/L. It was earlier established, that the sorption in these limits grows and has linear dependence on molar refraction. From graphic dependence is determined amount of adsorpted phenol. The results are given in the Table 2. It is necessary to note, that partial sorption of water/1–2 ml from 10 ml of a solution for 4 h sorption of a solution on sorbents/takes place.

TABLE 2. The sorption of phenol from a water (0.05M)* solution on sorbents/temperature 20°C, duration 4 h/.

N	Sorbent	ND20 after sorption	sorption g phenol/g sorbent
1.	Tuff	1.3326	0.0125
2.	Mordenite (purified)	1.3320	0.0240
3.	H-Mordenite	Full sorption	0.0380
4.	Granular Activated Carbon**	1.3315	0.0289
5.	Peach seeds breaking/crushing/	1.3321	0.0227
6.	Apricot seeds breaking/crushing/	1.3322	0.0219

*ND20 for initial phenol solution is 1.3324

**Peach seeds based activated carbon, apricot seeds based acid-activated has same activity

It’s visible from the given tables with increase of concentration of solutions the amount of absorbed phenol is increased. Fairly active has modified clinoptilolite by mono-ethanolamine. The H-form of mordenite shows activity, where, on all probability, the formation of hydrogen connections takes place.

For aniline sorption from water solutions the H-form of mordenite and clinoptilolite show activity, where, on all probability, the formation of hydrogen connections takes place. The sorption activity is higher also for modified zeolites with ethanolamine and catamin-AB.

As chlorine containing organic products here was investigated the sorption of di-chlorine-benzene. The results are presented in Figure and Table 3.

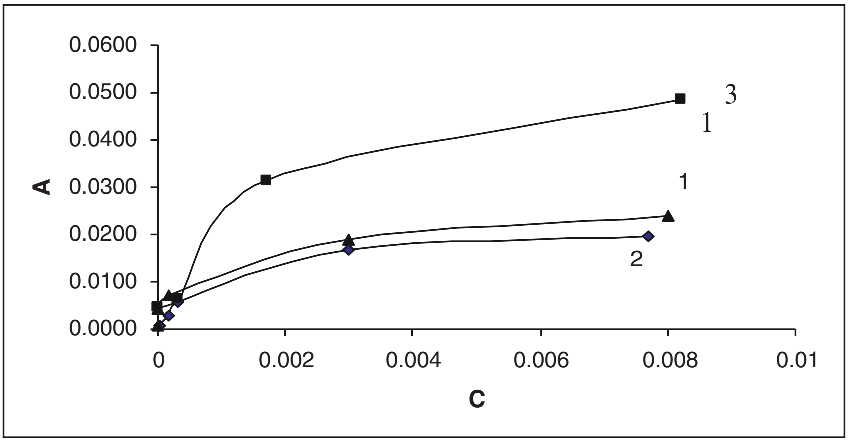

Figure 1. Adsorption isotherms for dichlorobenzene Clinoptilolite – treated by 1N $CaCI_2$ (1), Clinoptilolite-tuff (2), Clinoptilolite – modified by Catamine-AB (3).

From given results in Figure 1 and Table 3 appears, that the given method can be applied at rather low initial concentration for chlorine containing organic compounds as chlorinebenzene. There possibilities can be more important for waste water treatment process from pesticides.

TABLE 3. The adsorption of dichlorobenzene (mg) on the zeolites /10 g/.

N/N	Zeolite	The adsorption mg/g	The adsorption %
1.	Mordenite-tuff	0.12	22.0
2.	Mordenite - treated by 0.5N $CaCI_2$	0.19	25.0
3.	Mordenite- treated by 1N $CaCI_2$	0.28	40.0
4.	Clinoptilolite-tuff	0.22	30.0
5.	Clinoptilolite- treated by 1N $CaCI_2$	0.32	45.0
6.	Clinoptilolite- modified by ethanolamine	0.47	68.5
7.	Clinoptilolite- modified by Catamine-AB	0.50	70.0

6. Experimental Part

The tuff and zeolite – clinoptilolite and mordenite were dehydrated at 110°C.

In this study clinoptilolite and mordenite were prepared by heated pile method, using 0.5 and 1N solution of $CaCI_2$. Zeolites modified by catamin-AB and monoethanolamine were prepared according to Sargsyan et al. (2000).

The ammonia adsorption by zeolites was investigated by IR spectroscopy. After sorption of ammonia vapour produced by 1N NH_3 solution by natural zeolites and its treated forms for 10 days at room temperature the adsorption data were plotted.

Liquid chromatography is passed on HELCh/higher-effective liquid chromatography, detector Waters 486, controller Warers 600S, Pump, Waters 626, colon 250 × 4 mm, Si-100 C 18, P 150 Bar, V 1 ml/m, mobile phase acetonitryl-water (50:50), detector UV-254).

UV spectrometry is passed on UV-Specord spectrometr

7.2.a. On 1 g of sorbent added on 10 ml solutions of phenol in water. The mix was carefully shaken up within 4 h. The measurements of molar refraction of a solution were carried out before and after sorption. On a difference of concentration of an organic solution expected amount of adsorpted phenol.Here it has been check the results by liquid chromatography and UV spectrum dates also.

7.2.b. The removal of organic substances is carried out as follows. The precisely weighed portions of sorbents are brought in to the certain volumes of organic substances in water, which initial concentration vary. The mix is carefully shaken up during 6 h. Further test is settled. The quantity of the besieged substance on zeolites is determined by the precipitated organic fraction in the filtered solution by the methods of UV Spectroscopy, Highly Effective Liquid Chromatography and Refractometry.

6.1. MEASUREMENT OF PHYSICAL PROPERTIES OF SORBENTS TOTAL SURFACE AREA (M2/G)

The total surface area of the activated carbons was determined by the method Pendyal et al. (1999) using Micromeritics Gemini 2,375 surface area analyzer. The total surface area was measured by nitrogen adsorption at 77°K using 15 point BET.

6.2. BULK DENSITY (G/M3) MEASUREMENT

Bulk density was measured using the method of Ahmedna et al. (2000), which consisted of placing a known weight of granular activated carbon of 10–30 mesh size carbon in a 25 ml cylinder to a specified volume and tapping the cylinder for at least 1–2 min and measuring the volume of carbon. The bulk density was measured as:

$$\text{Bulk density}\,(\text{g/m}^3) = \frac{\text{weight of dry sample (g)}}{\text{volume of packed dry sample (g)}}$$

6.3. ATTRITION/ HARDNESS (%)

For determination wet attrition of the samples from agricultural by-products and activated carbon was measured using method described by Toles et al. (1999). One gram of granular activated carbon of 10–30 mesh was added to 100 ml of acetate buffer (0.07 M sodium acetate and 0.03 M acetic acid, pH 4.8) in a 150 ml beaker. The solution was stirred at 500 rpm for 24 h using Variomag Electronic Ruhrer Multipoint HP 15 stirrer (Daytona Beach, FL) with a 1/2 inch stir bar for agitation. The solution was then filtered through 50-mesh screen and the retained carbon was thoroughly washed and dried at 90°C under vacuum for 4 h and weighed. The % attrition was measured as:

$$\text{Attrition}\,(\%) = \frac{\text{Initial weight (g) - Final weight (g)}}{\text{Initial weight (g)}} * 100$$

7. Conclusion

It has been offered the convenient method for successfully sorption of ammonia and organic compounds from water for improve water quality. The given method can be applied at rather low initial concentration for non soluble or lower soluble in water aromatics and can be applied at waste water treatment processes by using domestic natural sorbents.

The treated natural materials, specially agricultural by-products, can be propose for using as sorbents and as promising materials for waste water treatment from small enterprises.

The advantages of zeolites, volcanic tuff, and agricultural by-products in comparison with other sorbents are their reserves in Armenia, a unique complex of technological properties as well as their natural origin, possibilities of they modification in various directions, regeneration and utilization.

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FEASIBILITY STUDIES FOR WATER REUSE PROJECTS: ECONOMIC VALUATION OF ENVIRONMENTAL BENEFITS

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Abstract. Water reuse is emerging as a promising alternative because it enables water resources to be increased and lowers pollution levels by reducing wastewater. In recent decades, significant technological progress has been made in the field of wastewater regeneration thus, water reuse projects feasibility are now mostly subject to just economic assessment. However, the economic aspect is the least addressed aspect of research into water reuse. Methodologies used to analyze the economic feasibility of these projects usually focus on internal costs while, the external effects are relegated to a series of statements about the advantages of water reuse. As a result, the true benefits and costs of many projects are not properly evaluated. This paper presents a methodology for assessing the economic feasibility of a water reuse project that takes into account the internal and external impacts. On the other hand, a monetary quantification of the environmental benefits is made. This assessment is made through an estimation of shadow prices for the undesirable outputs of wastewater regeneration. In this way, a useful economic feasibility indicator that includes both internal and external impacts is obtained for water reuse projects.

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1. Introduction

Recurrent droughts in recent decades have shown that water supply is not always balanced with demand (Hochstart et al. 2007). More than 70% of Europe's population face water stress problems: semi-arid coastal and highly urbanized areas being the most affected (AQUAREC 2006). In addition, global climate change will worsen this situation, especially in southern European nations where greater susceptibility to drought can cause serious environmental, social, and economic problems (Bixio et al. 2006).

Wastewater regeneration and reuse is emerging as an important future alternative because it performs two key functions: increasing water supply and so lessening the pressure on conventional natural resources; and reducing pollution by discharging less wastewater.

In recent years, there has been substantial technological progress in the field of wastewater regeneration. Examinations of the feasibility of wastewater reuse projects are mostly focused on economic considerations and social acceptance. In this sense, a detailed cost analysis is essential for assessing the potential of wastewater reuse projects (Asano 2007).

However, the economic viewpoint is perhaps the least studied aspect of research into the regeneration and reuse of wastewater. This is because only private costs are generally considered, while the external effects are relegated to a series of statements about the advantages of wastewater reuse (Seguí 2004).

The absence of a market for regulating prices creates difficulties when attempting to quantify externalities. Nevertheless, there is a growing interest in the monetary valuation of these externalities. An example of this interest is found in the works of Godfrey et al. (2009), Seguí (2009), Chen and Wang (2009), among others.

Many authors consider the conventional methods of economic valuation as consolidated techniques because they are supported by numerous empirical applications. However, in the scientific community (Diamond et al. 1994; Shabman et al. 2000, among others) there is no unanimous consensus regarding the validity of these methodologies because are expensive and their limitations.

From the pioneering work by Färe et al. (1993) and successive developments (Färe et al. 2001, 2006), a stream of research has been produced within the framework of efficiency studies that aims to provide a valuation methodology for those undesirable outputs that have no market. By using the concept of directional distance function, a shadow price is calculated for those goods arising from human and productive activities that have no market value – but create substantial environmental impacts.

This work shows a methodology to assess the economic feasibility of wastewater reuse projects where not only internal but also external impacts are considered. Also an empirical application is carried out to quantify the monetary value of environmental benefits arising from water reuse. This economic valuation is made by estimating shadow prices for the undesirable outputs resulting from wastewater regeneration.

2. Methodology

Economic feasibility studies of wastewater reuse projects must be made using conventional methodologies of economic analysis.

According to Seguí (2004) and Hernández et al. (2006), total benefit is calculated by considering internal benefit, external benefit, and opportunity cost. The function to maximize takes the following form:

$$MaxB_T = B_I + B_E - OC \tag{1}$$

Where B_T is the total benefit (total income – total costs); B_I is the internal benefit (internal income – internal costs); B_E is the external benefit (positive externalities – negative externalities); and OC is the opportunity cost.

2.1. INTERNAL BENEFIT

The internal benefit is the difference between internal income and internal costs. Internal income includes revenues from the sale of regenerated water and other recovered sub-products. If reclaimed water is used in agriculture, the nitrogen and phosphorus content in the water offer a saving in fertilizer costs; whereas if the reclaimed water is intended for environmental purposes, these nutrients can be recovered and then be sold. Internal costs are the result of the sum of the investment costs, operating costs, financial costs, and taxes.

The internal benefit is expressed as:

$$B_I = \sum_{n=0}^{n} \begin{bmatrix} (AVW_n * SPW_n) + (ACP_n * SPP_n) + (ACN_n * SPN_n) \\ -(IC_n + OMC_n + FC_n + T_n) \end{bmatrix} \tag{2}$$

where B_I = internal benefit (€); AVW = annual volume of reclaimed water (m^3); SPW = selling price of reclaimed wastewater (€/m^3); ACP = annual volume of recovered phosphorus (kg); SPP = selling price of recovered phosphorus (€/kg); ACN = annual volume of recovered nitrogen (kg); SPN = selling price of recovered nitrogen (€/kg); *IC* = investment costs (€); *OMC* = operational and maintenance costs (€); *FC* = financial costs (€); *T* = taxes (€); and *n* = year.

2.2. EXTERNAL BENEFIT

Water reuse projects create some externalities such as biological and chemical risks, health benefits, and especially environmental benefits. According to Equation 1, an economic feasibility study of wastewater reuse projects requires the consideration of internal and external impacts. The external benefit is expressed as:

$$B_E = \sum_{n=0}^{n} (PE_n - NE_n) \tag{3}$$

where B_E = external benefit (€); *PE* = positive externalities (€); *NE* = negative externalities (€); and *n* = year.

While any internal impact can be calculated directly in monetary units, the quantification of external impacts requires the use of economic valuation methods due to the absence of market prices. All this implies that decisions regarding wastewater reuse are generally based on the financial costs of the project without paying attention to non-monetary impacts such as environmental protection. However, a full economic feasibility study should consider both internal and external impacts. A method to estimate the environmental benefits derived from wastewater regeneration and reuse projects, as mentioned in section 1, involves quantifying shadow prices for the undesirable outputs obtained during wastewater regeneration.

According to Hernández-Sancho et al. (2010), wastewater treatment can be considered as a production process in which a desirable output (clean water) is obtained together with a series of pollutants (organic matter, phosphorus, nitrogen, etc.). The contaminants extracted from wastewater are considered undesirable outputs because dumping them in an uncontrolled manner would cause negative impacts on the environment .

The shadow price valuation methodology for undesirable outputs (Färe et al. 2006) is based on the concept of the directional distance function. Conceptually, a distance function measures the difference between the outputs produced in the process under study and the outputs of the more efficient process. Denote inputs by x = (x1,…,xN)϶RN, desirable outputs by y = (y1,…,yM)϶RM and undesirable outputs by b = (b1,…,bJ)϶RJ. Let g = (gy, gb) be a directional vector and assume g ≠ 0. The directional output distance function is defined as:

$$D_0(x, y, b; g_{y,} g_b) = \text{Max } \{ \beta : (y + \beta g_{y,} b - \beta g_b) \in P(x) \} \tag{4}$$

Directional distance function parameterization is carried out with a quadratic form. Given the directional vector $g = (1,1)$ the quadratic directional distance function for state k in period t is:

$$D_o^t(x_k^t, y_k^t, b_k^t;1,1) = \alpha + \sum_{n=1}^{N} \alpha_n x_{nk}^t + \sum_{m=1}^{M} \beta_m y_{mk}^t + \sum_{j=1}^{J} \gamma_j b_{jk}^t + \frac{1}{2}\sum_{n=1}^{N}\sum_{n'=1}^{N} \alpha_{nn'} x_{nk}^t x_{n'k}^t)$$
$$+ \frac{1}{2}\sum_{m=1}^{M}\sum_{m'=1}^{M} \beta_{mm'} y_m y_{m'}) + \frac{1}{2}\sum_{j=1}^{J}\sum_{j'=1}^{J} \gamma_{jj'} b_j b_{j'} + \sum_{n=1}^{N}\sum_{m=1}^{M} \delta_{nm} x_{nk}^t y_{mk}^t + \sum_{n=1}^{N}\sum_{j=1}^{J} \eta_{nj} x_{nk}^t b_{jk}^t \quad (5)$$
$$+ \sum_{m=1}^{M}\sum_{j=1}^{J} \mu_{mj} y_{mk}^t b_{jk}^t$$

$$Min = \sum_{t=1}^{T} \sum_{k=1}^{K} \left[(D_0^t(x_k^t, y_k^t, b_k^t;1,1) - 0 \right]$$

For parameter estimation the sum of the distance between the production frontier and individual observations for each period should be minimized:

$s.t.:$

$$(i) \quad D_0^t(x_k^t, y_k^t, b_k^t;1,1) \geq 0, k = 1,\ldots,K, t = 1,\ldots,T,$$
$$(ii) \quad \frac{\partial D_0^t(x_k^t, y_k^t, b_k^t;1,1)}{\partial b_j} \geq 0, j = 1,\ldots,J, k = 1,\ldots.,K, t = 1,\ldots,T,$$
$$(iii) \quad \frac{\partial D_0^t(x_k^t, y_k^t, b_k^t;1,1)}{\partial y_m} \leq 0, m' = 1,\ldots,M, k = 1,\ldots,K, t = 1,\ldots,T, \quad (6)$$
$$(iv) \frac{\partial D_0^t(x_k^t, y_k^t, b_k^t;1,1)}{\partial x_n} \geq 0, n = 1,\ldots,N,$$
$$(v) \quad \sum_{m=1}^{M} \beta_m - \sum_{j=1}^{J} \gamma_j = -1; \sum_{m'=1}^{M} \beta_{mm'} - \sum_{j=1}^{J} \mu_{mj} = 0; m = 1,\ldots,M;$$
$$\sum_{j'=1}^{J} \gamma_{jj'} - \sum_{m=1}^{M} \mu_{mj} = 0; j = 1,\ldots,J; \sum_{m=1}^{M} \delta_{nm} - \sum_{j=1}^{J} \eta_{nj} = 0; n = 1,\ldots,N;$$
$$(vi) \quad \alpha_{nn'} = \alpha_{n'n}; \beta_{mm'} = \beta_{m'm;} m \neq m', \gamma_{jj'} = \gamma_{j'j}, j \neq j'$$

The deduction of shadow prices for undesirable outputs means assuming that the shadow price of an absolute desirable output coincides with market price. If y is a desirable output whose market price is p and is equal to its shadow price pm, and if b is each of undesirable outputs and qj, is the shadow price of each undesirable, the absolute shadow prices are given by:

$$q_j = -p_m \frac{\partial D_0(x,y,b;g) \Big/ \partial b_j}{\partial D_0(x,y,b;g) \Big/ \partial y_m} \tag{7}$$

2.3. OPPORTUNITY COST

The opportunity cost is defined as the value of goods in terms of a lost alternative use of those goods. Therefore, the opportunity cost will be given by that use which provides greatest economic efficiency. In water reuse projects, the opportunity cost generally refers to land that the wastewater treatment plant occupies. Usually this land is not of great value, but there may be situations where alternative uses generate significant incomes.

3. Sample Data Description

The study was made from a sample of 35 wastewater treatment plants (WWTPs) of which 13 were selected because their effluent is reused for environmental uses. All the plants are located in the coastal area of the Valencia region (on the Mediterranean coast of Spain). All the WWTPs carry out a similar process and obtain a desirable output (regenerated water) and four undesirable outputs: suspended solids (SS); nitrogen (N); phosphorus (P); and organic matter measured as chemical oxygen demand (COD). The inputs needed are energy, staff, reagents, waste management, and others. These variables are described in Table 1. The statistical information comes from the Valencia wastewater management authority (Entitat de Sanejament d´Aigües) for the year 2007.

4. Results

Given that the aim of this paper is to quantify the environmental benefits of water reuse projects, the methodology described in Section 2.2 has been applied in the complete sample of 35 WWTPs. However, only those plants whose effluent is reused for environmental purposes have been selected.

The estimation of the directional distance function enables shadow prices to be calculated for each pollutant removed during the wastewater regeneration for each WWTP under study. These values, in €/kg, are shown in Table 2.

The shadow prices obtained for undesirable outputs are negative because, from the viewpoint of the production process, they are not associated with marketable outputs that can generate income. However, from an environmental point of view, these shadow prices can be interpreted positively because they represent environmental benefits obtained from the water reuse project.

TABLE 1. Sample description.

		Average for 35 WWTPS sample	Average for 13 WWTPs sample	Deviation for 35 WWTPs sample	Deviation for 13 WWTPs sample
Inputs (€/m^3)	Energy	0.054	0.072	0.037	0.021
	Staff	0.086	0.075	0.049	0.040
	Reagents	0.038	0.030	0.029	0.019
	Waste	0.046	0.025	0.038	0.011
	Others	0.011	0.008	0.008	0.006
Desirable output (m^3/year)	Waste water treated	4,203,312	3,166,290	3,192,313	2,400,849
Undesirable outputs (kg/m^3)	SS	0.297	0.380	0.239	0.246
	N	0.025	0.028	0.012	0.017
	P	0.004	0.006	0.003	0.004
	COD	0.678	0.667	0.387	0.323

Table 2 shows that the greatest environmental benefit for all the plants studied is associated with phosphorus removal followed by nitrogen. This is because an excess of these two nutrients in water creates problems of eutrophication. Nowadays, eutrophication is one of the major environmental problems

TABLE 2. Shadow prices for pollutants (€/kg).

WWTP	SS	N	P	COD
1	−0.010	−10.473	−62.840	−0.062
2	−0.001	−1.500	−9.000	−0.007
3	−0.008	−38.840	−45.826	−0.243
4	−0.002	−1.500	−2.166	−0.007
5	−0.059	−59.104	−70.792	−0.360
6	−0.004	−61.267	−367.602	−0.534
7	−0.001	−1.500	−3.519	−0.012
8	−0.007	−35.126	−42.126	−0.192
9	−0.003	−10.810	−28.579	−0.403
10	−0.010	−21.705	−130.227	−0.152
11	−0.016	−73.904	−167.671	−0.238
12	−0.006	−55.209	−63.809	−0.235
13	−0.007	−56.693	−78.794	−0.242
Mean	−0.010	−35.188	−82.535	−0.207

in continental water bodies because excessive growth of phytoplankton and algae reduces dissolved oxygen levels, and consequently, there is a loss of aquatic biodiversity. We must keep in mind that nitrogen and phosphorus do not equally affect the eutrophication. In the empirical application carried out, water reuse is performed for environmental purposes; and consequently, the regenerated effluent is dumped to inland water bodies. For this reason, the phosphorus shadow price is greater than the shadow price of nitrogen.

For the shadow price of organic matter, the obtained value is considerably lower than nitrogen and phosphorus. This is because water bodies have some capacity to self-purify this pollutant. However, an excessive discharge of organic matter into water bodies can cause oxygen deficiency.

Once the shadow prices of pollutants is quantified in €/kg and the amount of pollutants removed per cubic meter of reclaimed water are known, the monetary value of the environmental benefit of water reuse in €/m^3 and €/year is directly obtained.

The greatest environmental benefit, on average, is associated with nitrogen removal – representing nearly 60% of the total benefit. Phosphorus follows in importance with a percentage weight of 28%. These results reflect the fact that these pollutants have the highest shadow prices (see Table 2). The total environmental benefit derived from a water reuse project varies greatly between

TABLE 3. Environmental benefits of water reuse project.

WWTP	SS (€/m^3)	N (€/m^3)	P (€/m^3)	COD (€/m^3)	Overall (€/m^3)	Overall (€/year)
1	0.004	0.257	0.449	0.049	0.759	6,430,921
2	0.001	0.036	0.084	0.011	0.132	946,054
3	0.003	1.996	0.313	0.114	2.425	12,638,415
4	0.001	0.079	0.015	0.005	0.099	272,081
5	0.010	0.746	0.164	0.154	1.073	3,156,721
6	0.003	0.319	0.540	0.513	1.376	3,719,680
7	0.001	0.095	0.046	0.010	0.151	207,631
8	0.002	0.821	0.167	0.101	1.091	1,804,343
9	0.001	0.306	0.340	0.443	1.090	1,033,818
10	0.002	0.735	0.566	0.079	1.383	4,137,498
11	0.002	0.739	0.309	0.026	1.075	3,299,762
12	0.001	0.988	0.114	0.029	1.131	1,148,305
13	0.001	2.061	0.403	0.059	2.525	2,203,367
Mean	0.003	0.611	0.286	0.122	1.022	3,153,738

the different plants: the minimum value being 0.132 €/m^3 while the maximum is 2.525 €/m^3. The weighted average, depending on the volume of wastewater treated, is 1.022 €/m^3.

Finally, information about the environmental benefit expressed in €/year is given. The integration of this value in Equation (1) enables an indicator to be obtained regarding the economic feasibility of a proposed water reuse project. This indication considers internal impacts and externalities resulting from the project.

5. Conclusions

As a result of significant technological progress in wastewater regeneration in recent years the feasibility of a water reuse project is primarily subject to economic and social considerations. However, in most cases, economic feasibility studies are focused on internal impacts without consideration given to non-monetary benefits such as environment protection.

A monetary valuation of the environmental externalities arising from a proposed water reuse project is required to justify its economic feasibility. However, this is a complex task due to its non-market nature. This paper proposes quantification of shadow prices for the undesirable outputs of the regeneration process as an economic valuation method for the environmental benefits associated with water reuse.

An empirical application has been made with a sample of WWTPs that reuse effluent for environmental purposes. The results show that the greatest environmental benefit is the prevention of nitrogen and phosphorus discharges – since these nutrients are primarily responsible for problems of eutrophication in inland water bodies.

The monetary value of environmental benefits is expressed in €/year may be integrated into the economic feasibility study of a water reuse project; thereby obtaining a useful viability indicator that takes into account internal and external impacts.

6. Acknowledgement

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CASE STUDIES OF WATER RESOURCE MANAGEMENT

WATER RESOURCES IN JORDAN

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Abstract. Water resources in Jordan are very limited, among the lowest in the world on a per capita basis. The annual per capita share of water is currently estimated at 135 m^3 and this Figure is expected to drop to 90 m^3 in the year 2020 as a result of the disproportional increase in population relative to water resources development. Moreover, about 63% of the country's water resources are consumed in irrigated agriculture. Jordan with an area of around 90,000 Km^2 is characterized by Mediterranean semiarid climate in its western part to arid climate in its eastern part and in the Jordan valley. The arid climatic conditions occupy more than 90% of the area of Jordan. More than 96% of the area in Jordan receives less than 300 mm/year. The long term annual average of rainfall over Jordan is about 8,366 MCM/year. Surface runoff flow in Jordan was estimated to be around 885.6 MCM divided into 386.1 as base flow and 499.5 flood flow. For groundwater resources the safe yield is about 294 MCM/year while the pumped water was about 506 MCM making a deficit of around 212 MCM/year. The high consumption of water in agriculture sector made various sources of non-conventional supply mainly treated wastewater have been considered to meet water shortage. At present day treated wastewater was estimated to be around 84 MCM and expected to increase to 117 MCM in 2020.

Keywords: jordan, water resources, water demand management

1. Background

Water is the basis of the life and is the driving force for economic and social development. Jordan with its scarce water resources is considered one of the poorest four countries in the world therefore its management is a challenge for its expert.

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Jordan with its 90,000 km^2 area lies in a semi arid region making its water resources very scarce for around 6 million inhabitants. Topography of Jordan can be divided into three districts regions each with unique climate (Figure 1) The first region is central highland located in the western part of Jordan ranging in elevations from 600 to 1,600 m above sea level and characterized by Mediterranean climatic conditions with an average rainfall of around 580 mm/year, The second region is the desert area located in the eastern part of Jordan and comprise more than 90% of the area of the country. Its climate is arid with rainfall of less than 100 mm/year. The third region is the Jordan valley which extends along the western borders of Jordan from Lake Tiberius at – 220 m below sea level to the red sea in the south and characterized by arid climatic conditions.

Jordan is under water stress which indicates the degree of water shortage, is the value of annual rainfall divided by the total population (m^3/capita/year). When water stress indices below 500 m^3/capita/year therefore it is classified as absolute scarcity.

The share of water per capita per year is one of the lowest in the world; it is only 135 m^3/capita/year at the population of 6.0 million people and expected to be reduced for lower values under existence population growth of 2.2% and the same amount of water. The water resources in Jordan can be divided into conventional consisting of surface water, renewable groundwater and fossil groundwater as well as non conventional water consisting of artificial recharge, desalination of saline groundwater and sea water and treated Wastewater.

2. Rainfall

Rainfall is the main source of groundwater and surface water in Jordan. The average rainfall in Jordan ranges from 50 mm/year in the eastern desert part of the country up to 600 mm/year in the northern highland. Due to arid climatic condition in Jordan, more than 96% of the area in Jordan receives rainfall less than 300 mm/year. The rainfall distribution over Jordan can be illustrated in Figure 1.

As shown in Table 1 the highest volume of rain falls on desert areas rain cumulative fall less than 200 mm of rain and comprises around 80% of the country. The amount of rain in deserts is the highest 6,321 MCM/year but due to very high evaporation most of it is lost and return to the atmosphere.

By calculating the amount of rain falling on areas with different climatic conditions we found that in Jordan Valley where rain is 50–300 mm/year contributes only 5.7% and over the high land the rain is 400–600 mm/year contributing only 2.9% of total amount of rainfall and over desert area the amount of rain is 50–200 mm/year making most of the amount of rain with 91.4%. The Rainfall quantity falling on the whole country ranging from 5,800 MCM/Year in dry years to 1,100 MCM/year in Wet year.

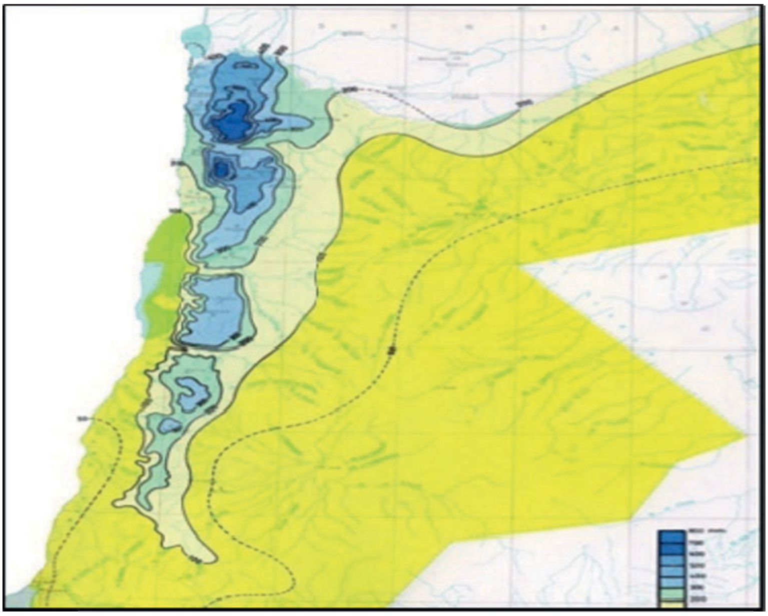

Figure 1. Rainfall distribution in Jordan.

TABLE 1. Annual average is 8,366 MCM/year.

Zone	Rainfall (mm)	Area (km^2)	Percentage to total area (%)	Volume of water (MCM)
Desert	<100	60,000	66.7	3,391
Arid	100–200	16,200	18.0	2,930
Marginal	200–300	10,000	11.1	530
Semi arid	300–500	3,080	3.4	1,110
Semi Humid	>500	720	0.8	405
Total	–	90,000	100	8,366

3. Surface Water

Surface water resources in Jordan are distributed among 15 basins discharging around 733 MCM/year. As shown in Table 2 the volume of discharge from each basin depends on the climatic conditions of that basin. Yarmouk basin which is located in relatively high precipitation area has the highest discharge of 166 \MCM while in the southern desert where precipitation is less than 100 mm/year discharge only 1 MCM in form of floods from thunderstorms although the area is very wide. The surface water quality depends on the anthropogenic activities in its basin as desert dams collecting desert floods are of good quality while King Talal dam collecting water from Zarqa River system which suffers water pollution resulting from industries in the Amman-Zarqa industrial area.

In Jordan around 26 dams were constructed to store the highest amount of surface runoff. The storage capacity of all dams is 254 MCM.

The quantity of surface water resources can be summarized as follow. Long term annual surface runoff is 733 MCM, annual surface water can be stored is 534 MCM and dams capacity in Jordan is 360 MCM.

TABLE 2. Discharge of surface water from different surface basins in Jordan.

Basin	Discharge (MCM/Year)	Basin	Discharge (MCM/Year)
Yarmouk	166	Hamad	24
Zarqa	84	Sarhan	18
Jordan Valley	124	Jafer	13
Mujeb & Wala	102	Southern Desert	1
Dead Sea	43	Northern Wadi Araba	46
Hisa	43	Southern Wad Araba	8
Azraq	41	Total	733

4. Groundwater Resources

Jordan's groundwater is distributed among twelve major basins. The safe yield of each groundwater basin is illustrated in the Figure 2. The groundwater budget for groundwater in Jordan are given in Table 3 below. It is clear that every year at present day situation there is around 104 MCM is pumped over

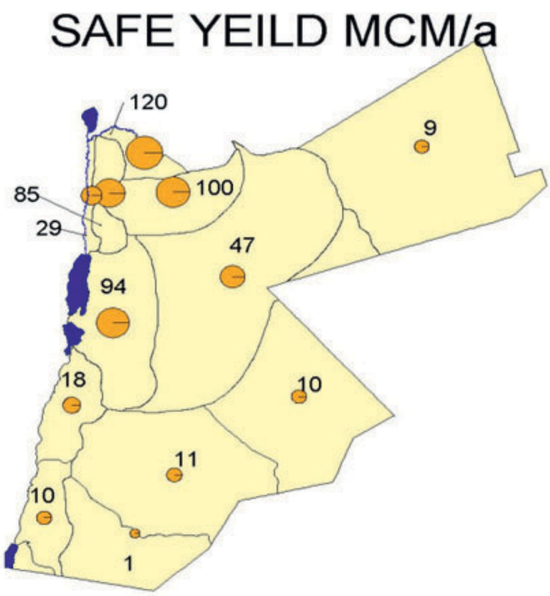

Figure 2. Safe yield of groundwater basins in MCM/year.

the safe yield of the aquifers. Over-extraction of groundwater resources has degraded water quality and quantity.

The safe yield of renewable groundwater resources in Jordan is estimated at 275 million m^3/year. Most of it is currently exploited at maximum capacity, and in some cases, beyond safe yield. There are two main groundwater basins for fossil water where discharge into these aquifers is very low

The main non-renewable aquifer presently exploited are the Disi aquifer and Jafr basins in southern Jordan and it was estimated that pumping water at a rate of 125 MCM/year from Disi basin will be sufficient for 50 years. For Jafr groundwater basin the amount is sufficient for forty years when it is pumped at a rate of 18 MCM/year.

TABLE 3. Annual water budget in Jordan.

Budget component	Annual quantity
Groundwater recharge from precipitation	395
Tran boundary groundwater from Syria	68
Network leakage, cesspool and irrigation return flow	70
Total Inflow	533
Groundwater abstraction	440
Base flow in various water courses	197
Total Outflow	637
Change in storage (Inflow–Outflow)	−104

5. Wastewater

Due to water scarcity in Jordan wastewater is considered as an important source for its water budget.

In Jordan there are 19 wastewater treatment plants generate more that 84 million cubic meters of treated wastewater per year. The biggest is Al Samra Wastewater Stabilization Pond (WSP) System was commissioned in May 1985 and by 1986 was receiving approximately 57000 m^3/d of domestic wastewater and septic tanks from the Metropolitan Area of Greater Amman, Jordan

The projected flow of wastewater in MCM for the next ten year are given in Table 4. It is clear that the amount of treated wastewater which is currently used in agriculture will increase dramatically and will play an important role in meeting future demands for water in Jordan.

In addition to treated wastewater, industry consume large amount of fresh water especially in phosphate production in addition to many mining industries. It was estimated that phosphate production consumes more than 4 MCM annually.

Research was done by Rimawi et al. (2008) showed that this water is suitable for grain production.

Septic tanks in all governorates are disposed in a remote site. Jiries et al. (2009) found that this source of water can be used for fodder production which was safe in term of organic and inorganic pollutants.

TABLE 4. Projected flow of wastewater (MCM).

	2010	2015	2020
Inflow to treatment plants	181	215	247
Treatment effluent	170	202	231
Effluent inflow into reservoir	−86	−100	−114
Total wastewater contribution	84	102	117

6. Water Supply Demand

As mentioned earlier, Jordan suffer from water shortage due to its location in a semiarid region where around 92% of rain fall on the country evaporates, therefore water management is a big challenge for decision makers in the country.

Summary of the supply demand in Jordan as shown in Table 5 shows a deficit of around 187 MCM in 2010 and expected to increase to 360 MCM in 2020 due to population growth and improvement of the standard of life.

TABLE 5. Water supply demand in Jordan until 2020 in MCM/year.

Year		2010	2015	2020
Population (million)		6.0	8.1	9.3
Water demand	Municipal	434	518	611
	Industry	99	122	146
	Irrigation	904	897	890
	Total	1,437	1,537	1,647
Water supply	Municipal	387	470	524
	Industry	99	119	136
	Irrigation	764	693	627
	Total	1,250	1,283	1,287
Total water deficit		187	255	360

The distribution of water use according to sector is shown in Figure 3. The highest consumption is used preliminary for agriculture which consume around 63% of all water consumed and the rest being for used primarily for domestic, industrial and other use. The volume of water demand for agriculture is 904 MCM from which treated wastewater contribute only 10% and the rest is from fresh water resources .

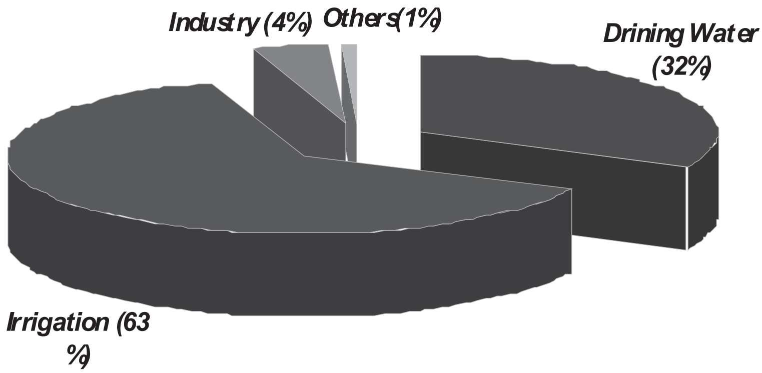

Figure 3. Water use percentage in Jordan.

The high demand on water is attributed to rural to urban migration, high natural population growth and influxes of refugees in response to political situation in the Middle East .

7. Conclusions

Jordan suffer from sever water shortage as the demand is much higher than supply. Strategies to meet unsatisfied water demand must include utilization of non-conventional water resources, privatization, and efficiency enhancement in distribution systems and demand management.

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TRANSBOUNDARY MIGRATION OF THE RIVER WATER POLLUTANTS BETWEEN UKRAINE AND ROMANIA: A CASE STUDY OF BUKOVYNA REGION

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Abstract. The paper deals with analysis of main sources, pollution agents and ways of migration of the river water contamination in the transboundary area between regions of Chernivtsi (Ukraine) and Suceava (Romania) within historical land of Bukovyna. Dynamics of the pollution agents content is analyzed in the light of monitoring of the river water quality in the cross-boundary points. The paper outlines main problems in the field and discusses possible ways of their mitigation.

Keywords: monitoring of the river water; transboundary migration of pollutants; small and medium rivers; mitigation of the water contamination

1. Introduction

Bukovyna is a historical land known since middle of 15th century. Today it is divided between Ukraine (part of Chernivtsi oblast) and Romania (part of Suceava judet) (see Figure 1). This region has several medium size rivers and many hundreds of small rivers and creeks. Many of them are shared between Ukraine and Romania. All shared objects belong to the river basins of Prut and Siret, which are tributaries of Danube.

Atmospheric precipitations in Bukovyna are quite abundant and usage of river waters for irrigation is rather unusual. On other hand, many areas are over-watered or swampy and require more or less intense drainage works. Excessive drainage waters are being discharged to local rivers and creeks.

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However, water intakes for numerous water supply systems and discharge of industrial and municipal wastewaters are the main factors of anthropogenic load on all water objects in the region of Bukovyna.

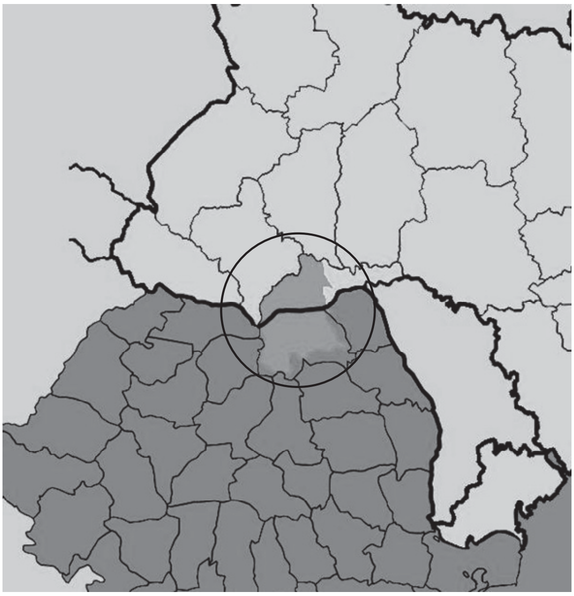

Figure 1. Historical land of Bukovyna (encircled) within modern Ukraine and Romania.

River flow is oriented from Ukraine towards Romania for all shared water objects due to the character of local relief and this imposes quite strict requirements towards quality of the river water in this transboundary region.

This work deals with extended analysis of anthropogenic impact on river water of Prut and Siret. We provide analysis of main pollution sources and dynamics of the concentration changes in course of the river flow towards Romania.

2. Analysis of Anthropogenic Load on River Prut

2.1. WATER INTAKES AND WASTEWATER DISCHARGES

River Prut flows within regions of Ivano-Frankivsk and Chernivtsi in Ukraine, then along the state border between Ukraine and Romania, then along border between Moldova and Romania and joins with Danube near the village of Giurgiulesti near junction of the state borders of Ukraine, Moldova and Romania (see Figure 2). About 40% of Chernivtsi region belongs to the Prut catchment area. River flow is rather fast, mountain-like in the upper Prut area and becomes rather lowland-like in the middle and downriver Prut.

River water in the upper Prut can be classified as conditionally pure while its quality drops to the technical or even worse in the middle and downriver parts. Wastewater discharges from the Chernivtsi wastewater treatment plant provides the most powerful anthropogenic pressure on the river ecosystem.

Figure 2. Map of Prut region.

Nevertheless of this fact, Prut is being extensively used as a source of water supply for many cities and smaller towns of the region.

City of Chernivtsi uses river water from Prut as one of source for the water supply (about 20% of the drinking water are being supplied from Prut; Annual reports of Dnestr-Prut river basin control department for 1986–2007 (2007)). The highest level of the Prut water intake has been reported (Solovey and Nikolaev 2006) in the beginning and middle of 1990th. Amount of the water taken was gradually lowering from 43 million m^3/year (1990) to 26 million m^3/year (1997).

Then this amount has been more or less stable during 1997–2002. Annual water intake was about 28.5 million m^3/year during this period.

Next lowering of the water intake has been registered during the third period (2003–2008) when this amount dropped down to 15 million m^3/year (2008).

This character of the water supply dynamics is caused by several reasons:

Decrease of the industrial production intensity, especially in the beginning-middle of 1990th;

Rise in the price of water, which is especially intense during few recent years. This pushes subscribers to be more thrifty and to cut down the volume of the water used (especially water losses at the households).

More and more subscribers start to use water counters, which also pushes them to more thrifty way of water usage. As reported (Gerasymchyk et al. 2000), an average water usage drops down for ~60% after the subscribers start to use water counters.

New individual subscribers in the private houses mostly use own underground water supply instead of the centralized sources.

All these factors cause decrease of the centralized water supply intake and lowering of this component of total anthropogenic load.

However, the situation with wastewater discharges is quite different.

Amount of the wastewaters discharged and, especially, their quality sometimes were critical or even unacceptable.

Chernivtsi wastewater treatment plant (WWTP) has discharged 40 million m^3 of wastewater in 1990 and about 2% of them were untreated.

An average annual amount of the wastewater discharge in 1991–1997 was 31.5 million m^3 and 93% were untreated.

In 1998–2002 an average discharge was 24.5 million m^3 and 54% were untreated.

In 2003–2008 an average discharge was 18 million m^3 and 18% were untreated.

Amount of wastewater can be higher than water supply from Prut because this source of water ensures only part of the city needs while another part of the needs is covered from other sources of water (river Dnestr, underground water intakes).

Very high part of untreated wastewater discharge in 1991–1997 was caused by hard economical conditions in Ukraine at that time. Local WWTP sometimes just didn't have enough finance to purchase reagents or pay for electricity to ensure proper cleaning of the wastewater.

Decrease in the wastewater discharge has been reported during last years nevertheless water supply is raising. This situation is caused by quite significant lagging in the sewage network development in the city. Some areas of Chernivtsi have water supply connection but do not have sewage because of the local relief character. No new small regional wastewater pumping stations have been constructed recently and citizens of many lower areas have to use cesspools together with centralized water supply.

Untreated wastewaters are mainly discharged during peak or overload periods (i.e. intense rainfalls) through the emergency outlets to small local rivers, which flow into Prut.

All collected wastewaters are being discharged from local WWTP into Prut and then travel downriver towards Romania.

Municipal sewage network was collecting significant amount of industrial wastewaters from various industrial objects located in Chernivsi. Industrial wastewaters consisted of heavy metals, acids, various organic substances including surfactants discharged from numerous galvanic stages, which were widely distributed at local plants. Food processing factories were discharging mostly organic pollutants and suspended particles.

Almost all galvanic facilities has been closed while food processing industry is still active. This process resulted in changes in the wastewater structure. Part of the industrial wastewater has decreased from 45–55% down to 25–30%. There is no more any sources of the chlorinated organics, heavy metals and other 'galvanic' pollutants. In general, municipal wastewaters become similar to the general household, not industrial discharge now.

River water quality is being controlled at some check points upriver, just near Chernivtsy, near main WWTP outlet (in ~750 m) and near the border with Romania (in ~40 km downriver).

As shown in (Annual reports of Dnestr-Prut river basin control department for 1986–2007 (2007); Winkler and Choban 2009), discharge of wastewater into Prut causes very serious decrease of the water quality. Some parameters remain above the maximum allowable level even in 30 km downriver.

However, the situation has been constantly improving during last years and most recent data proved better quality of the wastewater treatment.

Daily wastewater bio-treatment capacity has been increased up to 152,000 m^3 (it was 70,000 m^3 in 2004–2007). Effectiveness and technological regime of the bio-treatment has also been normalized. This resulted in decrease of the average BOD_5 of the treated wastewater from previously reported (Winkler and Choban 2009) 22.6 mg/l (2006–2008) down to 20.2 mg/l (2009).

However, some vital equipment is still missing or out of service at Chernivtsi WWTP. There is no sand bunkers at the sandcatchers, activated sludge dehydration equipment and emergency ponds are still in construction. This problem prevents further increase of the wastewater quality even though the plant has reached optimal treatment capacity.

Organic substances, suspended particles and the salt-NH_4^+ remain main pollution agents, which still travel with Prut water towards Romania. Therefore, construction of the activated sludge dehydration equipment is still considered as the most important step towards further improvement of the wastewater treatment in Chernivtsi.

This would eliminate risk of periodical discharges of insufficiently treated wastewater during hard rains. On other hand, all emergency sewage outlets should be directed to the wastewater network to prevent any effluent of untreated waters.

2.2. ANOTHER THREATENING ACTIVITIES

Chernivtsi region is rather densely populated. Many cities and settlements are located at the riverbanks. River gravel is very popular construction material and local inhabitants actively quarry this material and river sand from numerous gravel pits. Most of them are located very close to the river beds, which is illegal and dangerous for normal functioning of the river ecosystems. Even community pasturing areas are often turned into uncontrolled gravel pits because the latter activity seems more profitable.

Near-river gravel pits appeared in 1960s, then they were found dangerous for local ecosystems and banned. New legislation required to quarry gravel only aside the river bed. However, old gravel pits continued to work. Only deep economical crisis of the late 1980th turned many gravel pits out of regular usage. Riverbed pits were gradually filling with new sedimentary material and restored.

Economical raise of the beginning of 2000th breathed a new life into this activity, which was often concealed behind so-called riverbed cleaning works. However, advisability of such works is very doubtful. Any "cleaning work" results in the riverbed cut-off, increase of the river current speed, which causes fast changes in the river level and higher threat of flooding. On other hand, faster river current promotes erosion of the bridge foundations and other hydro engineering facilities. Two bridges in the region have been found in the emergency conditions because of intense erosion of the pies foundation.

Serious flooding happened in the summer of 2008 in the basin of many Western Ukrainian rivers. Uncontrolled riverbed cut-off and gravel quarry were found among main causes of that disaster.

We suppose that any gravel quarry activity in the riverside areas of Prut, Siret and other rivers of Bukovyna should be unconditionally stopped in the immediate future. Only this measure can facilitate normalization of the river current and prevent its fast changes, which currently endangers many installations and inhabited riverside areas.

3. Analysis of Anthropogenic Load on River Siret

River Siret originates in Chernivtsi region, flows within this region (109 km) then crosses border and flows within Romania (596 km) into Danube (Figure 3). Comparatively high content of the suspended particles in the water of Siret is caused mainly by the clay-like composition of the riverbed soils.

Water quality is controlled periodically at two border posts near Ukraine-Romania border crossing point. Wide variety of the quality parameters is registered at the posts:

Salt composition of water (total ion content, hydrocarbonates, chlorides, sulphates, ions of magnesium, sodium and calcium);

Important trophic parameters (content of suspended particles, dissolved oxygen, pH, total content of dissolved organic substances (through values of BOD_5 and COD), salt-NH_4^+, nitrites, nitrates and phosphates);

Specific pollution agents (oil products, surfactants, heavy metals (Fe, Zn, Cr, Pb and Ni)).

Figure 3. Map of Siret region.

There are no any heavy industrial facilities or big cities in the Siret basin. However, smaller settlements often discharge to the river poorly treated wastewater, which endangers its ecological state. For example, about 40% of municipal wastewaters of Storozhinets (population 14,000) are discharged into Siret without any treatment. Numerous sawmill factories in the region do not have any specialized wastewater treatment equipment as well. River Siret is rather shallow and even insignificant but constant discharges may worsen its water quality.

Results of the long-term monitoring of Siret water quality are represented in Table 1.

As seen from the Table 1, 14 facts of overriding MPL have been registered during the entire period of the Siret water quality monitoring. All these facts were registered during flooding time when the river overflew and washed down numerous cesspools, industrial and cattle-ranch wastewater storage ponds. Regular functioning of the near-river objects and settlements does not cause excessive pollution. No emergency discharge or significant overrides were registered, which proves satisfactory general condition of the river.

Water quality is constantly improving during recent years and only total content of organic substances sometimes overrides MPL. For example, only this parameter (calculated through the permanganate oxidation index) was found overriding MPL in the spring-summer season of 2008 (see Table 2). An year average value remained under MPL.

TABLE 1. Summary of Siret water quality parameters for a long-term (1989–2009) monitoring period.

Water quality parameter	Unit	Maximum permissible level (MPL) for the fish-producing water object (Khoruzhaya 1998)	Number of measurements/ Number of MPL overrides registered	Comments
Dissolved oxygen	mg/dm^3	>6.0	72/–	
pH	units	6.5–8.5	72/–	
BOD$_5$	**mg O/dm^3**	**2.25**	**72/6**	**Flooding**
Solid residue	mg/dm^3	1,000	72/–	
Chlorides	mg/dm^3	300	72/–	
Sulfates	mg/dm^3	100	72/–	
Mg^{2+}	mg/dm^3	40	72/–	
Ca^{2+}	mg/dm^3	180	72/–	
Na^{+}	mg/dm^3	120	72/–	
NH_4^{+}	**mg/dm^3**	**0.5**	**72/2**	**Flooding**
NO_3^{-}	mg/dm^3	40	72/–	
NO_2^{-}	**mg/dm^3**	**0.08**	**72/3**	**Flooding**
PO_4^{3-}	**mg/dm^3**	**0.17**	**72/3**	**Flooding**
Zn^{2+}	mg/dm^3	0.01	72/–	
Mn^{2+}	mg/dm^3	0.01	72/–	
Cr^{3+}	mg/dm^3	0.001	72/–	
Pb^{2+}	mg/dm^3	0.1	72/–	
Ni^{2+}	mg/dm^3	0.01	72/–	
Fe^{2+}, Fe^{3+}	mg/dm^3	0.1	72/–	
Oil products	mg/dm^3	0.05	72/–	
Surfactants	mg/dm^3	0.5	72/–	

Therefore, water of Siret can be classified as “pure”. However, some steps should be done in order to improve water quality and protect the river from additional pollution during flooding times.

Similarly, to Prut, riverbed of Siret is also used for the gravel quarrying, which provokes additional pollution and mudding of the river and increases speed of its current. This kind of activity should be stopped. Nearby riverside areas should not be used for any kind of crop production since this activity results in contamination of water with mineral and organic fertilizers. Existing agricultural areas should be bordered along the banks in order to protect the river from direct stormwater effluents, which bring additional mineral and organic contamination. Any hydrotechnic construction and/or reconstruction near such small river should be thoroughly examined for the purpose of possible ecological threats. Wide informative actions should be undertaken to prevent local inhabitants from periodical, often unconscious pollution of the river with various waste materials. Stormwater should be at least treated in settlers before discharge in order to decrease content of the suspended particles, which is very critical for Siret. Reforestation of the riverbank area will also be very helpful to prevent faster discharge of the naturally flowing muddy stormwaters in Siret.

TABLE 2. Summary of the organic compounds average content in Siret (2008).

Season	BOD_5, mg O/dm^3 (MPL = 2.25)	Permanganate oxidation index, mg O/dm^3 (MPL = 5)
Spring	1.89	5.63
Summer	1.35	6.87
Fall	1.38	4.95
Winter	1.68	2.15
Year average	1.57	4.9

All these actions would ensure increasing of the Siret water quality.

4. Conclusion

General condition of both rivers Prut and Siret near border-crossing points can be considered as satisfactory. There is no any regular override of the water quality parameters or any critical transboundary migration of the water pollution agents.

However, critical weather conditions sometimes result in overnormal pollution of water, which is mainly caused by washing down of waste collection areas and anthropogenic wastewater stored at ponds and cesspools.

Further upgrading of Chernivtsi WWTP capacity and discontinuation of the near-river gravel quarrying can ensure improvement of the water quality in Prut and decrease transboundary migration of pollutants.

Similar results can be achieved for Siret mainly by discontinuation of the riverside gravel quarrying and normalization of the agricultural activity along the river banks.

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IMPACT OF WASTE WATER TREATMENT FACILITIES ON GROUND WATER (AN EXAMPLE OF SVETLOGORSK CITY, BELARUS)

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Abstract. In the paper impact of waste water treatment facilities (WWTF) on ground water is discussed. The presented results are based on more than 20-year monitoring of ground water in impact zone of Svetlogorsk WWTF. The main factors of ground water pollution are shown. High concentration of sulphates, sodium and mineral forms of nitrogen and, as a result, high solute content in ground water is revealed. The formation of hydrogeochemical anomalies in impact zone is determined.

Keywords: urban ground water pollution, waste water, treatment facilities, main pollutants, hydrogeochemical anomalies

1. Introduction

Waste water is one of the main factors of environmental pollution, transformation of aquatic ecosystem and deterioration of drinking water quality. Problems of waste water collection and treatment, as well as sewage system management are very important on local and regional levels in different countries (Shah 2004; Landscape's Water… 2005; Stanko 2008; Mahrikova 2009; Progress and Prospects on Water… 2008).

The impact of waste water treatment facilities (WWTF) is connected with insufficient technology of water treatment, damages of dams, leakages during transportation, emergency situations, waste water infiltration, etc.

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Generally there are two main aspects of WWTF impact on environment. The first one concerns surface water pollution as a result of non-treated or insufficiently treated waste water discharges into rivers and spread of pollutants with water flows. Since treatment facilities are located near or on the bank of the main river, treated waste water is discharged into the river downstream (Landscape's Water… 2005; State water … 2009; State of Environment … 2009; Environmental protection in Belarus. Statistical Book (2007)).

The second aspect is connected with ground water pollution within impact zones of treatment facilities. In Belarus WWTF include several artificial reservoirs with dams (sewage tanks, disposal fields, storage ponds, etc.) which are not equipped with special nature protection facilities in order to prevent waste water leakage and pollutants infiltration. High concentration of ammonium nitrogen, nitrates, zinc, lead and others pollutants was revealed in impact zones of disposal fields, which were included into monitoring system (National system … 2009). In many cases the content of pollutants in ground water exceeds maximum permissible concentration (MPC) of sanitary and hygiene standards even in dozen of times.

Despite the fact that certain efforts have been undertaken, ground water pollution in impact zones of WWTF in Svetlogorsk city remains an acute problem (Khomich et al. 2002; Khomich 2005; Khomich, V. et al. (2004)).

2. Objects and Methods

Svetlogorsk is a young industrial city founded in 1961 with a population of roughly 75 thousand people. The largest volumes of sewage are formed at three enterprises: chemical plant (Khimvolokno Amalgamation), pulp-and-paper plant and heat power station. The study of chemical composition of ground water in Svetlogorsk has a long history: the first investigation was carried out in 1970th and permanent monitoring system was created in 1994 (Khomich 2005).

In Svetlogorsk both domestic and industrial sewage are treated at one WWTF which provides its mechanical and biological treatment. The area of this WWTF is 133 ha, waste water volume exceeds 20,000 m^3 per day. It has been operating for over 40 years. WWTF includes several sewage tanks, disposal fields, and storage ponds. Near the WWTF some sludge storages were built. Besides solid waste dump was constructed near the WWTF; the volume of solid waste continues to increase.

Industrial waste water is polluted with sulphates, sodium, mineral forms of nitrogen, heavy metals and other pollutants. The solute content in sewage reaches 3,000–5,000 mg/L (Khomich et al. 2002; Khomich 2005).

As a rule the aquifers are composed of sand with different granulation. Clay sand and loamy sand play a role of local confining layers.

There are more than 30 observation wells for non-pressure and pressure ground water monitoring. Sampling of ground water is carried out annually in spring and autumn by manual pumping.

3. Ground Water Pollution in Impact Zone of WWTF

3.1. GROUND WATER POLLUTION LEVEL

The comparison of obtained results with background levels and MPC is given in the Table 1. The results of investigation show that concentrations of main ions and heavy metals in ground water are higher in comparison to background values. The sum of ions in pressure ground water near the WWTF makes up to 2 g/L; water in many cases is alkaline; sulphates and sodium dominate among ions (up to 75–90%-mass and 50–76%-mass, correspondingly).

Pollutants enter the ground water due to a number of reasons: imperfection of technologies used, spillage of pollutants during waste water transportation, filtration of polluted water from sludge storages and filtration fields, as well as overflow of waste water during heavy rains, etc.

TABLE 1. Ground water chemical composition and maximum permissible concentrations, mg/L.

Indicator	Impact zones of WWTF	Background values (National system… 2009)	Maximum permissible concentration (MPC)
pH	6.2–9.3	7.9	6–9
Solute content	25.2–1,920	217.6	1,000
Cl^-	3.4–202.5	23.7	350
SO_4^{2-}	3.4–935	11.8	500
HCO_3^-	36.6–781	123.9	–
NO_3^-	0.1–51.9	3.87	45
NO_2^-	0.004–12.2	0.28	3
NH_4^+	0.02–21.4	0.3	–
Na^+	3.1–560	8.4	200
K^+	0.7–6.9	2.67	–
Ca_2^+	11.2–221.2	34.2	–
Mg_2^+	4.9–91.4	8.4	–
Cu	0.001–0.004	0.01	1.0
Zn	0.001–0.12	0.02	5.0
Cd	0.001–0.01	0.0003	0.001
Pb	0.002–0.04	0.0019	0.03

The highest concentrations of solute content, sulphates, sodium, and mineral forms of nitrogen were observed in different wells. Thus, in 2009 the exceeding of MPC was fixed in ground water of 7 out of 25 observation wells.

For example, MPC in water from the observation well number 35a (impact zone of disposal fields) was exceeded in regard to 4 indicators: concentration of sulphates exceeded MPC in 1.4–2.4 times, ammonium nitrogen – 2.6–8.2, nitrates – 1.2–2.9, sodium – 1.4, solute content – 1.2–2.0 times. Water from observation well number 3a (impact zone of sludge storage) was also one of the most polluted. Concentration of sulphates exceeded MPC in 1.7–2.2 times, solute content – in 1.5–1.8 times.

High concentration of oil products (>MPC in 1.5–2.1 times) was revealed in water from observation well number 33a (impact zone of solid waste dump).

The content of pollutants in ground water varies from season to season. For some compounds their variability reaches up to 2–3 times (Table 2).

TABLE 2. Content of main ions in ground pressure water in impact zones of WWTF in 2009, mg/L.

Site of sampling	Season	Water level, m	pH	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	NO_2^-	Ca_2^+	Mg_2^+	Na^+	K^+	NH_4^+	Sum of ions
25 m from disposal fields	Spring	3.20	8.9	61.0	8.4	685	52	1.1	35.3	15.6	280	6.9	21.4	1,179
	Autumn	3.15	6.3	24.4	10.1	1,200	131	0.04	96.2	18.5	500	6.0	6.7	1,993
250 m from disposal fields	Spring	3.80	7.4	48.8	8.4	40.4	5.6	0.08	22.4	5.8	3.9	2.0	1.72	139.2
	Autumn	5.10	7.4	61.0	10.1	26.5	55.0	0.59	33.7	5.8	5.3	0.8	0.20	199.1
15 m from sludge storage	Spring	2.46	6.5	183.1	27.0	852	1.5	0.08	221.2	91.4	100	4.7	1.36	1,482
	Autumn	2.86	7.1	207.5	22.0	1,100	4.7	0.08	160.3	121.6	170	4.2	0.70	1,791
300 m from solid waste dump	Spring	2.36	6.5	158.7	20.2	227.0	1.8	0.14	83.4	22.4	42.0	1.2	1.72	558.5
	Autumn	1.76	7.1	103.7	20.3	380.0	2.6	0.08	72.1	17.5	120.0	1.3	1.12	718.8

3.2. HYDROGEOCHEMICAL ANOMALIES IN WWTF IMPACT ZONE

The results of investigation show that in the impact zone of Svetlogorsk WWTF a hydrogeochemical anomaly was formed. Its boundary was identified by solute content of 500 mg/L. The hydrogeochemical anomaly has a heterogeneous chemical composition and pollution level. Within the range of anomaly two small areas with pollution level more than 1,000 mg/L were revealed (Figure 1).

The highest pollutants concentration in ground water was typical for "south" and "north" parts of anomaly. The level of solute content here reached 1,482 mg/L and 1,148 mg/L, respectively. Water pollution in the "north" part was caused by sludge storages and in the "south" part – by solid waste dump.

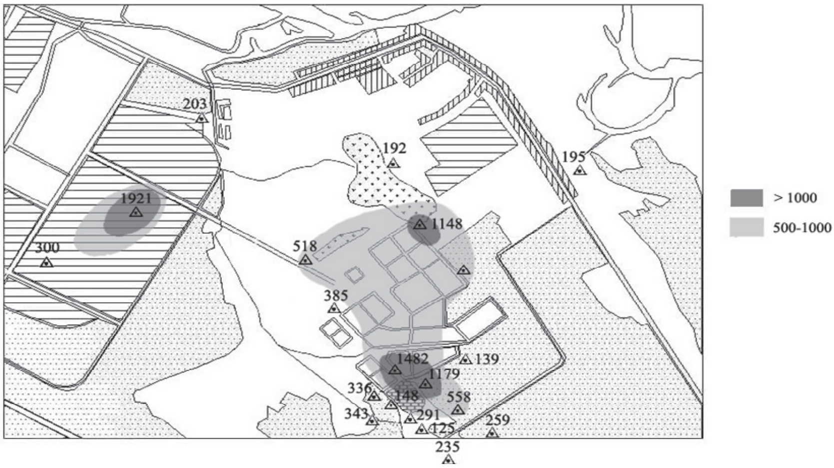


Figure 1. The area of hydrogeochemical anomalies in the WWTF impact zone in 2009 (solute content, mg/L).

As a rule, ground water in the majority of polluted areas has sulphate sodium water type which is untypical for boreal zone.

Vast area of polluted ground waters is also revealed on the drained wetland located between the industrial site of Khimvolokno Amalgamation and the WWTF. Ground water is polluted both by mineral and organic compounds. Ground water is also sulfate sodium in their composition, and solute content is over 1 g/L. The list of pollutants is rather wide: sulfates, ammonium nitrogen, sodium, iron, organic compounds. Their concentration exceeds MPC in 2–10 times.

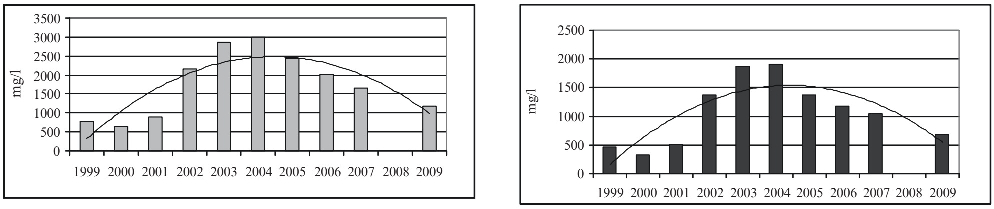
3.3. DYNAMICS OF GROUND WATER POLLUTION

According to analysis of pollution dynamics in WWTF impact zone, two different processes in ground water are revealed: "pollution" and "natural purification".

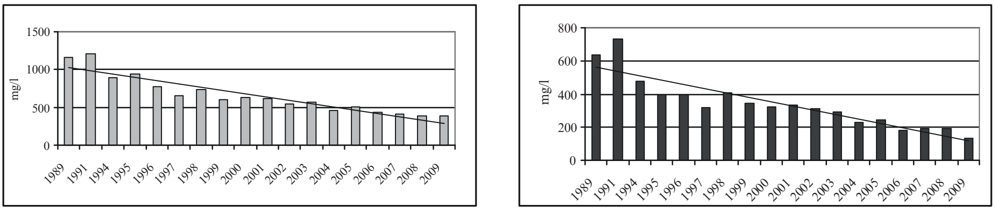
The process of "natural purification" is identified for water from the observation well near the former zinc-content sludge storage (Figure 2, well 11a). Due to reduction of chemical load after sludge extraction the solute content decreased here from 1,200 to 385 mg/L and sulphates concentration – from 750 to 135 mg/L.

The process of ground water "pollution" is revealed in impact zone of solid waste dump. Here the pollution of ground water continues due to waste volume growth, lack of protection facilities and week nature security of ground water. Starting from 2000, significant increase of pollutants concentration in ground

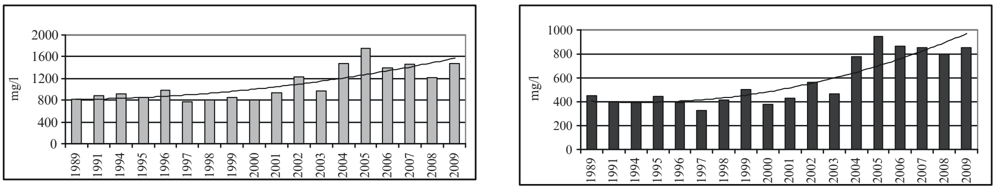
A B



Observation well between sludge storage and disposal fields (well 35a)



Observation well near the former zinc-content sludge storage (well 11a)



Observation well between sludge storage, disposal fields and solid waste dump (well 3a)

Figure 2. Dynamics of solute content (A) and sulphates concentration (B) in ground water in impact zone of Svetlogorsk WWTF.

water of observation well number 3a is revealed (see Figure 2): the solute content – from 800 to 1,500 mg/L, sulphates content – from 375 to 850 mg/L. Relative content of sodium in the chemical composition of ground water increased from 6% to 42%.

At the same time it should be stressed that significant improvement has been revealed within the area between the industrial site of Khimvolokno Amalgamation and the WWTF. Due to sludge extraction and treatment, as well as drainage amelioration, total solute content in ground water for a 20-year period decreased 4–5 times, natrium and sulfates concentration has decreased, too.

4. Conclusion

High level of ground water pollution in impact zone of Svetlogorsk WWTF is caused by several factors. They are: imperfection of waste water treatment technologies, spillage of pollutants during their transportation, filtration of polluted water from sludge storages and filtration fields, as well as overflow of waste water during heavy rains, etc. Hydrogeochemical anomaly is formed within the area of WWTF, sludge storages and waste dump. Many year investigation proves that the area of polluted ground water is quite stable, in spite of variability of pollutants and different trends of pollutants content in some observation wells.

Ground water pollution represents danger for further distribution of pollutants, as well as for contamination of drinking water sources. Therefore preventive measures for chemicals infiltration into ground water are needed. In order to improve the quality of ground water, serious abatement technology for waste water treatment is needed. And since solid waste dump still remains a very intensive source of ground water pollution, the improvement of waste storage and nature protection measures should be undertaken.

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SUSTAINABLE USE OF WASTEWATER AND SLUDGE IN JORDAN; RESIDUES OF PERSISTENT ORGANIC POLLUTANTS, A REVIEW

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Abstract. Water scarcity is the most important natural constraint to Jordan's economic growth and development. Jordan has very limited water resources which are classified among the lowest per capita worldwide. Two thirds of our water resources are currently used for agriculture; therefore, wastewater reuse is one of the priorities listed on the Jordanian water strategy for the year 2020 as an alternative water resource to meet agricultural water demand. However, with the realization of sustainable development, the wastewater reuse, which contains valuable nutrients, is becoming a key issue and a suitable water resource for irrigation purposes. Wastewater and sludge are considered the most realistic environmental sink for toxic organic and inorganic chemical pollutants produced from domestic and industrial sources. In addition to trace metals, it is worth mentioning that the impact of chemical pollution caused by the conventional "priority" organic pollutants, which displays persistence in the environment, especially those acutely toxic, mutagenic and/or carcinogenic such as pesticides, polynuclear aromatic hydrocarbons (PAHs), industrial intermediates, polychlorinated biphenyls (PCBs), phenols, chlorinated phenols, dioxins and furans, etc. Most of these types of persistent organic pollutants have been found in the Jordanian environment either in reclaimed water or in sewage sludge, as they are the main environmental sinks for most of these pollutants. It is believed that chemical pollutants could reach the food chain easily, and affects soil and crop properties, if wastewater is used for irrigation and sludge as fertilizer or soil conditioner. The present paper is a review of the future prospects for the sustainable use of wastewater and sludge in Jordan, mainly considering their content from the persistent organic pollutants (POPs).

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Keywords: sustainability, wastewater, sewage sludge, organic pollutants, Jordan

1. Introduction

Jordan is located in arid to semi arid environment that characterized by low amounts of wet precipitation, hot summer and cold winter. Jordan is facing a future of very limited water resources, among the lowest per capita worldwide. Water scarcity is the single most important natural constraint to the country's economic growth and development. All these factors have negative impacts on the agricultural activities in the area, despite the fact that Jordan soils are characterized by high nutrients contents. Therefore, more attention should be paid for wastewater reuse as alternative water resource for irrigation purposes. In addition, Sewage sludge is still considered a waste product in most developing countries such as in Jordan and its disposal or reuse are listed as one of the major priorities for the wastewater management plans for these countries and particularly the country of Jordan. However, with the realization of sustainable development the recycling and reuse of valuable nutrients contained in the wastewater and sludge is becoming a key issue (Lundin 1999). Sewage sludge from sludge treatment plants can be used for soil improvement as organic fertilizer or soil conditioner. Application of sludge in agricultural lands will reduce the quantities of chemical fertilizer used, improve soil fertility, and recycle waste products back to the cycle of soil and plants.

Jordan's water consumption in 2007 totaled 941 million cubic meter (MCM), of which 64% is consumed by agriculture, 31% domestic, 4% industrial, and 1% by other activities MWI 2007. Wastewater is currently treated in 23 wastewater treatment plants throughout the country, with total influent measuring 111.8 MCM yr^{-1} and effluent of 86.53 MCM yr^{-1}. Most of the effluent water is currently used in Jordan for agriculture purposes and groundwater recharge Al Nasir and Batarseh (2008). Liquid sewage sludge produced from 13 waste water treatment plants (WWTPs) in Jordan totaled 463,550 m^3 yr^{-1}, and the dominant treatment processes are classified as secondary, utilizing aerobic treatment processes. Excluding other existing stabilization ponds such as As-Samra, WWTPs typically receive 68.23 MCM yr^{-1} and discharge 52.23 MCM yr^{-1}. These plants accumulate sediment sludge, and require cleaning every 5–10 years MWI (2004). Sewage sludge byproducts produced from wastewater treatments are disposed of in landfills or stored in nearby treatment plants.

Wastewater and sewage sludge contain chemical toxic organic and inorganic components, such as polynuclear aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCBs), polychlorinated dioxins and furans (PCDD/F), pesticides, and heavy metals (Jiries et al. 2000; Parkpian et al. 2002; Morrison et al. 2004). When take out considering wastewater reuse for agriculture and land application of sewage sludge as organic fertilizer, there are many aspects concerning their quality that should be studied. Chemical characterization of wastewater and sewage sludge includes on one hand the nutrients amounts such as nitrogen, phosphorus, carbon, and other macro constituents that could be useful to be used for agricultural purposes such as nitrogen, phosphorus, potassium, calcium, magnesium, and etc. On the other hand, trace metals that are considered poisonous and have the greatest threat to the environment include zinc, copper, lead, chromium, nickel, and cadmium (Dowdy et al. 1997). The regulation in the USA for biosolids to be applied on agricultural land defines 10 toxic metals limited as maximum allowable concentrations (USEPA 1995). However, on an international scale it is evident that Cd, Zn, Cu, and Ni are of primary concern when ecological problems are studied (Berrow and Webber 1972; Hoffman 1980; Morrison et al. 2004).

In addition to the trace metals, it is worth mentioning the impact of chemical pollution caused by the conventional “priority” organic pollutants which displays persistence in the environment, especially those acutely toxic, mutagenic and/or carcinogenic such as pesticides, polynuclear aromatic hydrocarbons (PAH), industrial intermediates, polychlorinated biphenyls (PCBs), etc. (Hamscher et al. 2002; Batarseh et al. 2003; Thiele-Bruhn 2003). The European Commission has been limited guidelines for the content of some of these organic pollutants in sewage sludge to be used for agriculture such as PAH (6.0 mg kg^{-1}) and PCBs (0.2 mg kg^{-1} for each congener) on dry weight basis (European Commission 2000). The contamination of sewage sludge with various types of organic pollutants has been subject to intensive scientific research. For example, the sum concentrations of PAH in sewage sludge of Zabrze/Poland ranged from 7 to 10 mg kg^{-1} of dry mass (Bodzek et al. 1998), whereas, higher concentration levels of PAH was found for sludge samples collected from Jordan (Batarseh 2011). Further results are discussed within this review article.

The aim of this review article is to highlight some obstacles in terms of persistent organic pollutants as a main limitation factor for reclaimed water and sewage sludge reuse in Jordan.

2. Results and Discussion

Several studies have been carried out in Jordan concerning wastewater and sewage sludge quality and reuse. However, limited number of those studies concerned with persistent organic pollutants (POPs). The following sections discussed the occurrence of some priority organic pollutants and their environmental risk for reclaimed water and sewage sludge reuse on agricultural land. This paper is aimed to give a future prospective toward the obstacles and limitations to wastewater and sludge reuse in Jordan taking in consideration their content from the persistent organic pollutants POPs.

2.1. WASTEWATER

The residues of polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and phenols were investigated for soil, wastewater, groundwater and plants (Al-Nasir and Batarseh 2008). The uptake concentration of these compounds comparatively determined using different plant types which grown in a pilot site established at Mutah University wastewater treatment plant, Jordan. Environmental elevated concentrations of all targeted compounds were detected for wastewater samples much higher than for groundwater. The overall distribution profiles of PAHs and PCBs appeared similar for groundwater and wastewater indicating a common potential pollution sources. The concentrations of PAHs, PCBs and phenols for different soils ranged from 169.34 to 673.20μg kg^{-1}, 0.04 to 73.86 μg kg^{-1} and 73.83 to 8,724.42 μg/kg, respectively. However, lower concentration levels detected for reference soil samples. Furthermore, it was found that different plants have different uptake and translocation behavior. As a consequence, there are some difficulties to evaluate the translocation of PAHs, CBs, PCBs and phenols from soil-roots-plant system. The uptake concentrations of various compound from soil where plants grown are depended on plant variety and plant part, and they showed different uptake levels. Among the different plant parts, roots are found the most contaminated and fruits the least contaminated. Therefore, this study gave evidence on the pollutant transfer through water-soil-plant system and recommended that reclaimed water is preferred to be used for restricted agricultural practices.

Furthermore, the residue of persistent organic pollutants in sediments contaminated with wastewater effluents was investigated at Amman/Zarqa Area in Jordan (Batarseh et al. 2003a; Batarseh et al. 2003b). The results of this study reported relevant environmental concentration of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorobenzenes (CBs), and organochlorine pesticides (OCPs) for Zarqa River sediments which is contaminated with reclaimed water effluents from As-Samra WSP, Jordan. The results have shown that the total concentrations of PAH for summer season were 2–3 times higher than for winter season and they significantly correlated with total organic content (TOC). The sediment profiles were characterized by 2–3 rings PAH near the sources of Zarqa River as well as in the winter sampling period, while, 4–6 rings PAH dominated down stream and for the summer sampling period indicating a recent source of pollution. Moreover, the occurrence of pentachlorobenzene, hexachlorobenzene, 6 PCB congeners and 12 different organochlorine pesticides was investigated in sediments from Zarqa River too. The discharge of organic load from domestic and industrial waste disposals into Zarqa River have led to an environmentally relevant concentrations of organic pollutants in the river sediments. The distribution pattern of most organochlorine compounds in sediments was dependent on the organic carbon content, type of anthropogenic activities, and rainfall quantities. The summer sampling period indicated higher pollution levels than in winter season. This study was the first report for evaluating the environmental quality and measuring the environmental background concentrations of organic pollutants at the investigated area.

Municipal wastewater discharges have been recognized as a major source of PAHs, PCBs and phenols (Ng et al. 1997; Jiries et al. 2000; Abo-El-Seoud et al. 2003; Tor et al. 2003). Chemical waste produced at Mutah University laboratories was found to be adversely effect on wastewater quality in terms of trace metals and major ionic composition (Hussein et al. 2000). Furthermore, appraisal PAHs residues was detected for wastewater, sediments, sludge and plants for wastewater treatment plant in Karak Province (Jiries et al. 2000; Jiries 2001).

2.2. SEWAGE SLUDGE

In Jordan, the concentration levels of 16 PAH in domestic sewage sludge have been investigated in three sites in Karak province, their concentration ranged from 28.7 to 39.3 μg kg^{-1} (Jiries et al. 2000). Assessment of bio-solids quality at several domestic wastewater treatment plants of Wadi Mousa, Wadi Hassan and at Jordan University of Science & Technology for agricultural land application was conducted through Badia Research Development Program by Royal Scientific Society (RRS), International Arid lands Consortium (IALC), and University of Arizona in order to update the current Jordanian standards for sludge to be reused in agriculture (MWI 2005). Based on this study, the Jordanian guideline was updated for treated sewage sludge disposal and reuse for agriculture number JS 1145/2006 (JISM 2006).

Sewage sludge at As-Samra Wastewater Treatment Ponds WTPs, the largest waste stabilization ponds in Jordan, was investigated for the concentrations of macro- and micro-elements, and polynuclear aromatic hydrocarbons (PAH) for dry and wet sludge types (Batarseh 2011). The results showed that the sewage sludge is contaminated with low levels of trace metals. Furthermore, dry sludge characterized with higher concentration levels of trace elements than for wet sludge. Despite the fact that none of the trace metals concentration exceeded the guidelines threshold concentration for sludge to be applied for agricultural land, however, environmental relevant concentrations of PAHs were detected ranging from 62 to 70 μg g^{-1} for dry sludge and from 35 to 47 μg g^{-1} for wet sludge. These results were indicative an environmental risk for sewage sludge in Jordan to be reused as organic fertilizers without any further treatment. Although, high nutrient contents were found for both wet and dry sludge samples, thus the application of sewage sludge in Jordan for agricultural purposes would positively influence the soil properties in terms of nutrients contents such as organic carbon, nitrogen and phosphorus. The result of this study has been given a good understanding of the sewage sludge characteristics in semiarid environment and its risk for application on land.

3. Conclusion

The major parameters that might determine contamination levels with persistent organic pollutants of wastewater, sewage sludge, soil and sediments are the type of anthropogenic activities, point or non-point pollution sources, physical and chemical properties of the environmental matrix and the rainfall quantities in terms of runoff. For example, the direct discharge of the low quality reclaimed wastewater discharges of untreated industrial and domestic wastewater into Zarqa River are affecting the sediments chemical and physical properties. As a consequence, high concentration levels of total organic carbon and POPs were reported. Thus, water quality along the Zarqa River was degraded due to those anthropogenic inputs of inorganic and organic pollutants.

The studied Jordanian ecosystems were found less contaminated with polynuclear aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated benzenes (CBs), and organochlorine pesticides residues than other urbanized and industrialized sites in Europe as well as in North America. However, several studies showed that the contamination with various types of organic compounds were found for wastewater much higher than for groundwater samples in Jordan. Furthermore, the distribution profile of some organic pollutants for groundwater and wastewater indicating common potential sources of pollution. The concentration levels of organic compounds were higher for soil irrigated with wastewater than for the remote reference site indicating sources of contamination due to irrigation with wastewater. It was evident that organic pollutants are transferred through water-soil-plant system. Whereas, different plants showed different uptake concentrations of various organic compounds. Roots found the most contaminated plant part, however, fruits are the least contaminated.

Generally, organic pollutants might be transferred or translocated from the soil irrigated with wastewater and enter different plant parts. The uptake ratios depend on plant type and the physiochemical properties of the organic compounds. Obviously, it can be recommended a national monitoring program that can be designed for organic compounds for soils and crops irrigated frequently with reclaimed water. Finally, reclaimed water prefers to be used for restricted agricultural practices in Jordan.

In term of inorganic pollutants, it was concluded that sewage sludge can be applied after drying for agriculture soil without further treatment. As all trace elements that have the greatest threat to the environment showed lower concentration levels than the permitted threshold concentration by the European Commission Guidelines for sludge to be used as organic fertilizer. It is feasible to apply sewage sludge considering a monitoring program to control the potential environmental risk of heavy metals accumulation in the agriculture soil. However, in term of organic pollutants, it is concluded that sludge contained relevant environmental levels of PAH which could be restricted its application for agriculture soil without further treatment. Despite the fact that high nutrients content found for wet and dry sludges.

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REFLECTIONS OVER THE WATER CYCLE IMPACT ON THE PEACE PROCESS IN THE MIDDLE EAST

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Abstract. Throughout the years, many attempts were made to advance an overall Middle East peace settlement between Israel and its neighbors. Presently, only a fragile peace exists between Israel and the Arab countries Egypt and Jordan. The main obstacle to advancing the progress of peace in the region is the conflict between Israel and the Palestinians. In this dispute, the core issues are: borders, refugees, Jerusalem and water. It is this last issue's relationship to the peace process that will be discussed in this paper. Even though the essential need for a minimum quantity of clean water is understood and recognized by all parties to the conflict, there have not been any successful efforts to separate the issue of water from all of the other core issues. That is, while every discussion of peace treaties includes a discussion of water, there has been no regional move toward unilaterally addressing the need for regional cooperative water management. On the other hand, new, modern technologies for water production, treatment and recycling could serve as a driving force to try once again to revive the effort to produce a regional water solution. Aided by the personal experience of one of the authors (Dr. Shmuel Brenner), who served as the environmental affairs representative for Israel to the 1995 Oslo peace talks, this paper briefly outlines water and water management in the Middle East, discusses the water aspect of the regional conflict and reflects on how the peace processes have related to water. Finally, it suggests options for progress under the challenging present circumstances.

Keywords: water management, peace process, Middle East, Oslo Accord

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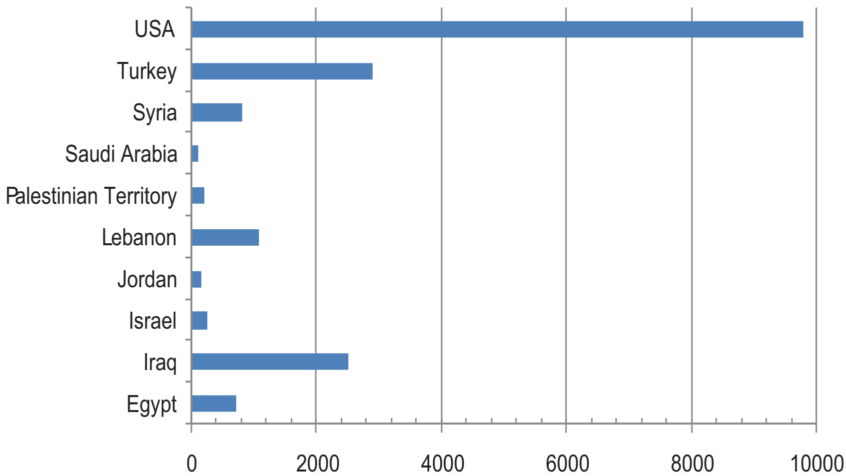
1. Introduction

In almost all regions of the Middle East, a secure and adequate supply of water is not and has never been the norm. The total renewable quantity of water available per person per year in the region is very low (Figure 1). Today, increased use of water for development compounded by exponential population growth has put new pressures on an already limited resource. Frequent and sometimes daily interruptions in supply occur in Amman, Damascus, Cyprus, and, very recently, Yemen (Laessing 2010). The projected impacts of climate change on scarcity will only exacerbate an already serious water issue.



AQUASTAT Online Database. 2010. Food and Agriculture Organization of the United Nations.

Figure 1. Water resources: total renewable per capita (actual) (m^3/inhab/yr).

Because water does not respect political borders, it is impossible for management decisions to be made in isolation or in consideration of one particular use. Many leading figures in the region and elsewhere share the view that conflicts over water and their solution in the area are crucial for sustaining peace and stability. After signing the 1979 peace treaty with Israel, for example, Egyptian President Anwar Sadat said his nation will never go to war again, except to protect its water resources. Similarly, King Hussein of Jordan identified water as the only reason that might lead him to war with the Jewish state, and Former United Nations Secretary General Boutros Boutros-Ghali warned bluntly that the next war in the area will be over water (Darwish 2003). Conflicts over water are not a new phenomenon. Between 2999 BCE and 2010 CE, there have been 203 recorded incidents of conflict over water, 54 of which occurred in the Middle

East (Pacific Institute 2009). Yet, times of crisis can also be times for dialog and enterprise. Ultimately, regardless of historical conflicts over shared basins, it has been shown that countries are more likely to cooperate over water than to fight over it. The fact that this resource is essential to life necessitates interdependence, and therefore can eventually force cooperation, between and among nations (Wolf et al. 2001).

While no wars have ever been fought strictly over water, the resource has certainly been a contributing factor to many wars in the Middle East. In the last 50 years, 30 of the 37 violent water disputes have occurred between Israel and one of its neighbors (Wolf et al. 2001). There was an early, serious attempt at compromise over the Jordan River in 1953 when the American delegate Eric Johnston led negotiations among Israel, Jordan and Syria (Israeli Ministry of Foreign Affairs 2010). Experts of both sides agreed to the division of the waters but at the end the negotiations failed because of the political conflicts. Later, in 1965, Syria and Lebanon unilaterally began constructing channels to divert the sources of the Jordan River which flows into Israel. The Israelis attacked the diversion works, the first in a series of moves that led to a regional war in 1967 (Darwish 2003).

It must also be acknowledged that, while this paper deals with transboundary water conflict, national and regional water issues will only intensify the international discussions. For example, a recent report from the Integrated Regional Information Networks outlines water issues in Lebanon, where scarcity is worsening despite the fact that the country has a relatively high average annual rainfall (Irinnews 2009).

It is beyond the scope of this article to provide comprehensive details and data about water quantities, qualities and needs in the region. All sides continue to disagree on the actual quantities of water available. Regarding the situation in Israel, the Ministry of Environmental Protection reports that the quantity of water available to Israel is 1,175 MCM. Natural water supply in 2008 was only 826 MCM, 63% of the multiannual average. Four successive years of drought have dramatically lowered water levels in all of the main reservoirs, with the total deficit reaching some 940 MCM meters over the past four years (Israeli Ministry of Environmental Protection 2008). Israel is therefore increasing its development and use of treated wastewater, brackish water, water harvesting and desalination while promoting water conservation and remediation of wells. In desalination, capacity is expanding from the current level of about 240 MCM per year to 750 MCM per year. However, these unilateral measures on behalf of Israel do not tackle the wider regional problems. Without Israel's neighbors on board, even without factoring in the adverse effects of climate change, it is obvious that the water situation in the region cannot improve.

2. Reflections on the Peace Process

After decades of hostility, all sides made the first formal move towards peace in 1991 at the Madrid Conference. These and other meetings among Israel, its neighbors, and other international players enabled the ultimate signing of both the Oslo Accords in 1993 and the 1994 Israel–Jordan Peace Treaty.

2.1. OSLO II

Dr. Brenner has contributed much to this subject in his twenty years of experience dealing with environmental and water matters inside Israel. He has been involved in negotiations with officials from both the Palestinian and Jordanian governments as well as other international parties. In 1995, as the representative of the Israeli Ministry for Environmental Protection, Dr. Brenner was appointed to lead the Israeli Subcommittee for Environmental Affairs in the Oslo II peace talks with the Palestinians. These meetings were dedicated to outlining collaborative solutions to various environmental problems as well as the means for conservation of natural resources (including water). At the same time, a parallel to subcommittee dealt solely with water issues related to water rights, quantity and quality. At the end of this extensive and difficult deliberation, the Oslo Interim Peace Accord included a specific article for environmental affairs, article 12 (Jewish Virtual Library 2010), as well as article 40 for water and sewage (Jewish Virtual Library 2010).

The teams dedicated to working on article 12 were headed by Dr. Brenner for the Israelis, and Dr. Mohammad Said Al Hmaidi for the Palestinians. This article not only outlined the environmental areas for which both sides were intended to be responsible for, but it also transferred the authority over these areas in the West Bank and Gaza to the Palestinians. Under the Cooperation and Understandings section, the article also outlined a number of principles and goals dedicated to ensuring both internal and transboundary environmental protection. At the time, many believed that a real peace would eventually emerge from the Oslo process, and so the articles that emerged from the negotiations addressed an ambitious list of issues, including air quality, water, solid and hazardous wastes, noise, radiation and others.

Article 12 also established a special committee tasked with supervising and evaluating the ability of both sides to address the various items included in these articles. The Environmental Experts Committee (EEC), headed by Dr. Brenner and Dr. Hmaidi, met several times between 1996 and 2000, until it faded out in the wake of the Second Intifada. As it had no power to enforce recommendations, the EEC had few tangible achievements and it was quickly realized that the environment needed more than just limited cooperation and soft agreements.

Article 40 manifested the fact that from the beginning, both sides realized that issues related to water struck at the core of the conflict. This was made evident in the first principle of the article: “Israel recognizes the Palestinian water rights in the West Bank.” The principle was, however, included only after an intense, protracted debate. It enabled the parties to continue discussing other water-related issues including water quantities and allocations, water quality and sewage treatment and, most importantly, the establishment of The Joint Water Committee (JWC), a permanent body responsible for addressing and enforcing issues related to water and sewage in the West Bank.. Practically speaking, the main element of article 40 was classified under the heading of Additional Water:

“Both sides have agreed that the future needs of the Palestinians in the West Bank are estimated to be between 70 and 80 MCM/year. In this framework, and in order to meet the immediate needs of the Palestinians in fresh water for domestic use, both sides recognize the necessity to make available to the Palestinians during the interim period a total quantity of 28.6 MCM/year” (Jewish Virtual Library 2010).

Compared to article 12, article 40 was more powerful in part because it gave responsibility to the JWC to approve or deny proposed water projects. Today, both sides are at odds as to whether the JWC has delivered on the “immediate needs” as stated in Article 40 (Jewish Virtual Library 2010). According to a report published by the Israeli Water Authority in 2009: “A scrutiny of the minutes of the committee’s meetings shows that the committee approved nearly all the projects that were submitted for its approval, even beyond the obligatory ones included in the Water Agreement” (Israel Water Authority 2009). On the other hand, a report published by the World Bank that same year states: “Of the 417 [Palestinian] projects overall presented to the JWC 1996–2008, 57% were eventually approved (World Bank 2009).”

The JWC is tasked to respond to water development requests in the West Bank. Because of the location of the West Bank, groundwater withdrawal, wastewater reuse and rainwater harvesting are the only truly viable sources of freshwater, with the majority of water coming from underground aquifers shared with Israel (Figure 2). In the West Bank, out of 417 water and wastewater projects put before the JWC in the period from 1996 to 2008, 202 well drilling projects were submitted, 32% of which were ultimately approved and 19% implemented (World Bank 2009). Regardless of whether the Committee has been effective, it is, despite many years of continued disagreements and hostilities, still an active organization. Out of 26 joint committees established under Oslo II, the JWC is one of only two that survives to this day (World Bank 2009). In 2001, following the start of the Second Intifada, the joint heads of the JWC signed the Joint Declaration for Keeping the Water Infrastructure out of the Cycle of Violence which underscored the ability of the negotiators to reach consensus during times of conflict (Israel – Palestinian Joint Water Committee 2001).

While the JWC may be effective in handling a few, local selected water issues, it is not an effective body to address the present and growing water needs of the overall growing Palestinian needs (Table 1).

Figure 2. The disputed aquifers.

http://www.utexas.edu/features/2005/water/graphics/water3_large.jpg

TABLE 1. Projected water demand in the West Bank and Gaza until the year 2040, according to the Palestinian Hydrology group (Rabi 2009).

Year	Population (million)	Projected water demand: Domestic and industry (MCM/year)	Agriculture (MCM/year)	Total (MCM/year)
2000	3.15	196	191.8	387.8
2010	4.95	416	301.5	717.5
2040	9.98	1,075	607.8	1,682.8

An Israeli interpretation of these demands vis-a-vis requirements from Israel was recently presented at a meeting of the Israeli Water Association Conference. If quantities demanded by the Palestinians were to be met with supply from Israel, that would mean 65% of Israel's total annual fresh water input contributed to the Palestinians (Gvirtzman 2010). It is therefore probable that a feasible solution would be a serious evaluation of regional needs and capabilities rather than comparison of numbers and demands.

2.2. ISRAEL–JORDAN PEACE TREATY

The Palestinians were not the only ones making agreements with Israel at that time. About a year before Oslo, in 1994, the Treaty of Peace between the Hashemite Kingdom of Jordan and The State of Israel was signed. The document included a special annex on water related matters in which it also established a Joint Water Committee, stating:

"Israel and Jordan shall cooperate in finding sources for the supply to Jordan of an additional quantity of (50) MCM/year of water of drinkable standards. To this end, the Joint Water Committee will develop, within one year from the entry into force of the Treaty, a plan for the supply to Jordan of the above mentioned additional water (Jewish Virtual Library 2010)."

This agreement was arguably more successful than the agreement with The Palestinians. Numerous reviews and opinions were written about it, and to the purpose of this article the following observations are based on the case study analysis for UNESCO by Haddadin and Shamir who concluded that "…the agreement has been in effect since 1994, and has worked well. This indicates that both Jordan and Israel view cooperation in water a matter of national interest (Haddadin & Shamir 2003)." Serious evaluation of the situation fifteen years later indicates that while there is peace and a quantity of water is delivered to Jordan each year, the complete water problems between the sides are far from a sustainable solution and a new and fresh inspection of the issue should be conducted in the framework of regional needs and capabilities.

3. Lessons, Possible Solutions and Conclusions

The agreements on water with Jordan and the Palestinian Authority are much more detailed and complex than what was described above. Inspection of the situation 15 years since the signing of the agreements reveals that Israel has fulfilled its obligations to both Jordan and the Palestinians. While the water situation has improved somewhat, this improvement relates only to segments of the water cycle and certainly not to all the countries in the region. Regarding the peace process the situation can be defined as deteriorated or, at best, stalled.

In addition, without addressing the whole water cycle, a satisfactory and sustainable solution cannot be achieved. For example, the linkage between water supply and wastewater treatment is an essential component in any modern integrated water management system; however it could not be implemented in the west bank mainly because of the political diversions. Dr. Brenner was involved in several cases in which potential cooperation was sought, in one of them, the inability of the sides to construct a modern wastewater treatment plant for East Jerusalem despite an offer of a generous grant from the German Government whose only precondition was that the project would be a joint Israeli-Palestinian venture. In another attempt, negotiations with representatives of the World Bank centered on the possibility to construct joint wastewater treatment plants based on international participation through investments on economical basis and granting services priced according to quantity and quality and disregarding the nationality of the customers or the future sovereignty of area under the jurisdiction of specific project. Israeli and Palestinian professionals indicated support to the idea and the World Bank's conditions to the loans included that (S.B. personal records (1997–1999)):

The service will be per capita service
The loans will be given only to the Palestinians
Guarantees from the bank will be given to investors (Israelis, Palestinians, others
The installations will be appropriate to the conditions in the area

Here again, even though the conditions were reasonable, the ideas could not pass the level of the politicians from both sides.

It is probably a very naïve approach to think that a win-win operational scheme can be out on the table to solve the water situation and at the same time decouple it from the other core issues of the dispute. However, the severity and the grave consequences do not allow for inaction and necessitate a continuous and serious dialog to reach collaboration. The need for regional management and cooperation over this vital resource can no longer be ignored. New management structures need to be implemented within a framework of Integrated Water Resources Management (IWRM). This framework requires that new governance mechanisms include not only the scientific, technological and economical aspects of the issue, but also the social, cultural, demographic and geographic. As defined by the Global Water Partnership (an intergovernmental water organization), IWRM is "a process which promotes the coordinated development and management of water, land and related resources in order to maximize the resultant economic and social welfare in an equitable manner without compromising the sustainability of vital eco-systems (Global Water Partnership 2008)." At the same time, all stakeholders must be involved in the process and understand the uncertainties associated with making strategic and progressive changes. The core need to have a fair and balanced program for the region is the ability for prompt, dynamic and efficient analysis of different scenarios as well as provision of immediate responses.

The solution to the region's water problem must be comprehensive and take into account the needs and the interests of all stakeholders. In that way, it must, by necessity, be linked to the peace process. Even if the focus is on water issues between Israel, Jordan and the PA, other countries like Syria, Lebanon and even Iraq and Egypt should not be neglected.

In addition to these practical solutions, the importance of collecting (either by an independent organization or cooperatively by both parties) accurate water data should not be underestimated. For example, there is still a question as to whether the Eastern Aquifer contains sufficient water resources (Selby 2003). Regardless of the true state of the resource, Palestinian distrust in this and many other data points mean continued lack of cooperation and inability to move forward. It is impossible to accurately collect data and it is meaningless if those impacted by the numbers do not trust them. It is essential to gain consent from the respective governments in the region to start the regional IWRM process, but in order to have chances to succeed, at least the data gathering and the planning stages should be based on NGOs and international economic bodies, able to operate independently. The emphasis on this consent of governments as a precondition to a fruitful process is the main contribution of this paper. There is no magic solution but combination of the basic parameters with the technologies available today with objective study of all the other factors may provide a small but significant chance for success.

According to the Israeli Water Authority the main elements of the Israeli IWRM are: saving and efficient use; water preserving building enabling seeping; remediation of polluted water source; recycling of wastewater; desalination of sea water; and import from sources outside the region. Naturally, a different weight is given to each of these components and desalination is at this moment the main component. However, based in part on personal experience, sincere cooperation between the rival parties may contribute to the proper IWRM with the same components for the whole region with a significant chance to contribute to peace as well.

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POSTER SECTION

NEW METHOD OF THE BOUNDARY RAINFALL CAPACITY COMPUTATION

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Abstract. The paper offers the new method of the boundary rainfall capacity computation, which is used for the CSO (Combined Sewer Overflow) structure design. The system is suitable for design the CSO parameters for the sewer system, which is flow into the non water supply recipients.

Keywords: CSO structure, boundary rainfall capacity, dilution ratio, allowed proportion of overflow water

1. Introduction

The Slovak republic operated mostly the combined sewer systems, where the significant role has the CSO structure. For the CSO structure design in Slovakia are valid the recommendations defined in the standard STN 756261 (1997), which define the significant boundary flow of mixed waste water Qč, which represents the determining parameter as a flow, which have to accumulate in sewer system and treat it before outflow to the recipient. The limitation value we can compute by the boundary rainfall method.

2. Boundary Rainfall Method

Boundary rainfall is defined as a block rain with the average rainfall intensity, which dewater the major portion of flush from the catchment surface from the

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CSO to WWTP (Waste Water Treatment Plant). After overrun of the boundary capacity start the overflow of mixed waste waters from the CSO into the recipient. Limitation flow Qč dewatering from the CSO to the WWTP during the rain event we can compute by the boundary rainfall method follow equation:

$$Q_{\check{c}} = Q_{b24} + Q_{dm} + \sum Q_{dmi} \tag{1}$$

where

Q_{b24} represent the average hourly flow of dry weather flow from the entire watershed upper the CSO,

Q_{dm} boundary rainfall flow from the local catchment Sp, directly belong to the designed CSO, which is computed by the eq. (2)

Q_{dmi} boundary rainfall flow from the CSO upper the designed CSO

$$\mathrm{Q_{dm}} = \mathrm{q_m} \sum \psi_{\mathrm{i}} \mathrm{S_{pi}} \tag{2}$$

where

ψ_i – runoff coefficient for the catchment i with the surface Spi with the same surface conditions, Spi – surface of the local sewerage catchment (hectares), belong directly to the designed CSO,

q_m – capacity of boundary rainfall (l s^{-1} ha^{-1}).

The Slovak standard STN 75 6261 recommend the boundary rainfall capacity by the eq. (3)

$$\mathrm{q_m} = 4{,}324 \ln\left(\frac{\mathrm{Q_{id}} (0{,}01 \mathrm{h_{ob}})^{\mathrm{x}}}{\mathrm{K_r}\, \mathrm{Q_{270}}} \right) + 12 \tag{3}$$

where

Qid represent the optimal contemporary flow of rainfall waters (m^3 s^{-1}) from the entire appraisal dewatering area. It is computed as the composition of reduced surface of sewer system catchment and minimal rainfall capacity, used for the sewer system design (Stanko 2006),

hob – average population density (inhab ha^{-1}), for the self catchment the value is 30, for the industrial catchments depend on the pollution rate, with the value 100 and more, x - exponent depend on population density. The value x=0.1 if the density is greater than 100 ingah ha^{-1}, otherwise x=3.0.

Kr – coeeficient, Kr = 1.0 – water supply stream, Kr = 1.5 – non water supply, if we assume the lower level of water quality protection in recipient,

Q270 – flow in the recipient excess 270 days in year (m^3 s^{-1}). Boundary rainfall capacity are evaluated for the one city or for the one continuous sewer system of urban agglomeration in relation with the one recipient of the same value, capacity is computed with the accuracy 0.5 $l\ s^{-1}\ ha^{-1}$.

By the standard STN 75 6261 boundary rainfall flow we need to compare with the equivalent flow of dilution ratio nr = 4, computed for the average hourly flow of concentrated dry weather flow Qm24 (domestic or industrial).

$$n_r = Q_{dm} . Q_{m24}^{-1} \quad \geq \quad 4{,}0 \tag{3a}$$

The lack of eq. (3) is the computation of only one value of designed rainfall capacity qm, which is the same for all CSO on WWTP watershed, which not respect the variability of watershed surface conditions.

The valid range for eq. (3) in Slovakia is qm = 7.5 till 25 $l\ s^{-1}\ ha^{-1}$. In the fact, respect the logarithmic form of the figure (3), the most values from this equation is in the range qm = 15 till 25 $l\ s^{-1}\ ha^{-1}$, which increase the investments and operational costs concerning the volumes of stormwater basins in WWTP.

2.1. NEW METHOD OF THE BOUNDARY RAINFALL CAPACITY COMPUTATION

The new method of the computation and recommended for the non water supply recipients was published by Urcikán and Rusnák (2004).

For non water supply streams with the B category of protection we can compute MD (boundary rain) by follow equation

$$q_{mB} = a + b + f(t_s) + k_c \ (l\ s^{-1}\ ha^{-1}) \tag{4}$$

with the valid q_{mB} = 7 till 15 $l\ s^{-1}\ ha^{-1}$

argument "a" is computed by the follow equations:
(a) for annual precipitation amount Hz = 500 to 1,000 mm,

$$a = (\beta + z)\ (0.01\ H_z^{0.6} - 0.145) + x\ (l\ s^{-1}\ ha^{-1}) \tag{5}$$

(b) for 15 min rainfall capacity q_{15} = from 95 to 155 $l\ s^{-1}\ ha^{-1}$ with the periodicity p = 1.0

$$a = (\beta + z)\ 0.003\ q_{15} + x\ (l\ s^{-1}\ ha^{-1}) \tag{6}$$

x – influence of streets cleaning, in the case of periodic mechanical-vacuum cleaning x = 1.0, for no regular manual cleaning x = 1.5, for rare cleaning x = 2.0.
argument "z" represent the influence of surface urban runoff pollution

$$z = 0.035\ k_M\ \Sigma\ z_i\ S_p\ (-) \tag{7}$$

where Spi is part of catchment CSO (%) characterized by the argument "z_i" (Table 1), k_M – coefficient – represent the number of inhabitants in CSO catchment, $k_M = 0.9 + 0.05 \ln M$, M – planned number of inhabitants in CSO catchment.

If the miss the data about the type of build-up area by Table 1, argument of pollution from the surface runoff "z" we can compute by the equation

$$z = \psi\,(6.0 + 0.3 \ln M)\ (-) \tag{8}$$

where ψ – average runoff coefficient (−) valid for the CSO catchment

For the argument "a" computation we use the bigger value by the eq. (5) or (6), also argument "z" by the (7) or (8), if we have the data for both equations.

TABLE 1. Average values of pollution concentration cd in stormwater flow from the urban surface runoff and the values of zi depend of the urban build-up area.

Urban build-up area	L (+) (kg COD ha^{-1})	φ (−)	Cd (mg l^{-1} COD)++)		zi (l s^{-1} ha^{-1})
			From–to	Average	
A	800–900	0.7–0.75	152–178	165	1.6
B	450–550	0.5–0.55	117–157	137	1.4
C	250–350	0.35–0.4	89–143	116	1.2
D	50–75	0.2–0.3	24–54	39	0.4
E	300–400	0.6–0.7	60–95	78	0.8

A – commercial centre with partial residential build-up, B – residential build-up, satellite residential build-up, block of flats build-up, C – single floor or lower built-up

D – single family houses, villa areas with gardens, E – industrial areas, (+) by Ellis, (++)

Computed by the average annual precipitation amount 700 mm by the 150 ombrographic stations

argument β – influence of wash away drift and sewer slime in sewers with stormwaters is in relation with the slope of sewers and terrain ip in tracks, when the sewers are loaded parallel with the terrain. Argument β is computed by the eq. (9)

$$\beta = 13.61 - 3.4\ SP_{pr}\ (-) \tag{9}$$

where SP_{pr} average value of the surface slope category in the sewer track in the entire catchment above CSO by the eq. (10)

$$SP_{pr} = (\Sigma\ S_{ri}\ SP_i)\ (\Sigma\ S_{ri}){-1}\ (-) \tag{10}$$

where S_{ri} area of partial reduced area above CSO, characterized by category of SPi (1., 1,5., 2., 3. or 4.) by the Table 3 and dependent from average slope of terrain ip (%) in the sewer track in entire catchment above CSO. Determination of β argument – influence of wash away drift and sewer slime, represent the most demanding time of computation of MD.

TABLE 2. Average annual values of pollution concentration cd in stormwater flow from the surface of urban catchment and the values of parameter zi by the type of urban build-up area.

Slope of surface ip (%)	$i_p < 1$	$1 \le i_p \le 2$	$2 < i_p \le 5$	$5 < i_p \le 8$	$i_p > 8$
SPi (−)	1.	1.5	2.	3.	4.

In the case of negative surface slope i_p = 0.1% base on minimal sewer slope. Parameter k_c, regarding influence of pollution concentration cb by the COD in dry weather flow is computed by the eq. (11)

$$k_c = c_b\ 800^{-1}\ (\mathrm{l\ s^{-1}\ ha^{-1}}) \tag{11}$$

where 800 mg l^{-1} COD is the average concentration of pollution in waste water with the specific production of waste waters qs = 150 l $inhab^{-1}$ day^{-1}. Validity of eq. (11) is in range kc = 0.5 až 3.0. Concentration cbCOD depend on measurement values in WWTP. Otherwise it is computed by the mixing equation.

$$c_b = (\Sigma\ Q_s\ c_s + \Sigma\ Q_p\ c_p)\ (\Sigma\ Q_s + \Sigma\ Q_p + Q_B)-1\ (\mathrm{mg\ l^{-1}\ COD}) \tag{12}$$

where Σ Q_s – total average flow of waste waters (l s^{-1}) from the entire catchment above CSO

$$\Sigma\ Q_s = 86\ 400-1\ q_s\ \Sigma\ M\ (\mathrm{l\ s^{-1}}) \tag{13}$$

where Σ M – planned number of inhabitants on the entire catchment above CSO, q_s – specific production of waste waters (l $inhab^{-1}$ day^{-1}), c_s – concentration of waste waters (mg l^{-1} COD) by the equation, c_s = 12.104 q_s^{-1}, Σ Qp – average flows of industrial waste waters (l s^{-1}) above CSO, cp – concentration of pollution of industrial waste waters (mg l^{-1} COD).

Computed value cb by eq. (12) is valid for cb ≤ 2,400 mg l^{-1} COD.

If c_b > 2400 mg l^{-1} COD, then into eq. (11) put c_b = 2,400 mg l^{-1} COD.

Inflow of infiltrated ballast waters Q_B is computed base on coefficient of infiltration k_i.

where k_i = 0 till 0.15 depend of underground water level. If this is under sewer bottom, then ki = 0.

$$Q_B = k_i\ Q_s\ (\mathrm{l\ s^{-1}}) \tag{14}$$

parameter $f(t_s)$ – influence of the time of concentration ts (min) from the catchment above CSO is computed by the equation

$$f(t_s) = 180\ (t_s + 120)^{-1}\ (\mathrm{l\ s^{-1}\ ha^{-1}}) \tag{15}$$

where t_s – time of concentration (min)

In the case of ts more than 100 min then t_s = 100 min.

Longer time of concentration allow to design the smaller capacity of boundary rain. Parameter "b" represent influence of stormwater ratio from WWTP catchment and characteristic flow in recipient. It is computed by the eq. (16)

$$b = 0.8 \ln y \qquad y = Q_{(1)}\, Q_{(270)}^{-1}\, S_{ri}\, (\Sigma S_{ri})^{-1}\ (\mathrm{l\ s^{-1}\ ha^{-1}}) \tag{16}$$

Equation (16) is valid for $y \geq 1.0$, if we compute $y < 1.0$, then we put into eq. (16) $y = 1.0$. Q270 – flow of 270 daywater in recipient ($\mathrm{l\ s^{-1}}$), Sri – entire reduction area above WWTP catchment (ha), Q(1) – comparable stormwater flow ($\mathrm{l\ s^{-1}}$) from the entire catchment with the periodicity p = 1.0 is computed by the eq. (17)

$$Q_{(1)} = K_{(1)}\, (\Sigma t_s + t_c + B_{(1)})^{-1}\, \Sigma S_{ri}\ (\mathrm{l\ s^{-1}}) \tag{17}$$

where: t_c = 5 min – surface time of concentration into the stormwater inlet computed by the rational formula, $K_{(1)}$ a $B_{(1)}$ local parameters in equation for the computation of block rainfall capacity $q = K_{(1)}\, (t + B_{(1)})^{-1}$ with the periodicity p=1.0, where t is the duration of block rain in minutes

Equation (4) is valid in the case of non water supply recipient, which is in category B by the reference Urcikán and Rusnák (2004).

Designed parameters of boundary rain qmA for the category A increase by the local conditions with capacity from 3.0 to 5.0 $\mathrm{l\ s^{-1}\ ha^{-1}}$, for category C capacity is decreasing from 2.0 till 4.0 $\mathrm{l\ s^{-1}\ ha^{-1}}$ comparable with values qmB computed by the eq. (4) for category B and adjusted by the table 3 with the correction coefficient α (Government Regulation of SR No 296/2005).

TABLE 3. Design values of correction parameter α.

Category of non water supply stream protection	Design rainfall capacity base on stream protection category ($\mathrm{l\ s^{-1}\ ha^{-1}}$)	Request for the non water supply stream protection			
		Undemanding	Average	Increasing	Generally
		qmB ($\mathrm{l\ s^{-1}\ ha^{-1}}$) by eq. (4)			
		7 ≤ qmB < 10	10≤ qmB ≤ 13	13< qmB ≤ 15	qmB = 7 till 15
		parameter α ($\mathrm{l\ s^{-1}ha^{-1}}$)			($\mathrm{l\ s^{-1}ha^{-1}}$)
A	qmA = qmB + α	3 till 4	4	4 till 5	qmA = 10 till 20
C	qmC = qmB − α	+ (1) 2 till 4	2 till 3	2	qmC = 5 till 13
(+) α = 1.0 as possibility, when qmB = 7.0 till 7.9 $\mathrm{l\ s^{-1}\ ha^{-1}}$					

Design values of capacity qm is recommended to use for:

1. for category A in range qmA = 10 till 20 $\mathrm{l\ s^{-1}\ ha^{-1}}$,
2. for category C in range qmC = 5 till 13 $\mathrm{l\ s^{-1}\ ha^{-1}}$, when qmC = 5 till 6 $\mathrm{l\ s^{-1}\ ha^{-1}}$ is in the case for huge amount watery streams,

3. for category B by eq. (4), when computed value is by eq. (4) is $q_{mB} <$ $7\ l\ s^{-1}\ ha^{-1}$, then design value is need to choose qmB = $7.0\ l\ s^{-1}\ ha^{-1}$, if the $q_{mB} > 15\ ls^{-1}ha^{-1}$, then design value is need to choose qmB = $15\ l\ s^{-1}\ ha^{-1}$.

Limitation flow $Q_č$ dewatering from CSO during the wet weather into WWTP we compute by the eq. (18)

$$Q_č = \Sigma\ Q_{b24} + Q_{dm} + \Sigma\ Q_{dmi} = \Sigma\ Q_{b24} + q_m\ \psi\ S_p + \Sigma\ q_{mi}\ \psi_i\ S_{pi}\ (l\ s^{-1}) \qquad (18)$$

where Q_{dm} – boundary flow ($l\ s^{-1}$) from catchment S_p (ha) CSO with runoff coefficient ψ (), $\Sigma\ Q_{dmi}$ – total of boundary flows from CSO above designed CSO ($l\ s^{-1}$), $\Sigma\ Q_{b24}$ – average dry weather flow ($l\ s^{-1}$) from entire catchment above CSO is computed by the follow equation

$$\Sigma\ Q_{b24} = \Sigma\ Q_s + Q_B + \Sigma\ Q_p = (\Sigma\ M\ q_s\ 86\ 400–1)\ (1 + k_i) + \Sigma\ Q_p\ (l\ s^{-1}) \quad (19)$$

where $\Sigma\ Q_s$ domestic waste water flow ($l\ s^{-1}$) from entire catchment above CSO, Σ M – total population on entire catchment above CSO, q_s – specific production of domestic waste waters ($l\ inhab^{-1}\ day^{-1}$),

Q_B – inflow of infiltrated waters ($l\ s^{-1}$), k_i – coefficient of infiltrated underground waters (k_i = 0 till 0.15); $\Sigma\ Q_p$ – inflow of industrial waste waters ($l\ s^{-1}$) only with the sewer operator agreement from the entire catchment above CSO.

Limitation flow $Q_č$ computed by the eq. (4) and (18) is appraised by the mixed ratio n_r by first reference by equation

$$n_r = (Q_m + \Sigma\ Q_{mi})\ (\Sigma\ Q_{b24})^{-1}\ (–) \qquad (20)$$

At which is demand

$$n_r \geq 7, \text{ for } c_b \leq 600 \text{ mg } l^{-1} \text{ COD} \qquad (21)$$

$$n_r \geq 0.017\ (c_b – 180) \text{ for } c_b > 600 \text{ mg } l^{-1} \text{ COD} \qquad (22)$$

where c_b – COD concentration (mg l^{-1}) in dry weather flow by the eq. (12).

3. Conclusions

Transported pollution from the CSO into the recipients which the new method makes provision for the boundary rainfall computation depend on:

- pollution contain in surface waters in stormwater flow from the urban catchment with various surfaces and type of build-up areas,
- influence of flush away drift from the sewer bottoms and sewer slime,
- flow of domestic waters Q_s and pollution concentration csCOD,

- flow of industrial waste water Q_p and pollution concentration cpCOD,
- inflow of infiltration ballast waters Q_B into sewer system,
- influence of the time of concentr. t_s from the specific catchment of CSO
- rainfall properties – rainfall capacity q, annual precipitation amount Hz.

The new method of the boundary rainfall capacity computation include the influence of all above properties, including quality characteristic of recipient protection by the three categories of the stream A, B, C, make provision for their exploitation, watery and oxygen regime.

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CONTRIBUTIONS TO THE DEVELOPMENT OF PHOTOMETRIC AND SPECTROPHOTOMETRIC PORTABLE KITS FOR WATER ANALYSIS

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Abstract. The contribution refers to concerns of an university border team from Romania and Ukraine involved in development and finished of a new concept for a quick analysis in situ of natural water resources on photometric and spectrometric way using modular cases with electrical autonomous input, with different optoelectronic components for many analytical applications, assembly for an application being ready in few seconds. The contribution presents concept and design elements for two cases. One of the same case is a photometric one and is designed to quick analysis for one ionic polluting specie and another case is a spectrometric one for a quick analysis of five ionic polluting species with simultaneous presence in a water sample. Both cases are expected to work interfaced with laptops, processing data being stored or forward by GSM, or satellite. The two cases integrate many original solutions proposed for inventions.

Keywords: portable equipments, photometry, spectrometry, turbidity, conductivity

1. Introduction

The nature of chemical species from water and their concentration can be determined only by specific reactions caused in the same number of samples and chemical species of interest. In order to determine the concentration of these

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species is used volume or colorimetric photometry. For reasons of sensitivity of the method, accuracy of calculations, possibility of on-situ analysis, photometry is preferred to volume. In turn colorimetric photometry can be achieved only in the visible spectrum (VIS), but this method of analysis is not directly applicable because samples are colorless. To determine, however, by photometric method the concentration of chemical species in water (Skoog and Leary 1966; Gary 1994; Schmidt 2005), first phase provides a color chemical reaction between chemical species in the monitored sample and a specific reactant, intensity of resulted color is proportional to the concentration of chemical species pursued. In the second phase the resulted colored solution is photometric measured at a specific wavelength length, the main goal being establishing the concentration value (Robinson and Frame 2005; Workman and Springsteen 1994; Hollas 1995).

2. Analytical Instrumentalities for Water Quality Control

2.1. COMPLEX PORTABLE APPARATUS FOR WATER ANALYSIS

Equipment described below relate to a portable electronic device for determining in situ concentration, turbidity and conductivity of water from natural untreated resources or from treated resources containing drinking water (Gutt and Gutt Patent proposals Nr.00855/2008, Nr.00152/2010, Nr.00858/2008, Nr.00153/2010, Nr.00156/2010, Nr.00160/2010; Gutt Patent RO 122.600/2007). Water turbidity is indicator of amount of suspended solids in water. Determination of turbidity is required so as to drinking water and rivers. Currently, water turbidity determination is made only by photometric test or irradiating a water sample with polychromatic light (American standard U.S. EPA 180.1., tungsten lamp as light source (2200–3000K)) recommended method to determine the small turbidity of drinking water, or irradiating a water sample with a radiation source in the spectral NIR LED at a wavelength of 860 nm (the European standard DIN ISO 7027:1999 and EN 27 027 similar.) Latter method is recommended to monitor the turbidity of flowing or standing water surface which usually have higher turbidity than drinking water.

Determination of water turbidity realized with an optical channel photometry, located in parallel with that of spectrophotometer used for determining the concentration of various chemical species present in water analysis, working with an LED radiation source in the near infrared wavelength 860 nm on all samples of water passing through the right channel photometry, optical absorbance, equation (1), being proportional with the amount of matter present in a given volume of water.

Electrolytic conductivity of water samples is a synthetic indicator which expresses the sum concentration of cations and anions in water without any possibility to identify their nature or the possibility of establishing the contribution made by each species concentration to the total concentration of anions and cations. However measuring conductivity of water natural resources but also of drinking water is the first operation in instrumental analytic of water. The value of water conductivity, compared with previous measurements of the same water resources, indicates where differences between the measured values exist, its overall inorganic pollution.

Water conductivity is usually measured using electrolytic conductivity meters which are in principle some electronic ohm-meters which comprise a movable probe with two platinum electrodes located in a precise distance apart. By soaking the probe in water sample between the two electrodes is interposed a water column which closes the circuit. To eliminate the phenomenon of electrolysis that occurs at the supplying of electrodes in DC current it is used AC power, usually at a frequency of 5 kHz.

Conductivity of the water column can be measured without contact by placing outside of rectangular or cylindrical glass cans with water for analysis of two electrodes which act as condenser armatures that is part of an oscillating circuit, frequency value of oscillation of the oscillatory circuit is a function of electrolyte conductivity. Plan condenser capacity expression is:

$$C = \varepsilon_0 \varepsilon_r \cdot \frac{A}{d} \tag{1}$$

where: C – condenser capacity with plan armatures

ε_0 – absolute electric permeability in vacuum
ε_r – environment relative electric permeability (permeability column of electrolyte between electrodes)
A – surface area of armatures (surface area electrodes)
d – distance between the armatures (the distance between electrodes)

Direct measurement of the capacity of a capacitor, due to changes in permeability of column water between the electrodes, is difficult enough, the capacitor formed is related to a type LC oscillating circuit whose oscillation frequency f0 is the expression (Gutt's Patent proposals Nr.00858/2008; Patent RO 122.600 /2007):

$$f_0 = \frac{1}{2\pi\sqrt{LC}} \tag{2}$$

Any ionic change of water composition between armatures determines another value of relative electric permeability which in turn causes a deviation Δf of the oscillation frequency f from resonance frequency f_0:

$$\Delta f = f - f_0 \tag{3}$$

where: L – inductance coil
C – condenser capacity

As such, changes in frequency of oscillatory circuit expressed in terms of a constant electrodes surface and a constant distance between them, the electrical conductivity of analyzed water samples:

$$\chi = k \cdot \Delta f \tag{4}$$

Conductivity value χ is automatically determined based on calibration curves in coordinates: Δf – by extrapolating values of drift frequency values on this curve.

The complex equipment proposed by authors for advanced analysis of ground water allows, Figures 1–4, simultaneous determination in situ, in a high productivity conditions, the concentration of important chemical species presented as pollutants in water, its turbidity and conductivity with a total replacement of chemical kits of single use, for which purpose: to determine in situ the concentration of chemical species in water spectrometric and water turbidity by photometry is used a portable dosing system and a system with photo barriers for measuring intensities of radiation absorbed by the sample.

Dosing system allows by manual sequential and successive rotations of some dispensers and water samples to be analyzed, precisely bringing a sample of water next to a dispenser containing a color reagent specific to a particular chemical species present in water sample. All six water samples passing through the right turn twice two lights barriers. At the first crossing takes place the determination of intensity of light radiation absorbed by water colored by five water samples, determination of turbidity for six samples of water from two different lights barriers and electrolytic conductivity determination of all six water samples.

At the second crossing through the first lights barriers take place the Spectrometer analysis of the five colored water samples at specific wavelengths of the five chemical species pursued, the wavelengths being provided by appropriate filters installed in front of slots for the five samples of water, the purpose of measurement being the determination of the intensity of radiation absorbed by colored water of five samples.

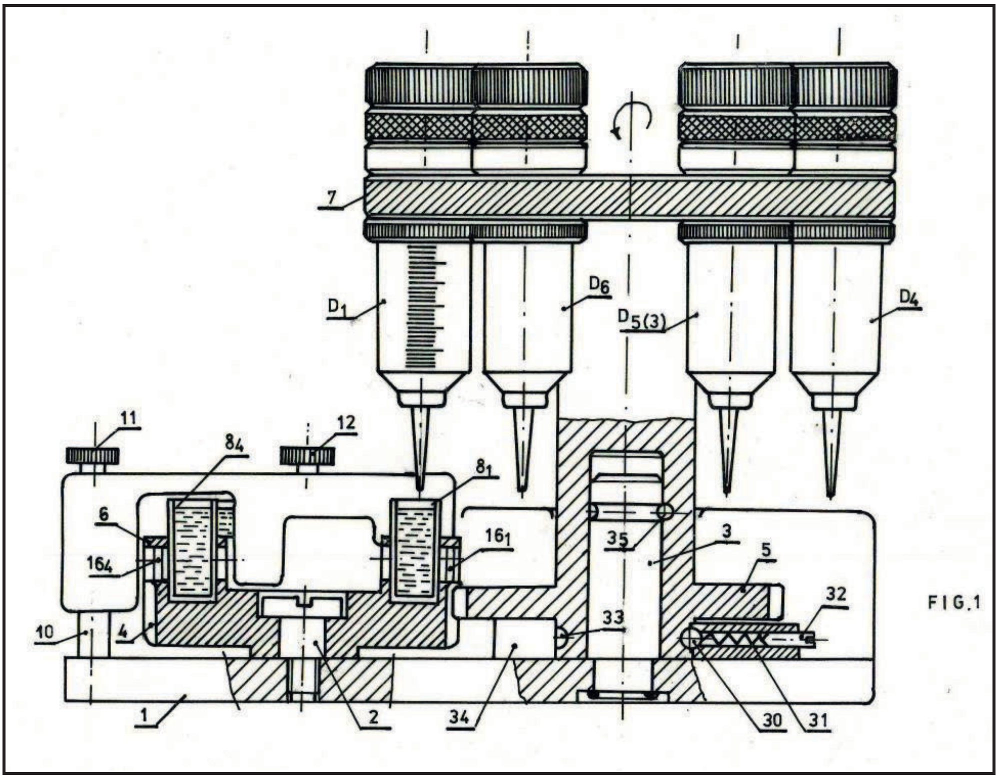

Figure 1. Side view section of portable complex device for water analyzing (Gutt and Gutt Patent proposals Nr.00855/2008, Nr.00152/2010, Nr.00858/2008, Nr.00153/2010, Nr.00156/2010, Nr.00160/2010; Gutt Patent RO 122.600/2007). 1-base plate, 2,3-axis of rotation, 4,5-identical gear head, 6,7-crown gear, 81-6–slots for glass tubes of analyzed water sample, 9-detector unit, 10-support column, 11,12-lock-nuts, 161,164-different optical filters whose color corresponds to maximum optical absorbance of the examined species, 30,33-balls, 31-compression spring, 32-screw, 34-electrical contactor, 35-pin screw locking, D_1-D_5- dosing systems.

in the determination of turbidity, the measurement occurs at the first passing of samples through the two light barriers and it is done differently by each lights barriers. The first photo barrier uses polychromatic light radiation and made the photometrical analysis of suspension in water for turbidity measurement, sample that is in slot containing no color filter, turbidity measurements made by this lights barrier is taken into account if they have low values. The second photo barrier is intended to photometrical analysis of the same water sample with monochromatic radiation to determine turbidity at high values. Decision on approval turbidity value determined by the first photo barrier or by the second being taken by microprocessor device by its specific programming.

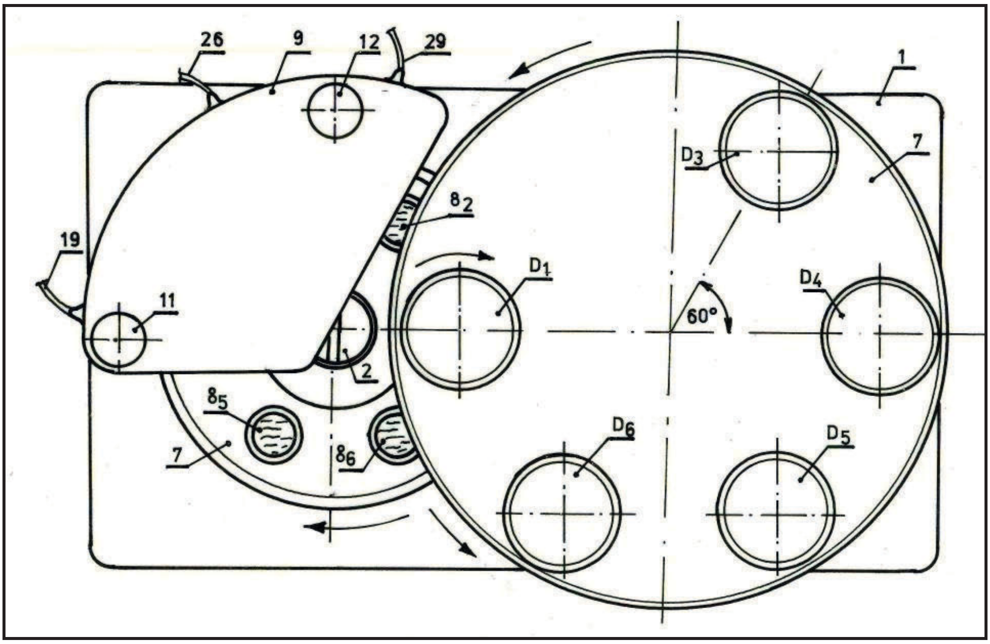

Figure 2. Overview of portable complex device for water analyzing. 1-base plate, 2-axis of rotation, 7-crown gear, 81-6 – slots for glass tubes of analyzed water sample, 9-detector unit, 11,12-lock-nuts, 19,26,29-electrical cable connecting to the electronics unit, D_1-D_5-dosing systems.

to measure the conductivity are used two elastic electrodes of stainless steel plate, slightly curved so as to cover the outer wall of the tube with water sample. Water samples for analysis are brought in turn in the front of the two electrodes, the conductivity is determined by the change in resonant frequency of an oscillating circuit due to capacity changes of capacitor made by the two electrodes and analyzed water column between his armatures.

Mode of work with complex equipment for water analysis is as follows: mount $D_{1–5}$ dispensers each in their appropriate slot in the crown *7* and locked in final position with appropriate safety nuts *40*, after that optical glass tubes $8_{1–6}$ containing analyzed water samples are introduced in cylindrical slots in the crown *6* and manually rotating the crown *7* which has the effect of proportional turning of the gear *5*, and by gearing the rotating it causes the rotating of gear *4* with the same angle (two gears having the same diameter), bringing in front dispenser D_1 the tube 8_1 with the first water sample for analysis. Continue to enable electronic unit *20* which causes the saving position of each sample of water saving through electrical contactor *34* and the electronic unit *20* by the end of determinations. Follows a complete handle rotation of the crown *7* to the right hand, stopping its rotation about one second to reach each division with *60°* made with ball *30* and spring *31*.

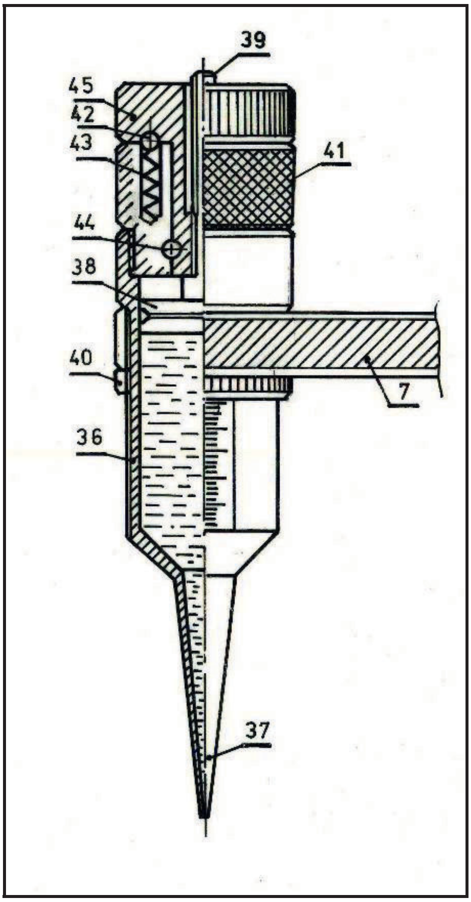

Figure 3. Section through a dispenser, 36-dose plastic syringe, 37-dose plastic tip, 38-plunger, 39-threaded right rod, 40-lock-keeper, 41-cylindrical body, 42-ball, 43-compression spring, 44-pin screw lock, 45-nut thumb.

The effect of complete rotation is the measurements of absorbed intensity I_0 of non colored water for five water samples with photo barrier f_1, measurement of turbidity of water from tube 8_3 which has no color filter mounted in front of the sample, first with photo barrier f_1 and then with the photo barrier f_2, and electrolytic conductivity measurement for all six samples of water when they parked a short time in the front of capacitor armatures *27* and *28*. If turbidity has high values the electronic system considers the turbidity values determined by photo barrier f_2, and if turbidity has low values electronic system decides taking into account the values determined by photo barrier, f_1.

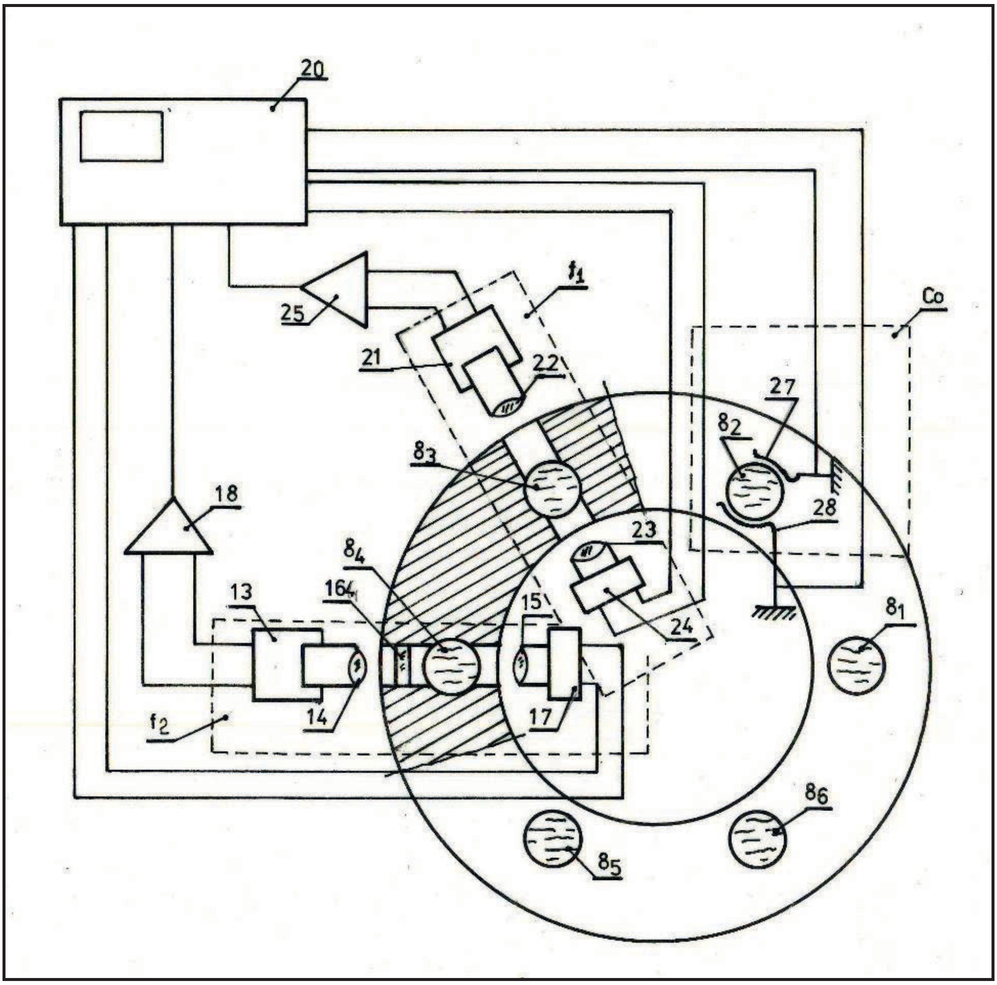

Figure 4. Schematic drawing of portable device for complex water analysis, 7-gear crown, $8_{1\text{-}6}$ - with six slots for glass tubes for water samples, f_1,f_2-photobarriers, 13-polychromatic radiation source, 14,15-optical collimator lens, 16-optical filter, 17-photodiode, 18-electronic amplifier, 20-electronic unit, 21-monochromatic radiation source in the near infrared spectral range, 22,23-collimator lens, 24-photodiode, 25-electronic amplifier, 27,28-electrodes for conductivity measuring.

After this operation it is bring back the dispenser number one by the next sequential rotation to a tube 8_1 containing the first sample of water, then turn the thumb nut *45* until the emergence click site indicated by the angular splitting system developed by ball *42* and compression spring *43* effect being the dosage of a reagent volume corresponding to the thread pitch displacement of rod *39* threaded right, in water sample where is initiated color reaction color.

The next stage crown *7* is easily rotated until it feels a new division click. Dosage specific reagent of the second chemical species presented in water is carried as a sample number one by turning the thumb nut *45* until the appearance of division's click. At the dosing of color reagent for the fourth sample of water, colored water sample number one is site of optical photometrical path consists of polychromatic radiation source *13*, collimator lenses *14* and *15*, optical filter 16_1 and photodiode *17*. Photometry is continued until all tubes 8_{1-6} crosses photo barrier f_1. At photometrical analysis occurs the measurement of light intensity I_1 absorbed by colored water samples and in the electronic unit occurs the calculation of absorbance A using Law Lambert Beer and the calculation of concentration *c* and calculation the extrapolation on the calibration curve:

$$A = log\frac{I_0}{I} = a \cdot b \cdot c \tag{5}$$

For design simplicity and to ensure high reproducibility of data is recommended that all dispensers used to have the same step of division, for example, one division by clicking on a thumb full rotation of the nut *45*, situation in which distributes in each sample of analyzed water an identical volume of color reagent corresponding to the amount of plunger displacement with screw thread pitch rods *39*, screwed to the right.

3. Conclusion

By using portable described equipments it is quickly determined and in situ, with a single device, without additional manipulation of samples, the concentration of important chemical species presented as pollutants in water. One of the constructive variants offers in addition besides the possibility of determining the concentration and simultaneous determination both of turbidity and of electrolytic conductivity of water. The complex device of water analysis eliminates chemical kits and glass tubes for single use classically used for color reactions caused in land and also allows the removal by electronic calculation of errors caused by turbidity on the concentration values determined for different chemical species in water. Other advantages of using this instrumental equipments are particularly a high productivity related to water analysis, their simplicity of design and low cost prices both in manufacturing and in using.

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A NEW GENERATION OF INSTRUMENTAL ANALYTICAL DEVICES FOR CONTROLLING AND MONITORING OF WATER QUALITY

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Abstract. Quantitative instrumental analysis of chemical pollutant species in water requires a complex laboratory logistics, difficult or impossible to travel on land. Concerns of research team have focused on design and implementation of simple and reliable field equipment to enable handling, dosing and quick analysis of water samples. All structures are portable and modular designed to work both with turbid water samples as well as clear water, also this equipment can work in the photometric analysis regime with Kit's, in spectrometric regime by scanning UV/VIS/NIR spectrofluorometric regime or combined, using besides these schemes for analysis in the same time analysis of the water conductivity. Achieved unitary concept, high flexibility, a large number of possible analysis in short time and original solutions incorporated, makes designed equipment from which some of them already made an outstanding technical means for water analysis and monitoring of performance both as primary natural resources and treated water resources. All means of instrumental analysis are interfaced with portable computers that allow an over ordering processing data, storing it and as appropriate their forward by GSM or satellite.

Keywords: portable photometer, in situ analysis, photometer probe, conductivity cell

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1. Issue of Photometric Portable Equipments

There are two important issues in the achievement of photometric portable equipments: the assurance of a high precision measurement close to those provided by laboratory equipments and production of different equipments covering a larger area as analytical field of analysis. The authors of this paper acted in this issue with the purpose of developing a family of portable equipments with applications mainly in water analytics. One of main factors affecting data reproducibility is the deviation from linearity, the parameter that influences accuracy in all experimental measurements. By statistical methods it is possible to express the calibration curve as a calibration function using the linear regression method, respectively the verification of according linearity by the method of least squares. In general case, the equation of a straight line with the intersection of ordinate in a point d can be expressed by the relation:

$$y = a \cdot x + d \tag{1}$$

And the calibration curve equation can be expressed by the relationship:

$$A = a \cdot c + d \tag{2}$$

where:

A – optical absorbance

a – molar coefficient of optical absorption

d – point of ordinate intersection corresponding for the amount of zero concentration.

If the value of molar absorption coefficient and blind signal value d are known, then the concentration c for each value of absorbance A using Beer-Lambert law (Skoog and Leary 1996; Gary 1994), can be calculated:

$$A = a \cdot b \cdot c + d \tag{3}$$

where: b – thickness of layer photometry

To determine the extent to which the calibration curve registers in linear field, factors a and d are determined by the method of least squares:

$$a = \frac{\sum x \cdot \sum xy - \sum x^2 \cdot \sum y}{(\sum x)^2 - n \cdot \sum x^2} \tag{4}$$

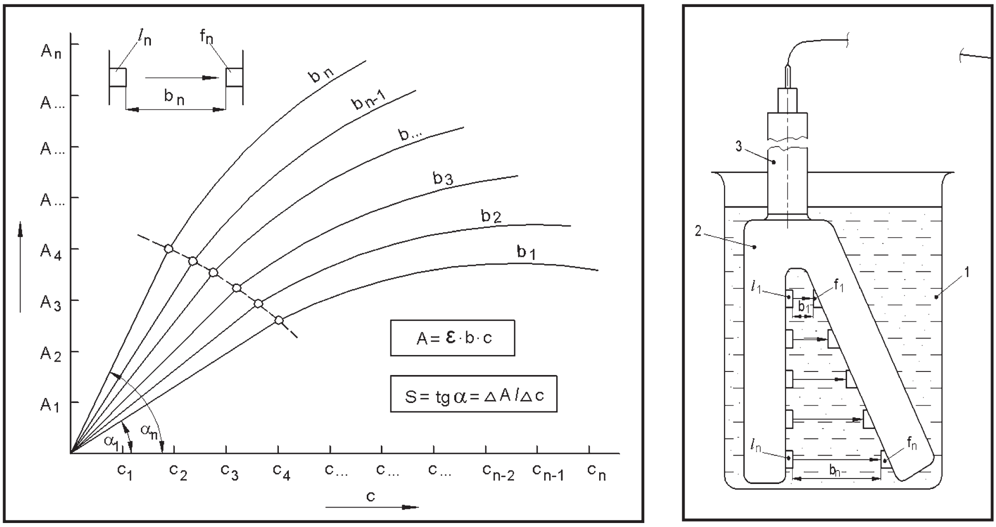
$$d = \frac{\sum x \cdot \sum y \text{ - } n - \sum xy}{(\sum x)^2 - n \cdot \sum x^2} \tag{5}$$

From the experimental values the correlation factor R is determined, factor which describes the correlation of linearity between the experimental calibration curve and the equation of a straight. If the correlation factor r is closer to the value 1, then the linear correlation is higher (Matter 1995). It is accepted that for a analytical method this factor should be greater than 0.98. Analytical tools for determining the linearity of calibration curve.

1.1. PORTABLE PHOTOMETRIC PROBE

At the same purpose of determining the limit of linearity a portable photometric probe as one represented in Figure 1a was designed and built. The probe is a miniaturized and compact structure, consisting of a series of laser diodes, all accorded on the same wavelength range and a receiving photodiodes, laser emitting diodes forming with receivers photodiodes optical channel with well known length but different from a pair diode to another. Probe has at the top a fixing and suspension rod and it is connected by a flexible cable of a portable electronic unit equipped with specialized software for acquisition, processing and displaying data. Considering that maximum sensitivity to determine the concentration of molecular species by photometric way is achieved at specific wavelength at which absorbance is maximum, therefore for each chemical monitored species it is necessary such a probe.

The working mode to determine the maximum limit of concentration of test solution is very simple: a photometric probe 1 is introduced in turns in vessels with known concentrations of monitored species. Between two different concentrations probe will be rinsed in distilled water. On each entry into a glass containing a certain concentration, on the electronic display unit of the probe, respectively on the display of calculation unit which is interfaced with the probe, appears the family of vertical points for that concentration, after photometry of all concentrations, the operator indicates the end of the measurement by pressing a key of electronic unit, and the display shows families of curves plotted in Figure 1b with marking area where begins the nonlinearity dependence of absorbance A and concentration c for different thickness of absorption layer b. In parallel with the graphical representation, in memory exists the data base tables which was the foundation for rendering the graphical representation. Photometric probe can be used for rapid determination of maximum sensitivity S, defined as the ratio between absorbance change and change of concentration in the linear field, in terms of known layer thickness. Another application (Gutt's Patent RO 122.598 /2007, 2007) of the probe is his using in the study of influence on the limit linearity concentration by various sizes and process parameters such as: changes of optical molar absorption coefficient due to the presence of chemical kinetics, temperature change, pH change, reflection, refraction or absorption of radiation by the walls of vats with test solution and because of the impossibility of ensuring a perfectly monochromatic radiation.



a) b)

Figure 1. Scheme design and principle of the probe (a) and the family (b) of curves obtained using the probe according to the invention to determine the concentration limit of linearity. l_1....ln-emitting laser diodes, f_1....f_n-diode receivers, b_1....b_n- photometric thickness of solution 1-sample solution, 2-photometric probe, 3-mounting rod, 4-flexible cable, A_1.... An absorbent solution, c_1... c_n - solution concentration, ε - molar absorptivity coefficient.

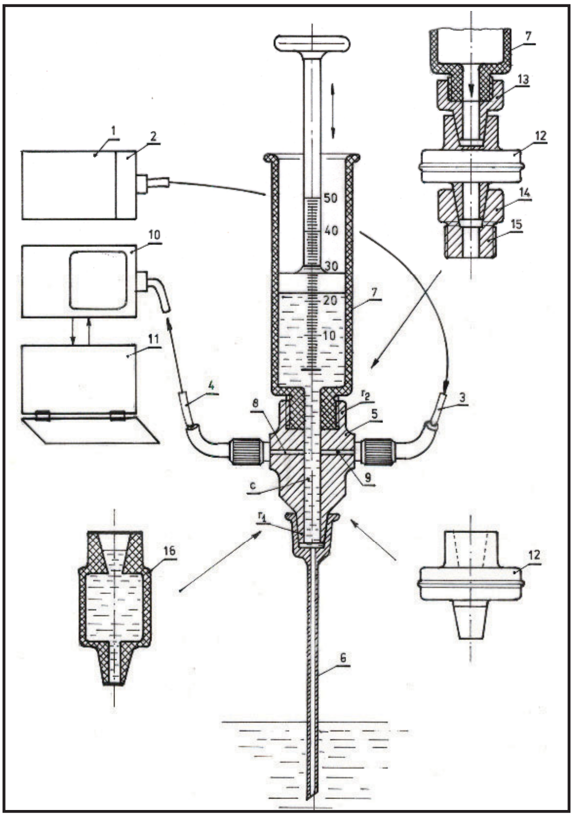
To this purpose, after showing family of curves and automatic determination of limit concentration for all layer thicknesses of solution, a solution with concentration clim will be prepared and the probe will be inserted into it. By varying sizes and all parameters listed above on the family of curves is obtained a view of the movement of concentrations corresponding to a limit of linearity according to concrete size or parameter value studied at a time.

2. Portable Spectrometric Systems

2.1. SPECTROPHOTOMETRIC SYSTEM TO DETERMINE THE COMPOSITION, CONCENTRATION AND DOSING A SOLUTION

Portable electronic spectrometry system described below uses for fast and precise chemical composition and concentration determination of a liquid solution, followed by appropriate its volume determination, both in laboratory conditions as well as in situ. The principle scheme of this system is illustrated in Figure 2.

The problem solved by that proposed scheme is to achieve a portable spectroscopy structure for measurement and dosing which consists in an extraction system of sample from water resources, laboratory or industrial containers, using a syringe or a dispenser, a spectrometric flow cell, coupled by optical fiber with a radiation source, Ocean Optics8, a miniature spectrometer, Ocean Optics8, and a computer unit with a specialized soft, Ocean Optics11.



1-polychromatic radiation source, 2-set of interchangeable optical filters, 3,4-optical fibers, 5-body flow cell, c-channel flow, r_1,r_2-fittings, 6-needle syringe, 7-aspiration/repression syringe 8,9-optical fibers, 10-miniatural spectrometer, 11-computer system, 12-single-use filter, 13,14,15-adaptation segments, 16-chemical KIT.

Figure 2. Schematic diagram of the spectrometric system to determine composition, concentration and solution dosing.

During sampling and/or tested solution repression chemical analysis occurs both qualitative and quantitative as well as its automatic data processing. These operations can be followed as appropriate by the volumetric determination of a part of tested solution based on spectrometric data obtained in the first part through quantitative analysis and material balance performed by electronic unit and specialized software.

The system allows to work in situ difficult conditions of access as well as laboratory work using some sets of syringes filled with water samples taken in different locations and then transported to the laboratory, also allows spectrometric measurements of turbid solutions and, with the using of chemical KIT for coloring reactions of species that do not absorb in the visible field, specific application for natural and drinking water resources (Gutt's Patent RO 122.598/ 2007, Patent RO 122.600 /2007, Patent RO 122.599 /2007, Patent RO 122.694/ 2007).

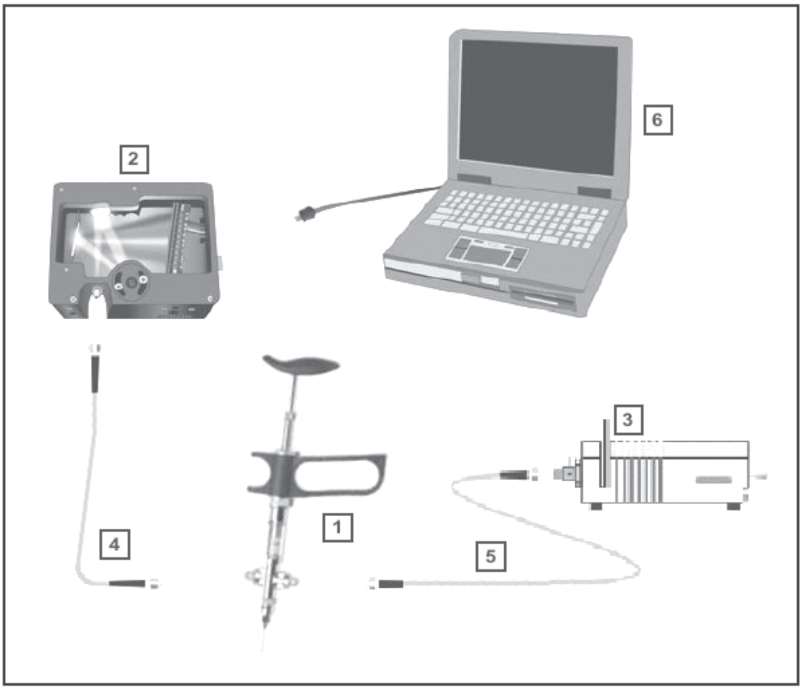


Figure 3. View of modular portable spectrometric system for determination of composition in situ, concentration and dosing of a solution. 1-syringe dispensers (www.socorex.com - Socorex syringes 187, catalogue SOCOREX, Swiss, 2009) and photometric flow cell, 2-miniature spectrometer with a fixed diffraction grating and diode-array detector (Miniature spectrometer USB4000 2007/2008), 3-radiation light source (Tungsten halogen Sources 2007/2008), 4,5-optical fiber (Optical fiber module 2007/2008), 6-laptop (SPECTRASUITE Software 2007/2008).

To ensure a good operability and high productivity, including access in difficult places, radiation source, flow cell of sampling system and spectrometer are interconnected by optical fiber. Sampling system, which ensures the spectrometric analysis of aspirated solution to, or spectrometric analysis of repressed solution, consists of syringe or dosing electronic dispenser coupled to the dosing syringe and comprises a flow cell for the sample solution provided at the bottom with a long syringe needle, in median area with a photo barrier perpendicular mounted on cylindrical channel of the flow cell. Spectrometric measurements of turbid solutions between the flow cell and syringe needle (for aspiration of fluid from analyzed environment by a syringe needle) and between syringe and cell flow (for pressing of liquids from syringes filled with solutions of various sites considered) is interpolated a miniature single-use cartridge filter.

Figure 3 presents a modular system for spectrometric determination of composition in situ, of concentration and dosing of a solution as it exists in the Instrumental Analysis Laboratory of Food Engineering Faculty of Suceava-Romania.

2.2. SPECTROPHOTOMETRIC SYSTEM TO DETERMINE IN SITU SOLUTIONS CONTAINING FLUORESCENT SPECIES

Process and a apparatus shown in Figure 4 are used to determine concentration and appropriate to dose solution volume, in laboratory, factory or field, a certain chemical species on the principle of fluorescence measurement. In order to achieve a new method and equipment for measuring the concentration of a fluorescent species presented in solution and appropriate dosing of this solution a portable structure is used to determine using fluorescent-photometric method with measurement at 180°, of a fluorescent chemical species concentration in solution during aspiration or repression a small part of it, through simple extracting respectively pressing the plunger of syringe attached to a optical photometrical device.

Equipment design, for measuring process, is a portable electronic photometrical system consists of a measuring probe type flow cell, a source of monochromatic excitation LED type, a miniature spectrometer, all connected by an optical fibers package and a calculation unit. Measuring probe consists of a volumetric dosing syringe mounted on a flow cell that has in bottom a syringe needle and in the case of turbid solutions and a typed single-use filter cartridge. Flow cell is traversed by a cylindrical channel on which moves liquid to be analyzed during its aspiration respectively repression of the syringe plunger action.

Perpendicular to the flow channel axis wall is poured into it a package of optical fiber consists of six excitation radiation fibers circular arranged around a central optical fiber with the role to direct fluorescence radiation, resulting from excitation, to the spectrometric system for measurement of fluorescence intensity and its conversion in concentration values of fluorescent chemical species pursued.

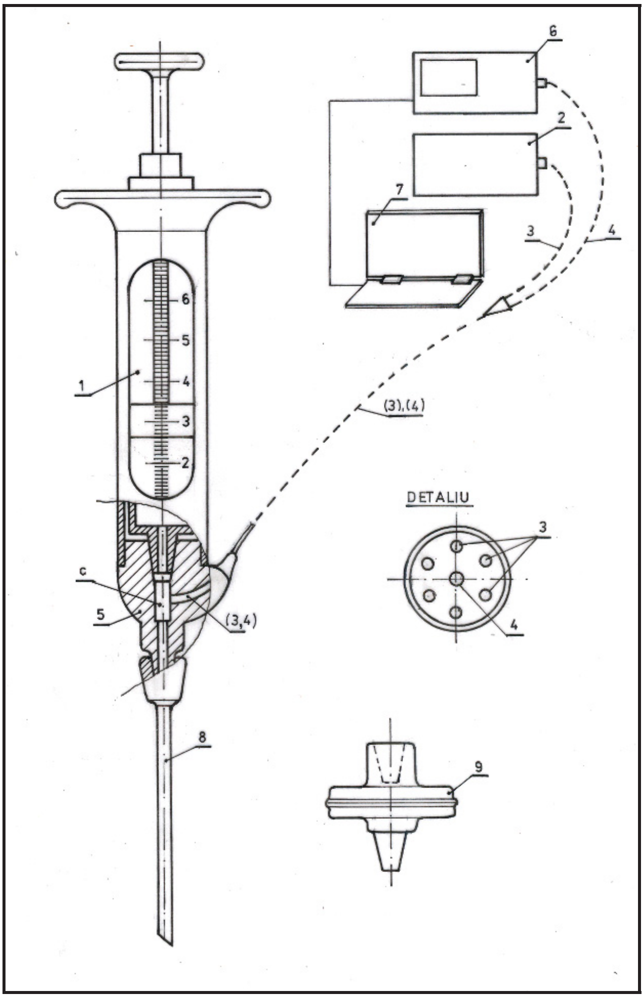


Figure 4. Schematic diagram to determine the fluorescent species. 1-dose syringe, (SOCOREX syringes 2009), 2-monochromatic radiation source LED, 3-radiation package consists of six optical fibers, 4-optical fiber transmission (OceanOptics Optical fiber module 2007/2008), 5-flow cell 6-miniature spectrophotometer with a fixed diffraction grating and detector Diode-Array (Ocean Optics Socorex syringes 2009)), 7-unit of calculation, 8-needle syringe, 9-single use filter, c-channel flow.

3. Combined Cell for Spectrometry in Situ of Solutions to Determine Composition, Concentration and Their Electrolytic Conductivity

Measuring cell is intended to measure the composition, concentration and electrolytic conductivity of a solution in fluid flow conditions, using the cell on-line and in-situ measurements both in recirculation system type by-pass and aspiration-repression mode achieved with a dosing syringe. Flow cell is a module, figure 5, that can be attached to any dosing syringes or dispenser unit.

It can also attach filters or kits for color reactions as in Figure 2. Measuring cell consists of a plastic body 1 with two joints 2 and 3 respectively for the entry and exit of tested solution, two short optical fibers 4 and 5 whose lower ends are placed at the level of wall of a cylindrical flow channel c solution and whose upper ends are connected by standardized connectors to other two optical longer fibers that are in touch with a source of polychromatic radiation, with spectral coverage UV-VIS-NIR, respectively with a miniature spectrometer

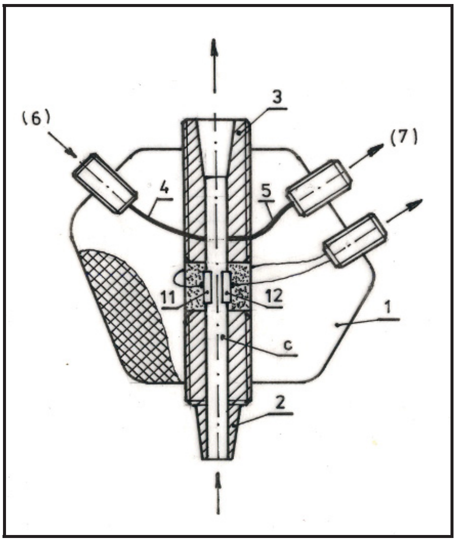


Figure 5. Section through cells to determine concomitantly concentration, composition and conductivity solution. 1-cell body measuring 2,3-fittings, 4,5-optical short fibers, 11,12- electrodes, c-channel flow.

with fixed diffraction grating and diode-array detector. Also in cell body 1, and at the same level of the wall cylindrical flow channel c, two electrodes 11,12, foil type of platinum, are integrated, designed for measuring with an electronic conductivity meter the conductivity measurements of researched solution. Data acquisition and processing were performed using a computer system supported by specialized software.

4. Conclusion

Portable instrumental means of analysis presented in the paper are a part of a new concept for automatic spectrophotometric analysis in situ offering the possibility of absorption or fluorescence analysis of water in the visible spectral range. By using modular optoelectronic structures such as those described turbid water analysis is possible, working both with chemical kits for single use as well as working with large volumes of reagents without kits using. Water productivity analysis is very high, an analysis is summarized in a suction and a discharge of water carried with a dosing syringe in a cylindrical flow channel where spectrophotometric analysis occurs, the outcome of concentration measuring of water analyzed species being an average of hundreds determinations made during the water flow. Field equipments presented have a high universality, allowing a high productivity of analysis, operation and maintenance are easy and lower acquisition and operating costs than current equipments used for water analysis in field.

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THE STUDY OF TOXIC EFFECTS OF WASTEWATERS DISCHARGED FROM THE VILNIUS TREATMENT PLANT ON FISH

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Abstract. The aim of this study was to assess the toxicity of wastewaters discharged from Vilnius treatment plant (VTP) using rainbow trout, at different stages of development, and evaluating alterations in fish biological parameters. The results of the present study demonstrated that untreated wastewaters (UTWW) could induce significant adverse effects in developing fish (the increase in mortality of larvae and juveniles of rainbow trout, reduced gill ventilation frequency, heart rate, relative body mass increase of larvae). Treated wastewaters (TWW) also caused negative alterations (reduced growth of larvae, decreased immunotoxicity responses in juveniles) of rainbow trout. Generalizating of our results, it should be recognized that treated wastewaters of VTP still are toxic to fish at sensitive stage of development (larvae, juveniles). The toxicity tests demonstrated the need of applying new treatment technologies for reducing the negative impact of effluents on natural water receivers.

Keywords: wastewaters, toxicity, embryos, larvae, juveniles

1. Introduction

Discharges from the industrial and municipal wastewaters treatment plants, receiving waters, and storm waters all contain unknown, or partially known, mixtures of chemicals: of natural and synthetic xenobiotics, household and

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agricultural chemicals, pharmaceuticals, hormones, and other compounds, many of which remain unidentified (Liney et al. 2006).

The toxicity of municipal effluents is dependent upon a variety of factors including the size and extent of industrial and urban development; the type and efficiency of the treatment and disinfection processes; and the physical, chemical and biological characteristics of the receiving waters (Chambers at al. 1997).

Harmful effluents discharged into the environment have the potential to reach water bodies and disturb aquatic ecosystems (Oliveira-Martins et al. 2009). Moreover, wildlife species in natural waters are rarely exposed to single chemicals, they mainly treated with complex, fluctuating mixtures of contaminants. Mixtures of contaminants may act in various ways and that may induce combination effects via the same or different mechanisms (Rajapakse et al. 2002; Silva et al. 2002; Sumpter 2003; Thorpe et al. 2001, 2003).

The freshwater organisms particularly fish are very sensitive to various pollutants, that generally manifested in survival, reproduction or growth due to physiological alterations occurred in the animal (Pathan et al. 2009).

Acute toxicity tests had been published in a review on the toxicity of effluents 43 (Methods for Measuring… 2002; Andreottola et al. 2008). These tests encompass the assessment of the effect of human activities on animals and they have wide applicability in evaluating the toxicities of mixture of pollutants in fish and other species of aquatic organisms. The parameters of short-term (toxicity) tests are the most common measures of toxicity (Sitre et al. 2009; Pathan et al. 2009). Whereas for evaluating the long-term effluent exposure on fish organism integrated health effects (reproductive, endocrine, immune, genotoxic, nephrotoxic) are measured (Liney et al. 2006).

The physical, chemical and biological components of the environment play an important role in manifestation of biological response to pollutants. The toxicity) of particular pollutants depended upon many factors such as animal sensitivity, weight, developmental stages, period of exposure and temperature, pH, hardness of water and dissolved content of the chemicals (Tišler and Zagorč-Končan 1997; Sisman et al. 2008; Pathan et al. 2009; Vosylienė et al. 2009).

In addition to dilution, factors such as hardness, pH, temperature, and organic matter in the receiving environment can affect the bioavailability and, thus, the toxicity of organic and inorganic chemicals (Chambers at al. 1997).

According to Pathan et al. (2009) the importance of potential damage to aquatic ecology by effluents had been advocated and demonstrated, informing through various toxicity tests used in the management of water pollution.

The aim of this study was to assess the toxicity of wastewaters effluents discharged from Vilnius treatment plant using rainbow trout, at different stages of development (embryos, larvae, juveniles), and evaluating alterations in fish biological parameters.

2. Material and Methods

Experimental treatment: Sampling of untreated wastewaters (UTWW) and treated wastewaters (TWW) was performed at the Vilnius treatment plant (VTP) in April–May 2008. Exposure of fish for the toxicity studies was performed at the Laboratory of Ecology and Physiology of Hydrobionts (Nature Research Center). Rainbow trout (Oncorhynchus mykiss) eggs and juveniles were obtained from the Žeimena hatchery (Lithuania). The toxicity tests were undertaken under semi-static conditions. Deep well water of high quality was used for storing control embryos, larvae, and juveniles. Embryos were incubated in a cold and dark room at 10 ± 0.5°C. The average hardness of water was approximately 250 mg/l as $CaCO_3$, dissolved oxygen concentration and pH were not less than 7 mg/l and 7.6–7.8, respectively. Control water, UTWW and TWW in aquaria were renewed on alternant days. During these studies, juveniles were fed with commercial DANA FEED fish food ad lib.

UTWW, TWW toxicity: Long-term 12 days (prior to hatching) toxicity tests were conducted with embryos, 24 days – with larvae (including hatching period), 12 days – with juveniles. The effect of diluted UTWW (12.5%), undiluted TWW (100%) on the mortality of embryos and larvae (N = 100), and physiological parameters, e.g., heart rate (HR, counts/min), gill ventilation frequency (GVF, counts/min), and relative body mass increase (%) of larvae (N = 10 in a group) were recorded. Studies with embryos and larvae were performed in three replications. Mortality observations were undertaken at 24 h intervals.

Long-term effect of diluted UTWW (12.5%), undiluted TWW (100%) on the mortality, and physiological parameters, e.g., gill ventilation frequency (GVF, counts/min) of juveniles (N = 10 in a group) were recorded. Blood was sampled from 10 fish. Erythrocytes (RBC, 106 × mm^3), haemoglobin concentration (Hb, g/l), haematocrit level (Hct, l/l), leukocyte counts (WBC, 103 × mm^3) were determined using recognized methods (Svobodova and Vykusova 1991). Giemsa – May Grünwald – stained blood smears were viewed under 12 × 100 magnification, in order to determine leukograms. For leukograms, 100 leukocytes were counted and following forms were distinguished: small and large (immature) lymphocytes, and four stages of neutrophils.

Statistical analysis: The reliability of the data was evaluated using the Student's t-test at $P \leq 0.01$, $P \leq 0.05$. Data significance was determined using the programme GraphPAD InStat (USA).

3. Results and Discussion

UTWW toxicity: Mortality of the embryos exposed to diluted UTWW (12.5%) in study during the 12 days did not significantly differ from the mortality of controls. In contrast, larval mortality significantly increased during the 24 days. No mortality of juveniles was found during the 12 days at 12.5% concentration of UTWW (Table 1).

TABLE 1. Effect of UTWW and TWW on the mortality of embryos, larvae (N = 100), and juveniles (N = 10) (M ± SD).

VTP wastewaters	Mortality, %		
	Embryos (12-day exposure)	Larvae (24-day exposure)	Juveniles (12-day exposure)
UTWW (12.5%)	10.3 ± 2.4	35.7 ± 2.2*	0
TWW (100%)	7.7 ± 2.8	15.2 ± 3.4	0
Control	7.3 ± 2.6	12.9 ± 2.8	0

* - Significant differences from control (P ≤ 0.05)

The gill ventilation frequency (GVF) of larvae exposed to 12.5% concentration of UTWW was significantly lowered as compared to the controls. No alterations in HR of larvae exposed to 12.5% concentration of UTWW were observed. After 12 days of exposure respiratory disorders (GVF) were observed in juveniles exposed to 12.5% concentration of UTWW (Table 2).

TABLE 2. Effect of UTWW and TWW on the HR and GVF of larvae (N = 10), and GVF of juveniles (N = 10) (M ± SD).

VTP wastewaters	HR, counts/min	GVF, counts/min	
	Larvae (24-day exposure)	Larvae (24-day exposure)	Juveniles (12-day exposure)
UTWW (12.5%)	116.9 ± 14.3	109.7 ± 10.0*	85.5 ± 2.1*
TWW (100%)	116.0 ± 11.8	136.6 ± 11.4	94.4 ± 2.0
Control	115.9 ± 6.8	125.1 ± 16.4	96.3 ± 2.1

* - Significant differences from control (P ≤ 0.05)

The growth of larvae treated with UTWW was lower as compared to controls. The estimated relative body mass increase (%) of treated larvae with 12.5% of UTWW significantly decreased (Table 3).

TABLE 3. Effect of UTWW and TWW on relative body mass increase of larvae (%) (N = 10) at the end of the test (M ± SD).

VTP wastewaters	Total body mass, mg (N = 10)		Relative body mass increase, %
	At the start of exposure	At the end of exposure	
UTWW (12.5%)	629 ± 3.8	723 ± 4.2	15 ± 3.4*
TWW (100%)	612 ± 3.6	770 ± 4.6	26 ± 2.2*
Control	634 ± 2.4	856 ± 3.4	35 ± 2.8

* - Significant differences from control ($P \leq 0.05$)

TWW toxicity. No mortality of embryos, larvae, and juveniles after long-term exposure to TWW was detected (Table 1). No significantly alterations in GVF and HR of larvae after exposure to TWW were observed (Table 2). No alterations in respiratory responses were determined in juveniles treated with TWW after a long-term (12 days) exposure (Table 2).

Meanwhile, the estimated relative body mass increase of treated with TWW larvae was significantly reduced (TWW – 26%, control – 35%) at the end of the tests (Table 3).

TWW induced significant alterations in selected blood parameters: the level of haematocrit, leukocyte count, and percentage of neutrophyles significantly decreased in effluent-exposed juveniles. Hct level reduced 26% and leukocyte count – 22.5% in treated fish, respectively. Neutrophyle percentage decreased two times, while share of large (immature) lymphocytes increased (Table 4).

TABLE 4. The changes in haematological parameters of juveniles after 12 days exposure to TWW.

VTP wastewaters	Er, 106 × mm^3	Hb, g/l	Hct,l/l	Leu, 103 × mm^3	Leukogramm, %		
					Lymph.	Large lymph.	Neutr.
TWW (100%) (N = 11)	0.98 ± 0.01	85.3 ± 4.0	0.40 ± 0.01*	14.5 ± 1.5*	187.1 ± 0.9	6.3 ± 1.2*	6.1 ± 1.4*
Control (N = 10)	0.98 ± 0.03	91.6 ± 3.7	0.54 ±0.03	18.7 ± 1.5	184.6 ± 2.5	3.1 ± 0.5	12.6 ± 2.2

Notes. Er – erythrocytes, Hb – haemoglobin, Hct – haematocrit, Leu – leukocytes, Large (immature) lymphocytes, Neutrophyles – all neutrophyle forms. * - Significant differences from control ($P \leq 0.05$)

The abnormalities of erythrocytes were observed, which included vacuolisation of cytoplasm, irregular cell shape, and higher percentage of old, and removal forms of erythrocytes (Figure 1).

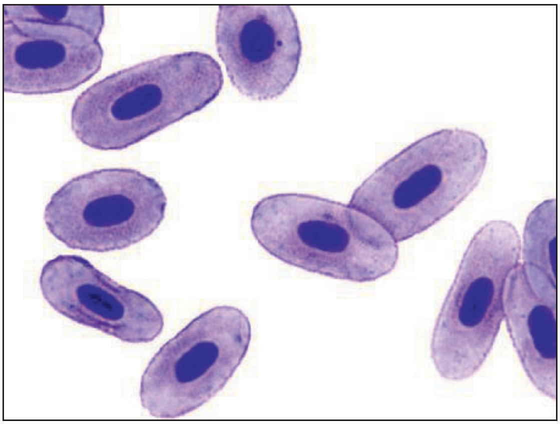

Figure 1. The effect of treated wastewater on erythrocytes forms of juvenile's blood.

Atypical lymphocytes were noticed in the blood smears of juveniles exposed to treated wastewater. Atypical lymphocytes were characterized by very intensely staining cytoplasm (deep basophilic colour), and enlarged or irregular-shaped nucleus (Figure 2).

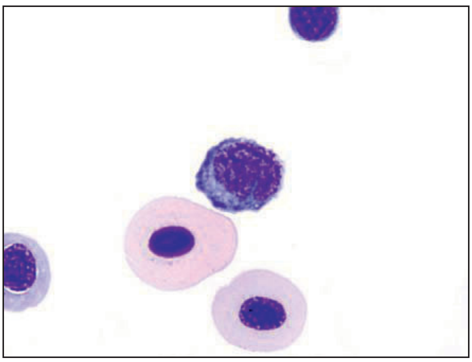

Figure 2. The effect of treated wastewater on lymphocytes of juvenile's blood.

Our tests performed under experimental conditions revealed that UTWW (12.5%) induced remarkable deleterious changes in various systems of the developing fish organism: the increase in mortality of larvae, reduced gill ventilation frequency (larvae and juveniles), heart rate, and relative body mass increase of larvae. The investigations of mortality of fish at different stages of development showed differences in toxicity of UTWW to fish: treated larval mortality was prolonged, whereas juveniles at the highest concentrations of UTWW died within 96 h (Vosylienė et al. 2010). These data confirmed that larvae were more sensitive to the negative impact of the pollutants (e.g., heavy metals, oil products) as compared to embryos (Vosylienė et al. 2003; Kazlauskienė et al. 2008); whereas, the acute toxic effect of UTWW on larvae and juveniles did not differ significantly (Vosylienė et al. 2010). Alterations in biological parameters of larvae and juveniles revealed the differences in toxic effects of UTWW on fish: survival of larvae mostly depended on the duration of exposure (Vosylienė et al. 2010).

Biotests with fish at different stages of development demonstrated toxicity of TWW. TWW caused negative alterations – reduced growth of larvae, decreased immunotoxicity of juveniles. The study of Kakuta (1997) showed that sewage treatment plant effluent can lead to potentially adverse effects on selected immune reactions and suppress the immune response in goldfish (Carassius auratus). Previous studies by Baršienė et al. (2009) demonstrated that treated effluents from Vilnius wastewater treatment plant caused significant increase in blood micronuclei. According to Liney et al. (2006) wastewater treatment work effluents (and the chemicals therein) have a multiplicity of biological effects and can be genotoxic and immunotoxic and/or can cause endocrine disruption in fish.

Meanwhile chemical analysis of UTWW and TWW did not indicate high amounts of any studied contaminant (Table 5). Concentrations of main xenobiotics varied in wide intervals in soluble and insoluble phases of wastewater. Percentage distribution between soluble and insoluble phases showed that from 60% to 96% of investigated pollutants were found in insoluble phase (Vosylienė et al. 2010).

TABLE 5. The average concentrations of some metals and xenobiotics in UTWW and TWW (Vosylienė et al. 2010).

Xenobiotics	UTWW Insoluble phase		TWW Insoluble phase	
	Average	SD	Average	SD
SS, mg/l	610.0	410.0	23.00	11.00
Cd, μg/l	1.10	0.52	0.38	0.24
Cu, μg/l	24.5	7.80	4.7	2.3
Pb, μg/l	12.7	10.4	3.9	2.0
Zn, μg/l	188.9	162.9	29.9	22.1
B(a)P, μg/l	0.080	0.041	0.017	0.005
Oil products, mg/l	0.74	0.25	0.15	0.08

Concentrations of petroleum hydrocarbons (C14–C28), benzo(a)pyrene, heavy metals (Pb, Cd, Zn, Cu, Hg) in treated wastewaters corresponded to their criteria for effluents discharged into receiving waters (Report on dangerous substances

2007). However, heavy metals in mixture even in low concentrations might have more-than-additive toxic influence on fish, and their toxicity could be revealed only after a long-term treatment (Kazlauskienė and Burba 1997). Whereas, wastewaters from Vilnius city can contain various chemicals at low concentrations, which can enter surface waters and induce negative effects in aquatic organisms. It should be noted, that according to the Report (Report on dangerous substances 2007), wastewaters of Vilnius city contain low concentrations of organotin compounds, phtalates, and organic chlorinated compounds, which were not analysed in this study.

The aim of the wastewater treatment always was focused to protect the environment from the adverse effects of wastewater discharges (Kreuzinger 2008), and new treatment technologies are developing for reducing of their impact on aquatic biota. However, a number of different kinds of xenobiotics can be found in effluents discharging into water receivers (Hollender et al. 2008), which, in turn, can negatively affect the fish. It should be noted that fish are especially sensitive and vulnerable to adverse environmental affects at early stages of development.

Generalizating of our results, it should be recognized that treated wastewaters of Vilnius treatment plant still are toxic to fish at sensitive stage of development (larvae, juveniles). The toxicity tests demonstrated the need of applying new treatment technologies for reducing the negative impact of effluents on natural water receivers.

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THE IMPACT OF IGNALINA NUCLEAR POWER PLANT WASTE WATER ON LAKE DRŪKŠIAI BEFORE THE DECOMMISSIONING OF THE PLANT (2007–2009)

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Abstract. Ignalina NPP (INPP) is located at Lake Drūkšiai utilized as cooler. Like Chernobyl NPP, INPP was equipped by RBMK–1500 type reactors. One unit was decommissioned in 2005, the other in 2009. The aim of this study was to evaluate activity concentration of radionuclide's in bottom sediments and macrophytes from the waste water (WW) channels of the INPP as well as assess the phytotoxicity of water and bottom sediments of the WW channels and Lake Drūkšiai zones directly impacted by these WW. The significant decrease of activity concentration of radionuclide's in bottom sediments of WW channels and Lake Drūkšiai after the Unit One decommissioning was determined. Phytotoxicity of water and bottom sediments of WW channels and Lake Drūkšiai also fluctuated in rather wide limits during 2007–2009. After the INPP decommissioning, chemical and radioactive pollution of the lake will persist during a long period of INPP dismantling works, consequently, the investigation of the radioecological and ecotoxicological state of the lake will be necessary.

Keywords: radionuclide, macrophytes, bottom sediments, waste water

1. Introduction

Ignalina Nuclear Power Plant (INPP) is located near the Lithuanian border with Belarus and Latvia. Like Chernobyl NPP, INPP was equipped by RBMK–1500 type reactors, i.e. graphite moderated, channel-type, boiling water nuclear reactors

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(Sarauskiene 2002). Unit 1 was put into operation in 1984 and Unit 2 – in 1987. Unit 1 and Unit 2 were closed on 31 December, 2005 and 2009, respectively. The cooling pond of INPP – Lake Drūkšiai is the largest lake of Lithuania.

Due to abiotic and biotic environmental factors, radionuclide's, which are discharged into the cooling pond together with NPP waste water s, are promptly (in 2–4 days) diluted and distributed among the main components of hydro ecosystem: water, bottom sediments and plants (Marčiulionienė 1998).

Water is the least informative component for the assessment of hydro-ecosystem's pollution with radionuclide's, because radionuclide's is quickly diluted and their activity concentrations in water significantly decrease (Marčiulionienė et al. 2001). Bottom sediments intensively accumulate radionuclide's that occur in the hydroecosystem. However, radionuclide's accumulation in bottom sediments depends upon their sedimentation rate, composition, the amount of mineral and organic matters as well as other physical chemical properties. Only those bottom sediments, which contain a large amount of organic matters, correctly represents a long–term radioecological state of the hydroecosystem. Such bottom sediments may become an environment for radionuclide deposition. Aquatic plants make up a large biomass and intensively concentrate radionuclide's occurring in the environment in micro amounts by assimilating them both from water and bottom sediments. Therefore, to assess the radioecological state of a hydroecosystem, the plants (bioindicators) are used. Radionuclide activity concentrations in bioindicators are integrated in time (a month, a year or even longer period) as well as in space, whereas in the environment they demonstrate fast alteration due to environmental factors. Radionuclide activity concentrations in bioindicators can be established comparatively accurately, even in such cases, when their activity concentrations in other environmental components are under the minimal detectable level (Marčiulionienė et al. 2001).

The aims of this work is to investigate INPP industrial storm water and process water discharge channel (ISW-1,2) and cooling water discharge channel (CW) pollution with 137Cs, 60Co, 54Mn and 134Cs and to asses the toxicity of waste water of these discharge channels as well as water and bottom sediments in the inlet zones (4th and 7th monitoring stations) before the decommissioning of the NPP; to evaluate the possibilities of contamination of Lake Drūkšiai with INPP channel wastes by chemical pollutants and radionuclide's (137Cs, 60Co, 54Mn, 134Cs).

2. Material and Methods

Samples of macrophytes, water and bottom sediments were collected in the INPP industrial storm water and process water discharge channel (ISW-1,2), in the cooling water discharge channel (CW), and in the route of the waste water

(WW) of the ISW-1,2 and CW into Lake Drūkšiai (4th and 7th monitoring stations) in 1988–2004 and 2007–2009 (Figure 1). Radionuclide activity concentration in the macrophytes and bottom sediments was estimated by the γ-spectroscopy methods (Gudelis et al. 2000). The values of radionuclide activity concentrations in the study are presented on the dry weight basis (Marčiulionienė et al. 2001). Toxicity and genotoxicity tests of the water and bottom sediments were carried out based on the biological tests widely used in the world (EPA 1996): Lepidium sativum L. (garden-cress) (Magone 1989; Montvydienė and Marčiulionienė 2004). The level of water and bottom sediments toxicity to Lepidium sativum was assessed following the method suggested by Wang (1992).

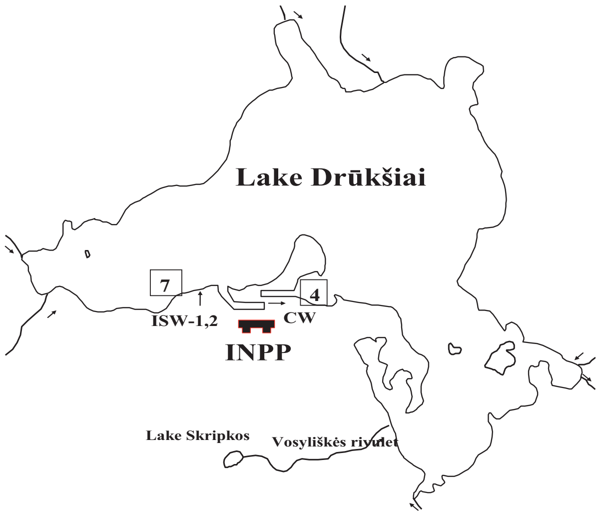


Figure 1. Scheme of the discharge channels of the INPP and monitoring stations of Lake Drūkšiai. Monitoring stations of Lake Drūkšiai: St. 4 – at the discharge zone of cooling water discharge channel; St. 7 – at the discharge zone of waste water of industrial storm water and process water discharge channel; CW – cooling water channel; ISW-1,2 – channel of industrial-storm water and process water discharge.

Statistical analysis was performed using Statgraphics plus for Windows Version 2.1. Statistical Graphics Corp. (USA) or GraphPAD InStat (USA). The data were expressed as mean ± standard error of the mean that did not exceed 15%. Differences between measured characteristics were tested by Student's t-test with $p \leq 0.001$ or $p < 0.05$.

3. Results and Discussion

The research data obtained before the INPP decommissioning (2007–2009) indicate that in 2007, in the ISW -1.2 channel, 137Cs, 60Co and 54Mn activity concentrations in macrophytes, reached correspondingly only up to 20, 34 and 2 Bq/kg (Table 1).

TABLE 1. Activity concentration (Bq/kg) of radionuclide's in macrophytes, and bottom sediments of Ignalina NPP industrial storm water discharge channel (ISW-1,2) (2007–2009).

Nuclide	Ceratophyllum demersum			Myriophyllum spicatum		Bottom sediments		
	2007	2008	2009	2008	2009	2007	2008	2009
137Cs	20 ± 2 **	392 ± 47** 406 ± 54***	22 ± 1.2 ***	166 ± 33* 271 ± 20***	18 ± 1.6* 13 ± 1.1**	<0.3*	4 ± 0.7** 11 ± 2***	<mdl* 0.4 ± 0.3** 1.3 ± 0.4 ***
60Co	34 ± 2 **	754 ± 51** 634 ± 50***	63 ± 3.0 ***	2185 ± 108* 463 ± 23***	46 ± 1.9* 37 ± 1.6**	<mdl*	1 ± 0.4** 5 ± 1***	<mdl* 3 ± 0.4** <mdl ***
54Mn	2 ± 0.6 **	2203 ± 147** 1774 ± 129 ***	75 ± 3.0 ***	6428 ± 372* 151 ± 88***	44 ± 2.3* 46 ± 2.1**	<mdl*	4 ± 0.7** 11 ± 2***	<md l* 0.5 ± 0.3** <mdl ***
134Cs	<mdl **	208 ± 27** 250 ± 30***	3 ± 0.2 ***	120 ± 4* 154 ± 81***	3 ± 0.4* 2 ± 0.2**	<mdl*	2 ± 0.3** 5 ± 0.8***	<md* <mdl ** <mdl ***

<mdl – minimal detectable level; INPP ISW-1,2 channel: outset – *, middle – **, end – ***

However, in 2008, the radionuclide activity concentrations in macrophytes considerably increased and came even up to 406, 2,185 and 6,428 Bq/kg, respectively. 134Cs was also ascertained. Its activity concentration in macrophytes reached 250 Bq/kg. Presumably, high radionuclide activity concentrations in this channel were induced due to scheduled reconstruction of INPP. It is known that the suspension of NPP operation increases the possibility of radionuclide discharge into the environment. It should be indicated that the highest 60Co and 54Mn activity concentrations in macrophytes were established at the outset of the channel, however, at its end, they markedly decreased: 60Co by 5 times, 54Mn by 43 times. 137Cs and 134Cs activity concentrations in plants differed insignificantly both at the outset of the channel and at its end. Such differences in radionuclide accumulation in macrophytes can be explained by varying chemical and physical chemical characteristics of these radionuclide's, upon which not only radionuclide accumulation in macrophytes, but also their dispersion in hydroecosystem depends. Although the investigated radionuclide activity concentrations in macrophytes sharply decreased in 2009 in comparison with 2008, however, they were higher than those in 2007 (Table 1).

The comparison of radionuclide activity concentrations in the macrophytes and bottom sediments of this channel clearly showed that in bottom sediments they were distinctly lower than in macrophytes (Table 1). Although in 2008, 137Cs, 60Co, 54Mn and 134Cs activity concentrations in macrophytes were extremely high, however, in bottom sediments they reached only up to 11, 5, 11 and 5 Bq/kg, whereas in 2007 and 2009 they were still lower.

It was ascertained that in 2007–2009, the investigated radionuclide activity concentrations in macrophytes and bottom sediments of Lake Drūkšiai discharge zone of waste water of ISW-1,2 channel were comparatively low and differed insignificantly (Table 2). In bottom sediments, radionuclide activity concentrations were lower than in macrophytes or they were similar. The comparison of radionuclide activity concentrations in macrophytes of both this zone of the lake and ISW-1,2 channel revealed that in 2008, in macrophytes of this zone, 137Cs activity concentration was 24 times, 60Co – 17 times, 54Mn – 24 times lower than that in macrophytes of ISW-1,2 channel. However, in 2009, in bottom sediments, radionuclide activity concentration in this zone of the lake was higher (137Cs – 24 times, 60Co – 6 times, 54Mn – 2 times) than in ISW-1,2 channel, because in bottom sediments, which consisted of sand, the amount of organic matters was significantly smaller than in Lake Drūkšiai discharge zone of waste water of ISW-1,2 channel, therefore, the concentration of radionuclide’s in bottom sediments of this zone was higher. Besides, high concentrations of radionuclide’s (accumulated in 2008) with already dead macrophytes from ISW–1,2 channel could occur in bottom sediments of this zone of Lake Drūkšiai.

TABLE 2. Activity concentration (Bq/kg) of radionuclide’s in macrophytes and bottom sediments of Lake Drūkšiai (St. 7 - discharge zone of WW of industrial storm water channel) (2007–2009).

Species	137Cs			60Co			54Mn		
	2007	2008	2009	2007	2008	2009	2007	2008	2009
Myriophyllum spicatum	4 ± 0.8	–	4 ± 0.4	<mdl	–	2 ± 0.3	< mdl	–	2 ± 0.3
Ceratophyllum demersum	17 ± 1.5	17 ± 7.2	–	42 ± 2.3	38 ± 7.5	–	3 ± 0.8	67 ± 11.4	–
Potamogeton sp.	–	4 ± 0.7	2 ± 0.3	–	3.0 ± 0.7	<mdl	–	8 ± 1.0	0.5 ± 0.2
Bottom sediments	7 ± 0.4	19 ± 2	31 ± 3.1	0.3 ± 0.1	<mdl	5 ± 1.2	<mdl	<mdl	2 ± 1.1

mdl – minimal detectable level

The investigated radionuclide activity concentrations in macrophytes of both INPP CW channel and Lake Drūkšiai discharge zone of waste water of CW channel were comparatively low and differed insignificantly (Table 3). However, the studied radionuclide activity concentrations, in particular those of 137Cs, in bottom sediments of this zone of the lake were significantly higher than in bottom sediments of CW channel. The obtained differences in radionuclide accumulation in bottom sediments might be conditioned by diverse composition of bottom sediments, different physical chemical characteristics of radionuclide's, and strong water current in this channel.

TABLE 3. Activity concentration (Bq/kg) of radionuclide's in macrophytes and bottom sediments of Ignalina NPP cooling water discharge channel (CW) and Lake Drūkšiai (St. 4 - discharge zone of WW of CW channel) (2007–2009).

Species	137Cs			60Co			54Mn		
	2007	2008	2009	2007	2008	2009	2007	2008	2009
INPP CW channel									
Myriophyllum spicatum	4 ± 0.8	5.7 ± 2	4 ± 0.3	< mdl	< mdl	< mdl	< mdl	< mdl	< mdl
Cladophora	–	11 ± 3	–	–	4 ± 1.2	–	–	< mdl	–
Bottom sediments	1 ± 0.1	1 ± 0.3	2 ± 0.4	< mdl	< mdl	< mdl	< mdl	< mdl	< mdl

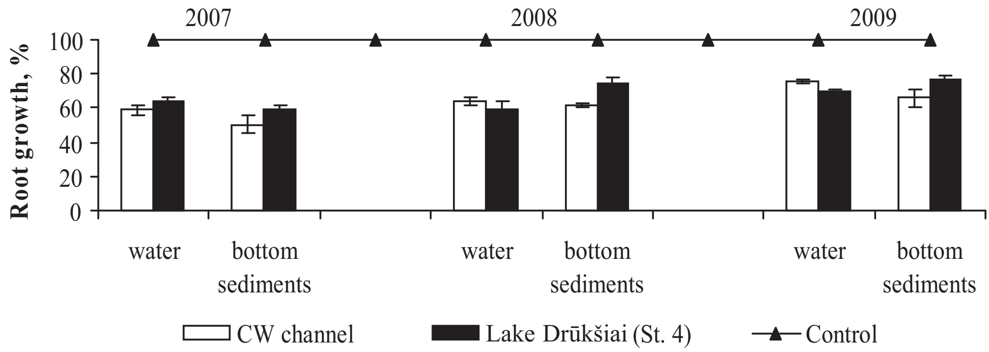
Species	137Cs			60Co			54Mn		
	2007	2008	2009	2007	2008	2009	2007	2008	2009
Lake Drūkšiai (St. 4 - discharge zone of WW of CW channel)									
Myriophyllum spicatum	–	6 ± 0.8	4 ± 1	–	2 ± 0.4	< mdl	–	3 ± 0.4	< mdl
Ceratophyllum demersum	7 ± 0.7	–	8 ± 1	22 ± 0.2	–	1 ± 0.4	< mdl	–	1 ± 0.3
Bottom sediments	145 ± 9	76 ± 4	78 ± 4	1 ± 0.1	6 ± 1	6 ± 1	< mdl	< mdl	< mdl

mdl – minimal detectable level

Basing on the obtained long-term research data, it was established that in the period of investigations, i.e. from 1988 to 2009, radionuclide activity concentrations, especially of 60Co and 54Mn, in macrophytes of Lake Drūkšiai discharge zone of waste water of ISW-1,2 channel were markedly lower than in macrophytes of ISW-1,2 channel (Marčiulionienė and Montvydienė 2009).

The discharge of radionuclide's from INPP to ISW-1,2 channel was higher than to CW channel, however, in some cases higher content of radionuclide's was dismissed with CW channel wastes than with the wastes of ISW-1,2 channel (Marčiulionienė et al. 2001). However, in most cases activity concentrations of radionuclide's released from these channels into Lake Drūkšiai in macrophytes varied insignificantly. The obtained data demonstrated that radionuclide dispersion from

INPP channels into Lake Drūkšiai varied. These differences were conditioned not only by chemical and physical chemical characteristics of radionuclide's as well as the composition of bottom sediments, but also by diverse environmental conditions in these channels. As far as water current in CW channel is very strong and there are few aquatic plants, radionuclide's were directly and fast dismissed from it into Lake Drūkšiai. In ISW-1,2 channel, radionuclide's were diluted and accumulated in macrophytes growing in it and in littoral helophytes, which make up a large biomass, particularly in the zone of inflow into the lake. The macrophytes growing in this channel performed the role of cleaning (phytoremediation) of the channel waste water by accumulating large content of radionuclide's. Therefore, the content of radionuclide's discharged from this channel into the lake was comparatively low.



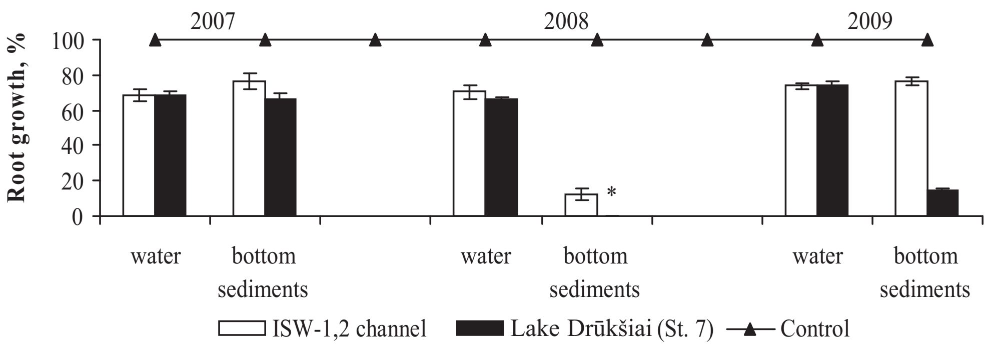


Figure 2. Toxic effect of water and bottom sediments from Ignalina NPP CW and ISW-1,2 chanels and Lake Drūkšiai (St. 4 – discharge zone of waste water of CW channel; St. 7 – discharge zone of waste water of ISW-1,2 channel) on Lepidium sativum root growth. * – root growth was inhibited.

The research data obtained in 2007–2009 show that the impact of INPP ISW-1,2 and CW channels discharge as well as the water of Lake Drūkšiai discharge zone of waste water of CW channel and bottom sediments upon the growth of Lepidium sativum roots was similar, except in 2008, when bottom sediments of both ISW-1,2 channel and Lake Drūkšiai discharge zone of waste water of ISW-1,2 channel were very toxic (Figure 2). Hence, we can maintain that in 2008, not only radioactive, but also chemical pollution in ISW-1, 2 channels increased, which contaminated Lake Drūkšiai, too. However, bottom sediments of Lake Drūkšiai discharge zone of waste water of ISW-1,2 channel were more toxic than those of ISW-1,2 channel. The long-term research data presented in Figure 3 also demonstrate that chemically polluted waste water is constantly discharged from ISW-1,2 and CW channels. Regression analysis of the data showed a tendency of increasing toxic impact of CW channel discharge water and bottom sediments as well as the water of ISW-1,2 channel discharge into Lake Drūkšiai zone and bottom sediments upon Lepidium sativum.

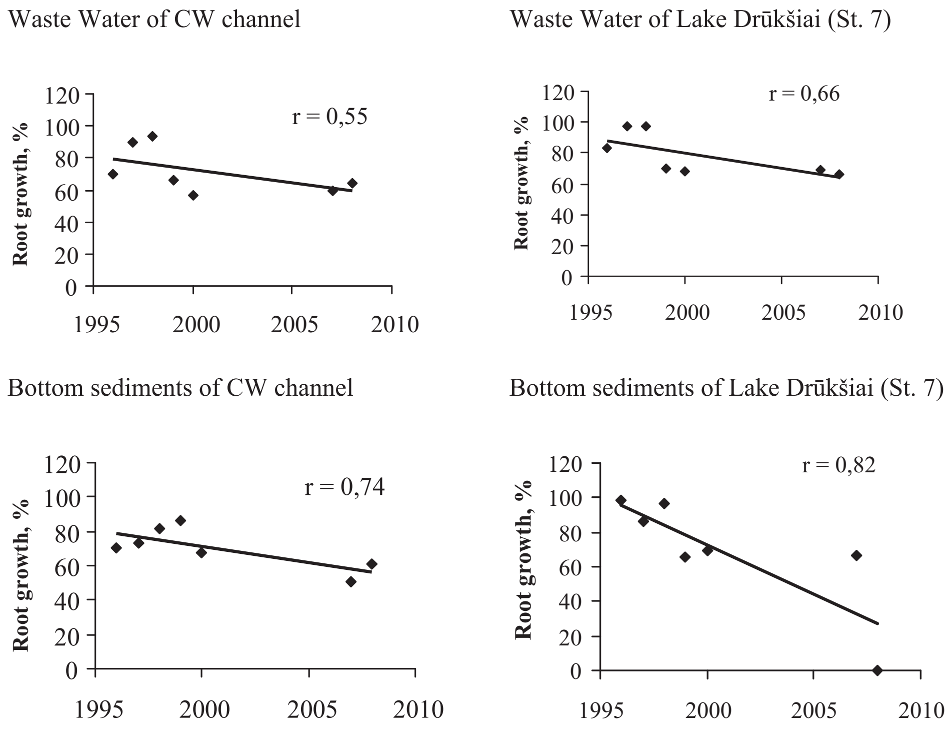


Figure 3. Changes in root growth of Lepidium sativum in water and bottom sediments of CW channel of Ignalina NPP and Lake Drūkšiai (St. 7 – discharge zone of waste water of ISW-1,2 channel) (1996–2009).

General analysis of the long-term research data (since 1988) and those obtained in discharge channels of the plant and Lake Drūkšiai before the decommissioning of INPP (2007–2009) enabled us to affirm that:

The content of radionuclide's discharged from INPP into ISW-1,2 channel was higher than that into CW channel, however, activity concentrations of 137Cs, 60Co and 54Mn dismissed from these channels into Lake Drūkšiai in macrophytes differed insignificantly, because in ISW-1,2 channel, self-cleaning of waste water (phytoremediation) from radionuclide's was taking place.

To assess the pollution of water body with radionuclide's, it is necessary to ascertain radionuclide activity concentration in macrophytes, because bottom sediments are not very good indicators of hydroecosystem's pollution with radionuclide's.

Macrophytes can be used not only for the assessment of radioecological state of a water body, but also for the phytoremediation of discharge water polluted with radionuclide's.

Waste water polluted not only with radionuclides, but also with chemical contaminants was constantly discharged from CW and ISW-1,2 channel of INPP into Lake Drūkšiai, which accumulated in bottom sediments. A tendency of increasing toxicity of INPP CW channel discharge and bottom sediments as well as the water of ISW-1,2 channel discharges into Lake Drūkšiai zone and especially bottom sediments was observed.

New ecological conditions will form in Lake Drūkšiai after the decommissioning of the Unit Two in 2009; the thermal pollution of the lake will particularly decrease. Chemical and radioactive pollution of the lake will persist during a long period of INPP dismantling works. However, in case of the changes in ecological conditions, hydrological and hydrochemical mode of Lake Drūkšiai, toxic substances that are present in bottom sediments would possibly penetrate into water again and having joined the biological circulation would accumulate in flora and fauna of the lake. Additionally, the construction of a new nuclear power plant after the decommissioning of INPP would be a great challenge for Lake Drūkšiai and the vicinities of the lake.

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PHYTOREMEDIATION OF WATERS AT AN URBAN STATION OF WATER PURIFICATION BY WATER HYACINTH WITH PREINDUCTION OF METALLOTHIONEINS

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Abstract. For maintenance of drinking sources and biodiversity actions on additional purification of urban rainfall runoff are required. Application of water hyacinth (Eichhornia crassipes) from the family of pontederia (Pontederiaceae) with increased level of metallothioneins is necessary as efficiency of wastewater phytoremediation increases. It has been shown, that the efficiency of extracting heavy metals from wastewater can be increased due to ionic preinduction of metallothioneins by means of ions Cd within the root system of plants (Eichhornia). The efficiency of this technique has been estimated in terms of the risk these heavy metals may present to the health of Moscow inhabitants.

Keywords: rainfall runoff, water hyacinth, phytoremediation, metallothioneins, health risk

1. Introduction

At present sewage disposal in the territory of Moscow is being realized via the network collector – open channel – collector. The total waste discharge amounts to 580 million m^3 a year. Three types of sewage treatment plants are used in

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municipal watershed areas: sediment ponds, chamber installations and shield barriers in the water area of Moscow river. These installations are intended for full-scale collecting of utility waste, partially suspended substances and oil products, however, they prove to be ineffective in case of heavy metals (HM).

Eichhornia crassipes or water hyacinth is among the plants of HM hyper-accumulators from the aquatic environment. This plant is widely used for tertiary treatment of waste phytoremediation water (Danilin, 2009). Actual prerequisites, however, suggest that the efficiency of HM extraction from waste-water can be improved thanks to preinduction (prestimulation) by protein synthesis of Cd ions – metallothioneins (MT) in the plant root system. Eichhornia crassipes tissues involve MT type 3 (phytochelatins) formed as a result of enzyme reactions with glutathione as well as MT, the synthesis of which is genetically controlled (Seregin, 2001). The feature of heavy metals is the presence of SH-groups which can fix heavy metal ions and inactivate free radicals (Danilin, 2004).

The paper investigates the ability of water hyacinth to extract HM ions (Zn, Cu, Pb) from water after preinduction of MT synthesis and estimates the efficiency of this technique from the viewpoint of HM health risk for Moscow population.

2. Materials and Methods

The efficiency of HM ions extraction as a result of Eichhornia crassipes cultivation has been studied in the SUE "Mosvodostok" sediment ponds (SP) ("Butovo" and "Bogatyrskoe-2") with the similar HM contamination level of wastewater ("Bogatyrskoe-2" was the reference sediment pond and "Butovo" – the experimental one).

To increase the content of proteins-MT, sprouts have been cultivated during 7 days in 10 l plastic vessels in distilled water added by nutrient solution and Cd ion concentration of 20 μm. Then the sprouts were transferred to the sediment pond and the purification efficiency was controlled. During vegetation in 30 days 10% of the grown mass (1-2 rosettes from $1m^2$) were taken and again held during 7 days in the above solutions with the subsequent return to the sediment pond.

Concentrations were chosen with the reference to data on the ability of Cd ions at the density of 10 and 20 μM to increase phytochelatin content. The content of MT was determined by a radioactive tracer method based on radioactive l09Cd displacement of metal ions chelated in MT. The signal-generated reagents are l09CdCl2 and CdCl2 in 0.01 M Tris-HCl-buffer, pH = 7.4 (the total Cd2+ concentration in a mixture is 2.0 μg/ml, radioactivity is 40.0 kBq/ml) (Van Hoof et al. 2001).

The content of Zn, Cu, Pb in all samples was assessed by atomic absorption spectroscopy (Varian Liberty AX Sequential ICP-AES plasma emission spectrometer) in the Radiochemistry and Analytical Chemistry Laboratory RIARAE RAAS (Obninsk).

The potential cancerogenic risk is calculated using the U.S. Environmental Protection Agency (US EPA) approach (Guidebook, 2004) and the linear model

$$CR = ADD \cdot SF,$$

where SF is the slope factor $(\text{mg/kg-day})^{-1}$, *ADD* is the average daily dose (mg/kg-day).

The average daily dose was calculated from:

$$ADD = \frac{C_w \cdot V \cdot EF \cdot ED}{BW \cdot AT \cdot 365},$$

where C_w is the substance content, mg/l; V is input rate (the average daily volume of portable water, l/day); *EF* is the impact frequency, days/year; *ED* is the impact duration, years; *BW* is the body mass, 70 kg; *AT* is the period of exposure averaging, years; 365 is the number of days in year.

The potential noncancerogenic risk is assessed from the calculated hazard quotient HQ.

$$HQ = \frac{ADD}{RfD},$$

where *ADD* is the average daily dose, mg/kg-day; *RfD* is the reference (safe) dose, mg/kg-day. The more the *HQ* value exceeds 1, the more hazardous may the analyzed exposure be.

In a combined heavy metal impact the risk of expected noncancerogenic effects is specified from the calculated hazard index HI:

$$HI = \sum_i HQ_i,$$

where HQ_i is the hazard quotient for some components in the mixture of affecting substances.

3. Results and Discussions

The analyzed post-purification by water hyacinth during 60 days gives evidence of the efficiency of tertiary treatment of sewage water by Eichhornia crassipes with preinduction of metallothioneines (Table 1).

TABLE 1. Zn, Pb, and Cu ion concentration, mg/l, in the sediment pond outlets after post-purification of rainfall runoff on the 1st and 60th day from Eichhornia crassipes bedding.

SP	Zn		Pb		Cu	
	1st day	60th day	1st day	60th day	1st day	60th day
"Bogatyrskoe-2" (control)	0.077	0.062	0.008	0.002	0.006	0.006
"Butovo"	0.089	0.021	0.009	<0.001	0.004	0.002

Data on the efficiency of MT synthesis preinduction in Eichhornia crassipes roots are presented in the Figure 1.

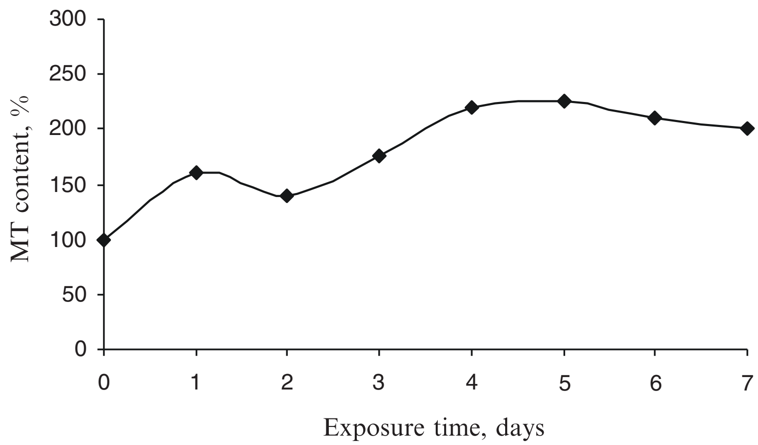

Figure 1. Changes in MT content in water hyacinth Eichhornia crassipes at different exposure time of Cd ions, percentage relative to the reference value.

The efficiency of Zn and Pb ion extraction has really increased by 25% and that of Cu ions – by 50% (Table 2).

TABLE 2. The efficiency factor of phytoextraction, percentage of Zn, Pb, and Cu ions from sewage water in its post-purification.

SP	Zn	Pb	Cu
"Bogatyrskoe-2" (control)	19.5	75	0
"Butovo"	76.4	100	50

It is unlikely that simply the impact of Cd ions on water hyacinth sprouts during 7 days has resulted in the increased efficiency of HM extraction. Zn is known to be one of the inductors of MT III type 3 (phytochelatins), and participation of Cu ions implies the synthesis of MT type 2 (Van Hoof et al. 2001). The observed enhancement effect of plant extraction properties is probably stipulated by the action of Zn and Cu ions continuously ingressed into the sediment pond with sewage water. Preliminary stimulation by Cd ions allowed the plants to accumulate only a certain quantity of MT and to avoid the toxic impact of Zn and Cu ions in the early stages of phytoremediation (during the first week) and to participate in the tertiary treatment of sewage effluents from the first days.

As the concentration range, within which post-purification has been carried out, is much lower than the maximum permissible concentration (MPC) for general-purpose and fishery-industrial waters and the industrial-resource standards have not been violated, the comparison of observed concentrations with MPC or their intercomparison is of a low value. Therefore the technique of health risk assessment when drinking water with a given HM content is used to analyze the efficiency of water purification (Guidebook 2004).

Table 3 presents calculations of the potential cancerogenic risk (CR) stipulated by the action of Pb ions.

TABLE 3. Changes in the risk of cancerogenic effects caused by Pb ions in the tertiary treatment of sewage water if it is used for public water supply take place on the 1st and 60th day from Eichhornia crassipes bedding.

SP	CR (Pb)	
	1st day	60th day
"Bogatyrskoe-2" (control)	$8{\cdot}10^{-7}$	$2{\cdot}10^{-7}$
"Butovo"	$9{\cdot}10^{-7}$	$1{\cdot}10^{-7}$

The analyzed calculated risk (Table 3) has stated that the life cancerogenic risk caused by HM water contamination is reduced by half as a result of water hyacinth treatment.

Calculating the risk, the authors assumed that runoff waters enter the potable water distribution. In actual practice water is certainly diluted by water of receiving reservoirs and HM content will be lowered, metal ions will be partly accumulated by aquatic organisms and deposited on silt. These processes are responsible for drinking water compliance at the level of SanPiN 2.1.4.1074-01, according to which the content of HM ions should not exceed 0.03 mg/l for Pb; 1 mg/l for Cu; 1 mg/l for Zn; these concentrations are much higher than those contained in waste runoff water. However, as calculations show, even these low concentrations may cause extra cases of cancer diseases (for example, in case with Pb ions), and the applied hydrobotanic method with MT preinduction in plants-hyperaccumulators becomes an effective means for reducing the potential cancerogenic risk caused by heavy metal ions.

So, the individual life risk of cancerogenic effects for all sources of heavy metal ingressed into Moscow water intake facilities is at the boundary of the accepted risk level recommended in WHO publications (10-6). Post-purification by water hyacinth, however, allows the accepted risk to be reached and the preliminary rise of MT level in plant roots makes the process of phytoremediation efficient twofold.

The assessed risk of noncancerogenic effects for the metals chosen is given in Table 4.

TABLE 4. Changes in the hazard quotient HQ as a result of sewage water post-purification on the 1st and 60th day from Eichhornia crassipes bedding.

SP	HQ					
	Zn		Pb		Cu	
	1st day	60th day	1st day	60th day	1st day	60th day
"Bogatyrskoe-2" (control)	0.007	0.006	2.8	0.7	0.004	0.004
"Butovo"	0.008	0.002	3.1	0.4	0.003	0.0015

The analyzed probability of noncancerogenic effects caused by Zn and Cu ions found in water for the proposed sources of risk does not give rise to concern because the hazard factors are well below 1, i.e. below the value that qualifies any accepted risk of noncancerogenic effects. The exception is a noncancerogenic risk stipulated by available Pb ions; however, the applied technology of sewage water post-purification by water hyacinth with MT pre-induction allowed the probability of noncancerogenic effects to be reduced below the accepted level.

Table 5 presents the risk of developing noncancerogenic effects in case of simultaneous ingestion intake of Pb, Zn and Cu ions. The obtained data clearly indicate that the realized post-purification by water hyacinth with the preliminary stimulation of MT synthesis in the root meristem allows the acceptance risk level to be reached (Table 5). The total HI < 1 for the sewage water under consideration, i.e. the risk of hazardous noncancerogenic exposure is negligible.

TABLE 5. The hazard index HI of a combined action of Pb, Zn and Cu ions in case of ingestion intake with tape water on the 1st and 60th day from Eichhornia crassipes bedding.

SP	HI	
	1st day	60th day
"Bogatyrskoe-2" (control)	2.80	0.71
"Butovo"	3.15	0.35

4. Conclusion

Assessed is the efficiency of Eichhornia crassipes application for storm sewage post-purification under megapolis conditions.

The technique of storm sewage post-purification by water hyacinth Eichhornia crassipes with the preliminary stimulation of MT synthesis by Cd ions is suggested and tested in the public treatment works system.

As a result of performed post-purification, the carcinogenic risk of diseases stipulated by heavy metals contained in water is reduced by half, the probability of noncancerogenic effects being below the permissible level (hazard index are below 1).

5. Acknowledgements

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ANOXIC GRANULATION IN USB REACTOR WITH ANAEROBIC GRANULATED SLUDGE AS AN INOCULUM

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Abstract. Anaerobic granulated biomass from high-rate anaerobic IC reactor was tested as a possible inoculum for anoxic granulation in post-denitrification USB reactor. The aim of the experiment was cultivate anoxic granules and to remove nitrates from wastewater after activated sludge process and secondary clarifier (20 mg l^{-1} NO_3-N; with external organic carbon methanol; COD methanol: NO_3-N = 6). Adaptation of anaerobic biomass to anoxic conditions and methanol lasted from 7 to 25 days. Anoxic granules with diameter of 3–5 mm and with excellent settling properties were cultivated by the anoxic granulation process. Maximum loadings of the USB reactor up to 22.4 kg COD m^{-3} d^{-1} and 3.2m^3 m^{-2} h^{-1} proved exceptional properties of this kind of biomass. Compact structure and clear difference between core and cover of the granules, with dominant filamentous bacteria Sphaerotilus natans on the surface of the granules were detected by microscopic observation of the granules.

Keywords: inoculum for anoxic granulation, granular sludge, post-denitrification in USB reactor, microscopic observation

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1. Introduction

This laboratory research was focused on the use of anaerobic granular sludge from IC reactor as an inoculum for anoxic granulation in denitrification USB reactor, which can be situated at WWTP as a process of tertiary post-treatment (after secondary clarifier) (Pagacova et al. 2009). The main advantages of granular sludge are excellent sedimentation properties and the resistence towards adverse conditions in composition of wastewater. As a result it is possible to keep extremely high concentrations of biomass in the reactor and to reach much higher mass loadings compared to reactors with flocculate or fixed film biomass (Pagacova et al. 2010).

Anaerobic IC reactor is one of the high-loaded systems with granular biomass, with typical loadings in the range of 15–30 kg COD m^{-3} d^{-1}. Characteristic sign is a very high concentration of anaerobic granular biomass, which is kept at high ascending rates of both wastewater and biogas and affords opportunity to reach high volumetric loadings. (Grant et al. 2002)

Anoxic Upflow Sludge Bed (USB) reactor (Figure 1) is the reactor with a sludge bed containing anoxic granulated biomass and internal three phase separator of biomass and biogas (it is an analogy to anaerobic UASB reactor). (Lettinga et al. 1980). The principles of anoxic granulation which is the main condition for successful denitrification in the USB were described in previous papers (Pagacova et al. 2009; Jonatová et al. 2010).

2. Methods and Objects

The main parameters of laboratory USB reactor (Figure 1) were: $V_{total} = 3.22$ l, $S = 7.85E\text{-}03$ m^2 and the temperature during the whole experiment was in the range 18–20°C.

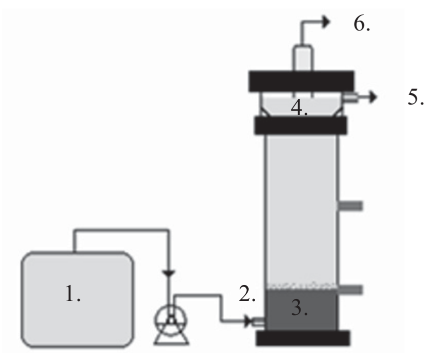

Figure 1. The scheme of laboratory USB reactor. (1) tank for synthetic laboratory wastewater (2) inflow of wastewater (3) sludge bed (4) G-L-S separator (5) effluent (6) outflow of biogas ($N_2 + CO_2$).

The synthetic wastewater contained nitrates ($NaNO_3$/20 mg NO_3-N l^{-1}), phosphorous (KH_2PO_4/1 mg P l^{-1}) and the source of organic carbon was methanol (COD: NO_3-N = 6).

Analytical assessments were carried out according to Standard Methods (Horáková et al. 2007). Microscopical observations were realized with microscope type NIKON ECLIPSE E600.

3. Results and Discussion

Presented experiments and results are a part of long-term research of slow and accelerated anoxic granulation in USB reactor, where flocculate oxic activated sludge and granulated anaerobic biomass were used as an inoculum (Pagacova et al. 2009; Pagacova et al. 2010).

In this paper two granulated anaerobic inocula from IC reactor are compared. Both of tested inocula were from anaerobic reactors with ORP less than −300 mV (what can be a disadvantage of this inocula because of its problematic adaptation to anoxic conditions and denitrification with methanol). The advantage of these inocula are their excellent sedimentation properties. In addition, they are not just an inoculum, i.e. source of microorganism, but they are also a slowly biodegradable carrier for new denitrification biomass.

Starting volumetric loading (B_v) was 4 kg COD m^{-3} d^{-1} in both experiments (this value is a safe starting value for the process of anoxic granulation; it was verified in our previous research (Pagacova et al. 2009). Bv was gradually increased during the whole granulation experiment; each increase was realized when the effluent concentration of NO_3-N + NO_2-N was less than 3 mg l^{-1} (this value was our internal requirement in all the experiments with anoxic granulation). The experiment was finished in a moment, when the mass and hydraulic loadings were so high that the volume of sludge bed in the USB reached the bottom of G-L-S separator.

3.1. ANAEROBIC GRANULAR SLUDGE FROM IC REACTOR IN PAPER MILL AS AN INOCULUM FOR ANOXIC GRANULATION

With this kind of inoculum the adaptation period was significantly longer. Anaerobic biomass was adapted to denitrification with methanol after 25 days. Just after this period the concentration of NO_3-N + NO_2-N in outflow was less than 3 mg l^{-1} (during the first 5 days this concentration was in the range 12–15 mg l^{-1}, from the 5th till the 25th day were the concentrations of NO_3-N less than 5 mg l^{-1}, but the concentration of NO_2-N was still between 5 and 15 mg l^{-1}).

During the anoxic granulation experiment B_v was increased from starting value 4 to $B_{v,max}$ = 19.7 kg m^{-3} d^{-1}. γ_{max} value was 2.8 m^3 m^{-2} h^{-1} and θ_{min} was 9 min.

In this case the anoxic granulation experiment was divided into three parts (with uptake of excess sludge as a new variant of the process). The additional aim was the complete exchange of the sludge bed and the measurement of parameters of a new, purely anoxic biomass without any residues of anaerobic inoculum (Figures 2 and 3).

Part 1. (till the 48th day) – The aim was to finish the anoxic granulation process and to reach the maximum loading in USB. A mixture of anoxic-anaerobic and anoxic granules was created in the reactor. The morphology of granules remained the same (3–5 mm), just the colour changed from black to grey. SVI and MLSS values changed only slightly. A spontaneous balance of biomass in the reactor was created without excess sludge uptake. Suspended solids in outflow were from 5 to 10 mg l^{-1}.

Part 2. (49–80 days) – Excess sludge was wasted every day (93 ml d^{-1}) and the sludge bed was completely exchanged. Mixture of anaerobic-anoxic and anoxic granules was changed to purely anoxic granules. The colour of this new biomass was light brown, but the diameter of granules remained the same (3–5 mm). Volumetric loading was kept during this period constant (19.7 kg COD m^{-3} d^{-1}). As a result of excess sludge wastage MLSS values decreased from 58 down to 17 g l^{-1} and SVI increased up to 40 ml g^{-1}. Efficiency of denitrification remained the same and NO_3-N+NO_2-N in outflow were constantly less than 3 mg l^{-1}. It is evident that the amount of biomass in USB during the part 1 was in significant excess.

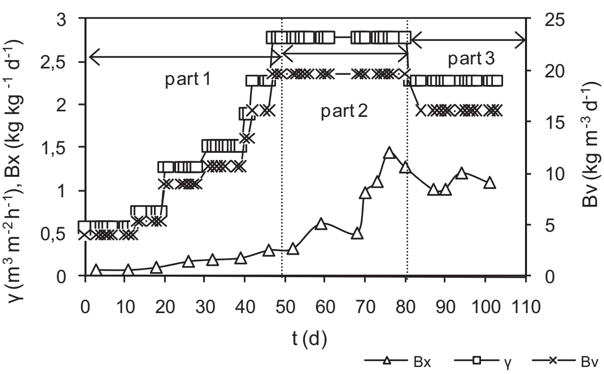

Figure 2. The course of B_v (volumetric loadings), B_x (specific loadings) and γ (hydraulic loadings) during the whole experiment (in kg COD). The anoxic granulation experiment started after the adaptation period.

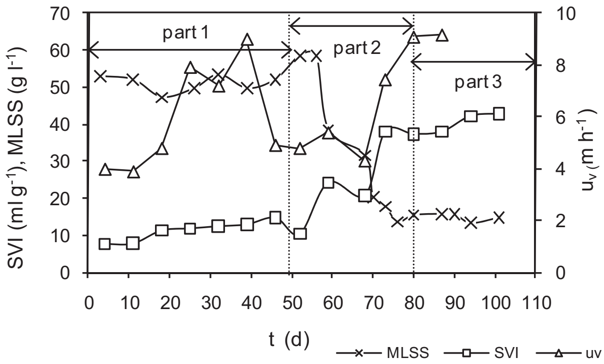

Figure 3. The development of MLSS (mixed liquor suspended solids) in the reactor, SVI (sludge volume index) and uv (sedimentation rate) of biomass throughout the whole experiment.

Part 3. (81–103 days) – There was only purely anoxic biomass in reactor, without residues of anaerobic inoculum. The volume of the sludge bed reached the bottom of separator and so the Bv was decreased to a safe value of 16.1 kg COD m^{-3} d^{-1}. During 23 days of this stage the process of denitrification was stable, spontaneous balance of biomass was created in the reactor (without a necessity to take out any excess sludge) and MLSS concentration remained on the level of 15 g l^{-1} and SVI of 42 ml g^{-1}.

3.2. ANAEROBIC GRANULAR SLUDGE FROM IC REACTOR IN BREWERY AS AN INOCULUM FOR ANOXIC GRANULATION

This inoculum was taken from mesophylic anaerobic reactor and 2 months was stored in laboratory at 18–20°C. Just after the experiment of anoxic granulation in USB started. The adaptation to completely new conditions was surprisingly short – after 8 days NO_3-N were denitrified with methanol to less than 3 mg l^{-1} NO_3-N + NO_2-N.

Starting value of B_v = 4 kg COD m^{-3} d^{-1} was gradually increased up to maximal value $B_{v,max}$ = 22.4 kg COD m^{-3} d^{-1} (Figure 4). Corresponding specific loading B_x was 0.56 kg COD kg^{-1} d^{-1}. Maximum hydraulic loading was γmax = 3.2 m^3 m^{-2} h^{-1} and minimum hydraulic retention time of wastewater in reactor was 7.7 min.

Change of anaerobic granules into anaerobic-anoxic and later anoxic was spontanous and connected with a change of colour from black to grey-brown- The diameter of anaerobic and anoxic granules remained the same (3–5 mm). Sludge volume index (SVI) was almost the same during the whole experiment (Figure 5). The sedimentation rates (uv) gently increased from 4 up to 7.5 m h^{-1}.

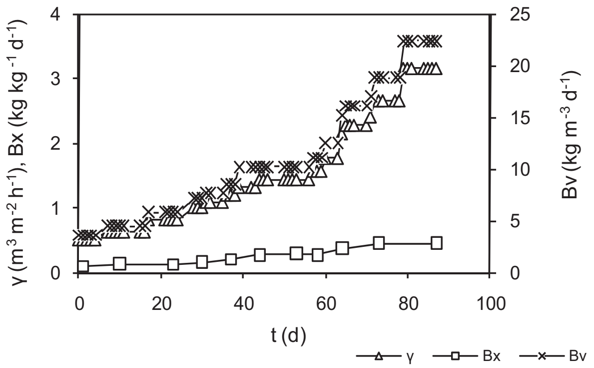

Figure 4. The course of B_v (volumetric loadings), B_x (specific loadings) and γ (hydraulic loadings) during the whole experiment (in kg COD). The anoxic granulation experiment started after the adaptation period.

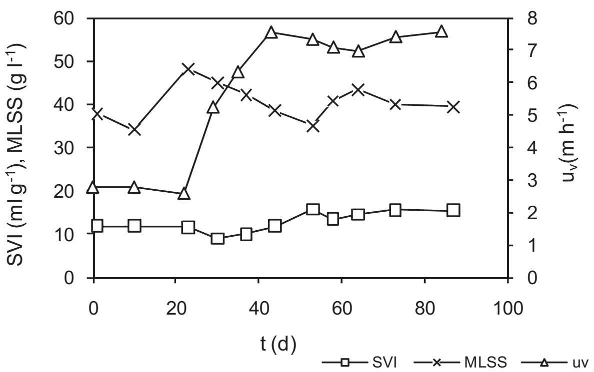

Figure 5. The development of MLSS (mixed liquor suspended solids) in the reactor, SVI (sludge volume index) and uv (sedimentation rate) of biomass throughout the whole experiment.

Concentration of biomass (MLSS) changed minimally and a spontaneous balance in reactor was created without excess sludge uptake (growth of biomass = decomposition of biomass + outflow of biomass).

3.3. MICROSCOPIC OBSERVATIONS OF ANOXIC GRANULATED BIOMASS CULTIVATED FROM ANAEROBIC GRANULATED INOCULUM

Microscopic observation of anoxic granulated biomass cultivated on external organic substrate – methanol proved compact structure and clear difference between core and cover of the granules. Granulated biomass in the centre was dense, with dominant occurrence of bacteria. On the surface of the granules filamentous bacteria Sphaerotilus natans appeared (oxic chemoorganotrophic organism which prefers easy biodegradable substrate as a source of carbon and energy; it grows under the conditions of low concentration of oxygen or basic macronutrients) (Wanner et al. 1996; Wanner et al. 2000) (Figure 6).

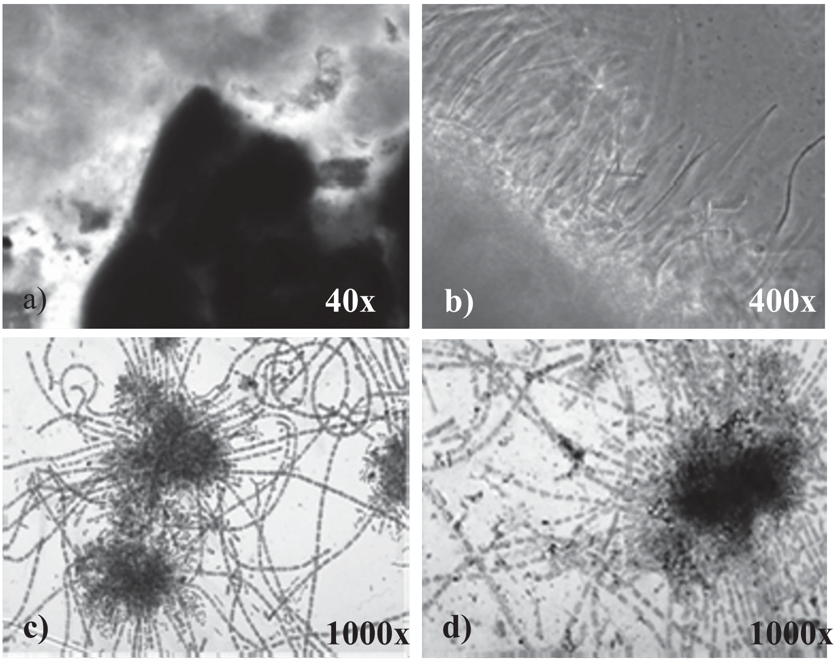

Figure 6. Microscopic observations of anoxic granulated biomass (extension is in figure). (a) clear difference between core and cover of granule (b) filamentous bacteria on the surface of the granules (c) Sphaerotilus natans from the surface parts of the granules – coloured according to Gram, reaction negative (d) Sphaerotilus natans from the surface parts of the granules – coloured according to Neisser, reaction negative colouring accord Neisser, reaction negative.

Appearance of this kind of filamentous bacteria indicated not only high loading of biomass, but also oxic conditions on the surface of the granules. Dissolved oxygen occurred in the water phase and on the surface of granules. Anoxic conditions without oxygen were present inside of the granules. This assumption was proved by the measurement of dissolved oxygen, which was regularly detected in the bottom of g/l/s separator and in the outflow from USB reactor (up to 1 mg l^{-1} O_2).

4. Conclusion

Anaerobic granulated biomass from anaerobic IC reactors was confirmed to be suitable inoculum for anoxic granulation. Anoxic granules with diameter of 3–5 mm and with excellent settling properties were cultivated in post-denitrification USB reactor. Maximum loadings of the USB reactor up to 22.4 kg COD m^{-3} d^{-1}

and 3.2 $m^3\,m^{-2}\,h^{-1}$ proved exceptional properties of this kind of biomass. Compact structure and clear difference between core and cover of the granules, with dominant filamentous bacteria Sphaerotilus natans on the surface of the granules were detected by microscopic observation of the granules.

5. Acknowledgements

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COMPARISON OF TWO FLAT SHEET MEMBRANE MODULES USED IN A REAL DOMESTIC WASTEWATER TREATMENT PLANT

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Abstract. The paper evaluates the results of obtained data from 2 years of observation of real household wastewater treatment plant (WWTP) with immersed membrane module. Two different commercial flat sheet membrane modules were investigated. The membrane modules, as well as whole WWTP, were tested with different fluxes and moreover the response of membrane and activated sludge to different conditions like real peak wastewater flows, extremes temperatures (winter below 5°C) and high pH values.

Keywords: household WWTP, membrane module, domestic wastewater, membrane flux

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1. Introduction

Increasing water scarcity coupled with stringent regulations have meant that a single-household MBR (membrane bioreactor), with the effluent being recycled for nonhuman contact applications such as irrigation, washing and toilet flushing, is potentially economically viable. However, a single-household MBR is believed to be costly compared with established freshwater supply and effluent discharge (Fletcher et al. 2007). The MBR technology integrates biological degradation of wastewater pollutants with membrane filtration, ensuring the effective removal of organic and inorganic contaminants and biological material from domestic and/or industrial wastewaters (Cicek et al. 1998).

2. Methods and Objects

2.1. PILOT HOUSEHOLD MBR WWTP

The tested household MBR WWTP (Figure 1) is installed in the garden of a four-person house. All the wastewater produced in the house flows to the treatment plant. The plant has no possibility of bypass or emergency overflow. The effluent is stored in an effluent tank and can be reused for watering lawns and gardens or cleaning floors etc.

The pilot-scale MBR plant consists of three chambers in series; the volume of each is 0.58 m^3. The first two chambers are used as a preliminary treatment stage. In these settlement chambers the majority of the solids are removed from the raw wastewater by sedimentation. The pretreated wastewater (from settlement chambers) flows into the biological activated sludge reactor equipped with an immersed membrane module.

During the experiment two flat sheet membrane modules from commercial suppliers were tested. The parameters are shown in Table 1.

A hydraulic retention time (HRT) in the whole household MBR plant is 7.2 days, the HRT in the preliminary stage is 4.8 days and HRT in the biological reactor is 2.4 days; a volumetric loading is around 0.35 kg COD m^{-3} d^{-1}.

Each membrane module was surveyed 1 year. At that time the research was divided into several phases of dependence on the necessity of membrane regeneration or technical changing.

The research of the membrane module “A” was divided into three phases and the membrane module “B” into two phases. The major difference between the compared membrane modules was the membrane area, the membrane pump and the technical arrangement of the WWTP.

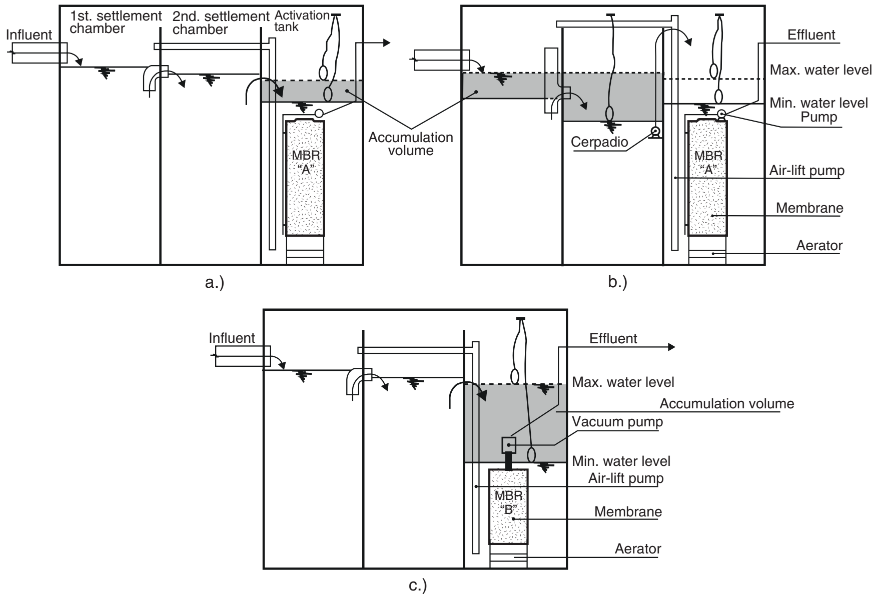

Figure 1. Scheme of household MBR WWTP : (a) membrane module "A" - concept 1 applied in the first and second phases (b) membrane module "A" – concept 2 applied in the third phase (c) membrane module "B" – both phases.

TABLE 1. Parameters of observed membrane modules given by suppliers.

Parameters given by suppliers			
Parameter	Unit	Membrane module "A"	Membrane module "B"
Membrane parameters	mm	185×1090×316	207×207×492
Membrane area	m^2	6.7	3.5
Pore size	μm	0.1	0.05
Pressure	bar	0.02–0,4	0.1–0.15
Max. flux	$l\ m^{-2}\ h^{-1}$	–	50
Average flux	$l\ m^{-2}\ h^{-1}$	–	15–30
Membrane material		PVDF	PES
Max. inflow	$m^3\ d^{-1}$	0.6	0.6
Pump		Submersible pump	Vacuum pump

3. Results and Discussion

3.1. THE QUALITY OF RAW WASTEWATER AND EFFLUENT

In the whole experiment there were monitored chemical parameters of the raw water (influent) as well as effluent. As seen in Table 2, values of effluent parameters were excellent, and they fulfilled legislative demands without problems for SR and ČR for the household WWTP during the whole experiment (Decree of the government 2007; Regulation 2006).

TABLE 2 The quality of raw wastewater (influent) and the effluent from the household WWTP.

Parameter	Membrane module “A”		Membrane module “B”	
	Influent (mg l^{-1})	Effluent (mg l^{-1})	Influent (mg l^{-1})	Effluent (mg l^{-1})
COD	917.59	53.35	776.97	60.09
BOD_5	593.79	2.32	543.88	2.60
NH_4-N	151.88	44.96	161.45	58.39
N_{tot}	213.78	137.13	211.97	154.34
P_{tot}	18.66	11.72	23.89	16.17

However, it is necessary to advert on high concentration of Ntot in influent (Figure 2). Ntot is usually higher in concentrated household wastewater and it can have a negative influence on nitrification.

European standard EN 12566-3 (2005) establishes conditions of tests of household WWTPs after which they may receive CE marking. CE marking provides the opportunity of selling these products on the European market. The standard is recommended in raw wastewater, besides other values, the values of KN = 25–100 mg l^{-1} and NH_4-N = 22–80 mg l^{-1}. According to our experiences and also measurements, these values are very low and for real household WWTP unreal.

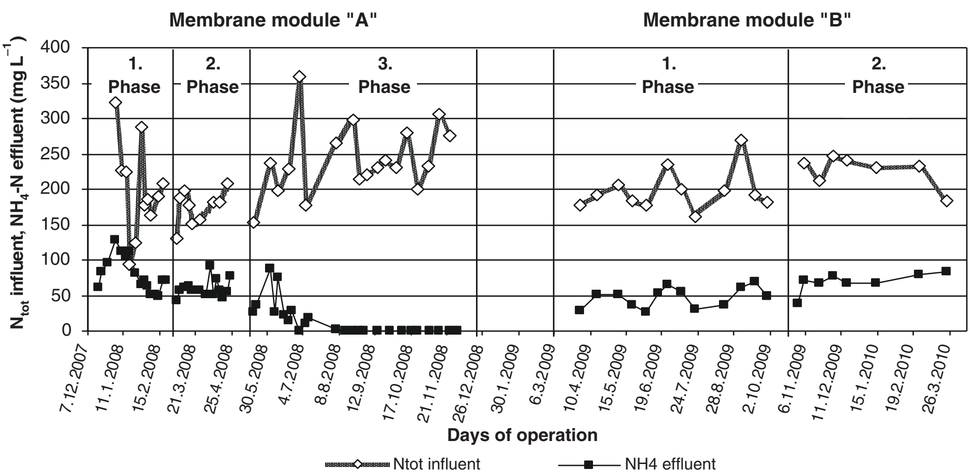

Figure 2. Ntot influent and NH_4-N effluent concentrations

3.2. EVALUATION OF MEMBRANE FLUX

3.2.1. *Membrane Module "A"*

Special attention was given to the flux. The filtration in the first period started without regulation of flux or transmembrane pressure. It was respected the probable situation that the majority of the owners and users of household WWTP would not be wastewater treatment experts, and they would not pay attention to the flux or pressure regulation. The initial flux was 45 L m^{-2} h^{-1} and we did not change the system. The flux decreased from the value 45 L m^{-2} h^{-1} below 10 L m^{-2} h^{-1} after approximately 3 months (it corresponds to 22 m^3 or 3.2 m^3 m^{-2} of filtered wastewater through the membrane).

The membrane module was changed for a new one, and it was started in the second period. Because of the possibility of flux regulation, a throttle at the effluent conduit was installed. At the start-up, the membrane module was operated under the flux 13 L m^{-2} h^{-1} for 3 days, and then the flux was set at 20 L m^{-2} h^{-1}. After 3 months, the flux rapidly decreased to 6 L m^{-2} h^{-1} again. Through the membrane module there was 12.1 m^3, or 1.8 m^3 m^{-2} of cleaned wastewater filtered.

The membrane was regenerated by a 0.5% solution of acetic acid before the start of the third period. The membrane module was operated at the low flux below 10 L m^{-2} h^{-1} and lower transmembrane pressure approximately below 0.1 bars in the third period. The operation of the membrane module at this value of lower flux appeared to be steady and suitable – after 184 days of operation the flux started to decrease. The membrane regeneration was necessary after 7 months (flow of 45.1 m^3 or 6.7 m^3 m^{-2} of filtered wastewater through the membrane).

When the lower filtration flux is used, it is necessary to pay attention to accumulation volume in the biological reactor. This accumulation volume should be as big as possible by the reason of peak wastewater flow, but it also depends on the height of the membrane module. In this case, the height of the biological reactor was 1.6 m and the height of membrane module with facilities (aerator and pump which had to be submerged) was 1.44 m, accordingly, the retention volume was just 60 L (Figure 1a).

The flux 15–25 L m^{-2} h^{-1} (common values given by the producer of flat sheet membrane modules) was calculated, when the conception of this household MBR WWTP was designed, but with regard to the third period, which was operated at the relative lower flux, the biological reactor was flooded (flux through installed membrane was so low, that it could not rise to the occasion off peak wastewater flow). This is a particularity of the membrane which must not be omitted by the designer. Therefore the gravity inflow from the second settlement tank was changed to pumped inflow. The first and second settlement chambers were then used as an accumulation (buffer) tanks with the accumulation volume of 200 L (Figure 1b). However this was not a convenient solution because there was another device which could break down.

3.2.2. *Membrane Module "B"*

The membrane module "B" offered bigger accumulation volume in the biological reactor because its height was considerably smaller compared to the membrane module "A". The conception of gravity flow of wastewater among the chambers was restored (Figure 1c).

The initial membrane flux was predetermined by the membrane producer at the value 25 L m^{-2} h^{-1} at the transmembrane pressure 0.1 bar. The flux fluctuated from 25 to 9 L m^{-2} h^{-1} during the operation of 6 months and then suddenly decreased to 1.1 L m^{-2} h^{-1} by the reason of membrane clogging. Through the membrane module 35.6 m^3 or 10.2 m^3 m^{-2} of treated wastewater was filtered. The mechanical cleaning and regeneration by citric acid pH = 3 and then by sodium hypochlorite pH = 11 had been done. During the mechanical cleaning big pieces of sludge cake were washing up, which thickness was approximately even 3 mm. Between particular sheets a continual layer of dewatered sludge cake was created, which caused an entire membrane blocking and so dysfunction of the whole system. Therefore it can be considered to be a big risk of flat sheet membrane modules.

In the second phase, the membrane module "B" was observed also at a lower flux about 10 L m^{-2} h^{-1}. However after 1 month, flux decreased and held about the value 5 L m^{-2} h^{-1}. The transmembrane pressure fluctuated between 0.12 and 0.20 bar. The flux decreased below 2 L m^{-2} h^{-1} after 5 months and the membrane module had to be repeatedly regenerated. After regeneration the flux was again 10 L m^{-2} h^{-1}. In household WWTP conditions, the obligation of membrane regeneration was confirmed even more than two times per year, whereby it is necessary count also with that the membrane would be necessary exchanged after half year.

During the whole experiment the flux fluctuated as can be seen in Figure 3. After these experiences, it is possible to assert that despite producer recommendations the flux decrease spontaneously and common proposed flux with regeneration demand two or three times per year is at the level 10 L m^{-2} h^{-1}. The membrane producers and suppliers normally recommended flux 15–20 L m^{-2} h^{-1}, nevertheless this value can be, after 2 years of research, considered as dangerous and irresponsible.

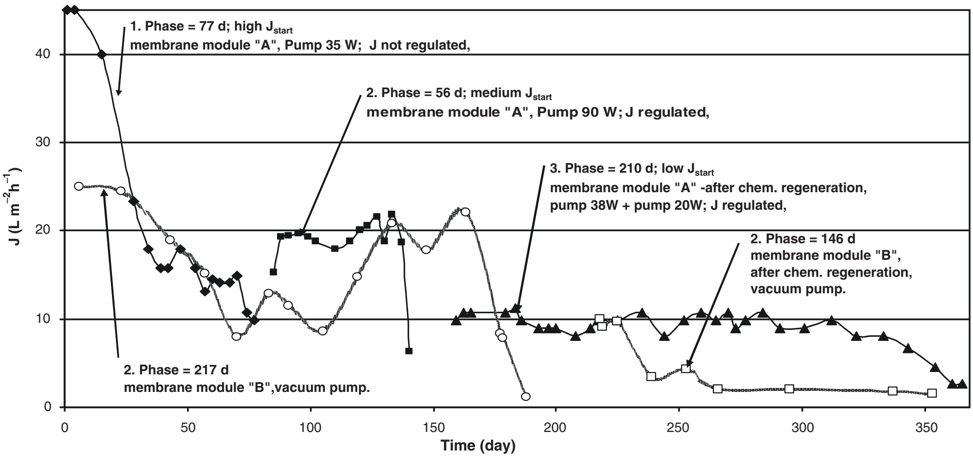

Figure 3. Flux evaluations of two different membrane modules during the experiment.

Membrane fouling probably was contributed by additional factors:

- high flux, mainly in the first days after start up,
- low temperature, mainly in winter season normally below 10°C. Temperature impacts on membrane filtration through its influence on the permeate fluid viscosity. Low temperature also resulted in incomplete nitrification, which started when the temperature was above 10°C,
- high concentration of Ntot (Figure 2.) in concentrated domestic wastewater caused higher pH levels and precipitation of phosphates PO_4-P. Incipient precipitation may foul the membrane. In winter this problem is more striking, because in the biological reactor the nitrification does not work and so the pH level does not decrease,
- sludge bulking. In the household WWTP a problem with sludge bulking occurred (the dominant filamentous bacteria was Microthrix Parvicella – the amount was 5 from 6 according to Jenkins method 1993) which had a tendency to flotation and foam during the whole experiment. The overgrowth of filamentous bacteria could result in a much higher release of extracellular polymeric substances (EPS) and did great harm to membrane permeation (Meng et al 2007; Jiang et al 2005).

The significant impact of temperature on MBR fouling suggests that winter is the critical time for membrane operation. To control the possible intensification of membrane fouling under winter conditions, it is suggested to run the MBR at lower filtration flux, if possible, and to intensify the coarse bubble aeration (Jenkins et al 1993).

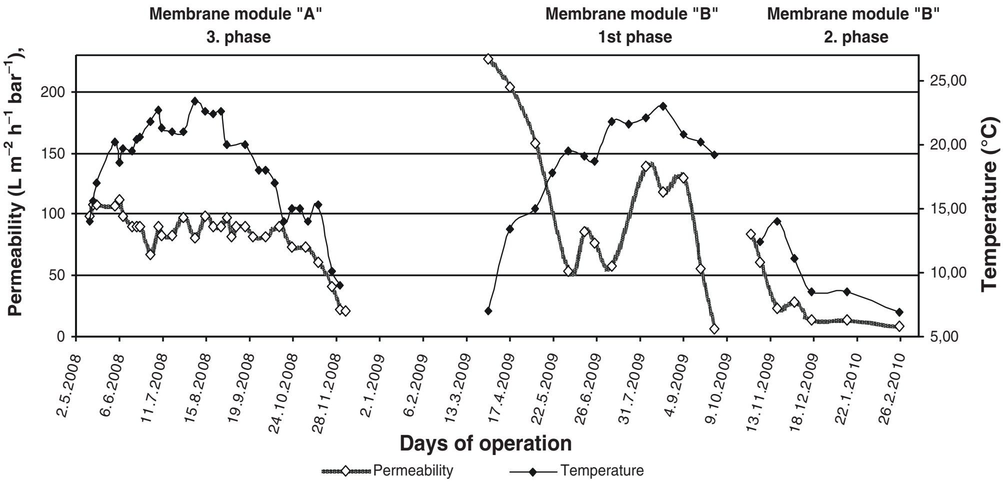

Figure 4. Temperature influences to membrane permeability.

3.3. EVALUATION OF ENERGY CONSUMPTION

For household MBR WWTP operation is also important to know energy consumption. During the experiment with the membrane module "A" in the second and third phases the energy demand was 2.1 kWh d^{-1}; 10.4 kWh m^{-3} and the price for electricity was approximately 4.9 € per month, that is approximately 58.8 € per year. It is necessary to take into consideration that during the operation was also added energy needed for the second pump operation (pump between second settlement chamber and biological reactor), which partly increased energy demand.

The energy demand of membrane module "B" furnished with vacuum pump and membrane area 3.5 m^2 was approximately 3.4 kWh d^{-1}; 17.4 kWh m^{-3} during whole investigation. The price for energy demand was approximately 6.5 € per month, that is 78 € per year.

In terms of effluent quality (particularly for the area where the treated water was reused) are not these values so high expense items. The difference of energy consumption between the two tested models can be seen, however, the difference is not so high and mainly each model has its own advantages as well as disadvantages. For example the membrane module "B" looks like more energetic exacting, but it is necessary to regard it as nearly half smaller membrane area, and so there is a longer filtration time at given flux in comparison to membrane module "A". On the other hand, the membrane is smaller and so it offered advantage of bigger accumulation volume in biological reactor and also fewer complications with pump system.

Operation expenses include besides energetic demand belong also membrane regeneration (1 regeneration = approximately 50 €) and maintenance (disposal of primary sludge 1× per year = 50 €) (Matulova 2009).

4. Conclusion

The paper should refer to the obtained results from investigation of household MBR WWTP placed in real conditions and with real wastewater. The task was to compare and evaluate two commercial membrane modules.

Both of the observed membrane modules offered excellent effluent parameters, which under the appeared condition, would be impossible for sludge separation by settling in a clarifier because of massive sludge bulking. Only the installed membrane module guaranteed the perfect effluent quality.

Membrane module “A” was furnished with a submersible permeate pump which turned out as problematic by reason of often defectiveness. The pump was exchanged four times during 1 year and this is for common user inadmissible. When the flux decreased below 10 L m^{-2} h^{-1} the height of membrane module (membrane area 6.7 m^2) the disadvantage occurred, because the WWTP started to be flooded at situations of peak inflows. The installation of another pump between the second settlement chamber and activation tank was necessary. However this was not a convenient solution, because there was another device which could break down.

The membrane module “B” was furnished with a vacuum pump, which was trouble free and so it was a very advantageous solution. The membrane module did have a smaller membrane area 3.5 m^2 which ensured adequate accumulation volume, and so the gravity flow through WWTP was possible. When the flux decreased below 10 L m^{-2} h^{-1} the filtration was longer, and it had to repeat more times. It tended to increase energy demand.

5. Acknowledgements

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PROBLEMS OF REGULATION OF ANTHROPOGENIC LOAD ON THE WATER OBJECTS WITH VARIOUS DILUTION RATIO IN UKRAINE

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Abstract. Main problems of the anthropogenic pressure regulation in Ukraine have been analyzed for two wastewater treatment plants (WWTP) in the cities of Chernivtsi and Khotyn (Ukraine). Current condition of the WWTP equipment has been evaluated and general quality of the treated water is described. Water condition of the receiving rivers upriver and downriver the discharge points has been compared and analyzed. It is shown that current legislation, which controls composition of the wastewater should be corrected.

Keywords: anthropogenic pressure, wastewater treatment technologies, monitoring of the river water

1. Introduction

Water objects are vitally needed to ensure life on Earth. However, this resources is very limited and quite vulnerable. Water contamination, discharge of industrial and municipal wastewaters can significantly worsen quality of water.

About 39% of the municipal and 42% of the industrial wastewaters in Ukraine are being discharged to the rivers without any treatment(Dmitrieva et al 2003). This results in significant changes in hydrobiological, thermal and chemical conditions of many rivers, which leads to decrease of the water quality and depletion of the phytoplankton biodiversity(Drenkalo 1999).

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Calculation of the maximum permissible discharge (MPD) of the treated wastewater is one of the control measures to normalize an anthropogenic pressure on some water objects. However, current recommendations on MPD calculation sometimes lead to ecologically illogical results. As shown in the work(Choban and Winkler 2008), calculation of MPD cannot be performed correctly for small rivers since the calculated values are close to the total dilution ratio of the rivers. Realization of such calculated MPD would definitely devastate any small river and transform it into the sewage collector, which transports the wastewater to a bigger water object with higher dilution ratio. On other hand, direct calculation of MPD for a river with higher dilution ratio can bring illogical results too. This problem has been analyzed for Chernivtsi and Khotyn WWTP, which discharge the treated wastewaters into river of Prut (lower dilution ratio) and Dnister (higher dilution ratio) respectively.

2. Analysis of Anthropogenic Pressure on Prut and Dnister

Main hydrological parameters of two rivers – Prut and Dnister – are shown in Table 1.

TABLE 1. Main hydrological characteristics of Prut and Dnister.

Parameter	Units	Dnister		Prut	
		Winter	Summer	Winter	Summer
Minimal water flow	m^3/s	13	31.6	9.97	12
Average width	m	50		35	
Average depth	m	1.2		0.7	
Average flow velocity	m/s	0.62	0.81	0.41	0.49
Sinuosity coefficient	–	1.064		1.087	

Chernivtsi wastewater treatment plant (WWTP) is the main object of anthropogenic pressure on river Prut. Capacity of full bio-treatment facilities of Chernivtsi WWTP is 152,000 m^3/day and the plant operates with following equipment: inlet chamber 12 × 9 m, inlet grate, rotating sand catchers, preliminary aeration units, flat sand trap, primary radial settlers, four-chamber aerators, aerators-settlers, secondary radial settlers, water pumps, activated sludge pumps, sludge storage areas, additional cleaning units.

Unfortunately, aerators-settlers and additional cleaning units are not currently involved in the wastewater treatment process because of some construction and assembling faults. Some other needful equipment is still missing at the plant: sand catchers are not equipped with automated sand unloaders and there are no activated sludge dehydration devices. This complicates normal functioning of the wastewater treatment complex.

Khotyn WWTP is smaller and its capacity is only about 1,000 m^3/day. Local inhabitants mostly use individual cesspools and only small part of the town (about 12%) is covered with the centralized sewage system. The plant provides mechanical cleaning and bio-treatment of municipal wastewaters.

The 5 years long monitoring of the wastewater quality ensures rather stable regime of the treatment at both WWTP (see Table 2).

TABLE 2. Average efficiency parameters of wastewater treatment in Chernivtsi and Khotyn.

Parameter	Value, mg/l	
	Chernivtsi	Khotyn
BOD_{full}	22.6±1.10	36.8±0.91
COD	31.1±1.10	96.2±1.15
NH_4^+	2.5±0.09	6.6±1.10
NO_2^-	0.4±0.04	1.0±0.05
NO_3^-	17.0±0.55	20.2±0.21
PO_4^{3-}	1.40±0.04	5.8±0.21
Cl^-	156.0±0.82	98.3±1.14
SO_4^{2-}	82.3±1.81	153.4±1.42
Solid residue	432.3±16.80	670.1±12.10
Suspended particles	15.7±0.50	29.7±0.64

As seen from the Table 2, efficiency of the Chernivtsi WWTP is much higher than in Khotyn. A range of BOD_{full} from 12 to 25 mg/l is considered as a technological standard of the bio-treatment efficiency and the Chernivtsi WWTP fits into this standard. Same situation is with the suspended particle content (12–25 is a standard). Only concentration of NH_4^+ is overriding the technological standard (2 mg/l). Efficiency of the Khotyn WWTP is significantly worse.

However, quality of the discharged wastewater is only at secondary importance. It is more important to evaluate influence of the wastewater discharge on condition of the receiving river water. Table 3 shows comparison of the river water quality upriver and in the control point 500 m downriver from the discharge outlet with corresponding maximum permissible levels (MPL) for the fish-producing water objects.

As seen from Table 3, the background water quality in Prut meets MPL for the fish-producing water except of content of NH_4^+. Water of Dnister is more polluted and three parameters (COD, NH_4^+ and NO_2^-) are overriding corresponding MPL.

TABLE 3. MPL and average actual values of some river water quality parameters.

Parameter	MPL	Value, mg/l			
		River Prut (Chernivtsi WWTP)		River Dnister (Khotyn WWTP)	
		Upriver	Control point	Upriver	Control point
BOD_{full}	3.0	2.3±0.12	2.80±0.14	2.60±0.12	2.65±0.08
COD	15.0	13.0±0.84	16.9±1.02	27.31±0.84	28.40±0.61
NH_4^+	0.5	0.8±0.07	0.9±0.09	1.3±0.04	1.49±0.03
NO_2^-	0.08	0.06±0.01	0.09±0.02	0.13±0.01	0.14±0.008
NO_3^-	40.0	5.1±0.25	6.2±0.31	3.03±0.22	3.12±0.21
PO_4^{3-}	3.12	0.31±0.04	0.62±0.05	0.042±0.01	0.045±0.02
Cl^-	300	34.0±0.12	44.4±0.11	82.2±0.21	83.4±0.24
SO_4^{2-}	100	40.7±0.81	47.8±0.68	73.2±0.27	73.8±0.45
Solid residue	1,000	331.5±12.80	357.0±11.80	416.2±3.80	420.0±6.20
Suspended particles	+0.25	9.2±0.24	11.3±0.22	17.4±0.22	18.3±0.31

As shown above, efficiency of the Chernivtsi WWTP is higher, however, discharge of the properly treated wastewater into Prut significantly worsens its quality. Concentration of PO_4^{3-} doubles while content of nitrites raises for ~50% and nitrates – for ~20%. BOD_{full} and COD also show raise for 23% and 30% respectively. Therefore, discharge of Chernivtsi municipal wastewaters into Prut results in excessive worsening of the river condition. Nevertheless normal efficiency of the water treatment, this fact is mainly caused by low dilution ratio of Prut.

On other hand, poorly treated wastewaters from Khotyn WWTP do not result in any serious worsening of the Dnister water quality because of much higher dilution ratio of this river.

This conclusion may look paradoxical but it only proves that taking into account quality of the wastewater treatment alone is insufficient for proper evaluation of anthropogenic pressure of various WWTP. Dilution ratio and self-purification ability of the water objects should also be considered.

3. Recommendations on Lowering of Anthropogenic Pressure on the Rivers

Taking into account current technological scheme of the wastewater treatment at both plants we can propose following steps, which will result in lowering of anthropogenic pressure on Prut and Dnister.

3.1. PRUT AND CHERNIVTSI WWTP

Wastewater cleaning equipment works in the stable and efficient regime, which should not be changes. The situation can be improved through installing of new devices and units.

Mechanical cleaning devices should be equipped with additional sand catchers and grates.

Mechanical dehydration equipment should installed at the activated sludge filtration stage.

Additional biological after-treatment devices can also be put into operation before wastewater is discharged.

This way we can reach better wastewater quality parameters and lower anthropogenic pressure on Prut and thus lower potential risks related to functioning of Chernivtsi WWTP(Winkler and Choban 2009).

On other hand, taking into account population of the city and dilution ratio of the river, we can state that Prut seems to be too small river for direct discharge of even properly treated municipal wastewaters. Further raise of the treatment efficiency would require higher and higher investments. Probably part of the treated wastewaters should be directed to special landfill areas.

3.2. DNISTER AND KHOTYN WWTP

This situation is quite opposite to situation with Chernivtsi. Total treatment efficiency at the Khotyn WWTP is low and bio-treatment seems incomplete because of the following:

Excessive amount of the activated sludge is usually collected in the secondary settlers. Decomposition of the sludge results in additional contamination of wastewaters with organic compounds.

Sand catchers are unloaded irregularly and part of the captured material slips through the catchers and raises content of suspended particles at the bio-treatment equipment.

WWTP works in a very irregular regime. Intensity of the night wastewater treatment is very low, which also shakes efficiency of bio-treatment. This problem can be eliminated through partial recirculation of the 'daily' waste-water and cleaning the recirculated waters together with the night portions. This way we can smooth down irregularity in the bio-treatment regime.

These steps would improve quality of the wastewater discharged into Dnister and lower small but negative influence of local WWTP on quality of the river water.

4. Conclusion

Advanced efficiency of the bio-treatment may not secure normal river condition if relatively high amount of the treated wastewater is being discharged into a river with low dilution ratio. On other hand, discharge of the poorly cleaned wastewater may not lead to any serious contamination of a river with high dilution ratio. Therefore, planning and estimation of environmentally safe capacity and working regime of any WWTP should rely on both parameters: calculated MPD level, which also refers to the dilution ratio of receiving river and current level of the wastewater cleaning at local WWTP.

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WATER SUPPLY OF CHERNIVTSI (UKRAINE): PROBLEMS AND POSSIBLE SOLUTIONS

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Abstract. The paper deals with main problems of supplying drinking water to the city of Chernivtsi (Ukraine). Main water supply sources are described and quality of water from each source is analyzed. We outline main problems of the water supply system functioning and propose possible solutions.

Keywords: drinking water supply; water intakes, river water quality assessment

1. Introduction

Quality of the drinking water is considered as one of the main factors, which ensure human health. A "Bill of Human Rights" (International Bill of Rights 1995) states that every human has rights to receive proper life means including meals, clothes, home, medical services to ensure normal health and wellbeing of him(her)self and his/her family. Of course, this definition includes a right to have access to the drinking water. However, this basic right remains unavailable for many thousands of people who have no access to normal drinking water, which causes numerous health problems.

In the light of this issue we would like to analyze main problems and possible solutions related to functioning of the drinking water supply system in the city of Chernivtsi. It is located in a water-rich region but existing water supply system faces various challenges. Some of them are rather common while the others are specific for this city.

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2. Description of the Drinking Water Supply System

History of the municipal water supply system begins in 1895–1912 when first installations and water supply network were constructed (History of cities... 1969). Today main water intakes use water from rivers Prut and Dnister. River Dnister is much bigger, however, river basin of Dnister occupies only small part of the Chernivtsi region (see Figure 1).

Figure 1. Comparison of river basin of Dnister (shadowed) and Prut within the region of Chernivtsi.

Dnister is being fed with rain water (50%), groundwater (30%) and snow melting water (20%). Main river flow is rather unstable since it is formed mainly in the hilly area, and this often causes floods. An average water flow in Dnister within Chernivtsi region is about 220 m^3/s but during flooding it sometimes raises up to 8,000 m^3/s. Water of Dnister is quite muddy and contains relatively high amount of the clay-like particles. Clay particles are delivered to the river because of very intense erosion of the river banks, especially in the upper and middle parts where Dnister flows in a deep river canyon. Only during the winter time the river can freeze-over and then the water becomes comparatively clear. This feature complicates production of the drinking water from this source.

On other hand, microbiological parameters of the Dnister water are very high. There are long pebble areas on the riverbed. The pebble is enriched with silicon minerals and numerous microalgae colonies, which ensure excellent micro-cleaning of the river water.

Many various industrial objects are working within the riverside area of Dnister. This imposes potential threat of chemical contamination of the river water with emergency effluents of toxic industrial liquids and/or wastewater. Such events were in fact registered and maximum permissible levels of nitrates have been exceeded for 13–19 times; copper – for 80 times; zinc – for 1.5 times and manganese – for 16–60 times (Zapolsky and Salyuk 2003).

TABLE 1. Average water quality parameters of Dnister and Prut (in MPL parts except suspended particles (mg/l)) within Chernivtsi region (Environment condition in Bukovyna 2007).

Control point	Water quality parameters						
	Suspended particles	BOD_5	Mineral–ization	Sulfates	Chlorides	Ammonium ions	Nitrates
Dnister							
1 (upriver)	7.8	1.5	0.4	0.2	0.1	0.5	0.1
2 (downriver)	8.9	1.6	0.4	0.1	0.1	0.4	0.1
Prut							
1 (upriver)	5.0	1.1	0.3	0.1	0.1	0.4	0.1
2 (downriver)	6.3	1.4	0.3	0.1	0.1	0.5	0.1

Prut is the second important source for the water intakes (Korzhik and Yuschenko 2002). River basin of Prut occupies about 50% of the Chernivtsi region area. This river is fed mostly with the rain water. Floods are also quite often for Prut. An average water flow in Prut within Chernivtsi region is about 75 m^3/s but during hard flooding it can reach up to 5,000 m^3/s. This river is also quite muddy however, chemical quality of the Prut water is higher than in Dnister. Soil and clay washout from the riverbanks is the main pollution source of Prut, especially during the floods. There is no any hard industry near Prut and only rare solitary exceeding of the total organic compounds content have been registered.

Average water quality parameters of both rivers within Chernivtsi region are shown in Table 1.

Local water supply system is also being fed from two underground water intakes, which supply 3,900 and 1,800 m^3/day. Both intakes are located near Prut and in fact use the under-riverbed water.

All rivers of the region are mainly fed with the rain water, which is quite abundant. An average rainfall can reach about 1,000 mm. The more warmer is a month, the more rainfall is registered (An educational atlas of... 2000) (see Figure 2). July rainfall is the highest and the most recent flooding of 2008 also occurred on July.

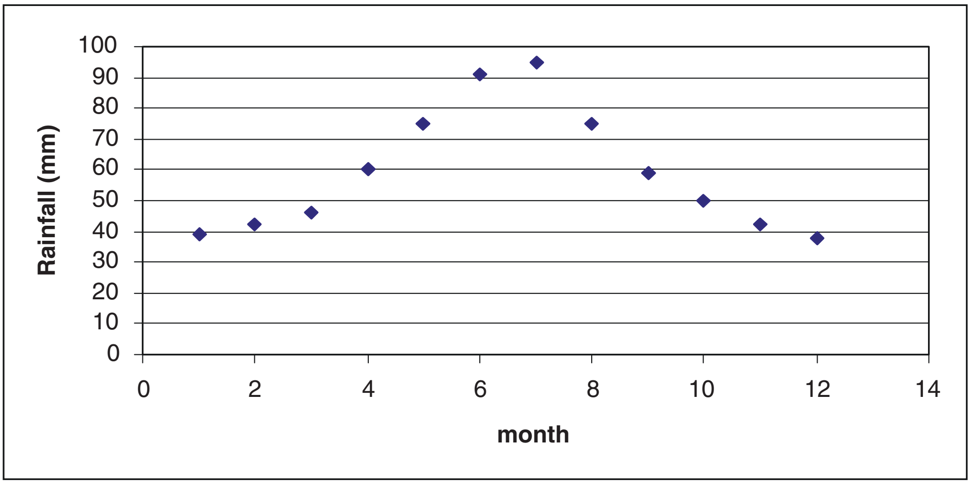

Figure 2. Monthly distribution of rainfall in Chernivtsi.

3. Changes in the Water Supply Character in Chernivtsi

Analysis of the water supply character in Chernivtsi shows some interesting results (Environment condition... 2008).

Part of the underground water in total water supply is constantly growing since mid-1990s. Now it can be estimated as about 40%. This is a positive trend because this kind of water is much clearer than any surface water. The water from underground sources does not require intense cleaning stages and can be converted into drinking water at significantly lower price. On other hand a high-outcome underground source with stable delivery characteristics is not always easily available.

Transportation water losses are gradually decreasing but remain too high. This parameter was about 45% in the beginning of 1990s and reached about 30% by the year 2008. It is still too high for an economically reasonable water supply network. This problem is mostly caused by too old water distribution network, which is quite hard to be renewed in an old downtown with very dense build-up character. On other hand, a water-supply line from Dnister to Chernivtsi is about 45 km long and passes through some land-sliding areas. This causes frequent breakings and leakages from the water transportation line. Gradual switching to the underground water sources near Chernivtsi should help to decrease water supply from Dnister and facilitate to minimization of the water transport losses.

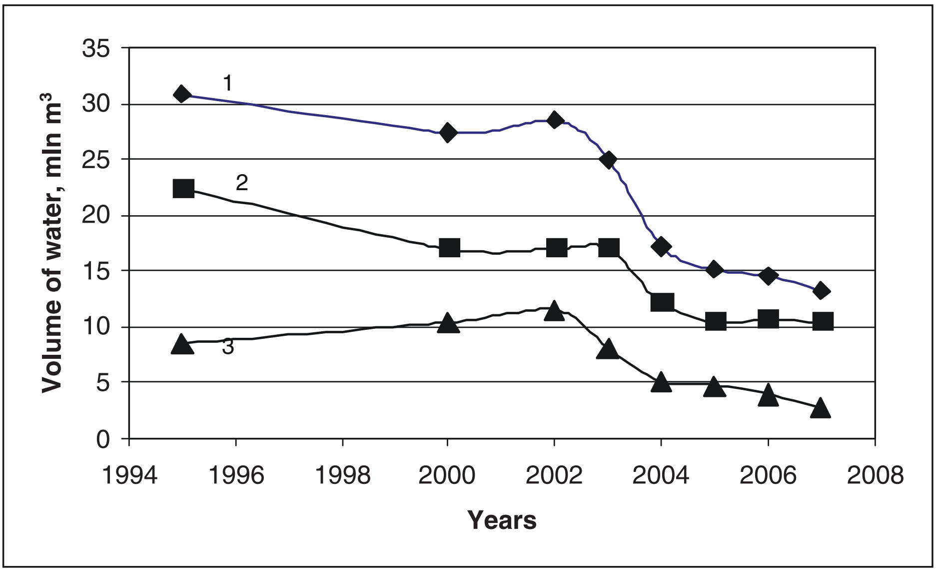

Figure 3. Total annual consumption of the primary water (1) and usage of the primary water for household (2) and industrial (3) needs.

Consumption of the primary water is constantly decreasing both for industrial and household needs (Figure 3).

Primary water is being gradually substituted with the water from own sources (household and industrial objects) and/or recycled water (at industrial objects). On other hand, total capacity of the heavy industrial productions is also decreasing, which also leads to decrease in the water consumption. Recycling or sequential consumption of the industrial water regained importance after 2002–2004, when water price started to rise faster than before (Figure 4). Percentage of the reused water has almost reached level of beginning of 1990s, when it started to decrease.

This tendency is positive, especially because it results in decrease of amount of the wastewater collected in the municipal sewage system and discharged into receiving river. As seen in Figure 4, this parameter has also decreased since mid-1990s. Taking into account constant widening of the sewage network in the city (though some areas still don't have connection to the network) this result can be caused only by wider involving of the recycled water into various technological processes.

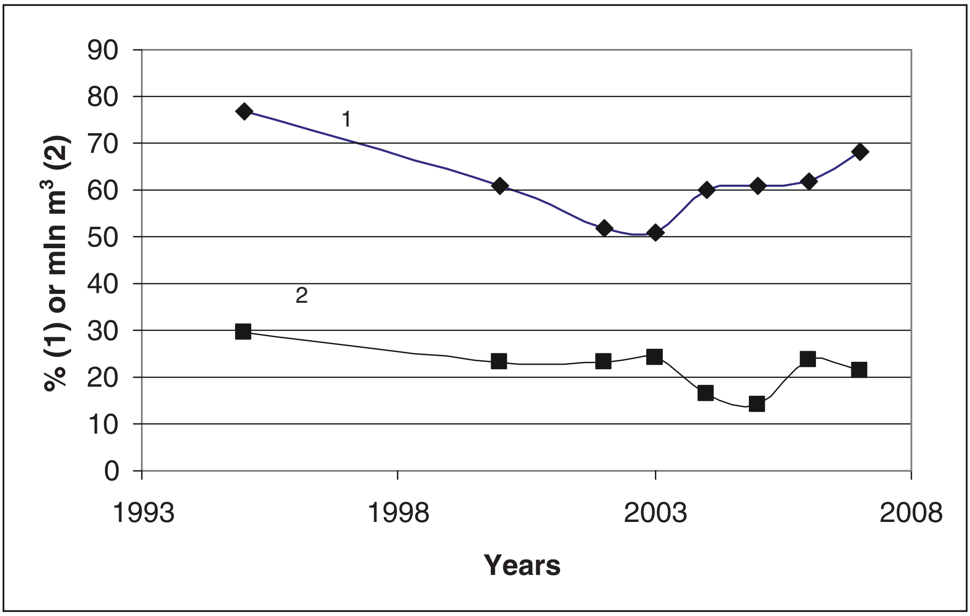

Figure 4. Percentage of the recycling and sequential usage of water for industrial purposes (1) and an average annual discharge of wastewaters (2).

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SORPTION OF AMMONIUM CATIONS AND HEAVY METAL IONS FROM THE NATURAL ARTESIAN WATERS WITH THE BASALT TUFA SAMPLES

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Abstract. Efficiency of sorption of some artesian water pollution agents has been investigated for various material based on the natural basalt tufa: unmodified and modified. It was found that surface modification with some agents can improve sorption activity of the tufa. Then this material can be proposed for cleaning technologies, which can be applied to the artesian water treatment.

Keywords: artesian waters; water cleaning; sorption activity; basalt tufa

1. Introduction

Deficiency of the drinking water causes worsening of social and economical problems and causes a need in searches of new sources for the water supply. Underground water can be considered as a prospective source of the water supply. An average daily output (Tugay and Prokopchuk 1999) of the underground sources in Ukraine is about 57 million m^3. However, underground waters often can be contaminated with various mineral and organic substances. For example, results of the chemical analysis of one example of the artesian water are shown in Table 1.

It is seen that some parameters are at sub-shoulder level or even override corresponding MPL. Wider usage of the underground water is impossible without deep investigation of theoretical and applied basic elements of their cleaning

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technologies. Previous works (Tarasevich 1981; Zhurba 1980) were mainly devoted to the plain filtration treatment.

TABLE 1. Chemical parameters of an artesian water sample.

Water quality parameter	Value, mg/dm^3	MPD, mg/dm^3	
		Drinking water	Underground water
Iron (total)	0.5	0.3	0.3
Manganese (total)	0.05	0.1	0.1
Copper (II)	0.12	1.0	1.0
Lead (II)	0.01	0.01	0.03
Zinc (II)	0.06	5.0	1.0
Chlorides	258	250	350
Sulfates	238	250	500
Ammonium	2.62	–	2.0

This work deals with experimental investigation of the sorption cleaning of some model systems, which represent natural artesian waters. The cleaning has been done with natural and modified basalt tufa materials.

2. Experimental Investigation of the Sorption Efficiency

An experimental investigation has been carried out in the dynamic sorption regime according to the methods described in Yurkov and Yurkov (2002). Granules of the natural basalt tufa (diameter = 1–2 mm) and the tufa granules modified with MnO_2 have been used in the experiments. Chemical modification has been performed according to the methods Yurkov and Yurkov (2002). Results of the iron (II) sorption efficiency by the natural and modified tufa and the concentrated MnO_2 are represented in the Table 2.

As seen from the Table 2, adsorption efficiency of the plain tufa is slightly lower comparing to the efficiency of the concentrated MnO_2. The latter material ensures higher adsorption efficiency comparing to the efficiency of the modified tufa if concentration of Fe^{2+} is higher than 24 mg/dm^3. Modified tufa shows higher efficiency at lower concentration of iron. This can be caused by different surface concentration of the active adsorption centers on the modified tufa and concentrated MnO_2.

Then the sorption efficiency of the modified tufa has been examined on the natural artesian water samples. Sorption efficiency is shown in the Table 3.

An organic-mineral composition sorbent BT-OM has been prepared according to the following method (Komarov et al. 1988). The basalt tufa (average grain diameter 180 μm) has been preliminary dried at 150°C and then mixed with a

15% solution of the phenol-formaldehyde resin in acetone. The resin was kept for polymerization at 70°C for 4 h and then the mixture was heated to 150°C. Further thermotreatment of the samples has been made in the airless conditions for 2 h at 700°C. Then the final product was ground and the fraction of 1–2 mm has been separated for investigation of the sorption efficiency.

TABLE 2. Efficieny of Fe^{2+} sorption on the basalt tufa samples and concentrated MnO_2 material. Rate of filtration – 5 m/h.

Initial concentration of Fe^{2+}, mg/dm^3	Sorption degree, %			Sorption value, mg/sm^3		
	Tufa	Modified tufa (with MnO_2)	Concentr. MnO_2	Tufa	Modified tufa (with MnO_2)	Concentr. MnO_2
3.0	80.3	94.6	91.5	0.016	0.019	0.018
10.8	77.6	93.1	90.6	0.056	0.067	0.065
24.0	70.3	90.0	89.4	0.112	0.144	0.143
42.5	68.4	88.2	88.4	0.194	0.249	0.250
85.0	68.0	86.0	86.8	0.385	0.487	0.492
115.0	67.8	75.4	78.3	0.520	0.578	0.600

TABLE 3. Efficiency of the ions sorption from the natural artesian water using basalt tufa.

Sorbent	Sorption degree, %			
	NH_4^+	Fe^{2+}	Cu^{2+}	Pb^{2+}
BT-N	80.2	77.7	63.7	77.2
BT-HCl	93.5	80.1	64.6	78.1
BT-MnO_2	90.8	90.3	71.2	84.6
BT-DK	91.7	94.7	88.4	96.4
BT-OM	100.0	84.5	80.6	81.2

Footnotes: BT-N – natural basalt tufa; BT-HCl – the tufa modified with HCl; BT-MnO_2 – the tufa modified with MnO_2; BT-DK the tufa modified with β-diketone; BT-OM the tufa modified with an organic-mineral composition sorbent.

The efficiency was measured in the dynamic experiment. Artesian water has been filtrated with rate 5 m/h through 100 sm^3 of the sorbent. An atom-absorption spectroscopy method (Alemasova et al. 2008) has been used to determine concentration of the metal ions in water and concentration of NH_4^+ ions was detemined using another photocolorimetry method(Arinushkina 1970).

As seen from the Table 3, sorption efficiency can be significantly changed as a result of the tufa modification. An organic-mineral tufa ensures almost complete elimination of NH_4^+ ions from the artesian water if initial concentration of the ions was comparatively low (see Table 1). Efficiency of adsorption of the heavy metal ions depends on the modification type and nature of the ion. The β-diketone modified sample shows the highest adsorption efficiency. This can be caused by active complexation properties of surface layer of this material.

Higher adsorption efficiency of the acid-modified samples comparing to the natural tufa can be caused by higher porosity of surface of the modified material. As shown inAbabi et al. (1980), an acid treatment of the natural tufa results in formation of the surface pores of 83-600 Å.

On other hand, processes of cation exchange, especially losses of aluminum and iron ions result in lowering of the surface concentration of the sorption active centers. This condition can be responsible for comparatively weak activation of the heavy metals sorption after treatment of the tufa with hydrochloric acid.

3. Conclusion

Basalt tufa can be used for cleaning of the artesian waters and lowering concentration of some agents to the limits, which are required for the drinking water. This technology would allow involving new water sources into regular water supplying. Underground waters are abundant in Ukraine and this would resolve many problems related to the water shortage in may regions of Ukraine. Comparatively simple surface modification of the tufa improves the sorption efficiency and ensures faster and better cleaning of the underground water.

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DEACTIVATION OF HAZARDOUS URANIUM CONTAMINATED WATER IN BLACK SEA BASIN

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Abstract. Protection of the rivers' waters, which get to the territories of other states, has recently become one of the most important and crucial issues and decisions to be make on those issues depending on the governments and scientists of the boundary countries. The plenty of the rivers runs into the Black See. Besides, it also runs on the territory of Ukraine where mining regions and many industrial and processing facilities are located.

Keywords: radionuclides, heavy metals, soils and wastes, permeable reactive barrier, sulfate-reducing bacteria, estimation of pollution, mining and processing industries, environment

1. Introduction

Ukraine nowadays has a diverse mining industry providing a wide variety of metallic and nonmetallic minerals and accounting for the main part of industrial output in Ukraine. Over 200 types of mineral resources are found in Ukraine

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and about 20,000 fields and ore deposits have been struck on its territory. The major minerals are iron, manganese, uranium ores, coal, titanium, zirconium, beryllium, sulfur, mercury, non-metallic raw materials for metallurgy, potash salt, and others. Ukraine is in the European and world leader in terms of the listed types of mineral raw materials.

The development of the mining and processing industry, the pollution, and degradation of the environment, particularly reservoirs and soils, and also the atmospheric air in large and medium towns and industrial centers due to industrial development have become threatening. These are, first of all, the areas contaminated with heavy metals and radionuclides in Donetsk, Dnipropetrovsk, Luhansk, Lviv and some other oblasts. To the point, the regions with critical ecological situation have the highest density of population (National Report... 1999; 2004; 2006).

Although the extraction of some minerals has decreased in recent years, the general state of environment in mining regions is getting worse. This occurs because of the obsolete production equipment, mining without any considerations for possible changes in the environment and noncompliance with preventive and rectifying measures.

The state of the environment is most complicated in the Kryvyi Rig Basin, where the iron, manganese, and uranium ores are mined. The enormous and relatively easily accessible reserves of iron ores, contained in the Kryvyi Rig deposits, stimulated their development and mining on such scales and in such volumes that were unprecedented in world practice.

The state of environment is very complicated now at uranium mines of the uranium ore province located in the Kryvyi Rig Basin, which is the largest in Europe and one of the largest in the world. By it energy potential this deposit is equivalent to the greatest Ukrainian coal province of Donbas. A major part of the reserves of uranium ores was found in the deposit of iron ores that represents a separate tectonic block.

Great potential pollution of the environment in the Kryvyi Rig Basin is related to the industrial activity in the town of Zhovti Vody. Zhovti Vody is of great importance for national economy as a unique Ukrainian center, where the milling and primary enriching of uranium and iron ores are performed.

The town of Zhovti Vody is situated in the western part of the Dnipropetrovsk region, bordering with the Kirovograd region. The area of Zhovti Vody is characterized by complex hydrogeological conditions, which are determined by geologic-structural features of the territory as well as by the intense economic activities of man.

The main water-way of Kryvbass is the Ingulets River. Five rivers flow into the Ingulets along its course in the Kryvbass region: left tributaries of the Zhovta and Saksagan' rivers, and right tributaries of the Visun', Bokova, and Bokoven'ka rivers. The drainage network in the district of Zhovti Vody and the water basin within the town are represented by the Zhovta River, as well as by three ponds: two of them are used as beaches and the storage basin is used as a reserve water body for potable water supply. The natural regime of the Zhovta River is now strongly disturbed, because of the presence of dams and the water intakes for the irrigation and domestic needs, as well as the discharge of domestic, industrial, and mine waters into the Zhovta River.

Eleven industrial enterprises of different branches of economy are located in the town. Liquid and solid process wastes (disposal sludge, waste of the washing, decontaminations of process equipment, etc.) are discharged via slurry pipelines. The tailing storage facility is located 1.5 km south from Zhovti Vody being a right tributary of the Zhovta River. The water ways nearest to the tailing storage facility are the Zhovta and Zelena Rivers running from the north to south at the distance of 1.0–1.5 km to the east of the tailing storage facility.

Hydrogeological conditions at the site of the tailing storage facility have been formed under the predominant influence of technogenic factors.

The dominant anion chemical components are sulfates and nitrates, contents of which in water are much higher than maximum permissible concentration limits. From the results of regime observations in the vicinity of the tailing storage facility, it can be seen that a halo of contamination with nitrates and sulfates was formed. Furthermore, the halo of contamination caused by nitrates practically repeats the halo of contamination caused by sulfates and remains within its limits. Currently, the border of the halo of contamination with sulfates well corresponds to the structure of the groundwater flow.

The levels of contamination with heavy metals and uranium in groundwater near the tailing storage facility are also rather high: 0.10 mg/L for Mn, 0.19 mg/L for Pb, 0.013 mg/L for Cd, and 0.35 mg/L for U.

At present a variety of methods has been proposed for remediating water, soil and sediments contaminated with hazardous substances. Depending on the type of contaminant, the degree of contamination, and the scale of the contaminated site, one or another method is usually proposed. A relatively new (in Eastern Europe) and potentially important in-situ methods is a permeable reaction barrier (PRB) that is constructed in the subsurface to intercept contaminated groundwater. Such barriers can be used to remediate hazardous organic compounds or metals (Interstate Technology & Regulatory Council 2005).

The contaminant treatment zone in PRB may be created directly using reactive materials such as iron or indirectly using materials designed to stimulate secondary physical, chemical or biological processes. The main PRB types in use today are continuous wall, funnel- and – gate systems, and injection well configuration.

Various materials have been investigated as possible materials for PRB. They include zeolite, hydroxyapatite, elemental iron, limestones, and others (Waybrant et al. 1998; Gu et al. 1998). It was shown that PRB were effective for the treatment of dissolved metals and radionuclides, acid mine drainage, and dissolved nutrients.

One of the most promising component for PRB is zero-valent iron that has been extensively studied in recent years (Blowes et al. 1997; Benner et al. 1999; Farrell et al. 1999). The biological approach in PRB remediation technology is also very promising. Many environmental biotechnological applications utilise microorganisms that have key role in the biogeochemical cycling of toxic metals and radionuclides (Landa 2004; Malik 2004;.Kalin et al. 2005; Spasonova et al. 2006). Biologically induced reduction reactions can promote the attenuation of inorganic cations through direct reduction of the cation or through indirect precipitation resulting from the oxidation or reduction of an inorganic anion. A lot of metals, including such dangerous ones as Cd, Cu, Zn, Mn, Pb, etc., can be removed by this method (Uhrie et al. 1996; Waybrant et al. 1998; Benner et al. 1999).

So the main objectives of this work are to evaluate the potential use and effectiveness of semi-passive permeable reactive barriers for metals contamination in Kryvyj Rig basin.

2. Materials and Methods

Contaminated groundwater sampled from wells near the tailing dump of uranium ore processing wastes at the Skhidnyi (Eastern) Mining and Processing Integrated Works were selected as the subject of investigation. The specified tailing dump is located near the town of Zhovti Vody (Kryvyi Rig basin).

The total uranium in contaminated waters was determined by the spectrophotometric method. The method of atomic absorption spectroscopy was employed for determination of the concentration of metal ions including Na^+, K^+, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Fe_{tot}, Co_{tot}, and Mn_{tot}. The determination of Ca^{2+}, Mg^{2+}, CO_3^{2-}, HCO_3^-, Cl^-, SO_4^{2-}, and the hardness was performed by the titrometric techniques of analysis. The potentiometric method was used to determine NO_3^- and NO_2^-, while the method of photometric analysis was employed to determine NH_4^+. The determination of pH for solutions and the control of oxidation-reduction potential were performed by using a pH-meter. Table 1 presents the chemical composition of the general mineralogical 4,007 mg/L of water based on the results of analysis.

TABLE 1. Chemical composition of the groundwater.

pH	Ca^{2+} mg/L	Mg^{2+} mg/L	Na^{+}, K^{+} mg/L	NH_4^{+} mg/L
7.4	576	209	370.4	0.75
U_{total} mg/L	Ni^{2+} mg/L	Cu^{2+} mg/L[3]	Co_{total} mg/L	Mn_{total} mg/L
4.0	<0.05	<0.033	<0.06	0.104
Cd^{2+} mg/L	Fe_{total} mg/L	Pb^{2+} mg/L	Zn^{2+} mg/L	Inflexibility, mg-eq/L
<0.013	0.05	<0.19	<0.01	46
Cl- mg/L	SO_4^{2-} mg/L	HCO_3^{-} mg/L	CO_3^{2-} mg/L	NO_3^{-} mg/L
213	2,189	402	0	49

The investigation of processes for the treatment of uranium-polluted waters was performed in cylindrical plexiglass columns having the diameter of 100 mm and the height of 270 mm under dynamic conditions that simulated the behavior of processes occurring in semipermeable reaction-capable barriers.

The first set of experiments involved the use of iron powder Fe^0 in the amount of 200 g as a reducing agent (the content of the main component was 99.6% by weight, the granulometric composition in terms of the sieve residues was as follows, weight %: 1.0 mm–0.4; 0.63 mm–21.7; 0.4 mm–16.9; 0.31 mm–10.5; 0.2 mm–19.9; 0.16 mm–13.9; 0.1 mm–11.6; 0.063 mm–1.8; 0.05 mm–1.0; <0.05 mm–2.3). The coarse-grained quartz sand in the amount of 0.95 dm^3 having the grain size of 0.6–2.0 mm and the apparent density of 2,400 g/L was used as an inert filling material for the column).

The second set of experiments involved the use of activated sludge from an aeration station as a reducing agent, while the coarse-grained quartz sand was also used as an inert filling material for the column.

The third set of experiments involved the use of activated sludge as a reducing agent, while the high-porous vitrocrystalline material manufactured by the method of duplicating the structure of polymer matrix made of sodium-calcium-aluminosilicate glass and montmorillonite was used as an inert filling material for the column.

The contaminated water was fed into the columns by the peristaltic pumps. The pump productivity was set equal to 0.05 L/ h. The treated water got to the storage tank via the hydraulic lock for eliminating a contact between the solution at the outlet of the columns and the air, and thereby preventing the progress of unwanted oxidation-reduction processes.

The U(VI) concentration in naturally contaminated water was further increased to the concentration of 10 mg/L by using the solution of $UO_2SO_4 \cdot 3H_2O$. In addition, for the second and third sets of experiments the solutions under investigation were supplemented with the nutrient medium consisting of ammonium acetate (0.5 g/L) and also the mono- and double-substituted potassium phosphate representing a phosphate buffer (0.01 M) for maintaining pH 7 and providing nutrition of microorganisms. For creating anaerobic conditions the treated water was additionally subjected to sparging with nitrogen during 4 h, while the space over the solution in the supply tank was filled with nitrogen from a special cylinder. The sampling of the treated water for the residual uranium analysis was carried out every day.

The experiment lasted for 100 days, following which the columns were unloaded and the layerwise analysis of uranium content over the column height was performed.

3. Results and Discussion

The quantity of the extracted uranium naturally increases with the rise of its concentration in the output solution. The mechanism of uranium extraction includes the primary sorption of its different soluble forms on the products of iron powder corrosion representing active iron hydroxides with high specific surface area. The reducing medium, created during the Fe^0 oxidation, gives rise to the simultaneous transition U(VI) = > U(IV) and the appearance of insoluble compounds of uranium that may form both the true and pseudo-colloids.

The results of experiments performed under dynamic conditions are presented in Table 2.

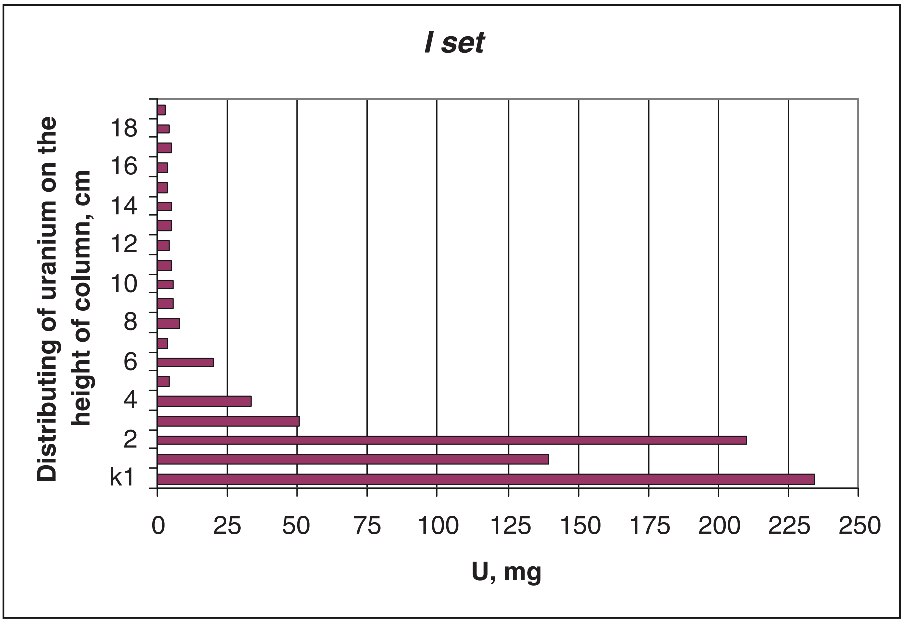
The analysis of findings indicates that during the entire experiment the use of inorganic reducing agent in the form of iron powder Fe^0 makes it possible to ensure the persistent decrease of uranium concentration in the final solution practically to zero level (I).

The use of microbiological reduction in the second set of experiments with activated sludge and quartz sand as a carrier makes it possible to ensure the decrease of uranium concentration in the final solution to the level just below 1 mg/L (II). The efficiency of decontamination of the output solutions achieved in the third set of experiments with activated sludge and high-porous vitrocrystalline material as a carrier was just above 1 mg/L in the final solution (III).

One of the possible causes for lower efficiency of the microbiological method as compared with the use of elemental iron is its higher sensitivity to the composition of the output solution and, correspondingly, to the form of uranium in the solution. As can be seen from data of the chemical analysis (see Table 1), the contaminated subterranean waters near the tailing dump of uranium ore processing wastes are characterized by high content of HCO_3^- and SO_4^{2-} anions. This gives rise to the formation of durable complexes with uranium that are more resistant to the microbiological reduction. The results of the layerwise analysis of uranium content over the column height are presented in Figure 1.

TABLE 2. Variation of the uranium concentration in the treated water: I corresponds to the first set, II corresponds to the second set, III corresponds to the third set of experiments.

Experiment continues, days	Contents of uranium in the treated water on an exit from a column, mg		
	I	II	III
0	0	0	0
10	0	0.15	0.75
20	0	0.7	1.08
30	0.01	0.75	1.10
40	0.02	0.75	1.14
50	0.025	0.75	1.18
60	0.025	0.75	1.20
70	0.03	0.8	1.25
80	0.03	0.8	1.25
90	0.03	0.8	1.25
100	0.03	0.8	1.25



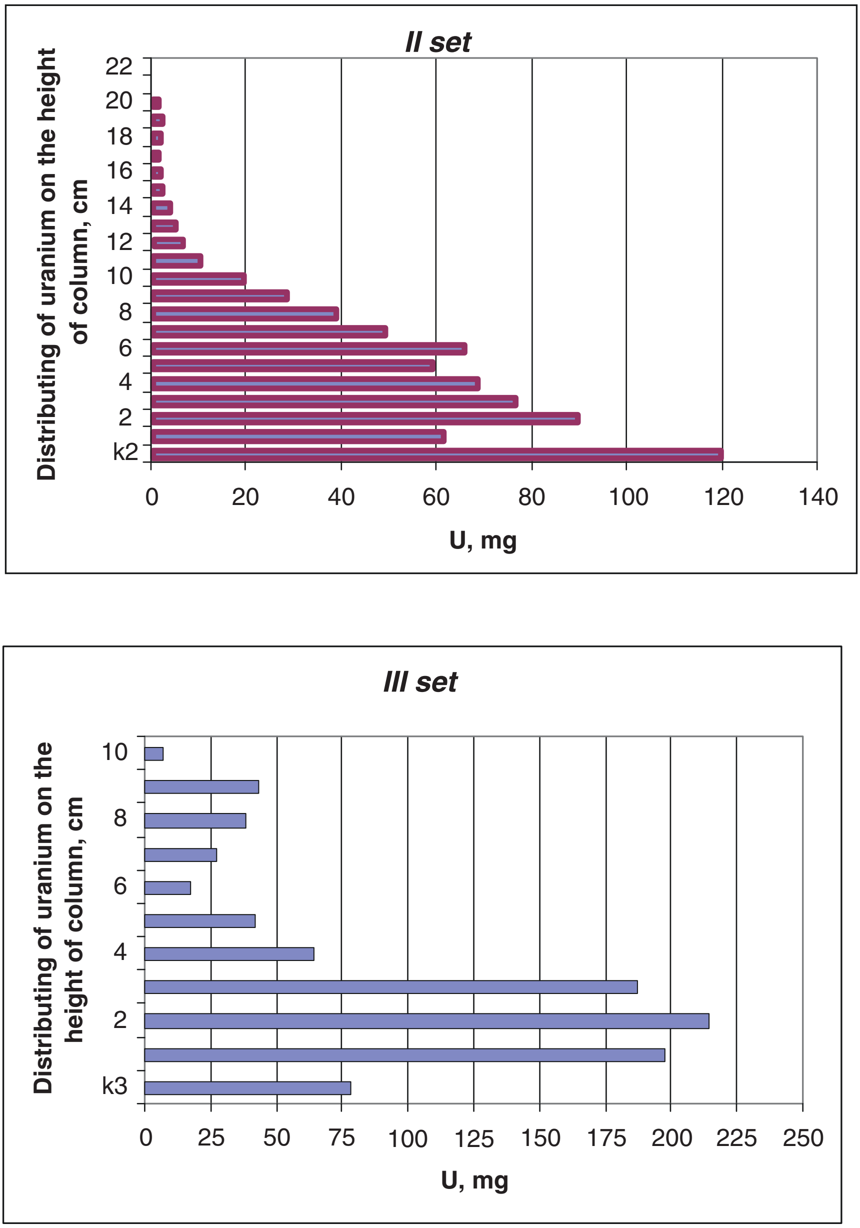


Figure 1. Layerwise analysis of uranium content in samples taken during the unloading of columns: (I) corresponds to the first set (II) corresponds to the second set (III) corresponds to the third set of experiments.

Based on the fact that only a minor part of the active charge over the height of reaction columns contains uranium in considerable quantities, the above data indicate that the potential resources of both the inorganic and microbiological materials are far from exhausted after the duration of experiment for more than 3 months.

4. Conclusions

A major reduction of the uranium concentration can be observed in all three sets of experiment as compared with the output uranium concentration in natural water. This corroborates the efficiency of using the sorption-reducing method for the treatment of contaminated groundwater near the tailing dump of uranium ore processing wastes in the town of Zhovti Vody. The use of iron powder as an active agent makes it possible to achieve practically zero levels of uranium in the treated water. At the same time, despite the use of microbiological reducing agent in the form of activated sludge makes it possible to achieve a tenfold decrease of the uranium concentration in the final solution, this does not satisfy the state-of-the-art world normative requirements with respect to the content of this toxicant in subterranean waters. Hence, for example, in the USA the admissible uranium content in subterranean waters is standardized at the level of 30 μg/L that is much lower than the levels achieved during the microbiological investigations.

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THE INFLUENCE OF WASTEWATER DISPOSAL SYSTEM ON THE QUALITY AND QUANTITY OF THE WASTEWATER TRANSPORTED TO A WASTEWATER TREATMENT PLANT

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Abstract. In the Czech Republic of the beginning of twenty-first century, over 80% of the population is connected to the public sewerage. Connecting the remaining part of population to drainage systems and the related choice of the right kind of sewerage is therefore a very topical problem. The traditional means of drainage is considered to be the integrated or divided sewerage systems, which are based on principles of gravity and free-flow transport of wastewater. The alternative means of drainage is the compressive and vacuum sewerage systems.

Keywords: wastewater disposal system, wastewater treatment plant, traditional means of drainage, alternative means of drainage, wastewater, pollution indicator, influence of wastewater disposal system

1. Introduction

The analyzed topic "The Influence of Wastewater Disposal System on the Quality and Quantity of the Wastewater Transported to a Wastewater Treatment Plant" presents comparison, characteristics, advantages and disadvantages of different kinds of sewerage in relation to landscape configuration, building density, wastewater treatment plant, etc. Integrated and divided sewerage systems and compressive and vacuum sewerage systems will be compared. It has been proved by monitoring a sample of sewerage systems, that the influence of the kind of

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system of transporting wastewater on its quality is obvious. The choice of a sewerage system has also a direct impact on the choice of technology and plans for parametres of a wastewater treatment plant. When planning a wastewater treatment plant, it is necessary to take into account the different mode of hydraulic and material load in connection to the kind of sewerage system. It is evident, that the right choice of wastewater disposal system, as well as wastewater treatment plant, can save a considerable amount of money within the bounds of the initial investment and in the course of operation, too (Hlavínek 2001).

2. A Comparison of Different kinds of Sewerage

If we suppose, that the demand for water for one person is 150 l/day, then wastewater can be characterized in the following way: BOD_5 400 $mg.l^{-1}$, COD_{Cr} 800 $mg.l^{-1}$, N_{total} 70 $mg.l^{-1}$, P_{total} 15 $mg.l^{-1}$, solids total 1,200 $mg.l^{-1}$, dissolved solids 830 $mg.l^{-1}$, suspended solids (SS) 370 $mg.l^{-1}$. The rate of COD_{Cr}: BOD_5 is usually 2. The proportion of C:N:P in wastewater, usually quoted as COD_{Cr}:N:P or BOD_5:N:P is very important for biological treatment. The efficiency of biological treatment may be influenced negatively by a shortage of nutrients (N, P), because preconditions for the production of activated sludge ($C_{118}H_{170}O_{51}N_{17}P$). Whereas sewerage and urban wastewater contains an excess of these substances, some trade effluents can be the opposite case. The proportion of some indicators are important, e.g. BOD_5 to COD_{Cr} or BOD_5 (COD_{Cr}) to total nitrogen and phosphorus. This last proportion is important for estimating the presence of sufficient content of nutrients (N, P) for effective biological treatment (Pitter 2009).

For effective biological treatment is the optimum of nutrients in relation to organic carbon approximately BOD_5:N:P = 100:5:1. The proportion of BOD_5:COD_{Cr} is a benchmark rate of biologically decomposable substances. Sewerage and urban wastewater contain mostly biologically decomposable organic substances.

2.1. A COMPARISON OF DIFFERENT KINDS OF SEWERAGE – THE QUALITY OF WASTEWATER

There have been long-term observations to compare different sewerage systems. Integrated sewerage system, compressive and vacuum sewerage systems have been compared for the purpose of the topic:

It is evident from the results, that in compressive and vacuum sewerage systems, where the access of oxygen is negligible, an increase in concentrations of COD and $N\text{-}NH_4^+$ in unprocessed wastewater takes place (owing to anoxic conditions), namely in comparison to gravity wastewater drainage.

TABLE 1. Average concentrations of indicators of pollution of wastewater flowing into wastewater treatment plants.

Kind of transport	BOD_5	COD_{Cr}	SS	$N\text{-}NH_4^+$
	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$	$(mg.l^{-1})$
Gravity wastewater drainage	161	347	97	32.2
Vacuum sewerage system	617	1049	590	124.6
Compressive sewerage system	507	1270	440	106.0

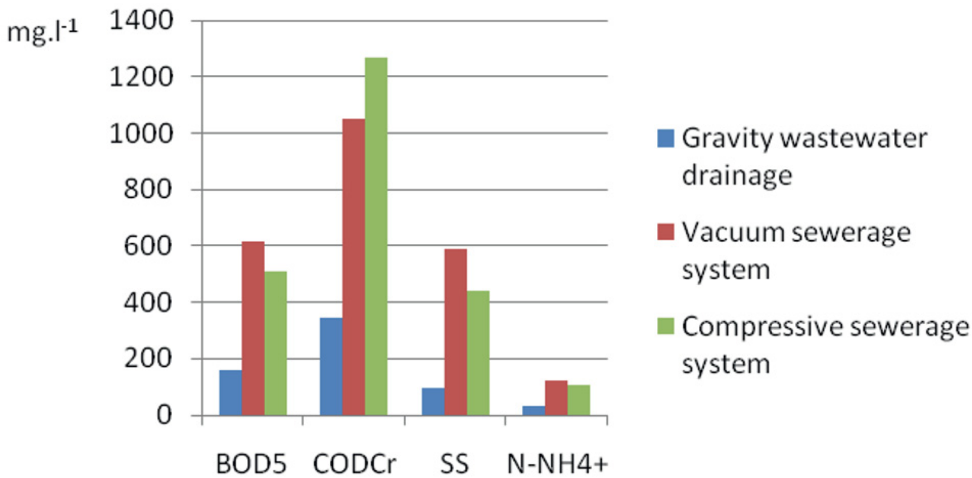

Figure 1. Average concentrations of indicators of pollution of wastewater flowing into wastewater treatment plants.

Monitoring the wastewater from different sewerage systems revealed significant differences in average concentrations of the studies indicators from vacuum, compressive and gravity sewerage systems. The results of monitoring the wastewater from compressive and vacuum sewerage systems demonstrated higher pollution of unprocessed wastewater. These are especially indicators, which are influenced by oxidation - reduction processes in the sewerage, i.e. BOD_5, COD and $N\text{-}NH_4^+$. Of greatest influence on the high concentrations is the fact, that there is a long detainment of wastewater in house shafts or water pumping stations, which can reach up to 16 h, and where the environment creates anaerobic conditions. In compressive and vacuum systems organic nitrogen is ammonificated in anaerobic processes – organic nitrogen substances decompose by microbial activity and nitrogen is usually released as ammonia nitrogen, which is utilized by organisms for synthesis of new biomass.

In gravity wastewater drainage the sewage is oxidized (this is also often influenced by a high gradient in the vertical alignment of the drainage), which influences indicators of BOD_5 and COD – BOD_5 and COD are degraded in oxic processes (Prax 2002).

Figure 2. Sampling

2.2. A COMPARISON OF DIFFERENT KINDS OF SEWERAGE – THE QUANTITY OF WASTEWATER

A high occurrence of check-up objects and the need for deep foundations of drains to secure gradients which transport waste in gravity networks complicates the achievement of the required impermeability of the system. Classic, gravity networks thus often infiltrate a great amount of ballast water, which can, to a considerable extent, affect adversely the effectiveness of treatment of the wastewater treatment plant.

A feature of alternative means of drainage is a minimum infiltration and undesirable intake in the closed pipe system. It has been discovered by an analysis of through-flow characteristics, that the daily inflow of wastewater from alternative systems in monitored areas fluctuated around 90 l per person per day.

3. Conclusion

The above stated difference in concentrations has a direct impact on the choice of technology and plans for parametres of a wastewater treatment plant. When planning a wastewater treatment plant, it is necessary to take into account the different mode of hydraulic and material load of the unconventional means, in comparison with traditional gravity sewer networks. When employing unconventional wastewater disposal systems, it will be appropriate to expect at least 20% increase in the volume of nitrification rates, compared to recipient on gravity wastewater drainage.

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