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Environmental Security

Dangerous Pollutants (Xenobiotics) in Urban Water Cycle

Edited by
Petr Hlavinek
Ongjen Bonacci
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Ivana Mahrikova

Springer

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Dangerous Pollutants (Xenobiotics) in Urban Water Cycle

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Dangerous Pollutants (Xenobiotics) in Urban Water Cycle

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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. In wastewater management, new challenges are caused by new chemicals of concern, including endocrine disrupters, pharmaceuticals, hormones, and personal care products, which often pass through wastewater treatment plants unabated, but may cause serious impacts on receiving aquatic ecosystems.

The topics focused on evaluation of impact of xenobiotics in the whole Urban Water Cycle are an interdisciplinary task which has a rising concern these days. Xenobiotics includes both inorganic elements like heavy metals, metalloids and man-made organic compounds such as pesticides, surfactants, solvents, fragrances, flavours, and pharmaceuticals as well as endocrine disrupters. It has been estimated that 70,000 xenobiotics may potentially be hazardous for humans and/or ecosystems. Water supply, urban drainage and wastewater treatment systems were originally designed to solve just conventional problems such as supply of potable water, flooding prevention and sanitation. The main problem within the conventional urban water cycle approaches is absence of design to deal with xenobiotics. Nowadays can be seen increased focus on rainwater use, wastewater reclamation and reuse in industrial and as well in domestic sector what increase the exposure to xenobiotics. Innovative approaches are therefore needed to prevent xenobiotics from being discharged into surface waters where they may give rise to impacts on the chemical water quality and ecological status of receiving waters as it is already recognized by the EU-Water Framework Directive. Under such circumstances it is needed to assess knowledge gaps within the integrated water management with a particular emphasis on xenobiotics.

Leaking sewer pipes, land application of treatment residues and increased focus on soil-infiltration of stormwater and wastewater further put the urban and peri-urban soil and groundwater resources at a potential risk that only rudimentary is accessed now. The integrated nature of the urban water systems and the ability of xenobiotics to spread across structural boundaries and into the environment where ecological systems and humans are exposed calls for an intersectorial and multidisciplinary approach to problem awareness and solution. Pollutants of interest have mainly been the conventional parameters (BOD, COD, N, P, SS and micro-organisms). Thus, there is a need to understand the sources, flow paths, fate (transport, treatment, natural attenuation) and impact of xenobiotics on both humans and environment in this technical system.

NATO Advanced Research Workshops (ARW) are advanced-level meetings, focusing on special subjects of current interest. This ARW on Dangerous Pollutants in Urban Water Cycle was held in Czech Republic under the auspices of the NATO Security Through Science Programme and addressed urban water management problems. It took place at Velke Bilovice (Lednice area), about 45 km from Brno.

The main purpose of the workshop was to critically assess the existing knowledge on Xenobiotics in urban water cycle, 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 31 papers on 4 topics, Challenges in Water Resources Management, Safety and Security of Water Supply and Sanitation, Xenobiotics and its treatment, Impact assessment and Wastewater Treatment and Reuse. 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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CHALLENGES IN WATER RESOURCES MANAGEMENT

A WHOLE-LIFE COST APPROACH TO SEWERAGE AND POTABLE WATER SYSTEM MANAGEMENT

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Abstract. To promote the efficient use of resources in the developed world there is a recognised need to make best use of existing infrastructure. Whole Life Costing in combination with computational modelling techniques can be used to satisfy this need. This paper outlines the development of WLC for the capital and operational management of water and wastewater networks based on the detailed consideration of holistic performance and the explicit linking of costs to their drivers.

Keywords: water, wastewater, whole-life costing, modelling, decision support

1. Introduction

Maintaining a reliable water supply and protecting human health and aquatic resources through adequate management of wastewater systems are essential to support all aspects of human life as well as dependent ecosystems. In particular, sustainable delivery of water and wastewater services has been identified as a key challenge (UNESCO, 2006). However, there is an existing financing shortfall across the whole water/wastewater sector of investment for the operation and maintenance of existing infrastructure (DFID, 2001; OECD, 2006). As water

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and wastewater service providers are subject to regulation, one common thread in meeting the above challenges is the need to demonstrate how levels of service can be maintained at least cost whilst meeting regulatory obligations. There is, therefore, a clear need for decision support tools that assist managers with better management and decision making. This need has long been recognized and over the last decade several advances have been made in the water/wastewater utilities sector (Skipworth et al., 2002; CARE-S, 2002). As part of two industry-relevant research projects funded by the UK Engineering and Physical Sciences Research Council and supported by five large UK water/wastewater companies, a set of whole-life costing (WLC) methodologies have been developed. This paper describes the methodologies and two decision support tools developed collaboratively by the Centre for Water Systems (University of Exeter) and the Pennine Water Group (University of Sheffield).

The crux of the methodologies is gauging the impact that each unit of investment has on many different levels of service (at different points in time) and assessing the whole-life cost (both capital and operational) of interventions associated with that investment. The methodologies developed are broadly in line with the UK Water Industry Research (UKWIR) Capital Maintenance Planning Common Framework that identifies the main steps in the process as: (1) historical analysis of maintenance expenditure and serviceability indicator trends; (2) forward-looking analysis to identify future maintenance expenditure to meet regulatory objectives; and (3) conclusions, where a comparison is made between the results of historical and forward-looking analysis and recommendations are made for the required level of future maintenance.

2. Whole Life Costing Approach

There are many definitions of whole life costing. For example, the UK Ministry of Defence defined WLC as "*the continuous process of forecasting, recording and managing costs throughout the life of an equipment with the specific aim of optimising its military output*" (UK MoD, 2007), while the Construction Research and Innovation Strategy Panel (CRISP) defines it as "*the systematic consideration of all relevant costs and revenues associated with the acquisition and ownership of an asset*" (BRE, 1999). The WLC approach to urban water systems management adopted in this paper aims to achieve the lowest urban water system provision and operating cost when all costs are considered to achieve standards enforced by regulation or otherwise.

The integrated performance of water distribution and urban drainage systems is not well understood in terms of the interrelationships between physical and economic behaviour, the integrated modelling of components that describe system performance and the impact of different management strategies on performance indicators and costs. Hence there is a need to develop a toolbox approach that is capable of taking account of system behaviour, performance and regulation within a sensible economic and engineering decision support framework. The efficient and effective management of urban water systems must be based on a number of prerequisites. These include: a proper and adequate knowledge of assets (e.g., condition state); an understanding of system performance; level of service provided and required; the management intervention options available and their impact; the costs associated with system performance and interventions and; the consequences of service failure. In addition, an intellectually robust, transparent and auditable methodology for combining these aspects to ensure that service providers are delivering value for money is increasingly upper most in the minds of regulators and customers (Ofwat, 2000).

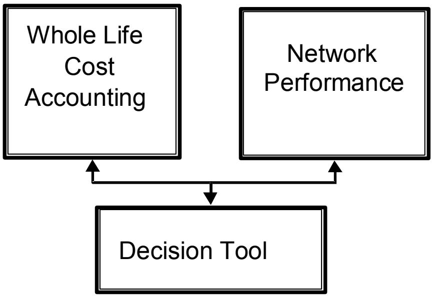

Figure 1. The framework for the WLC Methodology

The basic framework for the WLC Methodology has been configured around three main elements as shown in Figure 1. The “WLC Accounting” Module represents an accounting process that attempts to identify and report all costs, where possible as unit costs. The “Network Performance” module contains models, including a hydraulic model, that are able to simulate different aspects of performance with time under changing conditions, for example due to deterioration in the assets, changes in demand, and due to interventions. In summary, all costs and the quantities that drive them are identified in the “Whole Life Cost Accounting” and “Network Performance” Modules respectively. It must then be determined how this information is used in deriving management scenarios for operating and maintaining the network. This function is fulfilled by the “Decision Tool” element in Figure 1 which assimilates and links the information and models in the Cost and Performance modules.

3. Network Performance

Network Performance describes the state and performance of the network at any stage in time. As such it encompasses and keeps track of both current and future network configurations, models that describe the performance of the system and sets of intervention choices. A distinction is made between hydraulic-performance related features, on the one hand, and asset performance related modelling, on the other. In the first instance aspects such as hydraulic adequacy and sedimentation (for wastewater networks), and pressure (for water distribution networks) are included. Asset performance modelling includes asset deterioration (blockage and collapse for wastewater and pipe bursts and leakage for water distribution systems) although other performance models can be added.

The performance modelling components are used to generate sets of Key Performance Indicators (KPIs) based on the further development of indicators that are either currently in use or have been suggested (Matos et al., 2003; Alegre et al., 2006). The KPIs have been used to both evaluate performance and act as a mechanism to initiate intervention.

3.1. HYDRAULIC PERFORMANCE

Ofwat provides a definition of serviceability which stated that "Serviceability is a measure of the ability of the company assets to provide the service required by customers." A number of measures can be identified to measure an urban water asset's serviceability.

3.1.1. Hydraulic Performance of Water Distribution Systems

The number of properties at risk to receive their supply below 15 metres in head at their boundary, or 17 metres at the main, or the DG2 measure as referred to by Ofwat, is the main hydraulic KPI included in the WLC approach to management of water distribution systems. Other measures, like the number of customer interruptions, or the so-called DG3 measure and the number of bursts that have occurred (reported in terms of km/yr) are intertwined and obviously require the ability to predict main bursts and will be treated in the asset modelling section, while the first one requires hydraulic modelling.

The decision to include the hydraulic model enables all interventions which affect hydraulic capacity to follow the holistic nature of the proposed WLC framework. Mathematically, the required performance check is given by:

$$H_{i,t} \geq H_{min}$$

where $H_{i,t}$ is the head at each location i at time t and H_{min} is the minimum head requirement. The hydraulic modelling of a water distribution network requires that demands are aggregated at nodes. These demands are normally associated with customer service locations around the node. The above equation can be used at each demand node to check the number of services that do not receive an adequate supply. This, given the total number of service connections, gives a proxy to the DG2 measure of the percentage of properties that receive a supply below the minimum pressure level.

Within the WLC approach, the effects of increases in pipe hydraulic roughnesses with time can be considered through utilisation of empirically derived relationships. Equations can be assigned for each material type and possibly may change for each zone depending on water quality. If the water company does not hold information upon which to base such relationships, they must be derived or estimated by other means, for example from the limited available literature.

Water quality has, and will continue to play an important role in any maintenance strategy. In respect of a given water quality determinant (e.g., iron, lead, PAH, etc.), within the WLC approach an equation is used to reflect the operational cost of dealing with the risk (where actions are taken to mitigate the risk) or financial risk costs carried by the company (where no action is taken to mitigate the risk). For example, the operational cost of flushing corresponding to a given area, therefore, could be given as:

$$C_{Tflush} = F\sum_{j\in AM}\left[\left(v_j + w_j\right)L_j\right] + E_{flush}$$

where, C_{Tflush} is the total annual cost of flushing (£), j is a main in the network where AM is the complete set of all mains, L_j is the length of main j, F is the number of flushes per year, v_j is the annual cost associated with the particular main based on whether the main is thought to be a source of sediment build up (£/unit length/year), w_j is the annual cost associated with the particular main based on whether the main is thought to be a source of discoloration through corrosion and would equal to 0 if the main is not an unlined ferrous main (£/unit length/year), E_{flush} are the annual external costs associated with flushing. It is important to note that this is not a hydraulic performance model per se although the cost equations have a physical basis.

3.1.2. Hydraulic Performance of Wastewater Systems

A major operational concern for combined sewerage systems is their capacity and performance under wet weather conditions; at what point and under what conditions might the onset of in-system hydraulic incapacity, and any resultant flooding occur. Another aspect includes the question on what volumes of water which are in excess of the system capacity to convey onward. The project has developed a mathematical modelling tool to predict the hydraulic performance under two conditions: wet weather flow (WWF), dry weather flow (DWF). Dry weather flow conditions are also of interest from the point of view of the likelihood of deposition of sediments within the system and whether or not there is sufficient self-cleansing flow in the system.

The proposed performance measure for hydraulic incapacity under Wet Weather Flows (WWF) is based on a *performance assessment system* expressed either in terms of discharge (Q) or water level (H) (hydraulic head), Figure 2 shows this in terms of water level. The value H* (or Q*) represents the required or acceptable level of performance of an asset under WWF, with values dependent on pipe size, category, condition grade and possibly other factors.

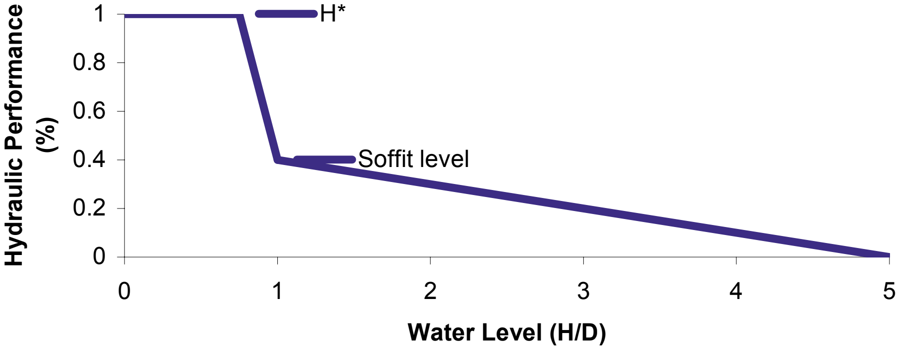

Figure 2. Hydraulic Performance Function Based on Depths

The hydraulic performance functions would be calculated for each of the WWF design events and for each asset a series of performance indicators produced. These would compare actual performance from the simulations against the requisite performance level for that particular asset. The performance functions would be further aggregated in the following steps: (1) by integration over the duration of wet weather event (and normalising over unit time); (2) by selecting critical values for each and every one of the different storm conditions; (3) by averaging with respect to probability of occurrence, i.e. by summing values for each return period multiplied by its probability; and (4) by aggregating to the system level with weighting proportional to pipe length. This step could be done either for the entire system in the same manner, or within groups.

In the cases where the simulation has identified flooding as occurring, a separate statistical routine is used to convert from flood volume, calculated through simulation, to the extent of the flooding caused at each location and the maximum water levels, for flooding caused by ejection from sewers. At a minimum the number of properties affected by flooding would be calculated for each incident and location indicated by the simulation.

Other considerations of hydraulic performance, such as Dry Weather Flows (DWF) and sedimentation, were subject to similar development. A system DWF performance has been characterised by its ability to transport DWF referenced to the total available capacity and actual flow rate as a simple ratio indicator called 'Sewage Available to Transport' (SATT). The indicator has been defined as the percentage of time during 24-hour dry weather flow simulation when the SATT score was greater than a pre-selected minimum. The flow simulations are also used to determine the actual velocity of flow in the system under dry weather flow conditions. These are compared against the critical or self-cleansing velocity to prevent sedimentation (Ackers et al., 1996).

3.2. ASSET PERFORMANCE MODELLING

3.2.1. Asset Performance Modelling for Water Distribution Systems

Within the WLC approach to distribution network management, there is the need to quantify the likely future cost of asset (structural mains) failure. Structural failure is often used as justification for asset replacement. However, within the WLC approach, the impact of replacement must be considered in its direct effect on, for example, leakage, water quality, customer interruption and in its indirect effect on, for example, additional purification and transmission costs and the demand for water placed on the environment. The probable rate of failure can then be attached to each length of pipe based on its asset and environmental description. The form of model used in the burst analysis to derive risk factors for homogeneous pipe groups, and the growth in these factors, for use in the WLC framework is given as:

$$\lambda(t_0)_i = \prod_k x_{ik} r_k$$

where, t_0 is the base year of the analysis, $\lambda(t_0)_i$ is the burst rate/unit time/unit length at time t_0 for the ith pipe group, k is a set of environmental factors (e.g., physical characteristics of assets and the conditions under which they operate), x_{ik} is a vector describing the asset and environmental variables, r_k is a vector of regression coefficients (Skipworth et al., 2002).

3.2.2. Asset Performance Modelling for Wastewater Systems

Blockages and collapses are a significant problem for the maintenance of the proper functioning and performance of sewer networks. They are responsible for 50% of all cases of sewer flooding. Two analytical approaches were adopted to accommodate the diversity of parameters on the one hand and reduce the impact of missing data on the other: multiple regression techniques (Shepherd et al., 2005), and evolutionary computing (Savic et al., 2006). From Shepherd (2005) it was shown that in respect of blockages that:

$$B_r = a(R_v \cdot L)^b$$

where, B_r is the blockage rate for a given category of pipe assets, a and b are coefficients dependent on the ICG band (ICG = Internal Condition Grade), R_v is the relative velocity of flow through the category of pipe assets and L is pipe length. Relative velocity R_v is defined by $D^{2/3}.s^{1/2}$, where D is the diameter and s is the gradient of the asset.

The second approach to modelling blockages has been based on a data mining technique, Evolutionary Polynomial Regression (EPR), which integrates the best features of numerical regression analysis with genetic programming (Giustolisi and Savic, 2006). Based on results of pervious studies (UKWIR, 2006) and by experimentation for this particular case study, the following expressions were derived for the number of blockages:

$$B_r = 0.212 \ln\left(\frac{D^2}{H \cdot L}\right)$$

where H is the hydraulic head at the blockage point. The equivalent expression derived by EPR for collapses is:

$$C_r = 0.00156 \frac{1}{L} \ln\left(\frac{K}{D}\right)$$

where K is the pipe cover depth.

4. Cost Accounting and Decision Tools

Costs are broadly associated with one of three cost categories: planned, unplanned-reactive and, planned-proactive, reflecting the level of activity occurring in the system. An Interventions Matrix, triggered by serviceability indicators and performance, has been development with the industrial collaborators such that the range of acceptable interventions is included. Within a time step the costs that accrue arise from the performance of the system at that time; either normal operational costs or costs resulting from a defined requirement to intervene. Thus for each time step a series of costs can be calculated that together make up the total cost accrued within that time step resulting from the provision of the service. Taking all the time steps together and their associated costs will give WLC for that particular configuration of service provision. This may not be the least WLC or the most cost-effective expenditure. Determination of any of these additional requirements would require further calculation steps in order to satisfy such conditions and would lead to modifying the intervention decisions.

Decision Tools developed for both water and wastewater networks allow the choice of different intervention strategies to be linked to not only their associated costs and cost profile over time but also to how they impact on performance within and between the time-steps. It is also important to be aware that there are constraints on both acceptable and unacceptable performance so that efforts to minimise costs that do not meet the required levels of service will not be acceptable. A key feature of the incorporation of the various performance models within the software platform is that it allows them to be integrated and provide the requisite feedback between the different performance models rather than treating different aspects of performance in isolation from each other. Different aspects of system behaviour and performance are inter-related and affect each other. Changes in performance manifest themselves across a system's performance both in terms of location and time. The integration of the hydraulic modelling with system asset performance models and the integration of the effects of different interventions not only offer a powerful tool to simulate network system behaviour over time as a predictive tool but also mirror, with an acceptable degree of rationalisation processes that are naturally at work.

5. Conclusions

A set of innovative methodologies has been developed that optimises both the engineering activities and the timing of investment within budgetary and levels of service constraints. The process relies on a whole-life cost management approach encompassing hydraulic performance modelling, asset modelling, whole-life cost accounting and decision support tools.

Input data to the models include investment required, engineering activities (interventions), existing levels of service and the impact of investment on the levels of service. Outputs include profiles of investment and individual levels of service over time, i.e. an explicit link between investment and service performance. The models are of generic type, i.e. it can be applied to other companies with other types of assets. The type of questions which the model can help answer include: (1) Can service target levels be delivered within budget? (2) What is the optimal mix of solutions for each asset type that should be adopted over a planning period? (3) What is the impact of investment timing on levels of service? (4) What is the minimum budget required to meet targets?

Short-term benefits of this type of modelling include greater certainty that investment decisions will bring about the improvements sought and greater efficiency from limited funds. Long-term benefits include stronger justification for investment decisions (to the Regulator and internally) and more direct management of customers' levels of service.

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REUSE OF URBAN WATER: IMPACT OF PRODUCT CHOICE

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Abstract. The toxicity of individual products has been measured in relation to a marine luminescent bacteria and a biological community within a grey water treatment technology. The results demonstrate that brand labeling provides no evidence about the relative toxicity of a product including those labeled as environmentally friendly. Overall, the only products seen to be a potential risk to reuse treatment technology is bleach and car oil with secondary risks associated with washing powder and vegetable oil.

Keywords: grey water, toxicity, reuse

1. Introduction

The availability of a sustainable supply of fresh water has always been central to the development of urban centres around the world. In more recent times, increased attention has been placed on water due to increases in both population and water demand per capita. Management of such issues involves multiple options including the decentralization of wastewater treatment and the potential reuse of water from either black or grey water sources. The distinction between the two is the input of water flows from the toilet in the case of the former and excluded in the case of the latter.

On a volume basis, 75% of the total wastewater flow to domestic sewers is derived from grey water sources yet there has been a paucity of investigation into the nature of these flows. In one such study Erisksson et al. (2002) revealed 900 potential substances in a survey of products used in Danish households.

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Similarly, around 200 Xenobiotic compounds (XOCs) were detected in an audit of grey water derived from bathroom sources (Erisksson et al., 2003). The dominating sources of XOCs are expected to be derived from the chemicals used within the household in combination with personal care products. The biggest sources by mass will be the laundry powders and washing products used on a regular basis yet relatively little is understood about the impact of such products on the toxicity of grey water and its treatability. Further, there is a need to understand the role of product choice on the nature of grey water and how this may affect its ability to be treated to an acceptable standard for reuse. In addition to the regular products discharged into the sewer a number of products can be discharged on a occasional basis and these may have a dramatic impact on the treatment processes and the overall acceptability of the water for reuse. The current paper aims to investigate these issues in order to begin to understand the role of consumer choice and habits on the characteristics of grey water and its ability to be treated for reuse applications.

2. Materials and Methods

A questionnaire survey on consumer behavioral patterns was distributed to 520 people of whom 341 replies were received covering a mixture of gender, age and social groups within the UK. The aim of the survey was to determine the following:

- What frequency different substances were discharged into a grey water sink
- Which substances were perceived as being harmful to the environment

The survey asked people to indicate the frequency which they dosed each substance into a bath/sink/shower. The survey then asked each respondent to indicate which 3 of the substances listed they considered to be harmful to the environment. Products were purchased from a national supermarket chain and selected as common examples of each category of product based on there relative coverage on the supermarket shelves. The toxicity of each product was assessed in relation to either response to a specific bacteria or to a active biomass used in the treatment of grey water. Specific bacterial toxicity was measured using a Microbics M500 toxicity analyser (Azur Environmental, UK) based on the response of a marine luminescent bacteria (Vibrio fischeri NRRL B-11177) to determine the median effective concentration EC_{50}. Biomass toxicity was measured in an 11 channel closed cell aerobic respirometer (CES ltd, UK). Biomass was taken from a membrane bioreactor treatment grey water under steady state conditions. In each cell 20 mL of washed biomass, 30 mL of grey water and 10 mL of the test component were combined and the standardized oxygen uptake rate measured for 24 hours. In each run, a control cell was measured by adding de-ionised water instead of the test product and data only analysed if the control was consistent with previous runs.

3. Results and Discussion

3.1. PRODUCT TYPE

Comparison of the toxicity of products revealed the most toxic products to be the bleaches and the laundry powders whilst the shampoos were the least toxic (Figures 1a and 1b). To illustrate, the $\log_{10}$ EC_{50} values for the branded version of each product were 2.01 $\mu L.L^{-1}$ for the shampoo compared to 0.83 and 0.30 $\mu L.L^{-1}$ for the laundry powder and bleach respectively. All other products had a $\log_{10}$ EC_{50} value between 1.00 and 2.00 $\mu L.L^{-1}$. Analysis of the data with respect to whether the product was commercially branded, an own brand or an environmentally labeled brand revealed no consistent trend with respect to toxicity ranking. For instance in the case of the shampoo and shower gel the ranking of products from most to least toxic was Own brand, branded and environmentally branded (Figures 1a and 1b). However, in the case of laundry powder the ranking was environmentally branded, branded and own brand. It must be noted that in many cases the differences in toxicity levels were below the error levels of the test and as such no real difference could be recorded. Importantly, the data indicates that product selection based on labeling is no indication of the toxicity of the product. More specifically, purchase of products labeled as environmentally friendly do not demonstrate a lower toxicity as is perhaps perceived by the consumer.

Comparing the two techniques employed revealed that in the majority of cases a lower EC_{50} value was recorded for specific bacterial toxicity as opposed to biomass toxicity (Figures 1a and 1b) by 1 to 2 orders of magnitude. To illustrate, the $\log_{10}$ EC_{50} values for the environmentally labeled washing up liquids were 1.01 and 2.22 $\mu L.L^{-1}$ with respect to the specific bacterial toxicity and 4.46 and 4.32 $\mu L.L^{-1}$ with respect to community toxicity. Comparison of the two techniques revealed no consistency with respect to toxicity level, indicated by the ratio of the EC_{50} values of both techniques, or the ranking of the products apart from that the bleaches and laundry powders come out as the most toxic.

More detailed analysis within each product group was conducted to assess the impact of product choice by labeling, price and profile of the most common users. The later was identified though a focused panel discussion and separated into broad grouping based on age, gender etc. EC_{50} values with respect to specific bacterial toxicity revealed no consistent trend based on any factor. For example in the case of shampoo the $\log_{10}$ EC_{50} varied between 0.89±0.61 $\mu L.L^{-1}$ and 9.93±5.85 $\mu L.L^{-1}$ (Figure 2). Whilst there is a clear difference due to product choice it was not consistent through the study indicating that there is no clear selection basis for ensuring lower toxicity products are used.

Investigation into the specific chemicals in each product is difficult but some common components can be identified. In the case of the human washing products, for example shampoo and shower gel, ingredients such as sodium lauryl sulfate (SLS) and essential oils are likely to be the most toxic components. Indeed, the US EPA toxicity database reports the EC_{50} of SLS to

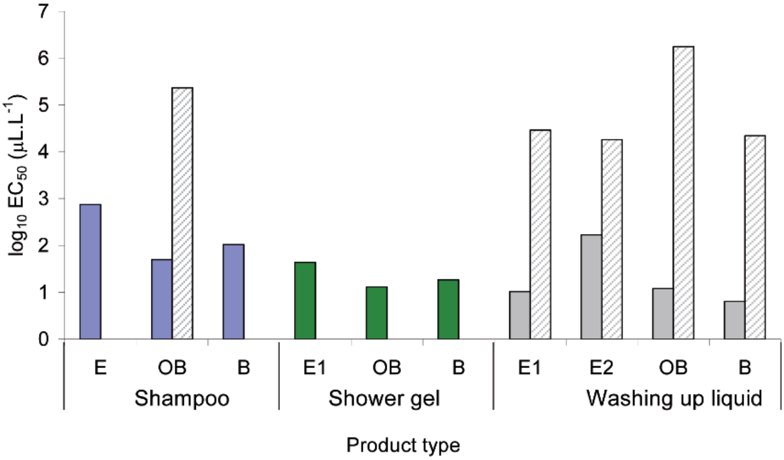

Figure 1a. Toxicity determination for generally used household products. For each product type the filled in box relate to microtox data and the hatched boxes relate to respirometry data

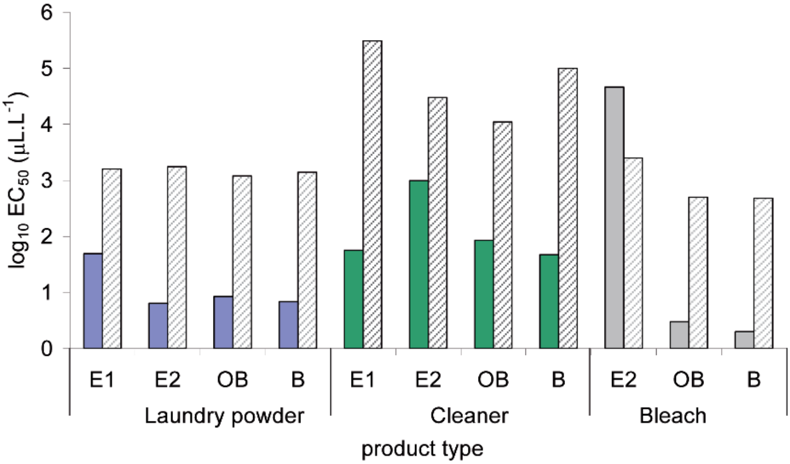

Figure 1b. Toxicity determination for generally used household products. For each product type the filled in box relate to microtox data and the hatched boxes relate to respirometry data

be between 8-41 mg.L^{-1} based on *daphnia magna* toxicity (Pidou, 2006) which is within the range measured in the current study. In the other products surfactants and sodium hypochlorite are the key ingredients with respect to toxicity. Specific surfactants are not commonly reported on product labels but previous studies have reported synthetic surfactants such as linear alklybenzene (LAS) and alklyphenol ethoxylates (APEO) which are know to be toxic and very resistant to biodegradation (Pidou, 2006). EC$_{50}$ levels for some potential compounds have been measured such as LAS with a level around 15 mg.L^{-1} (Pidou, 2006). Less commonly reported is the toxicity of essential oils which can be very toxicity and are known to be used as a disinfectant in some industrial situations. As an example, the EC$_{50}$ of clove bud oil is 0.01 μL.L^{-1} making the oil much more toxic than most of the other components.

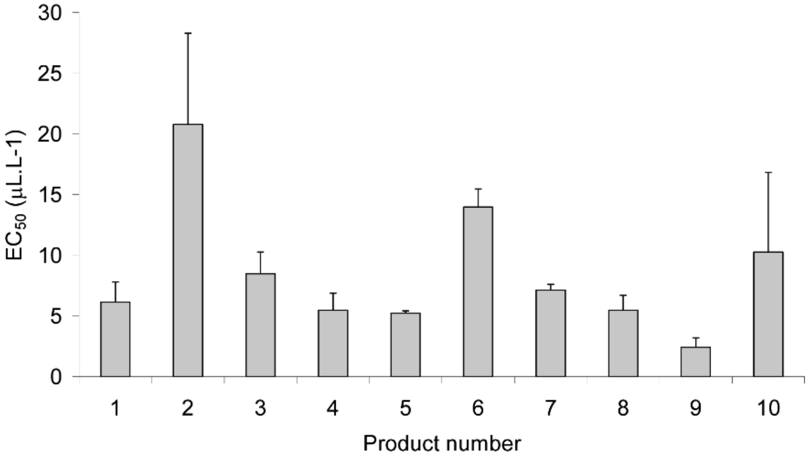

Figure 2. Toxicity of shampoo as measured by mircotox®

3.2. OCASSIONAL SUBSTANCE COMPONENTS

Results from the survey on discharge of occasional substances into grey water sources revealed that bleach (32%), body/food oil (32%), food (23%), cleaners (66%) and washing powder (27%) were identified as the most likely products to enter a grey water source as indicated by a high percentage response to the “at least once a week” category (shown in brackets) (Figure 3). Conversely, white spirits (87%), hair dye (89%), alcohol (84%), perfume (93%), body fluids (83%), Oil (94%), pet care products (96%), make up remover (84%) and caustic soda (91%) were identified are unlikely to enter a grey water source as they had a high combined percentage response to frequency ratings of “occasional”, “once” and “never” categories. Analysis of the responses with respect to gender and age showed that in most case neither significantly affected the likely frequency of discharge. The exception was an increased frequency of discharge of bleach among the older respondent age group.

Bleach (18.5%), white spirits (11.1%), oil (23.8%), detergents (13.7%) and caustic soda (11.1%) were identified as potentially harmful to the environment by a significant number of the respondents. Substances that are used for direct physical human contact or ingestion, such as make up remover and vegetable oil were considered to be the least harmful to the environment. No distinct correlation between age, gender and substance was found apart from the case of caustic soda where more female respondents judge it to be detrimental to the environment than male respondents. All females and males over 26 years old perceived car oil as being the most harmful substance of those listed, whilst younger males perceived bleach to be the most harmful. Interestingly, the perception of a substance being harmful to the environment did not significantly influence the likely discharge frequency. This was most pronounced with the older respondents although in part this is due to the opportunity of discharge as much as the behavioral choice.

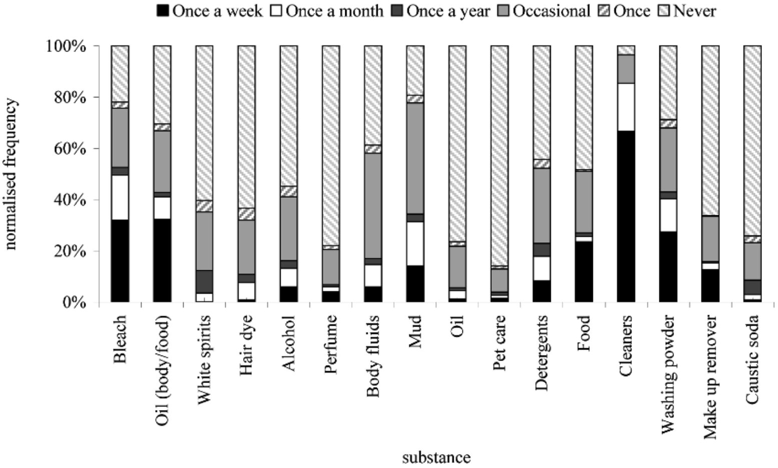

Figure 3. Normalised discharge frequency of different spiking substances

The addition of a test substance to active biomass revealed a similar pattern for most substances whereby the respiration rate initially increased then decreased once the concentration of the test substance had exceeded a critical value (C_{crit}) (Figure 4). Household cleaning products such as bleach and high strength chemicals such as car oil, caustic soda and perfume reduced the respiration rate at low relative doses (Table 1). For instance, in the case of bleach the

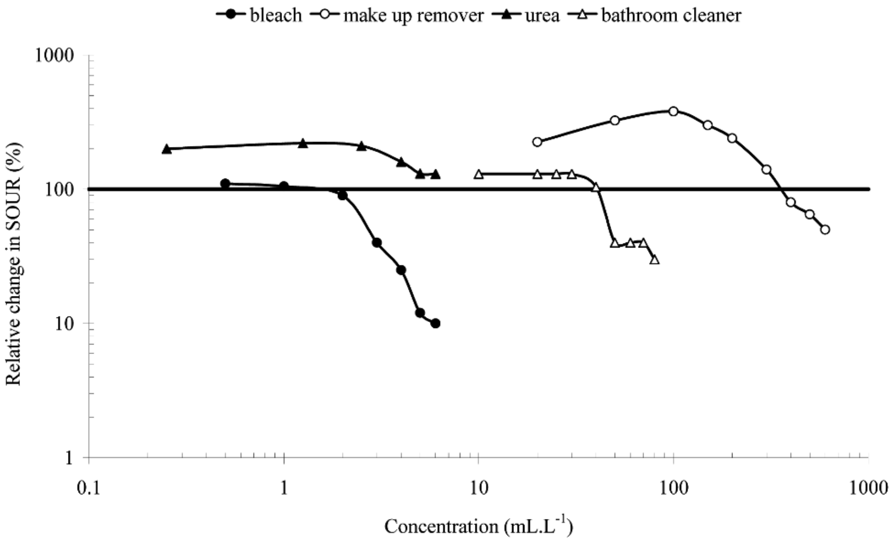

Figure 4. Relative change in SOUR when test substance is added to active biomass

TABLE 1. Critical concentrations of test substances

Substance	Ccrit $(\mathrm{mL.L^{-1}})$SOUR	Ccrit $(\mathrm{mL.L^{-1}})$pH	Spike vol. (L)	Vcrit (L)	Possible risk?
Bleach	1.4	4	4	2857	Yes
Caustic soda	4.5	<1	–	–	–
Vegetable oil	<10	Not found	4	400	Maybe
Perfume	12	Not found	0.5	41.6	No
Car oil	15	Not found	10	666	Yes
Washing powder	24	14	4	285	Maybe
Hair dye	>26	14	0.5	35.7	No
Carpet cleaner	30	Not found	4	133	No
Pet Shampoo	36	114	4	111	No
Bathroom cleaner	43	67	4	93	No
Food (soup)	60	40	1	16.6	No
White spirit	95	Not found	4	42.1	No
Alcohol (spirit)	130	240	1	7.6	No
Make up remover	320	Not found	1	3.1	No
Urea	Not found	Not found	1	–	No

SOUR fell below that of the control once the concentration had exceeded 1.4 $mL_{bleach}.L^{-1}$ (Figure 4). Beyond this concentration the respiration rate continued to decrease such that at a concentration of 6 $mL_{bleach}.L^{-1}$ the SOUR was 10% of the control value indicating that almost complete retardation of biological activity had occurred. Substances that provided relatively assailable organic material produced enhanced respiration over wide concentration ranges (urea, food, oil, alcohol). The test with food, washing powder, detergents, hair dye were restricted in concentration range due to operational problems associated with mixing or foaming indicating that spiking may cause other detrimental effects on the treatment process.

Analysis of the change of respiration rate and COD removal indicates the most probably pathway for the observed changes in activity (Jefferson et al., 2001). The observed increase in activity appeared to be due to metabolic stimulation in the case of carpet cleaner, alcohol, pet care product, make up remover, hair dye, washing powder and perfume. Whereas in the case of bleach, caustic soda and oil the observed changes appeared to be due to the uncoupling of metabolism, in which anabolism is inhibited and catabolism is not. In most cases when the dose exceeded its critical value the decrease in activity was due to metabolic inhibition. However, in the case of carpet cleaner, alcohol, pet shampoo and car oil the loss of activity appears to be due to chemical reaction between the grey water and the added substance. Analysis of the substances and there observed impacts revealed no discernible pattern or indicated any common chemical that caused a statistically apparent trend.

Another possible problem is the change in acidity of the grey water as a consequence of a spiking incident. As grey water contains little nitrogen critical pH ranges for carbonaceous oxidation are most relevant and lie between 6.5 and 8.5 (Gray, 1989). Further, depending on the probably standards that are imposed a pH criteria may exist which is likely to stipulate that the final grey water must be within the range 6–9. Critical concentrations of <1 $mL.L^{-1}$ (caustic soda), 4 $mL.L^{-1}$ (bleach), 14 $mL.L^{-1}$ (hair dye), 14 $mL.L^{-1}$ (washing powder) and 67 $mL.L^{-1}$ (bathroom cleaner) were observed due to increased pH beyond a value of 8.5. Whereas, in the case of food (40 $mL.L^{-1}$), and pet shampoo (114 $mL.L^{-1}$) the pH was reduced below the critical threshold. In the case of caustic soda, washing powder and hair dye the critical concentration due to pH was lower than that for respiration and was used in all further analysis.

To assess whether a potential chemical spiking event poses a process risk to a biological system it is necessary to estimate whether C_{crit} can be reached. The estimation comprises of two components: (1) what is likely volume of grey water the substance will be spiked into and (2) what is the maximum likely spike volume for each substance. Investigations into water saving efficiency in buildings have shown little improvement once the storage volume exceeds 150 L for single houses (Dixon et al., 1999a). In larger applications, which are more likely to involve biological processes, storages volumes are sized to avoid residence time beyond 24 hours due to concerns of water quality transformations and storage volume around 1 m^3 are often reported (Dixon et al., 1999b). Obviously the storage container may not be completely full at the time of any spiking event and so partial volumes need to be considered. Taking a grey water production rate of 100 $L.h^{-1}.d^{-1}$ and a minimum fill percentage of 50% of the storage volume then a sensible minimum grey water volume would be 500 L (equivalent to a 10 person occupancy building). Maximum spike volumes realistically can be assumed to equal the whole contents of one container of that substance (Table 1) and typically vary between 4 L for bleach to 0.5 L for perfume.

Combining the critical concentration and the maximum likely spike volume estimates a critical volume (Table 1). The critical volume represents a threshold level beyond which any storage volume would be able to buffer out any potential negative impacts. Comparison of the critical volumes indicates that bleach (V_{crit} = 2857 L) and oil (V_{crit} = 666 L) pose the only genuine process risks to biological activity. Under the current set of assumption bleach continues to be a potential risk up to populations of around 60 occupants. Vegetable oil and washing powder were indicated as possible risks if small storage volumes were used.

4. Conclusions

The experimental work described in this paper demonstrates that in terms of acute toxicity, as measured against either specific bacteria or an active community, brand selection has little relevance in informing about the impact of the product. Indeed, products labeled as environmentally friendly were shown to be no different to all the others tested within the framework of the study. A difference between specific bacteria and community is also shown suggesting that the impact of the toxicity is less likely to effect biological treatment systems than other potential areas of concern and that considerable volumes of the given products are required before any expected impact is likely to be observed. More detailed investigation into substances that can occasionally enter grey water sources reveals that whilst many substances have the ability to cause deterioration in the performance of biological systems the only products of real concern are bleaches and car oil. Secondary concerns exist for washing powders and vegetable oil.

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URBAN WATER RESOURCES MANAGEMENT IN ROMANIA - PERSPECTIVES FOR THE SUSTAINABLE DEVELOPMENT IN ORDER TO SUPPLY WATER TO HUMAN SETTLEMENTS

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Abstract. Romania is the beneficiary of an important complex of water resources. As various forms of water pollution can be found, some sources of water become unusable, so that the demand/supply ratio acquires a more complex significance. Generally, fertilizer, livestock industry waste, household effluent can be regarded as the sources of water pollution due to nitrates etc. The Environment Authority has established provisional guidelines concerning the controls on discharge of substances. The principles for the sustainable management of water resources, recommended by Rio Conference (1992), and the European Union regulations, lay at the foundation of the concept of integrated water management in Romania as well, where the problems of water usage are combined with the protection and conservation of natural ecosystems.

Keywords: romanian water resources, pollution, causes, quality standards, measures, sewerage systems, monitoring, conservation, management, sustainable development

1. Current Situation of Water Pollution in Romania

In Romania, measurements of water quality in nationwide public water areas were conducted from 1993 according to the new environmental quality standards of which the restrictions on substances that are harmful to human health, such as cadmium etc., have been revised. According to the results of the measurements, there were 33 measurement points which recorded a level of pollution

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exceeding the environmental standard, out of 5,708 measurement points nationwide, indicating that the points at which the standard was not achieved was 0.58% of the total number of measurement points.

As for conformity to the environmental standards concerning human health, because of the revision made to the standards, it is difficult to evaluate the status of conformity to the standards over the years. However, if calculated based on the conventional method to figure out the ratio of non-conformity (the ratio of the number of samples of which the level of pollution exceeded the standard, against the total number of samples examined), the ratio of non-conformity to the old environmental standard was 0.01%, which has improved steadily since 1989.

In the monitored areas where classifications of the environmental standards are applied concerning items pertaining to preservation of the living environment, the environmental standards per BOD (or COD), a typical water quality index used to measure organic pollution level, were achieved in 76.5% of all water areas; while 23.5% of total water areas have not yet met the standard. The breakdown of areas achieving the standard by water area is rivers 77.3%, lakes and reservoirs 46.1%, and sea area 79.5%. The achievement ratio is especially low in closed water areas such as lakes and reservoirs, and medium and small rivers in urban areas.

As regards other forms of water pollution, contamination of groundwater by substances such as: trichloroethylene etc.; contamination by organic tin compounds in vast areas; the pollution of public waters by the outflow of hazardous substances due to accidental long-term turbid water due to dam construction (applicable to limited areas); acidification, caused by natural factors, of rivers, lakes and reservoirs; impact on the environment by thermal drainage from large power stations pose problems (Compania Nationala Apele Romane, 2006).

2. Main Causes of Water Pollution in Romania

Tightened restrictions have proven effective to control pollution caused by effluent from factories and workshops. On the other hand, effluent associated with daily living such as cooking, laundry, bathing etc., has not been controlled satisfactorily due to inadequate sewage systems, and so on.

The cause of pollution in closed water areas such as lakes and reservoirs etc., is that due to physical features unique to closed water bodies, water often stagnates causing a favourable condition for contaminants to accumulate. The other cause of pollution in these areas is the socioeconomic factor. Population and industries are concentrated in water front areas.

In rivers in urban areas where population and industries concentrate along them, and in lakes and reservoirs of which the surrounding areas are increasingly urbanized, such as Tulcea or Braila, sewage systems can not catch up with the increase in population, and the pollution is encouraged by drain water, especially by household effluent (Galatchi, Vladimir, 2007).

As described above, recent water pollution is mainly caused by organic pollutants, and countermeasures against effluent from daily living are especially needed immediately. Besides this, water pollution is caused by unspecified sources i.e. contaminant effusing from urban areas, land creation sites, farming lands, often washed out by rain etc. Other causes include nutrient salts eluting from the bottom sediment consisting of deposits which are the result of long-term water pollution. Conditions of these factors should be studied and appropriate measures must be taken.

3. Threats Caused by Water Pollution

Approximately 70% of the sources of city water in Romania are from surface flowing water such as rivers, and can be affected significantly by water pollution. Underground water that accounts for approximately 30% of the total sources of city water was considered to be of good quality, until pollution caused by substances such as trichloroethylene etc. became actualized. There is a number of city water systems affected by water pollution in their sources.

Recently, the excess increase of algae due to eutrophication in reservoirs sometimes causes foul smell or taste in city water. In 2002, 28 city water systems were affected by foul smell and taste, disturbing approximately 3 million people (Negulescu, 2004).

To control water pollution occurring in the sources of city water systems, system operators are taking measures such as introduction of high-grade water purifying facilities. However, a contaminated water source is an enormous burden to the system operators from the stand-point of safety of city water, and can raise the cost of water treatment operations.

City water must be maintained at a safe and reliable quality for its users at all times, and the sources of water systems are desired to be maintained as pure as possible. Therefore, preservation of the quality of city water is becoming increasingly important.

Approximately 70% of the fresh water supply of industrial water in Romania depends on river water (approximately half of it is used for industrial tap water) such as surface water and infiltration water. Industrial water is used for many purposes such as for raw material, processing and washing of products etc., and is sometimes affected by contamination of river water.

Industrial water is generally treated by chemical sedimentation. Sometimes the disposition of sludge made from the contaminant of river water created through this treatment process raises a problem.

With the advance of recent urbanization, there are occasionally cases where effluent from cities flows into agricultural water, causing substantial damages to agricultural production as well as the living environment in farming communities.

Currently, the number of areas (of 5 ha or more) that are affected by polluted agricultural water is approximately 552 nationwide, total area of approximately 43,200 ha. The ratio of damages caused by the effluent from cities (including household effluent in agricultural communities) is highest of all, and accounts for 84% of total damaged area.

The result of the investigations conducted for two years since 2005 indicates that the number of areas damaged has increased by 10%, and the total area damaged has decreased by 2.9% as compared to the result from 2000. The total newly damaged area was approximately 12,000 ha, and 91% of the total area was damaged by effluent from cities.

Types of damage that the fishing industry is suffering from due to water pollution include:

1. deterioration of fishing environment and damages to boats and equipment due to floating objects on surface water, deposits etc.;
2. destruction or incomplete development of marine organisms due to algal blooming or even oil contamination;
3. soiled or rotten boats and equipment due to oil contamination etc.

4. Environmental Quality Standards in Romania

Environmental quality standards concerning water pollution are set as targeted levels of water quality in public water areas, and they should be achieved and maintained. The standards are classified in two categories:

1. the levels to be achieved and maintained to protect human health;
2. the levels to be achieved and maintained to preserve the living environment.

In the health category, uniform standards are set for public water areas, while in the living environment category standards are set for each classified type of water area depending on the purpose of usage of the water area. According to the type of area designated, a specific standard can be applied.

The environmental quality standards concerning the protection of human health were revised, substantially after 1989. The standards currently specify 23 items including:

- heavy metals such as cadmium, lead etc.;
- organochlorine compounds such as trichloroethylene etc.;
- agricultural chemicals such as simazine etc.

In addition to these, the standards were set as guideline levels for items that require close monitoring, in order to better understand the condition of water quality and further promote the prevention of water pollution (Guvernul Romaniei, 1999).

For items of the living environment category, standards per BOD, COD, and DO are specified. In order to prevent eutrophication, standards for nitrogen and phosphorus have been newly set for coastal areas, in addition to the standards for lakes.

Concerning the removal of the bottom sediment containing hazardous substances, provisional removal standards are established for bottom sediment containing mercury or PCBs.

5. Restrictions on Effluents in Romania

In an effort to preserve the water quality in public water areas, the Romanian Water Pollution Control Law sets nationally uniform standards for effluent discharged from specified factories into public water areas.

Some standards set for hazardous substances have been added to these nationally uniform standards, and some have been tightened, in conformity with the environmental standards concerning human health. New standards have been set for seven items of organochlorine compounds including dichloromethane etc., and 13 items of agricultural chemicals including simazine etc., and standards for lead, arsenic etc. have been tightened.

For those areas in which the environmental quality standards can not be met or maintained only by satisfying the nationally uniform effluent standards, can establish local more strict standards in addition to the national standards.

Corresponding with people's increased concern in the quality of city water, the "Basic Policies of Preservation of Water Quality in the Sources of City Water to Prevent Problems in Specified City Water and Irrigation Systems" was decided upon by the Government, in conformity with the Law Concerning the Measures for the Protection of Water Quality in Water Resources Area for the Purpose of Preventing Specific Trouble Drinking Water Supply. In the mean time, the Romanian National Environment Agency was inquired about the establishment of a range for specified effluent standards concerning the formation of trihalomethane, in consideration with the results from the effluent fact-finding investigations.

Requests were made by seven city water system operators from four counties for the concerned counties to promote the enforcement of the project for preservation of raw water quality used in city water systems. As a result of these requests, counties plans for the project have been determined for three operators of city water systems in two counties, and determination of other plans are under way for four operators in three counties.

The Romanian Environmental Protection Law specifies that, in case of a water pollution accident, the owner of the facility concerned is to take emergency measures, and that the facility owner is to notify the prefect of the concerned county of the measures taken.

6. Measures for Domestic Effluents

One of the problems that are contributing to water pollution in public water areas is effluent associated with daily living such as cooking, laundry, bathing etc.

In order to promote the measures to control domestic effluent it is important to improve not only sewerage systems but also various other drainage treatment facilities such as community plants, drainage facilities for agricultural communities, individual treatment equipment of mixed-effluent etc., according to the actual condition of each area. At the same time, measures such as increasing people's awareness toward the issue, encouraging people to participate in activities to reduce domestic effluent, should be promoted as well.

The National Environment Agency in Romania formulated the "Guideline for Guidance on the Promotion of Measures to Cope with Domestic Effluents", and holds a Water Environment Forum periodically as part of measures. By the partial amendments made to the Water Pollution Control Law, stipulations on measures for domestic effluent such as clarification of responsibilities to be assumed by the administration and the people concerning domestic effluent; and systematic promotion of measures for domestic effluent, have been improved according to the revised Water Pollution Control Law, prefects of counties are working on the designation of the areas for which intensive measures should be taken. Support was provided toward designated municipalities for their determination of a program for the promotion of measures against household effluents, establishment of facilities to purify water channels severely polluted by household effluent, development of facilities for collection of used oil and making soap from it and so on.

7. Sewerage System in Romanian Human Settlements

To support healthy growth of a city, improve public hygiene, ensure a good living environment, and to preserve the quality of public water areas, sewerage systems are vital and fundamental facilities.

Currently, a systematic project to improve sewerage systems is under way. One of the major objectives of this project is to improve sewerage systems, in middle-and small-sized municipalities, where the provision of sewerage systems are significantly behind. Another key objective of this project is to promote sewerage system operations as well as their high-grade treatment technologies to meet the requirements of the European Union. Moreover, it is also aiming at the achievement of the water environmental quality standards, prevention of flood and improvement of the living environment in urban areas, conservation of the natural environment in lakes and reservoirs, improvement of the living environment in agricultural communities, mountain villages, and fishing communities along the Danube River and in the Danube Delta; and promotion of effective use of treated sewage water and sludge.

Various projects to develop sewerage systems were conducted. These projects include: public sewerage systems; watershed sewerage systems; sewerage channels in urban areas; specified public sewerage systems; and specified public sewerage systems for environmental preservation. For those areas in which drastic improvement is needed, a project to promote improvement of sewerage systems by fully utilizing projects that are operated independently by the local authorities, in conjunction with the projects supported by the Government, has been enforced.

From the standpoint of the effect that the improved sewerage systems can produce in conservation of water quality in public water areas, a project has been enforced, having as objective to foster the relation between the residents and the clear water in the community. And in addition to the measures for controlling domestic effluent which have been enforced on days with fine weather, a project aiming at collecting and treating polluted urban runoff has been established.

In an effort to revive small streams in urban areas in response to people's need for a peaceful and pleasing urban living environment, various projects are being carried out. These include:

- sewerage system model project of sewerage system with amenities being carried out in five locations, a sewerage system utilizing treated sewage water;
- recycled water sewerage system projects in 13 locations (two new projects), a system utilizing treated sewage water for flush toilets in urban areas where demand for water is pressed;
- sewerage system with improved appearance model projects, a project aiming at improving the appearance of sewerage facilities by planting trees and creating promenades around rain-water ditches in urban areas;
- sludge recycling model projects, whose objective is to promote the utilization of sludge generated in sewage treatment processes for construction purposes, by aggressively using the sludge products in construction projects of sewerage systems.

Also a project was started with the objective to develop a sewerage system that can provide diverse service functions for urban life by actively utilizing added values of the sewerage system facilities such as the space around facilities, treated water, sludge etc., and the project also aims at promoting a strategic urban development utilizing these functions provided by the sewerage facilities. Additionally, the sewerage system project to cope with snow which is aiming at maintaining city functions during winter in areas with heavy snow fall was implemented in nine cities, and a project to promote incorporative development of sewerage and park facilities, was also implemented.

In an attempt to help promote sewerage projects smoothly, studies on various issues were conducted. These issues include:

- the basic policies of the sewerage development program and its rationalization;
- design and construction methods of sewerage facilities;
- rationalization and raising efficiency of sewerage technologies treatment and disposal methods of sludge generated from sewage treatment;
- technology for small-scale sewerage systems;
- upgrading of treatment facilities, the environment of treated water, and utilization of treated water;
- measures for rain water from a standpoint of sewerage system management;
- collection and utilization methods of energy resources generated in sewerage systems;
- improvement of durability of sewerage facilities;
- sewerage technologies to cope with environmental changes;
- measures for the diversified role of sewerage systems;
- maintenance and justification of sewerage systems.

Also, in order to improve sewerage technologies and efficiency of operation, application of new technologies model projects, in which various new technologies and construction methods are actively introduced, are being carried out.

8. Monitoring System of the Water Quality in Public Water Areas

The National Environment Agency continuously carried out monitoring plans, and surveys of water quality in public water areas, out of all necessary support to execute constant monitoring of the water quality in public water areas, in accordance with the Water Pollution Control Law. The monitoring is conducted in the areas where the necessity of the water quality monitoring is high, such as the areas that have been designated to be applicable for the environmental quality standards.

In order to strengthen the monitoring system of water quality in public water areas, it is necessary to promote the automation of monitoring at certain points where intensive monitoring is needed. Currently, measurements taken by automatic water quality monitoring devices are approved as an official measurement method for the environmental quality standards concerning pH and DO. Investigations have been conducted to study the possible official approval of measurements by automatic water quality monitoring devices for COD as well (Galatchi, 2006).

The Romanian National Environment Agency provided support toward local pollution research centres, etc. for their purchase of water quality analyzers, in an effort to enhance the monitoring systems of prefectures and administrative ordinance-designated cities.

In order to monitor the status of conformity to the effluent standards, the local authorities of administrative ordinance-designated cities demand factories or workshops for pertinent reports, or make on-the-spot inspections as necessary. Depending on the results of these monitoring activities, they take necessary administrative measures, such as orders for improvement against factories and workshops. The National Environment Agency also provided support toward the concerned local authorities for their development of telemetric water quality monitoring systems.

9. Purification of Lotic Waters

As measures for purifying rivers, various projects have been conducted. These projects include:

- the purification water induction project, in which the condition of a polluted river with a low flow rate is improved by mixing in the purification-purpose water induced from a large river;
- the direct purification project, in which heavily polluted river water is purified by the gravel contact oxidation method;
- the sludge dredging project, where the bed of a river containing large amount of accumulated organic matter is dredged to reduce the sources of offensive odours and pollution.

As measures to control turbid water and eutrophication in dam reservoirs, aeration and the removal of nutrient salts are performed in watersheds.

Within the areas requiring extensive measures against domestic effluent, there are a number of areas where development of domestic effluent treatment facilities such as sewerage systems etc. is not expected to be constructed in the near future, despite the fact that the pollution in the area caused by domestic effluent is substantial and measures should be taken immediately to preserve the living environment. To solve this problem, the Romanian National Environment Agency has been enforcing projects for installation of purifying facilities of waterways polluted by domestic effluents. This project is to execute a purification process directly to the polluted waterways and small streams which do not fall under the categories of "rivers" or "city sewage waterways".

In areas outside those that have been designated as requiring extensive measures against domestic effluent, waterway purifying projects that are established independently by each municipality have been implemented.

10. Conservation of Water Quality of Lentic Water Bodies in Romania

For lakes and reservoirs and other enclosed water bodies particularly with significant pollution sources, the rates of achieving environmental quality standards are lower than for other areas, because the loads of pollutants are significant and pollutants tend to accumulate. In, addition, the inflow of nitrogen, phosphorus and other chemicals leads to the progress of eutrophication.

To improve the water quality of vast closed water areas, it is necessary to reduce total amount of pollutants flowing into the waters. Area wide total water pollutant load controls were institutionalized for overall reduction in the loads of pollutants flowing into waters, but it is still necessary to improve the water quality of these waters.

They specify the reduction targets of loads at target year by source (industry, household and other). The reduction targets by source are 12% from domestic sources, 9% from industrial sources, and 2% from other sources. To achieve these targets, the improvement of sewage systems has been promoted and other comprehensive measures depending on the circumstances of each area have been taken. These measures include: measures for domestic effluents such as development of community plants, drainage facilities for agricultural communities, combined-purpose septic tanks etc. measures for industrial effluent, such as effluent standard for area wide total pollutant load control and so on (Romanian Waters National Agency, 2001–2006).

Since lakes and reservoirs are enclosed water bodies, pollutants tend to accumulate easily. Thus, the achievement status of the environmental quality standards is lower than that of rivers and sea areas. Eutrophication in these areas is creating various problems in irrigation systems. Lakes and reservoirs that need immediate measures to meet the environmental quality standard are to be designated, and the water quality conservation plan for lakes and reservoirs is to be determined for those lakes and reservoirs, so that various measures can be taken comprehensively and systematically. These measures include:

- projects for conservation of water quality, such as development of sewerage systems etc.;
- restrictions against sources of pollutants;
- preservation of the natural environment around lakes and reservoirs.

There are ten lakes and reservoirs that have been designated as above. Eutrophication originally referred to the phenomenon in which the water of lakes is gradually fertilized by nutrient salts such as nitrogen, phosphorus etc., that are supplied from its watershed, followed by consequences on the living organisms. However, due to the centralization of population and industries, nutrients are flowing into sea areas, and into the lakes and reservoirs. Overflow of these nutrients causes the bloom of algae, thus the water quality is deteriorated progressively, causing serious environmental problems.

Eutrophication not only lowers the clarity or mars the appearance of lakes and reservoirs, but also causes filtration hindrance in water purification plants, offensive odor or taste of drinking water etc. It also contributes to occurrences of algal blooming in sea areas, resulting in damages to the fishing industry.

In consideration of these issues caused by eutrophication, measures have been taken against nitrogen and phosphorus which are nutrients causing the problems. The environmental quality standards concerning nitrogen and phosphorus for lakes were established, and the designation of types of areas was completed, and effluent standards concerning nitrogen and phosphorus were established. Restrictions of pollutant load concerning nitrogen and phosphorus in accordance with the laws have been enforced.

11. Concluding Remarks

The water supply deficit in Romania is caused by the absence of, or insufficient infrastructure in some regions, as 66% of the rural population (representing approximately 6.75 million people), does not have access to centralized water supply, and only 92% of urban inhabitants in Romania have access to the system. The ability to pursue infrastructure expansion, rehabilitation and modernization has been limited by a lack of investment and financial resources. Supply issues are further influenced by excessive consumption of water resources due to low water tariffs and a general lack of awareness of the importance of water conservation among the population. A major cause of nutrient pollution in Romania is the inadequate treatment of wastewater. Inadequate treatment is rooted in inefficient, or absence of infrastructure. Industrial pollution is also a consequence of outdated infrastructure, weak enforcement of regulations and the absence of economic incentives to promote cleaner production. In turn, infrastructure weaknesses are rooted in the limited availability of finances for upgrading and modernization. The trends in development of water resources aim at enhancing the water storage capacity by damming some river courses and by optimizing water consumption. Romania's current water policy is based on international recognized principles of good water management – namely integrated water resources management.

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WATER QUALITY AND WASTEWATER TREATMENT SYSTEMS IN GEORGIA

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Abstract. The paper considers water resources availability, quality and wastewater treatment systems in Georgia. The main pollution of water resources in the country comes from the municipal, industrial and agricultural sectors that cause pollution of water bodies by organic and inorganic matters, chemicals and toxins. The quality of surface water resources are low as a result of dumping of insufficiently treated and untreated sewage heavily urbanized areas. The main wastewater treatment plants in Georgia that discharge municipal sewerage to the Black Sea and Caspian Sea basins are in poor condition and do not operate well. Actions for sector improvement need to be feasible and focused on areas that can make a real difference in the future. Significant investment effort should be in the pipeline to improve situation in wastewater management sector, to provide monitoring on the quantity and quality of wastewater and renew of municipal wastewater plants.

Keywords: water availability, water quality, wastewater treatment systems, Republic of Georgia

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1. Introduction

Successful management of water resources is one of the most critical issues facing humanity. Clean and safe fresh water is vital for the life organisms, human health and ecosystem. It is also a central resource for economic and social development. Water security is indispensable for sustainable development.

Historically, water management has tended to compartmentalize the human relationship to water resources by considering each activity and use separately. Water for drinking, agricultural and industrial activities, navigation, fisheries and recreational use, for energy generation (hydropower plants) and environmental health has each been treated as distinct political, economic, or management issues[1].

One of the growing consensuses on how to achieve water security is through a proper use of water recourses and sufficient treatment of wastewater. This approach sets out a participatory planning and implementation process, based on sound science.

In the water supply and healthy environment sectors, the wastewater treatment, water conservation and hygiene play the vital role in improving healthy living environment.

2. Water Resources in the Republic of Georgia: Availability and Quality

2.1. WATER AVAILABILITY AND USE IN THE REPUBLIC OF GEORGIA

The Republic of Georgia is situated in the south-east of Europe and occupies a territory of approximately 70,000 km^2 with approximately 5 million populations. The length of Georgian frontier is 1,969 km. 32.2% of the territory is covered by forest, 10.9% by water bodies, and 39.6% by agricultural lands[2].

The rivers in Georgia are drained in two main drainage basins: the western part rivers drain into the Black Sea, and the eastern part rivers drain into the Caspian Sea. Georgia is abandoned by water resources and the amount of water discharged is about 820,000 tons per km^2 that is 2.5 times the world average. About 78 per cent of water resources are concentrated on the western area and only 22 per cent in the eastern area. The country's water stock is about 56.5 km^3 per year. Approximately 67 per cent of water resources are surface waters[3].

There are approximately 26,000 rivers in the country with total length of 59,000 km and about 860 lakes and reservoirs with total area of 170 km^2. Most of the rivers, approximately 93% of all rivers are less than 10 km long. The longest rivers of the country are: Alazani – 390 km (basin area – 12,000 km^2), Kura – 351 km (21,100 km^2), Rioni – 333 km (13,400 km^2), Enguri – 206 km

(4,100 km^2)[2]. The Kura River flows for more than 300 km through Georgia. The river basin is approximetly 15,000 km^2, or 23% of the country's territory. The biggest lakes are Paravan – with a 37.5 km^2 mirror area and Kartsakhi with 26.3 km^2.

Water supply in the country is at an average level, and a safe drinking water supply is the key component of the general objective to ensure the environmental safety and health of the people of Georgia.

The Rioni River is the largest tributary to the Black Sea in Georgia, draining approximately 20% of the country. Additional contributions to the Black Sea come from smaller rivers such as (moving southerly) the Enguri, Kodori, Supsa and Cholokhi. Drainage to the Caspian Sea is dominated by the Kura River[4] (known in Georgia as Mtkvari) (Table 1).

TABLE 1. General data of the major rivers of Georgia

River		Length, km	Basin area, m^2	Average Area, km^3	Basin height, m
Caspian Sea Basin	Alazani	390	12,000	3.1	1,900
	Kura	351	21,100	7.2	2,100
Black Sea Basin	Rioni	333	13,400	12.6	2,800
	Enguri	206	4,100	5.9	3,050

Source: Financing Strategy for the Urban Water Supply and Sanitation Sector in Georgia. EAP task force. 2004

The Kura-Araks river system is the principal source of water for industrial, agricultural, residential uses and hydropower plants in Armenia, Azerbaijan, Georgia, Iran and Turkey[5]. The rivers are important to regional cooperation in the region as they cross and form many of the borders. Both rivers are very seriously degraded. Water quality is seriously impaired by the dumping of untreated municipal, industrial, medical and agricultural wastes. The average amount of pollutants exceeds the established norms by 2 to 9 times and often represents a substantial threat to human health[6]. Various fragmented efforts applied on intergovernmental level by the country have not led significant improvement as it requires cooperation among of all the states involved in the initial pollution of the river waterbodies.

2.2. WATER QUALITY

Water quality is one of the major environmental concerns not only for Georgia, but also for the whole Southern Caucasus region. During the Soviet period, large volumes of effluents were discharged into surface water bodies from the municipal, industrial and agriculture sectors, causing pollution of both surface and ground waters[7]. The sources of water pollution in the country were from the municipal wastewater, agricultural and industrial sectors. Municipal wastewater polluted rivers by the organic matters, suspended solids and surfactants. In the country large industrial facilities producing manganese, ammonia, arsenic, copper and gold mining, and processing plants, oil refineries and power plants polluted the river bodies of the Black and the Caspian Sea basins with heavy metals, oil products, phenols and other toxic substances (Figure 1). Also wastewaters from copper mining operations heavily polluted the Kazretula River (tributary of the Kura River) with heavy metals.

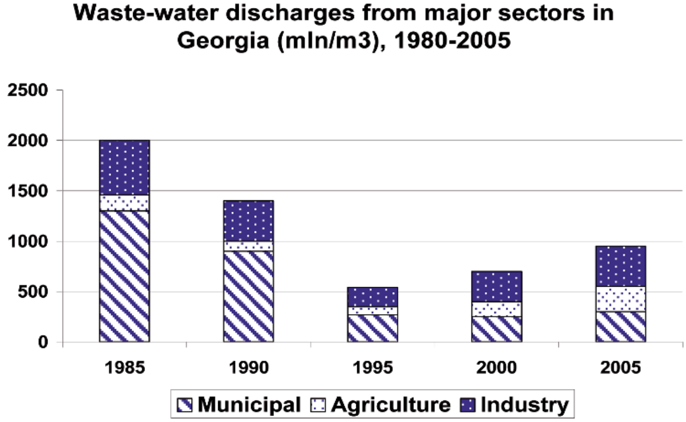

Figure 1. Caucasus Environment Outlook (CEO), 2002; Report of the Ministry of Environment and Natural Resources Protection of Georgia, 2005

After the break-up of the Soviet Union, contamination of surface waters has decreased, due to sharply decrease of industrial production and subsequent wastewater discharges. This could have resulted in the temporary improvement of water quality. However, this is off-set by the fact that the majority of wastewater treatment facilities ceased to function or work at very low levels of efficiency, caused the discharge of larger quantities of untreated wastewater directly into water bodies.

Data surface water quality in Georgia is extremely limited. The water quality in Georgia is collected by the Environmental Baseline Monitoring Center of the State Department of Hydrometeorology (Hydromet). According to the Hydromet, 131 sampling points are chosen in Georgia for baseline water quality monitoring in the rivers and reservoirs. Due to the lack of funding, only 26 points are monitored at regular basis (i.e., samples are taken and analyzed each month), another 26 at irregular basis (i.e., samples are taken and analyzed 2 or 3 times per year), and the remaining 70 points are not monitored at this time. The collected data are provided by Hydromet to the Ministry of the Environment of Georgia[3]. The infrequency of monitoring, and questions as to the quality control on sample collection and analysis compared to international norms, complicates any ability to draw conclusions on true ecological health and threats to Georgian water resources. Based on published and unpublished data and qualitative interpretations by experts, the following tentative observations were drown:

- mostly ambient surface water quality exceeds Georgian (and comparable international) norms many times over throughout the main stems of both the Rioni and Kura rivers;
- as it is reported, the main stem of the Kura affected downstream from the cities of Borjomi, Gori, Tbilisi and Rustavi; Tributaries to the Kura of concern include the Vere River in the Tbilisi area, the Alazani River downstream from Telavi, the Mashavera River downstream from Madneuli, and the Suramula River downstream from Khashuri;
- also relatively greater impacts on the Rioni River are to downstream from Kutaisi and at Poti near the Black Sea;
- surface waters have high nutrient readings (especially ammonia) as a result from untreated discharges of municipal wastewater. Synthetic organic chemicals, oil products and metal contamination probably originate from industrial sources since only 10% of industrial discharge is treated;
- mainly groundwater quality is believed to be very good but essentially no data are available to support this claim. Data are insufficient to assess whether more vulnerable groundwater is being contaminated by municipal, agricultural or industrial pollution[8].

The quality of drinking water also is of particular concern. The Ministry of Labor, Health and Social Affairs has been able to maintain the minimum level of water system surveillance, though questions of quality control do arise, and this must be taken into account in interpreting official statistics. Test methods, especially for microbiological constituents, are not directly comparable to the World Health Organization (WHO) recommendations. Drinking water standards were set by the Ministry of Labor, Health and Social Affairs in August 2001, and were generally adapted from old Soviet norms. Despite these limitations, concerns over systems' violations are real. In total (and depending on data source), approximately 18% to 24% of samples collected from centralized water systems violated Georgian norms for chemical and microbiological constituents. Samples from 13 towns and cities exceeded microbiological norms by 50% or more. Except for the larger cities, monitoring by water utilities for even such basic parameters as disinfection residual is not carried out. Perhaps a more direct measure of concern regarding drinking water is the occurrence of water-borne disease outbreaks.

3. Wastewater Management in the Republic of Georgia

3.1. WASTEWATER COLLECTION

Perhaps nowhere in Georgia is the decline in water sector investment and conditions as obvious as in the area of wastewater management. Wastewater collection systems operate in 41 cities and districts, 30 of which have wastewater treatment facilities with a total design capacity of 1.6 million m^3/day (including regional treatment facilities in Gardabani with a capacity of 1.0 million m^3/day, serving Tbilisi, Rustavi and Gardabani). All wastewater treatment facilities were designed and constructed as mechanical-biological treatment plants. The total length of the wastewater networks and sewers is 40,000 km^2.

In Georgia wastewater is collected through centralized municipal sewerage systems. At present none of the treatment facilities operates with the design capacity[9] (Table 2).

TABLE 2. Water supply and wastewater collection services in Georgia

City group	Covered by centralized water supply	Covered by centralized wastewater collection
Large cities (above 140,000 inhabitants)	100.0%	93.2%
Resort towns of the Black sea coastal zone	81.5%	32.3%
Other settlements	63.7%	28.7%

Source: Financing Strategy for the Urban Water Supply and Sanitation Sector in Georgia. EAP task force. 2004

3.2. WASTEWATER TREATMENT

Only 5 of the 23 municipal wastewater treatment plants are operating in the country currently, albeit at the reduced efficiency of mechanical mode. Biological treatment units (which are more effective at reducing organic and nutrient loading to surface water) are not operational at any of the 19 facilities. According to unpublished reports (prepared in 1999 for a possible donor grant), while the plant was initially designed to treat 1 million m^3 per day, only an estimated 600,000 m^3 per day passed through the plant. This reflected the fact that only 43 out of 100 connections to the sewer collectors had been actually installed. The rest of the wastewater (estimates range from 30% to 50% of the total) from Tbilisi discharged directly to the Kura River without even rudimentary treatment. Some components within the treatment plant (such as the sludge digesters) had never been completed. Needed improvements to wastewater collection and treatment systems were extensive and encompassed all components[8].

All wastewater treatment facilities were constructed before 1990. The design technology is now outdated and does not comply with modern requirements, especially with regard to sludge treatment. Moreover, the technology relies on almost free electric energy and natural gas. The energy crisis which followed the dissolution of the Soviet Union, the significant electricity tariff increase and the lack of financing have negatively influenced almost all wastewater treatment facilities of the country. The technological processes were interrupted, the microorganisms used for biological treatment were lost, and pipes and conduits were clogged up[2] (Figure 2.).

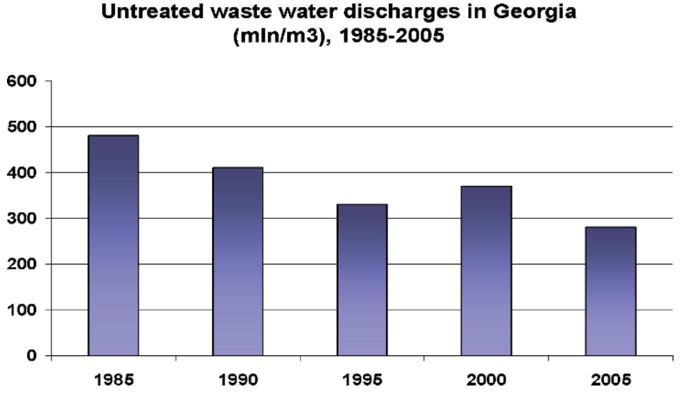

Figure 2. Source: Caucasus Environment Outlook (CEO), 2002; Report of the Ministry of Environment and Natural Resources Protection of Georgia, 2005

The condition of wastewater infrastructure in other settlements is rather lamentable: many facilities are being destroyed, and the equipment is completely worn out and partly lost. However, despite the difficulties related to the wastewater sector of Georgia, there are possibilities to treat wastewater and reconstruct treatment facilities. Regional treatment facilities in the Gardabani (serving Tbilisi, Rustavi and Gardabani) presently are reconstructed at the expense of Gruzvodocanal LLC with participation of the Association of Vodocanals of Georgia[3].

The situation regarding industrial wastewater reflects the extensive downturn in industrial production in the country. Water use, one measure of productivity and pollution impact, dropped from a reported 1,542 million m^3 to 975 million m^3 from 1985 to 1992 and to 211 million m^3 in 1998. One of the principal industrial categories is food processing, which can generate organic contamination. Pretreatment of wastewater by the vast majority of industrial users is the exception rather than the rule. The Ministry of Environment and Natural Resources Protection of Georgia estimates that more than 80% to 90% of industrial wastewater is not treated before being discharged to sewers and municipal wastewater treatment plants (where there is a network), or directly to surface waters (where there is no network). If biological treatment units were in operation at municipal wastewater plants (which unfortunately they are not) pretreatment to neutralize metals, acids and other contaminants would be essential for good operation[8].

4. Conclusions and Recommendations

4.1. CONCLUSIONS

Georgia is rich by ground and surface waters, but the infrastructure and management systems are currently in a place to use these resources effectively and in sustainable way. More than 80% of urban wastewater systems fail to provide even the most rudimentary treatment. Water utilities are unsuccessful at raising sufficient revenue from water tariffs to meet even basic operating expenses for energy and treatment chemicals. Given the expense of treatment chemicals and the high cost of energy faced by water utilities, it is reported that 70% of utilities do not disinfect their water supplies. The majority of wastewater utilities have not performed the required routine repair and restoration work for a long period of time[8].

The most dramatic situation exists in the domestic and industrial sewage collection and treatment systems. The majority of wastewater treatment plants are not operating well, and therefore wastewater discharges without treatment into open water bodies. This causes pollution of rivers, the Black and Caspian Seas. Such contamination of water resources has become the main reason for mass intestinal and infectious diseases in Georgia.

Given the scope of these difficulties and serious budget constraints in the country, recommendations for sector improvement need to be both feasible and focused on areas that can make a real difference in the near to mid term.

Investments are needed to reduce water losses, eliminate cross-connections with wastewater collectors, and improve cost-recovery through water metering and other means.

Donor assistance could be used to finance infrastructure investments with the greatest health benefit, for example disinfection technologies and strengthening of surveillance laboratories.

Nevertheless, cooperation with industrial sub-sectors that are relatively more viable economically can set the stage for broader improvements in the future.

4.2. RECOMMENDATIONS FOR THE IMPROVEMENT OF WASTE WATER TREATMENT SYSTEMS (WWTS)

- The Ministry of Environment and Natural Resources Protection of Georgia, in cooperation with other relevant ministries, should begin long-term strategic planning both at the national and at the utilities level the problems of wastewater management through the launching of a wastewater program for the most urgent hot spots;
- The agencies which are responsible for developing and implementing the wastewater treatment programs should start regulating this sector, developing sector investment programs and mobilizing resources for their implementation (budgetary funding and/or external loans and grants), practically to address these tasks;
- Support the establishment and strengthening of water-sector institutions, improve water quantity and quality indicators, enforcement of wastewater regulations, and promote legal and policy reforms in the country would be a positive sign for overall sector reform;
- To strengthen the involvement of the private sector in the provision of water and wastewater services in Georgia to renew and rebuilt the system of wastewater collectors that the majority of wastewater treatment facilities start to function at high levels of efficiency.

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STORMWATER MANAGEMENT IN URBANISED AREAS

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Abstract. Paper deals with storm water management in urban area. Present methods of stormwater management are focused on protection of real property against flooding. Securing of long term function of sewerage network and wastewater treatment plants is linked with increasing cost and is clear that this method cannot be implemented worldwide. Present methods of storm water collection endanger state of water bodies and water resources. Rigorous application of modern trends of drainage of urban areas, whose fundamentals are discussed in paper, storm water runoff can be minimized and problems with storm water collection can be eliminated.

Keywords: stormwater; retention; infiltration; water pollutants; management

1. Introduction

The present method of treating storm water in urbanised areas focuses primarily on protecting buildings against flooding, ensuring the long-term functioning of sewers and wastewater treatment plants.

This conception has successfully resolved the protection watercourses and resources; however, the existing method urban drainage brings about a number of problems including:

- Rapid drainage of stormwater flows from hardstanding surfaces increases the natural flow-rate in small watercourses, which results in growing requirements for their capacity.

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- Rapid drainage of stormwater run-off from built-up areas in urban areas (instead of the potential infiltration) reduces the groundwater renewal.

By thorough implementing the modern trends of urban areas drainage, the stormwater run-off may be minimized and thus it will be possible to signifycantly eliminate the problems related to its drainage.

2. Use, Retention and Infiltration of Storm Water in Urbanized Areas

The use, retention and infiltration of stormwater in the individual buildings are amongst measures that may be called as the “source control” (= measures at the source, intervention focusing on the causes of the identified problems). These measures are usually not only efficient but also economical. When deciding on the selection of the aforementioned measures, it is necessary to consider certain aspects. These are namely:

- Protection of watercourses, protection of groundwater and protection of soil against contamination
- Protection of civil structures (mainly buildings) in the vicinity of infiltration structures
- Hydrogeological conditions of stormwater infiltration
- Mass loading in the stormwater run-off
- Interests of the inhabitants (drainage comfort, health risks etc.).

2.1. STORMWATER IN URBANIZED AREAS

The stormwater run-off from urbanised areas lays one of the major roles in the field of municipal drainage. During heavy storm events, the stormwater run-off exceeds by far all other types of wastewater and thus has a major impact on the designs and dimensioning of a number of civil structures in the urban drainage systems. The stormwater run-off from the urbanised areas contains a major share of pollutants, which is reflected in the sewer system, the wastewater treatment plant and the receiving body of water and it also has an effect on the potential use of stormwater and its infiltration.

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

- possibility of using the stormwater as service water in households for purposes that do not require the quality of drinking water,
- reduced flow rate in the sewerage during storm events and a support of the function of the technical system, mainly in the combined sewerage,

- reduction in the hydraulic loading and mass loading at the WWTP during storm events,
- reduction in the hydraulic (mechanical) effects on organisms in watercourses with a low yield,
- reduced mass loading of pollution by overflows from the combined sewerage during storms,
- support of renewing groundwater renewal etc.

3. Use of Stormwater

The most common solution to the use of stormwater is for irrigating green vegetation, either manually or automatically using a time-controlled automatic device or on the basis of the measured soil humidity. The retained water is also used as service water for washing, above all in areas where the groundwater is hard or contains a higher share of iron and manganese. It is also used for toilette flushing, (the capacity of the cistern supplying WC and laundry washing must correspond to a one-year water consumption), washing machines, dishwashers, for cleaning purposes, as service water for crafts and industries etc.

The level of stormwater pollution is generally defined as follows:

- slightly polluted – stormwater run-off from residential areas (streets, bicycle tracks, pavements, green areas etc.)
- normally polluted – water from residential-industrial areas, villages, parking lots and roads
- strongly polluted – water form motorways, heavy-traffic primary roads, open warehouses, transit warehouses for harmful and poisonous substances.

Thus, the stormwater loading is greatly dependant on the local marginal conditions. Stormwater run-off from the streets should infiltrate only through an enlivened soil layer or after a preliminary treatment in a corresponding plant. There is a number of possible preliminary treatments; divided according to the physical and biological principles, possible utilization is presented, possible combinations, advantages and drawbacks, as well as maintenance and cleaning capacity.

4. Stormwater Retention

At present, there is a rising trend of building up the urbanized catchments resulting in an increasing stormwater volumes and peak flow rates. Each urbanized area causes a change in the character of the direct stormwater run-off in an effort to define a potential suitable solution to the run-off conditions in the town residential areas in the form of stormwater retention. The problem of large drainage area may be handled by retention – water storage and it's controlled discharging into the receiving body of water. Retention tanks replace the natural retention capacity of the environment, ensure protection against high water, stormwater run-offs, but they also retain flushes. However, their protective function is prevailing. Other tanks provide this function as an auxiliary function. The actual design and water management solution to the retention tanks must be preceded by detailed survey work.

The group of retention tans includes:

- Dry retention tanks (retention of stormwater run-off, reducing stormwater flow rate, being emptied once the flow wave passes)
- Retention tanks with a precisely defined protection room (transforming the flood wave and once it passes, the protection room is emptied in a controlled way down to the level of defined storage room)
- Anticorrosion tanks (retention of sediments)
- Stormwater tanks (for retention, short-term water storage, its treatment and use of water from storm events)
- Infiltration retention tanks (short-term retention of excess inflow, partial use for irrigation purposes)
- Baffle tank (used to balance out the shock flow waves in distant profiles during flow rate controlling).

4.1. DECENTRALIZED STORMWATER RETENTION

Decentralized retention is stormwater retention in the individual buildings. To reduce the run-off, use is made of run-off control equipment (throttling line, vortex regulator, and filtration bed).

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

- Pond with biotope
- Retention in pipes, horizontal and sloping roofs
- Stormwater retention tank
- Retention in parking lots and industrial premises
- Retention channel
- Filtration pit
- Plastic honeycomb blocks
- Infiltration with retention room
- Retention system combined with a pipe infiltration.

5. Stormwater Infiltration

Various methods employed include: direct infiltration, infiltration with overground water storage, infiltration with underground water storage, and important combination options. It includes the design of retention tanks, used to retain stormwater before infiltrating. A number of European countries the infiltration of unpolluted or little polluted stormwater run-off is supported by administrative and legislative instruments. The principal and a questionable issue handled so far is the definition of "unpolluted" and "little polluted" stormwater run-off.

The main marginal conditions of infiltration:

- stormwater run-off pollution
- requirements for groundwater protection
- requirements for soil protection
- type of infiltration (type of building).

The systems for stormwater run-off infiltration may be divided according to the following criteria:

- central or decentralized
- retention capacity (storage)
- surface demands
- method and distribution of hydraulic load.

The main technical principles of infiltration:

- surface infiltration
- shallow trench infiltration
- combination of shallow trench and trench (multi-component infiltration element)
- trench and pipe infiltration
- shaft infiltration
- infiltration tanks
- multi-element system.

The run-off from hardstanding surfaces are divided into three categories for the purposes of intended infiltration in terms of the concentration of the pollution and the potential effects on groundwater:

- harmless (wholesome)
- tolerated
- intolerated.

Harmless stormwater run-off may be infiltrated via unsaturated zones without pretreatment. However, such a run-off is not unpolluted. Nevertheless, the concentrations are considered to be so low that there is no need to be afraid of groundwater or deterioration of its quality.

Tolerated run-off may be infiltrated following a suitable pretreatment, with the use of cleaning processes in the infiltration system. Infiltration through a grassed area may be sufficient depending on the properties of the catchment surface and retention time of the infiltration area.

Intolerated run-off of stormwater should only be infiltrated following a suitable pretreatment or it should be conveyed to a sewer system.

Stormwater infiltration is enabled by an infiltration system. At first sight, these are usually simple civil structures. However, practical examples show that a proper functioning of these structures, subject to a suitable structural design and careful construction, is not possible without special knowledge and experience. Want is also important is professional maintenance of these systems.

6. Stormwater Management

Drained wastewater is always contaminated by e.g. flushes from roofs hardstanding areas and roads and therefore their treatment must be monitored and the pollution must be reduced.

There are presently several strong arguments why stormwater should be utilized:

- ever growing costs of potable water;
- restricted number of quality potable water resources;
- retention and storage of a share of stormwater during heavy storm events = protection of the individual catchments against flooding;
- stormwater is a suitable source of softwater (washing, irrigating, WC and installations).

6.1. REQUIREMENTS THE QUALITY OF STORMWATER

The composition of stormwater fro urbanized areas is affected by:

- a number of pollutants (CO_2, sulphurous dioxide, NOx, hydrocarbon compounds, dust heavy metals etc.);
- local conditions (polluted air, character of the land from which stormwater runs off);
- concentration of mass load (during storm events, it changes substantially in a number of substances).

By using stormwater in terms of its composition, the following must not occur:

- endangering the users health;
- endangering the drinking water quality (as a result of a potentially faulty installation);
- restricted comfort of the water use;
- environmental contamination (above all, soil and groundwater).

The decision on the stormwater management method must be preceded by a careful mapping of the local conditions and analyses:

- evaluation of the permeability and characteristics of the subsoil;
- depth and direction of the groundwater flow;
- ground slope;
- water protection zones;
- old ecological pollution;
- use of land etc.

Results of stormwater management:

- reduced share of stormwater in the sewer system → new sewers may have smaller profiles, or the existing profile need not be increased;
- reduction in the number of overflows from the sewer system to the receiving body of water;
- reduced share in the run-off from urbanized catchments during extreme flow rates in the river;
- reduced mass loading of surface water;
- substantially reduced need of constructing retention tanks in the sewer system (lack of space, private plots, major investment funds, operating expenses etc.);
- improved quality of life by bringing water to drains, passes and ponds;
- improvement of the microclimate in residential zones.

7. Conclusion

With respect to environmental protection, but also with respect to technical and economic relations, it is necessary to reduce the volume of drained stormwater while exploiting all possibilities, through the “permeable programmes implementing when reconstructing hardstanding areas”, retention, use of stormwater and direct discharges to watercourses.

With the intention to reach a new generation it is clear that it is necessary to bear responsibility for protecting this source and to concentrate the attention as soon as possible on “substitute sources” of water useable with individual restrictions in all areas of human needs.

The stormwater retention is governed by two principal methods of stormwater management:

- water is retained in surface or buried retention tanks;
- water is infiltrated into underground.

As the stormwater infiltration into the underground entails a number of risks, the stormwater in our local conditions will be retained prevailingly in local retention systems. This solution is more universal also with respect to the future standard use of stormwater in buildings.

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SAFETY AND SECURITY OF WATER SUPPLY AND SANITATION

SMALL URBAN RIVERS OF CHERNIVTSI: LEVEL OF ORGANIC POLLUTANTS CONTENT, MAIN SOURCES AND EFFECTIVE GREEN SOLUTIONS

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Abstract. This paper provides results of systematic monitoring of the organic pollutants content in small urban rivers of Chernivtsi, Ukraine. It has been found that this content continuously exceeds maximum concentration limit for any weather conditions. We supposed that unorganized and spontaneous urban effluents provided main part of this pollution. One year long monitoring proved that organic pollutants level lowered significantly even after partial elimination of unorganized effluents of residential waste water (RWW). We suppose that further elimination of RWW effluents would bring organic pollutants content under maximum concentration limit even in the presence of the organized sources of urban rainwater and wastewater.

Keywords: small urban rivers; organic pollutants; maximum concentration limit; residential waste water

1. Introduction

Problem of pollution of small urban rivers with various pollutants including most dangerous xenobiotics is going more and more severe for many European cities and megapolises. While main rivers are being systematically monitored by numerous official and non-government environment protection organizations controlling many parameters of the water condition, small rivers usually remain unmonitored and out of attention. Main rivers are very important as water

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sources, water-transportation lines, recreation areas, etc. However, antropogenic loadinging on the small rivers often exceeds loading level for the main rivers. Small urban rivers often flow just through the most populated and industrial heart of modern cities and take organized rainwater, industrial and residential wastewater discharges. Various emergency effluents also often get into local small rivers.

As a result, water condition of many small rivers can be estimated as disastrous. Ecological systems are seriously misbalanced and many living species are missed or almost missed.

Urban ground waters are also in a very poor condition. Modern chemistry and other industries produce tons of toxic products and dangerous xenobiotics, which finally get into waste and ground water. We regularly use about 100 thousand of various chemical compounds, according to a very approximate estimation[1]. Most of these compounds are xenobiotics, which do not meet any appropriate mechanism of natural compensation. In that way toxic compounds get into small rivers and accumulate in the tissues of plants, fishes and other organisms. This process seriously damages normal life cycle and causes diversity depletion leading to gradual extinction of the small river's ecosystems.

We can classify the following aspects of negative urban influence on the water condition of the small rivers[2]:

- Hydrological regime trouble (river-bed cutoff or digging the rivers into underground pipes, excessive regulation of the river flow;
- There are many artificial ponds on the small rivers. Their total volume can be much larger than the river-flow;
- Incorrect and excessive antropogenic activity in the water protection areas;
- Incomplete or even missed land recreation and melioration actions;
- Numerous municipal and industrial objects are usually placed near small rivers causing significant discharge of wastewater;
- Riverbanks are often littered within city limits with numerous unapproved scrap-heaps, which seriously pollute river water (see Figure 1);
- Old and poor city sewerage lines can cause small but numerous effluents of RWW, which finally get to the local small rivers;
- There are many old municipal rainwater drainage lines, which bring collected water directly to the local small rivers. Non-cleaned rainwater brings to the rivers road-washed grease, oil products and suspended dirt particles.

Four latter problems are considered[3] as the severest for the small urban rivers.

Figure 1. Littered riverbanks of Molnitsa within the city of Chernivtsi, Ukraine

Various rivers suffer of various problems. Sometimes one or two of the above mentioned troubles can provide main part of the river pollution. Therefore, finding such major problems and aiming environment protection efforts to relieve or eliminate those problems can significantly improve condition of the small urban rivers and bring them back to life.

Our project was aimed to determination of the water condition of the small rivers of Chernivtsi. There are several small rivers in the city and we selected one of them, river Molnitsa as an example. This river can be taken as a characteristic one since it has several branches, which join within the city. The branches flow through industrial and municipal parts of the city and there are several municipal rainwater drainage line outlets to Molnitsa.

2. Experiment

2.1. RIVERBANKS AND SAMPLING AREA

River Molnitsa flows to Prut, which is a tributary of Danube. Molnitsa flows within the city of Chernivtsi for about 11 kilometers. It has two sources outside of the city and two branches, which enter Chernivtsi in the upper flow.

Right branch (A) is fuller-flowing and runs through the low-populated part of the city. There are several ponds on this branch. Some of them are still functioning and they also collect organized and irregular wastewater discharges. Other ponds have been drained out and formed small abandoned marshy areas.

Left branch (B) is much shorter and shallower than A. It runs through heavy populated area of the city, partially through the underground pipes. Several rainwater lines have outlets ending to the B branch. These lines collect rainwater from the downtown area with very tough traffic. Obviously, this water can bring some amount of the transport-related organic compounds and other water impurities.

Both branches join within the city limits, further Molnitsa flows through other heavy populated areas, some industrial objects, small woodland area and finally flows into river Prut.

There is also old municipal sewerage collector, which was built along the river-bed of Molnitsa about fifty years ago. We found several damaged places where the sewerage water overflowed from the technical access gulley and run directly to Molnitsa.

We located sampling area at the junction place of A and B and were taking samples simultaneously from the A and B branches and below the junction point. Previous investigations proved that water of Molnitsa is very poor of living organisms while its riverbanks are seriously littered[4]. River water was found yellowish, turbid (especially after atmospheric precipitations), and with rather strong smell. Therefore, one can conclude that the water from Molnitsa fails to meet sanitary requirements towards regular river water.

Finding main source of the organic pollution and developing of effective solution for its reduction was the main aim of our investigation.

2.2. EXPERIMENTAL DETERMINATION OF THE OXIDIZING FACTOR

Organic compound content can be found through determination of the modified permanganate oxidizing factor[5]. We were taking sets of three simultaneous samples. Each set consisted of one sample from the A branch, another one – from B, and the other sample (C) was taken below the junction point of A and B. All the samples were taken irregularly, at different weather conditions during 3–4 months of the winter/spring season of 2004/2005 and then of 2005/2006. More than 40 sets of the samples have been taken.

3. Results and Discussion

Our results prove that the oxidizing factor was constantly over its limit value of 5 mg O/l for all the samples taken (See Table 1). Oxidizing factor of the

B-samples was always higher than that of the A-samples and the values of oxidizing factor of the C-samples had been found between the A and B values. Oxidizing factor of the B-samples was higher than that of the A-values even for the samples taken at the dry weather when there should be no rainwater effluents to the B branch. This fact proved that there were some additional sources of organic pollutants flowing into the B branch water. Initially we supposed that it could be RWW effluents from the damaged city sewerage lines, which got into the ground water and then gradually infiltrated to the nearby branch B.

TABLE 1. Average permanganate oxidizing factor (mg O/l) for the samples taken in 2004/2005 and 2005/2006

Sampling Point	Atmospheric Precipitations	Oxidizing Factor
Season 2004/2005		
A	No	8.0
A	Yes	8.5
B	No	15.2
B	Yes	20.0
C	No	9.6
C	Yes	16.8
Season 2005/2006		
A	No	7.5
A	Yes	7.8
B	No	11.1
B	Yes	12.7
C	No	8.1
C	Yes	11.4

Experimental measurement error was 3–7%.

On other hand, one can see that the precipitations-taken samples always show higher oxidizing factor than those taken in the dry weather. This result is correct for all the samples and can prove that some amount of traffic-related organic compounds is actually being washed out of the city roads to the rainwater drainage and then to the water of Molnitsa. Obviously, this kind of impurities can get to the river through irregular, non-drainage waters too. This result proved our assumption of the influence of traffic-related organic compounds on the overall level of organic impurities in the water of Molnitsa.

Comparing data for 2004/2005 to 2005/2006 one can see that oxidizing factor for the A-samples changed insignificantly while the B-samples factor became almost twice smaller in 2005/2006 series. Since there were some fixing works on the nearby buildings sewerage lines in the meantime between two series of our measurements, we can conclude that wastewater effluents really bring significant part of the organic impurities of the B branch. B-branch water is the most polluted, therefore further fixing of the sewerage system can significantly improve quality of the water in the B branch and, consequently, water quality of Molnitsa.

Basing on our results, we can conclude that RWW effluents bring main part of the organic impurities of Molnitsa. Left branch of Molnitsa is the most polluted one and main water improvement efforts should be directed to the nearby buildings sewerage system fixing, which can bring water quality closer to the sanitary conditions. Traffic-related organic compounds provide another part of the water impurities, however, their influence is smaller than the one of RWW.

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RECONSTRUCTION AND REHABILITATION OF SEWER SYSTEMS IN SLOVAKIA

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Abstract. The one way of urban water cycle is moving the waste waters from the producers to the recipient through moving and cleaning system. The missing of this part of water cycle cause the non only hygienic problems, the danger of population in urban areas, but the quantitative problem with dry weather and storm-water flow. The basic system for collection of waste water called sewer system is for a long time a basic system of urban areas. Because the sewage system is one of the oldest systems in the cities, they allocate too much malfunctions. This failures cause by age of the sewer system or/and poor quality build. Age of the sewers is from 50 to 100 years, and that's why many sewer systems in all the world cities need reconstruction and/or rehabilitation. *Rehabilitation* is any action for restoration or improvement of the functional service of existing sewer network or sewer pipeline system. *Reconstruction* is the repairing and restoration of the sewer pipelines, which changes the original technical parameters. Both words meanings the same goal, to improve the functionality of existing sewer system, with using variously of techniques to rehabilitate pipelines. Paper shows the known techniques of reconstruction and the way of capacity appraisal of sewer systems in Slovakia by the own software tool SeWaCAD.

Keywords: sewerage system, pipeline, reconstruction, rehabilitation, recalculation

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1. Introduction

The historical development of sewer system was consists from systematic and unsystematic approach. The first sewer systems were constructed with the goal to dewater small parts of urban areas from waste waters- from inhabitants and dewatering the waters from the rain. It was the base for systematic sewer system, which started as the connection of non-systematic sewer systems. The first goal was easy dewatering the waste waters directly to the nearest recipient, but this process had to be change, because the contamination of recipient causes the other hygienic and sanitary problems. The one of interesting systematic sewer disposal systems was “Heidelberg barrel system” or the “Kiel exchange bucket system” in Germany. The problem in sewer history was to liquidation the pollution in sewer system. The resolution was WWTP – Waste Water Treatment Plant. We could say that today sewer systems were come from last era, from last century. This is the typical in Slovakia. The all sewer systems in Slovak cities were built mainly after the second of world war 1945, but the large cities, capitol of Slovakia Bratislava, the relative big cities in Slovakia Košice and Banská Bystrica had sewer system build before the 2nd of World War. That’s why the majority of present sewers in Slovakia immediately needs reconstruction respectively rehabilitation.

2. The Reasons of the Sewers Rehabilitation

The sewer systems build in Slovakia in the last century are in very poor conditions. The construction of sewer system was very fast in the most of the regional cities. The occurrence was not takes in this era to the quality of sewer systems, but the priority was only quantity. The expansion of the cities in 50–70 years of the last century involved build of many kilometers of sewer systems. The fast construction with the non professional approach in this period causes, that the sewer were constructed with very poor quality. There were many problems, to keep the slope, to make a waterproof weld connection of the pipes, to keep the conditions of firm up over the pipe.

Many pipes were broken during the building, and insufficient of supervision caused the poor quality of execution. The knowing of the people, (which constructed the sewers, mainly workmen), were at low level, and they hoped, that it is impossible to reveal the bad quality of execution.

The new modern approach of appraisal of sewer systems shows with using the TV systems or excavation the sewer failure shows, that the actual conditions of the majority of sewer systems in Slovak cities are in deplorability. The first appraisal of the sewer system by the TV camera started approx. in 90 years of last century, but more years ago, when operational companies repaired the breakdowns – failures, shows that the sewer conditions is very bad, but it was not very important. The concept of impact on environment was foreignism.

The other problem outgoes form the present time of expansion of the cities, the peripheral parts of the urban areas. The increasing of the living standard in the big urban areas involved the bigger demanding of expansion of sewer systems and put the bigger demands for the quality actual water supply, distribution of water system waste water collection by quality sewer system. The Slovak building regulations make press to the constructors to connect new and reconstructed buildings to the public sewer system. But on the other hand, in many cases the public sewer system shows very bad quality, and to make the household connection to the sewer pipe is sometimes insolvable problem. The water operational companies know this situation of their system, and they have to repair the part of sewer pipe, if they want to connect the private/household connection.

The poor quality of sewer pipes causes the leakage to the underground water. It is very danger, because the waste water contains dangerous pollutants very often, and it can be danger for water supply, especially in the hills parts of Slovakia.

3. What Next?

The solution of rehabilitation of sewers in Slovakia became the very important and interesting problem. The water companies started to solve these problems in 90 years. The Slovak legislation, the rise of the water price, the Regulatory Office for Network Industries – URSO, the Environmental organizations, the Ministry of Environmental and the public opinion started the press to renew the not only sewer systems, but the water distribution system with approx. 30% loses of water, and Waste Water Treatment Plants too. The sewers in Slovakia dewater too much amount of ballast waste waters – depend on location, from 20–200%. In last years the Department of Sanitary and Environmental Engineering fetched the measurements of ballast waters in some cities in Slovakia – Levice, Roznava, Trebisov, Banska Bystrica, Ruzomberok, Pezinok and Malacky, Devinska Nova Ves and obtained the imagine about sewer systems in Slovakia, bad waterproof, bad build conditions.

For the evaluation of sewer systems were make the evaluation procedure based on criteria for evaluation. These studies were a relevant basement for water companies for start the process of rehabilitation, reconstruction of sewer system, mainly in cities.

The scientific aim of solution was the NATO Linkage Grant ENVIR.LG.950.445 – scientific program entitled Integrated Management of the Morava River Basin – Strategies and Tools. The results from this program had two outputs, A) Complex investigation of sewer system Malacky including CSO monitoring during rainfall, modeling of storm water discharge in sewer system and the evaluation of transport pollution to the recipient, B) Evaluation of settling tanks function during rainfall in selected WWTP Devinska Nova Ves close Bratislava.

4. Sewer Rehabilitation Depend on Investments

The Slovak authorities after negotiations decided to solve the poor quality of sewer systems. This process was divided into some stages.

- discovery issue of facts
- proposal of solution (expert studies)
- preparation the project – the input for application form preparation
- implementation of rehabilitation.

The rehabilitation of sewer system is in many cases much more expensive process then construction of new sewer systems. The water companies, which are not rich, must solve it. The best one solution was exploitation of entry process to EU – European Union. The exploitation of EU challenges – Operational Programs, for improvement of environmental based on protection of health of inhabitants, protection of water supply, protection of underground waters, protection flora and fauna in Slovakia. The various operational programs concerning waste water disposal from various funds of EU started the process of projects preparation, as base for application forms.

The majorities in water companies decided very wise to exploit these funds. So we can says, that the Slovak Republic had luck with this opportunity. But the conception of exploitation of EU funds goes through MoE (Ministry of Environmental), or MoCaRD (Ministry of Construction and Regional Development) of Slovak Republic. These institutions are responsible for effective exploitation of the funds. Both Ministries has the departments concerning the project preparation. There are some possible funds, cohesion, structural, depend of the high of investment demands.

Because the most important reason in decision process is the quality of project preparation, which implicates the serious approach in water companies. It needs to mention, that the EU investments doesn't cover 100% of investments, depend on the challenge. Approx from 5–25% covers the water company respectively applicant/beneficiary. This smaller part of cofinancing is significant amount of investments too, for beneficiaries.

4.1. ACTUAL STATE IN SLOVAKIA

Only 56% of Slovak inhabitants are connected to the public sewer system. In "Conception of water management policy in the Slovak Republic in 2005" approved by NR (national council) SR is planned perspective percentage of connection to year 2015 approximately 75%. Till 2004 Slovakia had 7 006 km sewers and 226 423 sewerage connections which overall length was 1 785 km. From noticed length of sewers and sewerage connections is significant percent broken and a lot of undesirable underground and strange water is getting to them (ballast waters). Ballast waters overloads capacity of sewers and subjects of Wastewater Treatment (WWT), reduces temperature of wastewater and the result of it is getting worse efficiency of biological process in WWT. The amount of underground water from whole quantity outgoing wastewater in SR reach up to 30.54%. According to data in professional literature the part of sewers, that needs constant renewal except other also from the reason of expiration of usage time of drainage pipes. Slovakia needs to renew up to 908 km of the sewers, what is approx. 14.6% of overall length of public drainage in administration of water companies.

TABLE 1. Estimate costs sewerage pipeline demands in SR

Inhabitants	Rehabilition demand	New pipes demand	Total costs	Rehabilitation costs
mil.	km	km	mil EUR	mil EUR
5,4	908	11 556	2400	703

5. The Ways of Sewer System Rehabilitation

The first stage when the operator of sewer system wants to sewer system rehabilitate, is appraisal of existing condition of the sewer system. This stage we can divide into two roles:

- capacity appraisal and evaluation of sewers
- appraisal and evaluation of structure conditions of sewers.

The reconstruction of combined sewer system is present time take consideration on the environmental too. The new conception of storm water management brings the trend to build separate sewer system for storm water and municipality waste water. These concept need to reconstruct the old combined sewer system to only sewer system for dewatering the rain waters. The sanitary sewer system is build separately. It need to exchange the household connections from combined pipes to pipes for sanitary waste waters. This approach is very useful, but very costs demanding.

5.1. CAPACITY APPRAISAL AND EVALUATION OF SEWERS

Appraisal of sewers is possible to perform with measurement on the catchments/ sewers or recalculation by the software, respectively by software modeling with defined operational conditions of system behaviour. The combination of both approaches, computer and measurement, brings better results. Many various software programs are possible to use for the appraisal of sewerage systems not only in capacity but with pollution transportation too. The Slovakia uses the Europe and overseas products for the sewer system evaluation, but the domestic software tools too. The system MOUSE is very often used for solving these tasks.

This paper wants to show, that for the quick and proper evaluation with Slovak standards performance, the software SeWaCAD is used for the capacity sewer system evaluation. The main advantage of this software is based on traditional approach of sewer design, with Slovak standards compliance.

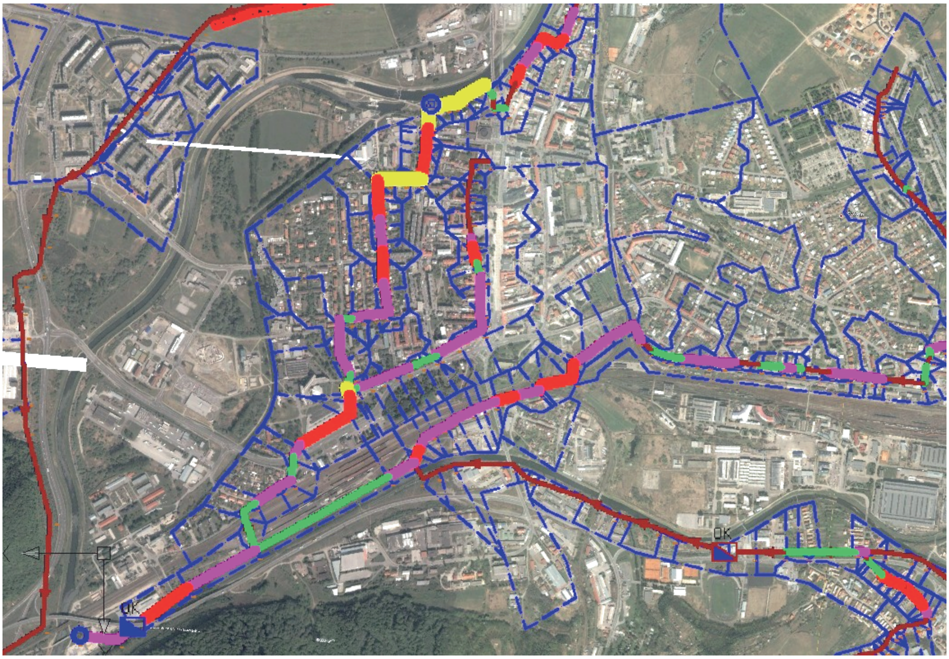

Figure 1. Situation of overloading the sewer network

System knows in very short time to show, where and how is network system overload, in which percentage and offer the solution for renew the sewers. (Fig. 1 – the color lines show the percentage of discharge overload of the sewers) Model SeWaCAD offer the tool for input data generation to model MOUSE, and it is possible to compare the both model outputs. Figure 2 shows the working screen, where is on the same picture existing and designed sewer. User can see, which existing profile and can get information, the replacement diameter of pipe, or know, if the system is overloading or no. Figure 3 is final output from the system in DWG, DXF format. The owner/operator of the sewer system can see the exact parameters of both network – existing and designed in the same trench. It possible to change the slope conditions separately of existing and designed pipes. Every pipe is described with overloading percentage, the recommendation for renewing the pipe with hydraulic parameters.

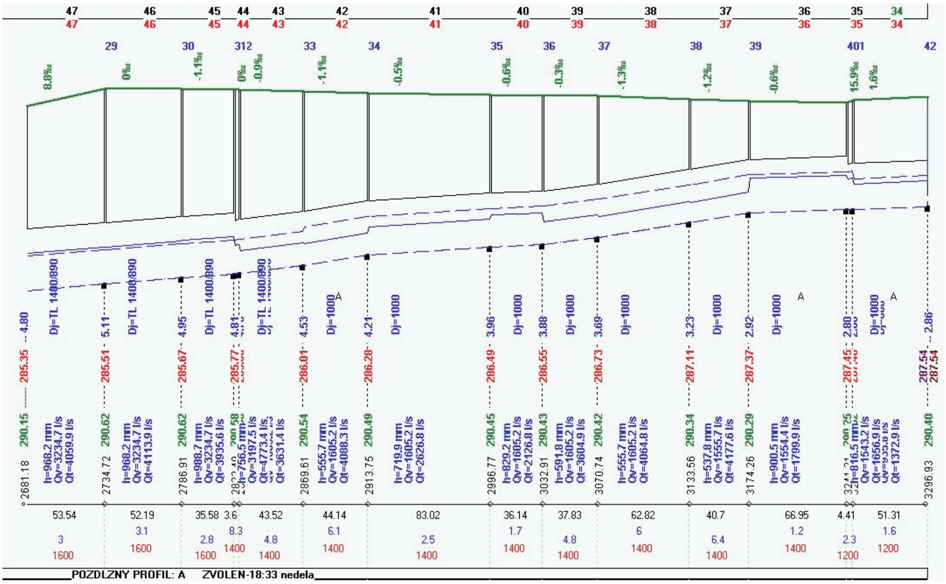

Figure 2. Example of overload longitudinal profile with renew offer (draft sheet)

5.2. APPRAISAL AND EVALUATION OF SEWERS STRUCTURE CONDITIONS

The Slovak standard STN EN 13508 “Determination of sewer system conditions and sewer pipelines outside structures” specify the general requirements for sewer system and sewer pipelines detection. The determination/detection of sewer system, pipelines and the elements on the sewer is the necessary part of system functionality appraisal.

Appraisal and classification of failures are made after detailed inspection and from the operational experiences. The significant is the age of pipes. Slovak standard STN EN 13508-2 determine the specific code system for sewerage evaluation, which is the base for next elaboration process. The pipes are sorting to the categories, depend on rehabilitation urgency. Categorization depends very often on the processor office.

The possibilities of rehabilitation uses in Slovakia:

1. maintainance and local repairs
2. renovation/restoration
    - insole of cement mortar
    - retraction of continuous conduit
    - inserting/plug in and connecting of continuous conduit
    - inserting/plug in and connecting of single pipes
    - insole of tight-fitting pipes
    - covering by pipe segments
    - insole of local tempered pipes
    - insole of plug-in and fixing water-hose

- Trench-less methods for rehabilitation
    - replacement with pipe disruption
    - replacement with pipe extraction
    - replacement with micro/mini tunneling exploitation
- Reconstruction in open excavation

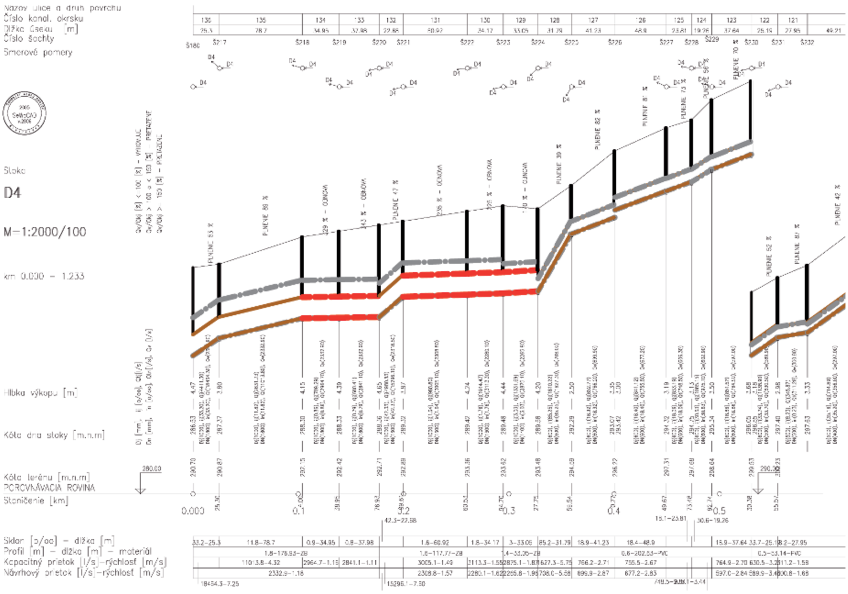

Figure 3. Example of overload longitudinal profile with renew offer – final output

6. Proposals for Slovakia

Slovak needs for sustainable of sewers a modern approach to rehabilitation of sewer networks. Present time offer numbers of decision support tools for analyzing of conditions, expert systems and optimization models. (such as CARE-S, COST-S, Gemini VA, KureCAD, SCRAPS, APOGEE etc.) The continuous deterioration process of pipelines with age is obvious – it can be proved by statistical failure analysis.

General framework for sewer rehabilitation should be given by Drainage area plans or Master plans processed for particular regions. Many water management companies concerning operation of sewer systems keeps records about surcharging, flooding or other failures on the network as well as compliances of clients dissatisfied with sewer operation. All these information can be stored in Asset Management System (AMS), the unique database, from which data on a particular catchments is available from one source. It also enables easier overview of problems on the network, tracking change in the system and keeping it up to date.

7. Conclusions

The reconstruction and rehabilitation of existing sewer networks are very important in present. These problems must solve the operational companies together with owners of sewer networks. The very important is conceptual approach with optimization methods. These processes need the planning based on evaluation of issue. It needs the systematic approach with expert system exploitation based on observation and modeling simulation by the special software. Based on elaboration of evaluation technical and hydro-technical view is possible to accept method of the solution, to plan the investments. From the expert view, considering the needs of water companies and telecommunication companies, to improve the quality of environment, to bring multifunctional exploitation of sewer pipes, the new approach is planned, exploitation the sewer pipes as the collector for the fiber optics cable implementation to into the sewers.

ACKNOWLEDGEMENT

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WASTE WATER TREATMENT FROM SMALL URBAN AREAS

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Abstract. This paper describes some actual specific problems by sewage systems in small urban centres. It is dilemma to find compliance with measures, which is following the strict requirements of EU by discharging of waste waters in receiving waters with lack of funds required for the construction of new sewage systems and WWTPs in small municipalities. In 2002 a new Water Act came into force in Slovakia. It is in line the requirements of Directive Nr. 91/271/EEC. The harmonisation of the waste water treatment in Slovakia with the requirements of this Directive will require substantial amount of funding for construction of new and reconstruction of existing WWTP's. This problem concerns especially municipalities with the equivalent population over 2,000 (EO). This paper discusses some possibilities to address this problem. There are some specific aspects and problems, as well as technical design of solutions for sewage systems in small municipalities. Under a small municipality we understand smaller urban units. In terms of water management Slovak Technical Norm (STN) 756402 Small Waste Water Treatment Plans, this group includes municipalities or urban centres, which produce up to 100 m^3/day of waste water, assuming specific consumption of 200 litres/day per head of population. This concerns municipalities with population up to 500.

Keywords: sewage systems, waste water treatment, small urban areas, legislation in Slovakia

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1. Introduction

Since 1,174 out of a total of 2,891 municipalities in Slovakia belongs in the small municipality category and predominantly they are located in areas with less affected environment, the sewage solution needs to meet the technical and financial requirements, but also the aforementioned dilemma must be reduced to the acceptable degree and the sewage network must be integrated sensitively with the environment. Preferred approach is sewage network – Waste water treatment plant (WWTP), as well as sewage – natural environment – life environment. These links need to be given a priority not only in terms of design planning, execution and operation of the construction, but also in terms of contradiction waste water – surface water. Whereas the waste water, carried off via a sewage network represents progress for the society, mainly in terms of improved health and hygiene, the waste water is detrimental to the surface water and subsequently also to the natural environment.

2. Sewage, Division and Execution Status

Sewage is a set of equipment allowing harmless removal of waste water, including its treatment. It consists of two sub-systems – sewage network with construction objects and waste water treatment plant.

There are a number of municipalities, which have addressed waste water treatment partially, or not at all. In terms of the world standard in this area the municipalities can be split into the following categories:

- ideal status, municipality with sewage network with waste water treatment, located before the receiving water
- interim status, sewage system prior to expansion, reconstruction
- interim status, sewage network in place, insufficient effectiveness WWTP
- unsatisfactory status, sewage system without WWTP in place
- critical status, no sewage system.

2.1. SEWAGE SYSTEM IN PLACE

In this case the whole activity is focussed on operation and maintenance, or fixing of small breakdowns. In case of fully built sewage system we can encounter these problems: low quality construction (seepage, deficiencies in detail), insufficient and non-qualified operation, low effectiveness of WWTP, difficulties with sludge utilisation.

2.2. SEWAGE PRIOR TO RECONSTRUCTION

Each expansion or reconstruction even in small municipalities represents certain distinctiveness. In the first place we need to take into account the inspection of existing structure. Expansion can be delayed by application of new trends in sewage management and increased intensity of treatment processes.

2.3. SEWAGE SYSTEM IN PLACE, INSUFFICIENT EFFECTIVENESS OF WWTP

Solution to this situation is very similar to case no. 2, with the only difference being more focus on WWTP. Again, crucial factor is determining the amount and quality of waste water, hydraulic, technological and operational parameters of WWTP. Over the past decades the development of sewage systems has been the focus also in small municipalities. Considering that the financial and time requirements for the construction of WWTP are lower than the sewage network for the whole municipality, the waste water treatment plant was usually, and also due to legal reasons (waste water without treatment must not be drained in the river system), constructed as the first sewage system element. Following the launch of the operation, the WWTP has, as a result of incomplete sewage system, significant capacity reserves and it is a problem to maintain it in optimal operation regime.

2.4. SEWAGE SYSTEM IN PLACE, WITHOUT WWTP

When constructing a new WWTP, emphasis needs to be placed on establishing the volume and quality of waste water, treatment effectiveness, technological design, as well as proper operation. Of course, other factors are also important, such as costs, lifespan of materials and incorporation in the environment.

2.5. SEWAGE SYSTEM NOT EXISTING

Construction of sewage systems in small housing centres requires the preparation of warranted, prudent and forward looking concept. Formulation of such concept needs to be entrusted with experienced specialists with know-how on the subject. Considering the required distances, sewage cost per person in smaller estates are higher than average. Therefore a great care is necessary when deciding, which technical solution to apply. Two possible solutions for the treatment of household effluent are available:

- Central drainage and treatment of waste water
- Individual waste water treatment

3. Central Drainage and Treatment of Waste Water

This is a case of a construction of new municipal sewage network and its connection to the existing regional waste water treatment facility or a construction of a new local WWTP. From the technical and operational aspect, it is the optimal solution. Currently a Water Act has come into force in Slovakia, stating, that by the year 2015 every municipality with population over 2,000 will have to be connected to the public sewage system and waste water from this sewage must be subsequently treated in WWTP with biological treatment level effectiveness, which will be determined by the respective water management body according to the pollution degree of the receiving waters, which will be receiving the treated water. At the same time however it is necessary to consider the question of financial effectiveness of the given solution. The sewage system construction and its financing will be the responsibility of the municipalities, who find it increasingly difficult to raise the substantial amounts of funds required for such purposes. For example a construction of 1 metre of gravity-fed sewage system, outside the road, costs 100 Euro – 300 Euro, depending on the contractor. Considering the adverse financial position of our municipalities we are encountering more and more often individual solutions for household waste water storage and treatment.

4. Individual Waste Water Treatment

Household effluent can be drained from individual houses into drain-wells, septic tanks or into individual waste water treatment facilities.

5. Drain-wells

Drain-wells are used as storage tanks for household effluent. In majority of cases they are built as enclosed monolithic concrete tanks in the vicinity of the house. Disadvantage of the drain-wells is that they are used only for storage purposes and not as a separation or stabilisation tanks and therefore the content has to be removed and transported to the WWTP. Effluent removal truck operators are charging 10 – 15 Euro per 1 m^3 of household effluent.

6. Septic Tanks

These are flow-through tanks used for accumulation, sedimentation and partially stabilisation purposes. They were known and used already towards the end of the last century, when waste water from cities across England was treated in this manner. They work as a small anaerobic filter. The sludge is separated from the water, which is then filtered through a filtration layer. Thus reducing substantially the amount of sludge, which needs to be removed from the septic tank. However this sludge is not sufficiently stabilised and therefore it needs to be further processed. In principle there are three solutions available: removal, stabilisation and final treatment at the municipal WWTP.

Removal – the sludge is taken to agricultural and other lands, sludge lagoons, possibly can be used for composting purposes.

Sludge stabilisation – carried out in the form of wet oxidisation or aerobic – thermal processing.

Final treatment in municipal WWTP – currently this is the only realistic method in case of high volume of sludge. However, WWTP must be suitable for sludge processing, since the sludge causes uneven peak loads for the treatment plant and therefore causing the run-off quality deterioration. It is accompanied by a strong odour and at the same time it has detrimental effects on the facility's equipment. When draining the sludge from septic tanks to WWTP, compliance with the following principles is recommended:

- max. distance, effective for sludge transportation to WWTP is 20–25 km,
- minimal size of WWTP, for sludge processing is 10,000 EP.

Sludge drainage represents a technical problem. If the sludge is drained directly, it can disrupt the treatment plant operation and reduce the quality of treated water. Current trend to combat this problem is by building as storage tank for sludge. The size of the tank depends on the number of EP, which the WWTP is capable of handling. From this tank the sludge is evenly fed, even prior to the mechanical treatment. The technology in the processing of sludge prior to treating in WWTP has been addressed also by several domestic companies. The approach adopted abroad was to bring the sludge directly to heated putrefaction tanks. However, the practice has shown that this sludge does not have sufficient sedimentation properties. Therefore it is simpler to introduce the sludge into the waste water feeder at the WWTP. Of course, construction of such tank requires additional funding required for reconstruction of the treatment plant, which needs to be secured by the operator, i.e., the municipality.

7. Household Waste Water Treatment Plants

As a last of the offered solutions are household waste water treatment plants. Over the past several years we have been witnessing their construction with increasing frequency also in Slovakia. In price terms they are comparable with quality septic tanks, without having to deal with the problem of residual sludge.

This sludge is aerobically stabilised, which means that it is hygienically harmless. It can be used in agriculture, thickened in concentration tanks or drained in sludge presses. Its thickening or drainage properties are comparable with properties of excess sludge produced in municipal WWPT.

8. Function of Household Waste Water Treatment Plants

Treatment plants are designed for treating normal household effluent. They are scaled to accommodate approximately 5–20 population equivalent. Waste water treatment takes place in two steps. In the first step, during the mechanical pre-treatment, mechanical debris is removed from the water. Second step represents biological treatment in the form of fine-bubble aeration activation. At the same time the treatment process is extended by removal of biological elements of nitrogen and phosphorus in the form of denitrification and nitrification, which makes the majority of household treatment plants compliant with the European requirements with respect to effluent treatment. Waste water treatment plant itself comprises of the delivery unit placed on the concrete plate. It is necessary to ensure that the whole unit is watertight, since often it is placed below the water-table level and also to prevent the waste water seepage.

9. Technological Treatment Line Design

Household waste water treatment plants are offered on our market by several companies in various technological modifications. They use either bio-filtration or a long-term activation with aerobic sludge activation. In our paper we will focus on the description of household WWTP technology and operation, which was used also by residents of a new housing estate in Bernolákovo. Since it is a new development within the boundaries of municipality, which does not have a public sewage system, it was necessary to conduct a study of effluent management for the area. Following the assessment of investments required for the construction of effluent sewage and related connection to the municipal WWTP, a decision on behalf of about 25 households was made, to construct individual household waste water treatment units to address the household effluent issue. Waste water treatment takes place in a circular tank, in the form of long-term activation with aerobic sludge activation. The principle of comprehensive waste water treatment in the proposed technological solution is based on biological treatment by heterogeneous biological sludge, maintained in the deposit, with prior denitrification, where the source of carbon for denitrification processes is the introduced organic contamination of waste water. In order to oxidise the biological treatment process and to maintain the concentrate in the deposit, an aerating system of fine-bubble aeration is applied. Air is delivered through fan powered by electric motor. Treated waste water is lead to the collection tank, where tertiary treatment, using disinfectant agent is introduced. Excess, aerobically stabilised sludge, is removed from the treatment process by effluent truck once or twice per year, depending on the sludge production.

10. Operation of Household WWTP

It is very important to know that well functioning WWTPs, not requiring regular maintenance and audit do not exist. Therefore it is necessary to look after your WWTP and to follow the supplier instructions for maintenance and operation. Biological treatment is based on the biomass growth, which needs for its existence regular supply of nourishment in the form of organic contamination in waste water and also sufficient amount of oxygen, which is supplied to the system through fine-bubble aeration. Any disruption of this system can lead to deterioration of treatment effectiveness. Long-term incorrect operation of WWTP results in dying of the biomass, followed by total disruption of the treatment process. Although the treatment plant operation is automated, it still requires supervision. At least once a week the fan needs to be checked and the treatment process in the reactor, as well as the quality of treated water in the accumulation tank, need to be checked visually.

Household waste water treatment unit is designed for treating normal household effluent, therefore it can be disabled by the introduction of excess amounts of substances, which should not be present in municipal waste water. These are mainly the following:

- greases in higher concentration (frying oil)
- household softener solutions
- paints, varnishes and solvents
- powerful disinfectants and acids
- low degradability materials (plastics, rubber, textiles).

Reliable treatment requires daily supply of effluent, in order to facilitate biological processes in the treatment unit. In case of absence over a period of 2 to 4 weeks, without new effluent for the WWTP, the micro-organisms start slowly to die. However, following the re-introduction of regular effluent supply they have the capacity to adapt and recommence their reproduction. However the air supply must be maintained also during the absence of waste water supply, otherwise organisms could start to decompose and rot. Only in case of absence from home for several months it is recommended to shut down the whole unit and remove the content.

11. Handling of Treated Water

Treated water can be used for watering of lawns and fruit trees. However it is not to be used for watering of plants for direct consumption, since it can contain substances harmful to human digestive tract.

12. Handling of Excess Sludge

When the separation tank is filled with sludge, it needs to be removed in order to prevent the sludge entering the treated water, hence reducing the quality at the exit point from WWTP. Excess sludge is sufficiently stabilised, i.e., hygienically harmful and it can be used in agriculture or used for further treatment in the municipal WWTP.

In closing, we would like to present several price comparisons, which can assist the consumers in selecting the most suitable solution for the treatment of their household effluent. These are for reference purposes only, since there is a number of suppliers and operators of sewage systems and waste water treatment plants.

13. Conclusions

Currently the trend is the preference for individual solution and each home owner has the freedom to select the most suitable equipment. Be it a drain-well, which is more affordable, but the operation requires regular emptying the full content, hence increased cost of removal or more costly septic tank, where only thickened sludge is being removed. However it is not stabilised and therefore a hygienic treatment at the municipal WWTP is necessary. Available is also a third solution, being highly promoted in the past few years – household waste water treatment unit. Although it is more demanding in terms of operation, there are however no problems with excess sludge and treated water.

TABLE 1. Price comparison for various treatment methods of waste water from small sources

Building, facility	Cost (Euro)
construction of 1 m of sewage system in green belt (except road)	100 – 300
drain-well capacity – 20 m^3	1000 without foundations
septic tank capacity – 10 m^3	1000 – 1400
WWTP for 5 – 10 PE	1800 – 2500
effluent removal per m^3	1 – 2

ACKNOWLEDGEMENT

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ALLIUM-ASSAY IN EVALUATION OF DRINKING AND SURFACE WATER MUTAGENICITY

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Abstract. Analysis of genotoxicity is of a great importance due to the pollution of the environment by genotoxicants. The most harmful anthropogenic pollutants as heavy metals, surface-active substances, pesticides and radionuclides are mutagens or/and carcinogens. At date many biotests for determination of genotoxicity in our environment are proposed. Plant assays are known to have a lot of advantages in compared to other bioassays. Our numerous data on studying genotoxicity of urban water samples demonstrate that *Allium*-assay may be used for complex assessment of nature water reservoirs as well as of tap water samples. Results obtained demonstrate the mutagenic activity in some samples of drinking and reservoirs water.

Keywords: water quality, environmental pollution, mutagenicity, *Allium*-assay

1. Introduction

The problem of drinking water quality is important in many countries because of environmental pollution. Surface, ground and even drinking water may be polluted by dangerous chemicals, not only toxic but also genotoxic. The most harmful anthropogenic pollutants as heavy metals, surface-active substances, pesticides and radionuclides are mutagens or/and carcinogens. It is known the chromosome instability is supposed to be significant in cancer processing, birth

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defects and others therefore studying of chromosome instability is very important[1].

Common method of drinking water preparation in Ukraine is chlorination, and different chemical mutagens (Cl_2, ClO_2, chlorinated hydrocarbons etc.) in this process are formed. In most cases, only the methods common accepted in hygiene are usually used for estimation of polluted environment. Under the circumstances, the problem of mutagenicity is underestimated because simple chemical analyses do not include information on mutagenicity.

At date many biotests for determination of mutagenicity in our environment are proposed[2–4]. Being easy for use, inexpensive, well developed and good correlated with others assays, plant test-systems have a lot of advantages in compared with others test-systems. They are recognized as good indicators of mutagenic and clastogenic effects of environmental factors and are applicable for the detection of environmental mutagens both in laboratory condition and in situ[5]. A lot of plant assays were used to determine the mutagenicity of chemicals, physical mutagenic factors, polluted environment, wastes etc[6–13] .

In the present study we used *Allium*-assay to investigate the total mutagenic activity of Kyiv surface and drinking water samples.

2. Materials and Methods

The experiments were carried out in several series. Firstly, water samples collected for mutagenicity analysis were: 7 samples from Kyiv drinking water pipeline in different location (tap water – TW 1-7), 1 sample of boiled tap water (BTW1), 4 samples from urban natural reservoirs (RW1 – pond outside Kyiv, RW2 – small river Lybid, RW3 – river Dnipro, RW4 – pond inside Kyiv) and 1 well-water sample outside city zone (WW).

In second experiment effects of water boiling (during 5 min) on total mutagenicity were studied when 4 samples from Kyiv drinking water pipeline (TW1, 3, 8) and 1 sample from well-water (WW) were collected and boiled (BTW1, 3, 8 and BWW). In this case the content of chlorine in all samples using iodometry was determined. Minimal concentration of Cl_2 identified by this method was 0,05 mg/l.

In the next experiment 6 samples from lakes within Kyiv city (LW 1-6), 6 samples from river Dnipro sites in Kyiv (DW 1-6) and well-water (WW) sample outside city were collected.

These experiments were carried out at different times, therefore probes taken twice (TW1, TW3) or three times (WW) from the same sources should not be considered as identical samples. All water samples were tested immediately after collection. Distilled water as a control was used.

Allium seeds (*Allium cepa* L. (common onion) or *Allium fistulosum* L. (spring onion) were grown in Petri dishes with the water samples evaluated during 72 hrs. Cytogenetic effects of different water samples were studied in stained microscopical slides of root tip cells by anaphase method[14–16]. The frequency of aberrant anaphases and mitotic indexes were determined. All results were statistically processed, comparison between the experimental variants and controls were conducted by $\chi 2$-method. Results were supposed as significant when $P<0,05$.

3. Results and Discussion

The low level of chromosome instability in the control (1,24±0,26) in the first experimental series was determined, and 6 samples tested demonstrated mutagenic activity (Fig. 1). The level of aberrant cells was significant higher in comparison with the control when seedlings grown in 4 samples of drinking tap water and in 1 sample of reservoirs water. This reservoir is one in tandem ponds system inside Kyiv, much polluted by domestic, motorway and other wastes. The boiled tap water (BTW1) also demonstrated mutagenic activity in comparison with the control, but not in the comparison with the same non-boiled sample.

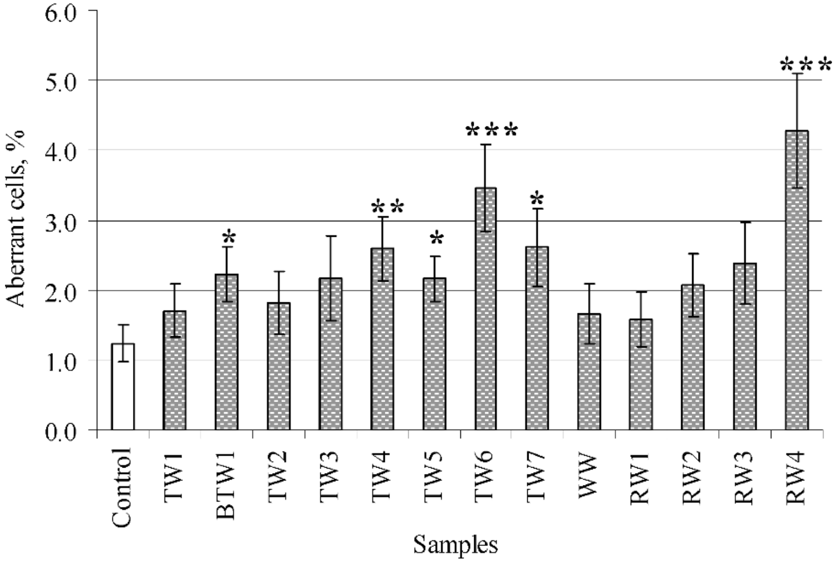

Figure 1. Diagrams showing the frequencies of aberrant anaphases (FAA) in *Allium fistulosum* induced by tap water (TW), boiled tap water (BTW), well-water (WW) and reservoirs-water (RW) samples. Significance of differences determined concerning the control; *– $P<0,05$, **– $P<0,01$, ***– $P<0,001$

The levels of chromosome instability in *A. fistulosum* in next experimental series were higher then in previous experiment. It is caused by seed ageing, because we used the same seed population with 1-year interval, when spontaneous level of chromosome instability was higher.

It is well-known, chlorine disappears of chlorinated water during boiling, and this fact was confirmed (Table 1), because there was no chlorine detected by iodometry in all boiled tap and well-water samples. Then pipeline samples of water were investigated for mutagenic activity before and after boiling, significant decrease of chromosome aberrations level due to boiling of water samples was revealed in one of four variants (BTW8) (Fig. 2). The chlorine amount in this sample was lowest (0,11 mg/l). Boiling of other two tap water and well-water samples was not effective for reducing their mutagenicity. There was no correlation between chlorine amount and frequency of aberrant cells. Previously, chlorinated water was shown to have strong mutagenicity in *Salmonella*-assay (Ames-assay), but under concentration much higher than in drinking water[17]. So, we can suppose chlorine was not an only mutagenic factor in tap water, another mutagenic chemicals may be present, for instance different chlorinated compounds.

TABLE 1. Content of chlorine in drinking water samples before and after boiling

Sample	Cl_2, mg/ml
TW1	0,21
BTW1	n.d.
TW3	0,36
BTW3	n.d.
TW8	0,11
BTW8	n.d.
WW	n.d.
BWW	n.d.

n.d. – chlorine was not detected in iodometric method.

Biotesting of water samples collected from surface reservoirs are presented in Fig. 3. All these sites are not supposed to be high-polluted because there are rest areas there. But some of these reservoirs may be polluted by domestic, motorway and/or railway wastes. The frequencies of aberrant cells were significant higher when the seedlings grown in water taken from four lakes, well-water and one site from river Dnipro. LW1, LW2, LW5 and DW5 sites are located closely to the intensive motorways, LW1, LW2 – closely to the railway also. The highest levels of mutagenic activity were determined in the samples LW2 and LW5 where the lakes likely may be high-polluted by mutagens (heavy metals, surface-active substances, benzo(a)pyrene etc.).

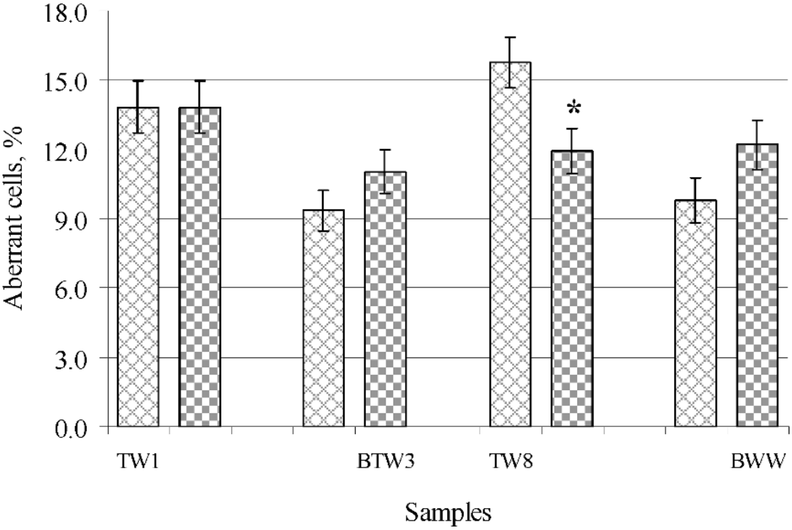

Figure 2. Diagrams showing the frequencies of aberrant anaphases (FAA) in *Allium fistulosum* induced by tap water (TW), boiled tap water (BTW), well-water (WW) and boiled well-water (BWW) samples. Significance of differences was determined between each TW and BTW accordingly, *– P<0,05

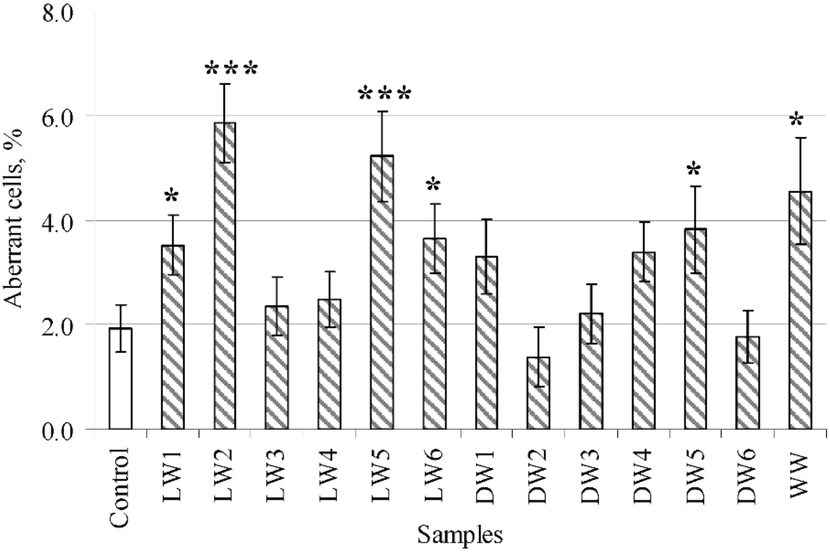

Figure 3. Diagrams showing the frequencies of aberrant anaphases (FAA) in *Allium cepa* induced by lake-water (LW), well-water (WW) and samples from river Dnipro (DW). Significance of differences determined concerning the control; *– P<0,05, ***– P<0,001

It is surprisingly, well-water sample for the first time within three experiments demonstrated mutagenicity as well as LW6 sample. This last lake located in forest recreation territory, there is no strong highway, railway or industrial pollution closely, only domestic wastes are supposed to pollute it. Other two forest lake samples (LW3, LW4) demonstrated no mutagenicity. Five samples from sites on river Dnipro were not mutagenic also, and they are located far from any strong pollutants. In addition, because of running river water is characterized lower mutagenic activity than standing lake water.

Results obtained demonstrate the presence of mutagenic pollutants in drinking and reservoirs water samples. Assuming, we can conclude that samples of drinking water sometimes had mutagenic activity as well as water from lakes and ponds. On the contrary, river water samples were not mutagenic in most cases. As our data demonstrated *Allium*-assay is effective bioassay, it may be used for complex assessment of nature water reservoirs as well as of tap water samples.

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MODELLING WATER QUALITY FOR INTEGRATED WATER RESOURCES MANAGEMENT AT THE BASIN SCALE

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Abstract. The concept of Integrated Water Resources Management (IWRM) is a powerful tool for satisfying needs for freshwater, protecting the environment and ensuring sustainable socio-economic development. After explaining the meaning of IWRM, mathematical modelling of water quality is applied at the basin scale as a first step towards achieving environmental protection. In view of many uncertainties, a risk-based methodology is proposed for IWRM at the basin scale with special reference to transboundary river basins.

Keywords: integrated water resources management; modelling water quality; risk assessment; transboundary water resources management

1. Introduction

When considering the different needs for water for human activities, for the natural environment and for different ecosystems, very often problems can be found due to conflicting or competing demands and situations. Such problems may arise between sectors using water for different purposes, such as water supply, agricultural irrigation, hydropower production and industrial water use, and concern available water quantity and/or water quality.

For example, industries producing large amounts of wastewater may pollute groundwater in the surrounding aquifer, which in turn affects the quality of water pumped for drinking purposes. The increase of water pollution from

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industrial activities may also affect the quality of river water used for irrigation. When groundwater is over-pumped from a series of wells, the groundwater table is lowered and can affect agricultural production, as less water will be left for feeding crop roots. Lowering the water table in a coastal zone may also increase seawater intrusion and soil salinisation, with negative impacts on agriculture and ecosystems.

Obviously, when actions are taken for different water uses, as can be seen in the examples above, there is a need to coordinate the related activities in various perspectives, such as between different:

- *sectors of water uses* (water supply, agriculture, industry, energy, …)
- *types of natural resources* (land, water and others)
- *types of water resources* (surface water, groundwater)
- *locations in space* (local, regional, national, international)
- *variations in time* (daily, monthly, seasonal, yearly, climate change)
- *impacts* (environmental, economic, social, …)
- *scientific and professional areas* (engineering, law, economy, ecology, …)
- *water-related institutions* (governmental, private, international, NGOs, …)
- *decision-makers, water professionals, scientists and stakeholders*

This basic need for coordination between different water related activities, impacts and institutions gave rise to the concept of IWRM. This concept will be clarified further in the following chapter and a risk-based methodology for tracking the degree of achievement of this concept in practice will be suggested.

In order to implement IWRM in its member states and also in neighbouring countries, which may share transboundary surface waters or aquifers with European Union (EU) member states, the EU issued in 2000 the EU-Water Framework Directive 60/2000[1] (EU-WFD). The purpose of the WFD is to create a framework, which:

- promotes sustainable water use based on a long-term protection of available water resources;
- aims at enhanced protection and improvement of the aquatic environment;
- prevents further deterioration and protects and enhances the status of aquatic ecosystems;
- ensures the progressive reduction of pollution of groundwater and prevents its further pollution;
- contributes to mitigating the effects of floods and droughts.

Tools and methodologies for key issues such as monitoring, river basin planning and management, institutional structures, water economics, environmental protection and public participation are included in the Directive.

2. The IWRM Methodology

The actual term "Integrated Water Resources Management" (IWRM) was first coined in 1977 at the UN Conference in Mar del Plata. The term is very broad and is therefore subject to different definitions.

In the Background Paper No. 4[2] of its Technical Committee, The Global Water Partnership (GWP) – an NGO based in Stockholm – defines IWRM as "a process which promotes the coordinated development and management of water, land and related resources to maximise the resultant economic and social welfare in an equitable manner without compromising the sustainability of vital ecosystems." The "Tool Box" being developed by GWP promotes IWRM and makes recommendations on how it can be achieved.

The World Water Council (WWC) stated that IWRM is a "philosophy that holds that water must be viewed from a holistic perspective, both in its natural state and in balancing competing demands on it – agricultural, industrial, domestic, and environmental. Management of water resources and services needs to reflect the interaction between these different demands, and so must be coordinated within and across sectors. If the many cross-cutting requirements are met, and if there can be horizontal and vertical integration within the management framework for water resources and services, a more equitable, efficient, and sustainable regime will emerge"[3].

As shown in Fig. 1, IWRM could be achieved by coordinating two different categories of issues, namely natural issues (type of resources, space and time scales) and man-related issues (water sectors, scientific disciplines, impacts, institutions, participants).

There is no general rule about the optimum degree of integration or how to achieve it. In terms of the spatial scale, that of the river basin is the most appropriate, taking into account the hydrological cycle and the water budget. The basin scale is also recommended by the EU-WFD[1]. The effect of possible climate change should also be taken into account, although large uncertainties still persist for quantifying such effects. In this context, mathematical modelling may play a major role for producing alternative scenarios for sustainable water resources management.

3. Modelling Water Quality

During the 1980s pollution from point source discharges was largely controlled in Europe and elsewhere through the construction of wastewater treatment plants under stringent pollution control laws. The major threat now actually comes from non-point sources, such as agricultural activities and surface runoff, and concerns surface water pollution and more importantly groundwater contamination.

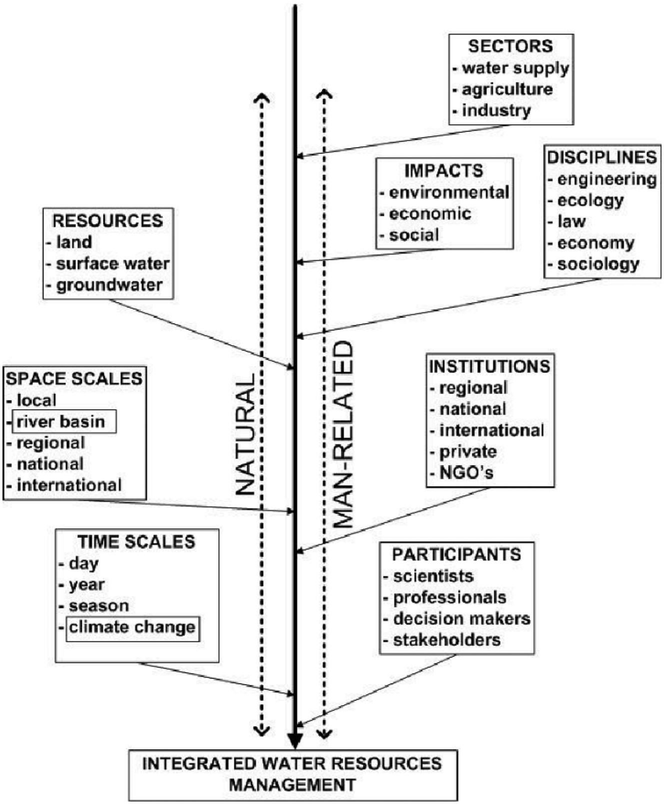

Figure 1. Areas and topics of IWRM[4]

Results of water quality simulation at the river catchment scale, obtained by a European funded research project called "A Regional Model for Integrated Water Management in Twinned River Basins (RIVERTWIN)," are presented. The main objective of the project was the development and application to different river basins of an integrated water resources management model, including the surface water quality simulation component. Two different mathematical models were used, namely the MONERIS and QUAL2K models. Results of numerical simulation and comparison with available data are summarised for the case of the Neckar River Basin, Germany.

3.1. THE MONERIS MODEL

The MONERIS (MOdelling Nutrient Emissions in RIver Systems) model is a conceptual, quasi-static model developed to estimate annual emissions of nitrogen and phosphorus from various sources on a subcatchment scale and the resulting loads at the sub-catchment outlet[5, 6].

As shown in Fig. 2, the model estimates annual loads from seven different pathways, which derive from point (direct and WWTPs) and diffuse sources (atmosphere, agriculture and urban areas). Each pathway has its own Excel file where the calculations are made and these files are further linked to an input data file and an output data file.

The model is dependent on statistical data (i.e. inhabitants, nutrient surplus and information on sewer systems) and geographical data stored and analysed in a Geographical Information System (GIS).

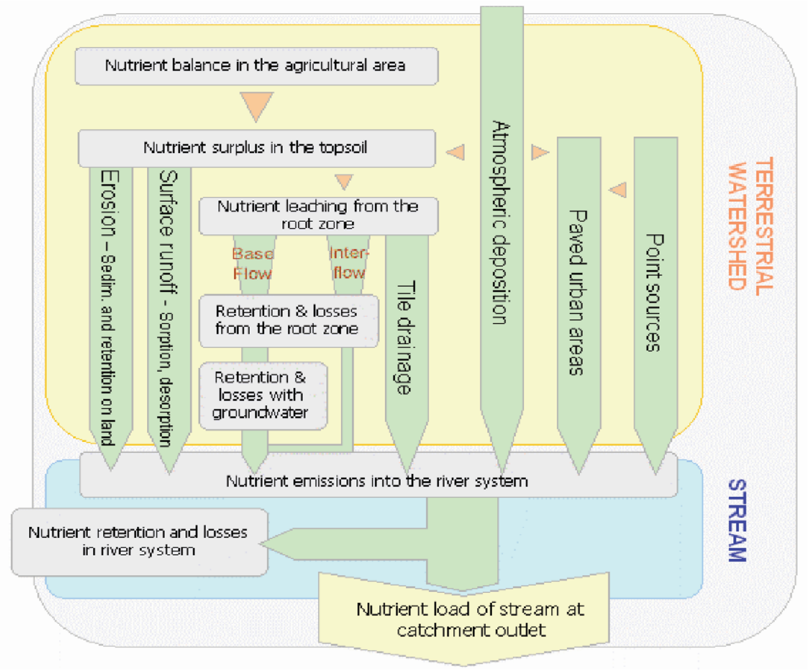

Figure 2. Pollutant pathways in the MONERIS model[8]

3.2. THE QUAL2K MODEL

The conceptual representation of a stream used in the QUAL2K model[7] is that of an element that has been divided into a number of unequally spaced reaches or computational steps equivalent to finite difference elements (Fig. 3).

For each computational element, a hydrologic balance in terms of flow, a heat balance in terms of temperature, and a mass balance in terms of constituents' concentration are formulated. The model presently simulates the main stem of a river. In addition, multiple loadings and abstractions can be introduced for any reach. Tributaries are not modelled explicitly, but can be represented as point sources.

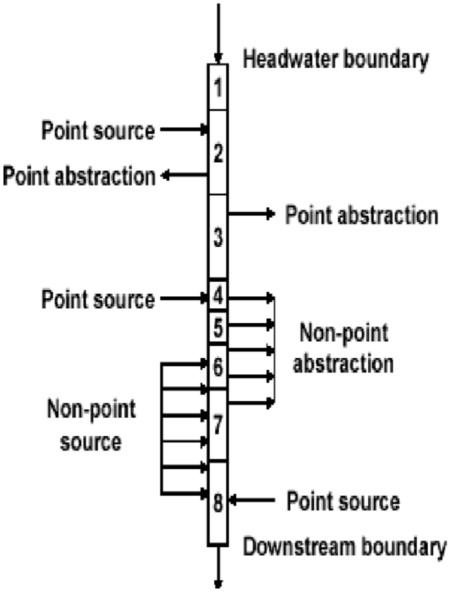

Figure 3. Operational scheme of the QUAL2K model[8]

3.3. SIMULATION RESULTS

The MONERIS model was run for the whole Neckar basin. The basin was divided into 42 subcatchments between 134 and 505 km^2. Some of the model outputs for the Neckar basin are shown in Fig. 4 below.

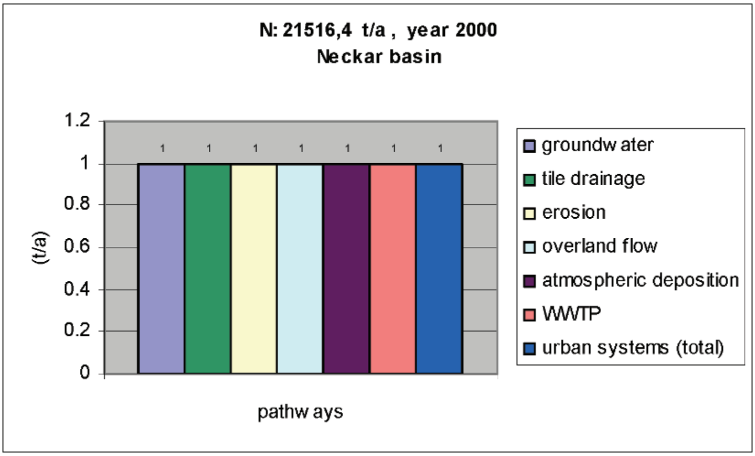

Figure 4. Nitrogen emissions at the outlet of the Neckar basin for the reference year 2000[8]

The lower part of the River Neckar from Hofen to Mannheim was selected for model calibration and validation, since there is better data coverage for this lower part of the river. The reference year for the first run of the model was 2000. Some of the model outputs and comparison with available data are plotted in the graphs below (Fig. 5).

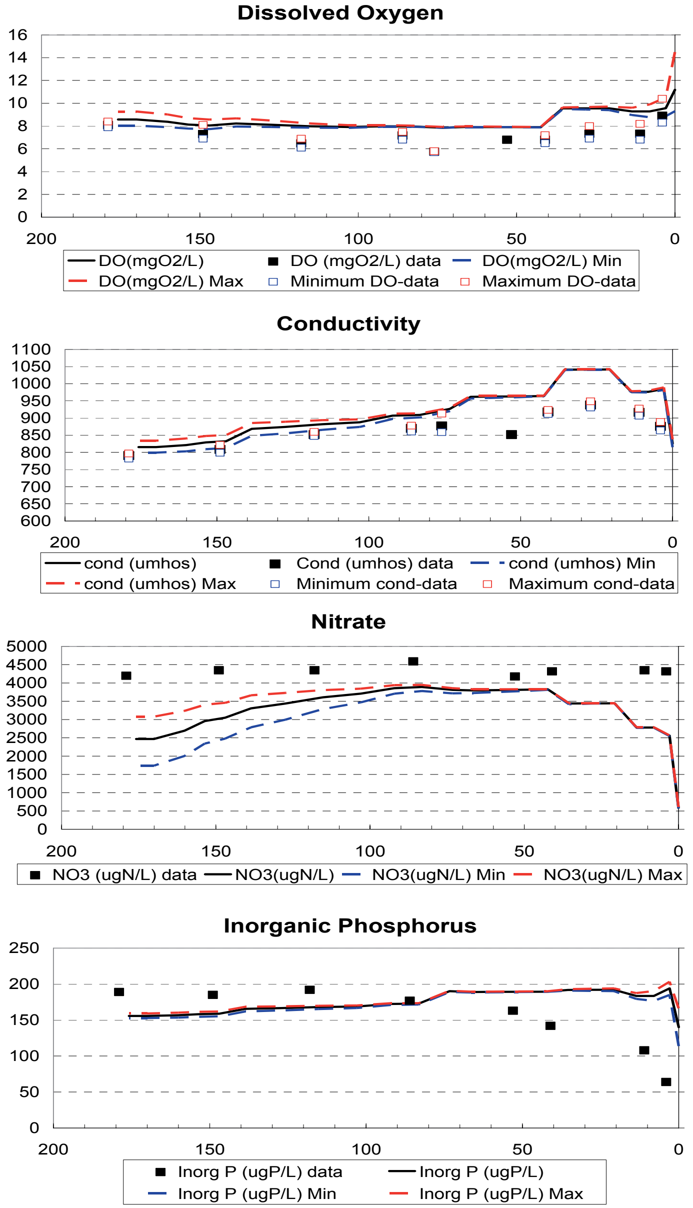

Figure 5. Comparison between QUAL2K simulation and available data[8]

4. Risk-based Integrated Water Resources Management (RIWRM)

In the past, traditional approaches for water resources management emphasised technical reliability versus the effective use of available economic resources in planning, construction and operation. Whilst still providing a reliable framework for water resources use, investment and maintenance costs were to be minimised.

According to IWRM, apart from the above technical and economic criteria, at least two more additional general objectives should be considered, namely environmental security and social equity. In terms of an integrated approach, management issues should be considered at the basin scale and groundwater aquifers should be managed in relation to surface waters.

In what follows, the Integrated Water Resources Management (IWRM) approach is formulated in terms of a risk-based multidisciplinary methodology called RIWRM. Furthermore, a Risk-based Multicriterion Decision Analysis (RMCDA) is presented as a tool for risk management and conflict resolution in internationally shared groundwater resources.

4.1. DEFINITION OF THE ENGINEERING RISK

In a typical problem of technical failure under conditions of uncertainty, there are three main questions, which may be addressed in three successive steps:

- When should the system fail?
- How often is failure expected?
- What are the likely consequences?

The first two steps are part of the uncertainty analysis of the system. The answer to question 1 is given by the formulation of a critical condition, producing the failure of the system. To find an adequate answer to question 2 it is necessary to consider the frequency or the likelihood of failure. This can be done by use of the probability calculus. The consequences of failure (question 3) may be accounted for in terms of economic losses or profits.

As explained in the book by Ganoulis[9], a variable reflecting certain external conditions of stress or loading may be defined as *load* ℓ. There is also a characteristic variable describing the capacity of the system to overcome this external load. This system variable may be called *resistance* r. A *failure* or an *incident* occurs when the load exceeds this resistance, i.e.

Failure or Incident: $\ell > r$

Otherwise we have:

Safety or Reliability: $\ell \leq r$

In a probabilistic framework, ℓ and r are taken as random or stochastic variables and the chance of failure occurring is defined as the *engineering risk*. In this case we have

Risk = *Probability of failure* = $P(\ell > r)$

This simple definition of engineering risk as the probability of exceeding a certain value of load is not unique[10]. Generally speaking, risk is a complex function of the probability of failure and its consequences. In the literature the product of the probability and its consequences are often taken as the risk function. However, different risk indices may be found in the literature for describing economic and social risks.

4.2. TECHNICAL, ENVIRONMENTAL, ECONOMIC AND SOCIAL RISKS

The Risk-based Integrated Water Resources Management (RITAM) approach for transboundary groundwater resources planning and operation aims to reduce not only technical and economic but also environmental and social risks in order to achieve four main objectives (Fig. 6):

(1) Technical reliability,
(2) Economic effectiveness,
(3) Environmental safety, and
(4) Social equity.

After the definition of the objectives, the steps to be undertaken for the RITAM method are the following[9, 11, 12]:

- Define a set of alternative actions or strategies, which includes structural and non-structural engineering options.
- Evaluate the outcome risks or risk matrix containing an estimation of the risks corresponding to each particular objective (technical, environmental, economic and social).
- Find by use of an averaging algorithm the composite risk index for technical and ecological risks (eco-technical composite risk index) and the same for the social and economic risks (socio-economic composite risk index).
- Rank the alternative actions, using as criterion the distance of any option from the ideal point (zero risks).

As shown in Fig. 6, in the two-dimensional plane with coordinates the composite eco-technical and socio-economic composite indices, strategies 1, 2 and 3 are ranked 1-3-2 using as criterion the distance of any strategy from the ideal point (0,0).

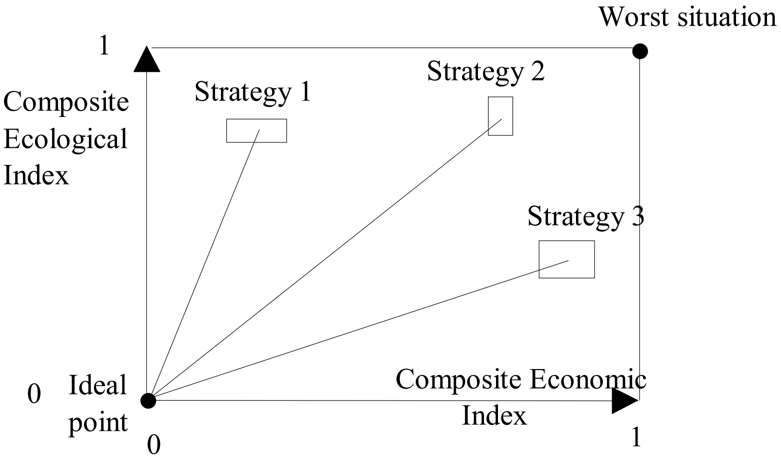

Figure 6. Ranking of different strategies in RITAM

5. Conclusions

Risk-based Integrated Water Resources Management (RITAM) methodology is proposed in order to integrate multiple risk indices into a multi-objective planning and decision-making process for sustainable water resources management. In order to achieve sustainability of water resources management, multiple risk indices are defined, such as technical, environmental, economic and social.

Modelling techniques like those reported in this paper for simulating water quality may be used to evaluate not only technical reliability and cost effectiveness, but also environmental safety and social equity.

ACKNOWLEDGMENT

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XENOBIOTICS AND ITS TREATMENT, IMPACT ASSESSMENT

POLAR ORGANIC MICROPOLLUTANTS IN THE WATER CYCLE

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Abstract. Emerging contaminants such as pharmaceuticals and biocides are released from sewage treatment plants and also from agricultural fields. They are increasingly monitored in surface and groundwater but are not yet included as priority compounds in European guidelines. Analysis of these mostly polar compounds and their sometimes relevant metabolites is more and more carried out by LC-MS-MS. The main elimination processes in sewage treatment plants are sorption and biodegradation. Both processes are difficult to predict in case of polar compounds and therefore fate studies are essential.

Keywords: micropollutants; pharmaceuticals; biocides; metabolites; emerging contaminants; priority compounds; tracer; chemical analysis; LC-MS; monitoring; surface water; groundwater

1. Definition and Origin of Micropollutants

Micropollutants are compounds which are detected in the concentration range of ng/L up to µg/L in the environment. In general, synthetic chemicals are meant, but natural substances, which are of anthropogenic origin such as estradiol, are often included.

An overview on different sources of products containing micropollutants and their release to the environment is given in Table 1. In general, point sources such as effluent of sewage treatment plants (STPs) and diffuse sources such as run-off of agriculturally used fields can be differentiated.

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Emissions into the environment are difficult to estimate. On one hand, emission data is often not available. Sales data on industrial chemicals, e.g. ingredients of personal care products, are very difficult to obtain. For pharmaceuticals, sales data were becoming available in several countries, thanks to the effort of researchers investigating their behavior in the environment in the last decade. Still, for many countries only rough estimations are available. According to IMS Health the equivalent of USD 96 billion was spent on drugs in retail pharmacies in the top five European markets during the year 2006.

TABLE 1. Overview of origin, type and pathways of organic micropollutants in the environment (main pathways are marked bold)

Source	Substance groups (examples)	Pathways in the environment
Urban settlements	Personal care products, human pharmaceuticals, detergents, chemicals used in construction business (dyes, lacquer, binder, wood preservatives), flame retardants, pesticides, biocides	Wastewater diffuse landfill site
Agriculture	Pesticides (insecticides, herbicides, fungicides), veterinary pharmaceuticals	Wastewater diffuse
Industry	industrial chemicals (polymers, dyes, varnishes, oxidants, reductants, detergents, corrosion inhibitors, biocides)	Wastewater landfill site
Traffic	ingredients of motor oils, lubricants, combustion products	diffuse landfill site

On the other hand, sales data are sometimes given but emission pathways are not known. For examples, pesticides are expected to be released mainly in agriculture. However, a study in Switzerland revealed that similar amounts of pesticides (approx. 1300 t/y) are used in agriculture as in urban settlements (Stamm et al., 2006). A study conducted for the catchment of lake Greifensee showed that 10–30% of the pesticides which are used only in agriculture reached the lake through sewage treatment plants (Gerecke et al., 2002). For pesticides with additional urban applications such as diuron, 60–80% of the load derived from STPs. The different emission pathways to the environment, as is the case for pesticides and biocides, need to be distinguished in order to determine realistic exposure scenario. As a result, effective reduction measures can be developed.

2. Selection of Priority Compounds

2.1. PRIORITIZATION USING ENVIRONMENTAL BEHAVIOUR DATA

In the European Inventory of Existing Commercial Chemical Substances (EINECS) approx. 100'000 chemicals are registered, which were marketed before 1981. There from ca. 30'000 substances marketed in volumes above 1 t/y and ca. 10'000 above 10'000 t/y. Since 1981 approx 3'800 new compounds came on the market. Until now an extensive risk assessment was carried out for approx. 3'000 compounds. The ranking of the relevance of compounds with regard to their aquatic pollution is complex and because of missing data often not possible. Apart from the production volume, the environmental behaviour and the toxicity is important for priorisation.

The environmental behaviour is mainly determined by the following processes:

- Transport (run-off, sedimentation, leaching, atmospheric deposition)
- Distribution between different phases (volatilization, sorption, bioaccumulation)
- Biological degradation (aerobic, anoxic, anaerobic; primary degradation versus mineralisation, cometabolism)
- Abiotic degradation (photolysis, chemical reactions like oxidation, reduction, hydrolysis)

Especially for new compounds the environmental behaviour is a priori not known. For an estimation e.g. of the distribution between different phases and transport processes physical chemical properties such as water solubility, log Kow, Koc, Kd, Henry coefficient, bioconcentration factor (BCF), and pKa are used. These data can be found in databases (e.g. scifinder, Beilstein, www.syrres.com/esc/datalog.htm, www.chemfinder.com, www.epa.gov) or, if not available, can be predicted by use of quantitative structure activity relations (QSAR). Some correlation between the different physical chemical properties exist, e.g. with decreasing water solubility and decreasing vapour pressure the log Kow and BCF increase indicating accumulation in lipophilic media. However, it should be emphasized that the prediction is mainly possible for non-polar compounds, while the prediction of the behaviour of polar or charged compounds is often not correct. For example, the use of log Kow values lead to an underestimation of the sorption of fluoroquinolones to sludge (Golet et al., 2003) or sulfonamides to soil (Stoob et al., 2006). The fluoroquinolone Ciprofloxacin has a Kow value of 1.8, but nevertheless sorbs to sludge in the STP by 80%, indicating that sorption is the main elimination process (Fig. 1).

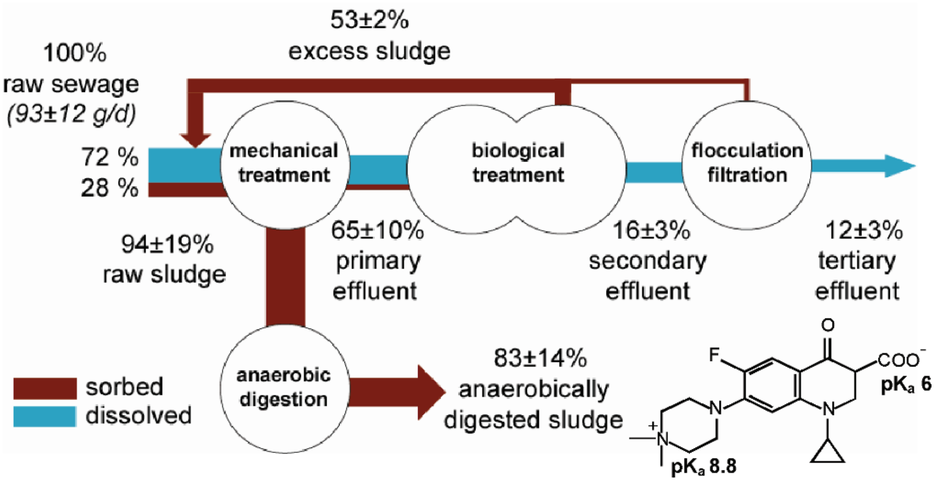
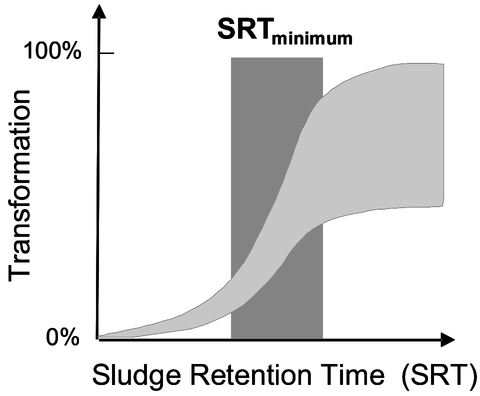


Figure 1. Significance of sorption as elimination process for the polar antibiotic Ciprofloxacin with a log Kow of 1.7 (modified from Golet et al., 2003), Copyright © 2007 American Chemical Society

The prediction of biological degradation (QSBR) with tools such as BIOWIN (EPISUITE), Catabol (Jaworska et al., 2002), or UM-PPS (Hou et al., 2003) is still at the beginning and until now almost exclusively possible for the aerobic degradation. So, biological degradation has to be tested by use of standardized OECD/ISO tests, preferably with real inoculum under realistic environmental conditions (TGD, 1996).

Biological degradation of different pharmaceuticals was studied within the EU project POSEIDON in a pilot plant membrane bioreactor with increasing sludge retention times (SRT) (Joss et al., 2005, Ternes and Joss 2006, Göbel et al., 2007). SRT was shown to be a major factor influencing the microbial transformation, as a minimal SRT is necessary to degrade the compounds (Fig. 2). Maximal achievable degradation occurs for many pharmaceuticals at SRT of 10–12 d, which is normally achieved in conventional STPs with a nitrifying step. Only for a few compounds like the antimicrobials Clarithromycin and Trimethoprim higher sludge retention time is needed for a substantial degradation to occur, indicating that the transformation of these compounds may be inversely correlated to the sludge loading, i.e. the ratio of substrate and sludge concentration, which decreases with increasing sludge retention time. Reduced sludge loading may cause an increase in the biodiversity of the active biomass, which seems to have an influence on the elimination of compounds undergoing co-metabolism, as assumed for antimicrobials. The observed degradation rates of various compounds differ significantly without showing any evident correlation to specific molecular structure: currently no quantitative structure activity relationship (QSAR) can be identified. The observed removal rates vary form very fast (e.g. Estradiol, Paracetamol) to zero (e.g. Carbamazepine, Amidotrizoate). Therefore the degradation of each compound has to be determined experimentally until better prediction tools are available.



SRT	Transformation [%]
2 - 5 d	Bezafibrate (> 95%) Ibuprofen (> 90%) Sulfamethoxazole (50-75%)
5 -15 d	Diclofenac (15-40%) Ethinylestradiol (> 90%) Iopromide (30-90%) Roxithromycin (0-60%)
60 -80 d	Clarithromycin (90%) Trimethoprim (85%)
< 20d	Carbamazepine (0 %) Diazepam (0 %)

Figure 2. Dependency of transformation rate on sludge retention time for pharmaceuticals in STPs: maximal transformation of pharmaceuticals at minimal SRT is listed (Joss et al., 2005; Ternes et al., 2004; Göbel et al., 2007)

2.2. EXISTING PRIORITY COMPOUNDS IN EUROPE

In Europe und the USA several lists of priority compounds are assembled which partly are valid only for specific applications (Table 2). Parameters were weighted to a different extent depending on the focus of the list. For the aquatic environment the 33 priority substances of the water framework directive (WFD) are most relevant. For these compounds monitoring programs have been or will be developed in the next years. Besides some anorganic compounds (e.g. lead, nickel), several agro chemicals (Alachlor, Chloropyrifos, Isoproturon), industrial chemicals (Nonylphenol, Chloroform), combustion products (PAHs) and traffic emissions (Benzene) are included.

Emerging contaminants such as pharmaceuticals, personal care products and biocides, which are increasingly investigated in recent years (Bester 2006; Kolpin et al., 2002; Richardson and Ternes, 2005; Ternes and Joss, 2006), are not yet included in the lists of priority chemicals. These compounds often do not bioaccumulate to a high extent and are therefore not relevant for many lists since they are based on bioaccumulation and persistence criteria.

TABLE 2. Lists of priority compounds in Europe and USA with focus on water (modified from Schuelp et al., 2006)

Priority list	Based on	Focus	No. of compounds	Year
HELCOM Helsinki Convention	HELCOM Helsinki Commission	water pollution (marine environment)	47	1988/2000
North Sea Conference List of Priority Hazardous Substances	3rd declaration The Hague, Annex 1	water pollution (marine environment)	36	1990
IKSR	International Commission for the Protection of the Rhine	water pollution	92	2000
The 2000 OECD List of High Production Volume Chemicals	Decision-Recommendation of the Council on the Co-operative Investigation and Risk Reduction of Existing Chemicals	Existing Substances, High Production Volume Chemicals	about 5000	2000
Stockholm List/UN-POP	Stockholm Convention on Persistent Organic Pollutants (European Commission, UNEP)	Persistent organic pollutants POP	12	2001
Priority PBT Profiles	US EPA PBT Initiative	PBT pollutants	12	1998/2003
Proposed Priority Substances Water Framework Directive	Water Framework Directive and COMMPS-Procedure (European Commission)	water pollutants	33	2001
OSPAR List of Chemicals for Priority Action	OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic	water pollution (mainly marine environment)	42	2002
EPA National Primary Drinking Water Standards	Safe Drinking Water Act and CCL-Procedure	drinking water	87	2003

Recently, Muir and Howard (2006) used also bioaccumulation, persistence and long-range atmospheric transport criteria for their screening of possible new emerging contaminants in the environment and so there list contains also only compounds with large Kow values.

In order to protect the aquatic environment polar compounds, which contain polar and often bioactive functional groups, have also to be considered. Currently, there is an ongoing discussion about the amendment of several polar compounds such as x-ray contrast media, pharmaceuticals, detergents, pesticides, perfluorinated compounds and personal care products to the priority list (Draft proposal to Directive 2000/60/EC). Within one year the European commission has to make a proposal for their final classification. Especially critical are those compounds for which acute or chronic toxicological tests showed low effective concentrations. For instance, the anti-inflammatory drug Diclofenac exhibits a low no observable effect concentration (NOEC) in rainbow trout (Schwaiger et al., 2004; Triebskorn et al., 2004). Taking into account a safety factor of 10 a quality value of 0.1 µg/l results (Jahnel et al., 2006). This is in the range of concentrations found in surface waters influenced by STP effluents (Ternes 1998, Öllers et al., 2001). The same holds for Carbamazepine for which a quality value of 0.5 µg/l is proposed. Critical values in the range of concentrations of contaminated surface water derived by scientific risk assessment are discussed also for Bisphenol A, tin organic compounds, as well as several pesticides (Jahnel et al., 2006).

2.3. ENVIRONMENTAL SIGNIFICANCE OF TRANSFORMATION PRODUCTS

Transformation products which can be formed during chemical, biological or photolytic degradation are, apart from Nonylphenol, also not included in the above mentioned lists, due to the scarce knowledge of the transformation processes and the non-availability of reference compounds. However, the exposure of transformation products can be relevant as shown for pesticides in groundwater in the USA (Kolpin et al., 1997; 2004, Boxall et al., 2004) as well as in Switzerland (Hanke et al., 2007). In both studies several pesticide metabolites such as Metolachlor-ESA or -OXA were found in higher concentrations in groundwater than the parent compounds. While Metolachlor in groundwater of Swiss wells was found in the concentration range of 3–32 ng/L, the maximal concentration of the metabolites were at 480 ng/L for metolachlor-ESA and 210 ng/L for Metolachlor-OXA (Hanke et al., 2007). The parent compound was found in 13% of the wells in concentrations above the detection limit whereas Metolachlor-OXA were found in 12% and Metolachlor-ESA even in 33% of the wells.

For pharmaceuticals there is only little knowledge on the environmental exposure of human metabolites which are excreted from the human body instead of the parent compounds, often in considerable amounts. Some metabolites like Sulfamethoxazole and Ethinylestradiol conjugates are cleaved in STPs to the parent compound (Göbel et al., 2005, D'Ascenzo et al., 2003). Only a few recent studies include the fate of persistent human metabolites. Bendz et al. (2005) detected human ibuprofen metabolites not only in the STP but also in the receiving river and carbamazepine metabolites were found in STP effluent and even in drinking water (Miao et al., 2005; Hummel et al., 2006). Nearly no information is available until now about transformation products formed in the environment or STPs.

3. Analysis of Polar Micropollutants

In the last 15 years the analysis of polar organic compounds has dramatically improved. Main reason is the development and increased application of the HPLC-MS technology. Until the nineties of the last century mainly classical contaminants such as PAHs, PCBs, and pesticides which are detectable by GC-MS were studied. The coupling of mass spectrometry with HPLC opened up the sensitive quantification of polar compounds without time-consuming derivatization. State of the art is the analysis of polar compounds by HPLC separation followed by electrospray ionization and tandem mass spectrometric using selected reaction monitoring detection (McArdell et al., 2007). After appropriate enrichment e.g. by solid phase extraction (SPE) and use of the described technology detection limits in the lower ng/L-range can be achieved. One disadvantage of LC-MS in comparison to GC-MS is that the ionization of the compounds is not standardized and so no spectra libraries are commercially available. Therefore a screening of unknown compounds by interpretation of fragmentation pattern using large spectra libraries such as those available for GC-MS is nearly impossible. A new approach is the use of new hybrid tandem mass spectrometers. The combination of LC-Time of flight (TOF) (providing accurate mass measurements to generate elemental compositions of ions) with LC ion trap (providing structural information from fragmentation studies) is recently been applied for screening and identification of pesticides and their metabolites in environmental samples (Thurman et al., 2005; Hernandez et al., 2004; 2005). The limitation of TOF instruments in comparison to quadrupoles is their lower sensitivity, which hampers the detection and identification of analytes at low concentrations (Hernandez et al., 2005). The hybrid system of linear ion trap combined with the new orbitrap technology (LTQ-Orbitrap) enables higher sensitivity and higher mass accuracy up to 2 ppm and better (Hu et al., 2005; Makarov et al., 2006; Hollender et al., 2006).

As an example, in Figure 3 the approach for the sensitive identification of selected target compounds in an acquired LTQ-Orbitrap chromatograms is illustrated for the pesticide Metolachlor (15 ng/L) in an enriched surface water sample (Hollender et al., 2006). The target compounds can be extracted from the Orbitrap full scan chromatogram (Figure 3, I) using their exact mass. Reliable identification can be carried out by (1) comparing the measured and the theoretical mass of the molecular ion, (2) comparing the measured and predicted isotopic pattern (Figure 3, IIa and IIb) and (3) further confirmation by comparing the MS/MS spectra received in the iontrap with literature data or data predicted by appropriate software (Figure 3, IIIa and IIIb).

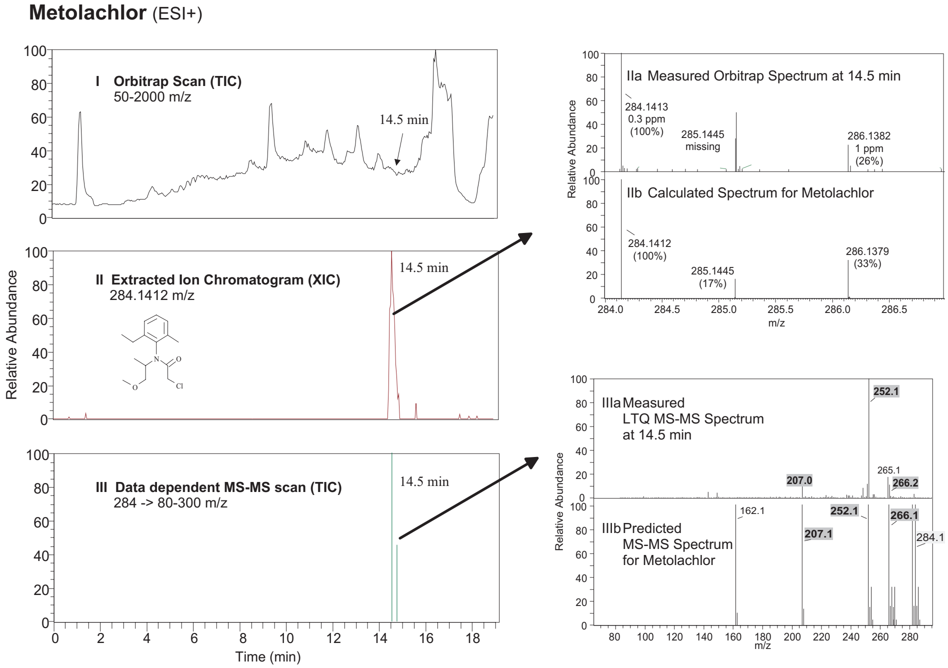


Figure 3. Identification of Metolachlor in a surface water sample using linear ion trap combined with orbitrap analyzer

4. Monitoring of Micropollutants in the Water Cycle

In the last 5–10 years large monitoring programs focusing on emerging contaminants in aquatic systems analyzed with LC/MS were carried out by research institutes, universities, but also federal environmental offices on the national and european level (Kolpin et al. 2002, Ternes 1998, BLAC 2003). Emphasis is on the discharge of micropollutants from wastewater in STPs into surface water. The results of the European project Poseidon and P-three are important contributions in this field (Ternes and Joss, 2007, Reemtsma et al., 2006). In general, surface water which is influenced by wastewater, contains several polar compounds in concentrations above 0.1 ug/L. In Table 3 different micropollutants are listed which are very persistence or which often appear at elevated concentrations in surface water.

TABLE 3. Persistent organic micropollutants of urban and agricultural use which are often detected in surface water (Giger et al., 2006; Reemtsma et al., 2006; Schluep et al., 2006; Stamm et al., 2006; Ternes, 1998)

Substances from urban settlements	Pesticides, Biozides
Amidotrizoate (contrast medium)	Atrazine (herbicide not longer permitted in the EU, restricted use in Switzerland)
Benzotriazole (corrosion inhibitor)	Desethylatrazine (metabolite of Atrazine)
Bezafibrate (lipid regulators)	Desisopropylatrazine (metabolite of Atrazine)
Benzothiazolsulfonate (biocides)	2,6-Dichlorobenzamide (herbicide)
Carbamazepine (Antieptileptic)	Diuron (herbicide, biocides)
Clarithromycin (Antibiotic)	Diazinon (insectizide, low concentration but high effect)
Diclofenac (analgesic)	Glyphosate (herbicide, increasing application)
Ethylenediaminetetraacetic acid (EDTA, complexing agents)	Isoproturon (herbicide)
Iopamidol, Iopromid (contrast media)	Mecoprop (herbicide)
Methyl-tert-butylether (MTBE, gasoline supplement; restricted use, substituted partly by ETBE)	Metamitron (herbicide)
Naphtalinsulfonate (detergent)	Metolachlor (herbicide)
Metoprolol (beta-blocker)	Metolachlor-ESA (metabolite of Metolachlor)
Sulfamethoxazole (antibiotic)	2,4-Dichloro-phenoxy acetic acid (MCPA, herbicide)
Sulfophenylcarboxylate (metabolite of linear alkylsulfonates)	Simazine (herbicide)
Perfluorinated compounds (e.g. PFOS)	Terbutryn (herbicide, biocides)

Substances from urban settlements show different input dynamics compared to substances from agricultural use. The contamination of surface by wastewater from STPs is continuous whereas pesticides show a high time dynamic resulting from run-off events and seasonal applications (Leu et al., 2004).

Some of the compounds listed in Table 3 (e.g. Amidotrizoate, Carbamazepine, Sulfamethoxazole or Benzotriazol) can be also found in groundwater after aquifer passage (Blüm et al., 2005, Hanke et al., 2007, Ort et al., 2007, Sacher et al., 2001) as shown in Figure 4 for Switzerland. The X-ray contrast media Iopamidol was found in the highest concentrations up to 88 ng/L, while the X-ray contast media Amidotrizoate was found more often but in lower concentrations (max. 50 ng/L). Sulfamethoxazole was the most abundant antibiotic found in concentrations up to 30 ng/L. These contaminants can be used as tracer for municipal wastewater because of their exclusive use in urban settlements. They are more persistent than Caffeine, which has recently successfully applied as indicator (Buerge et al., 2006) but is highly degradable in STP. The identification of tracers is more difficult for agriculture because some pesticides have additional urban application or are disposed through the sewage network as mentioned above.

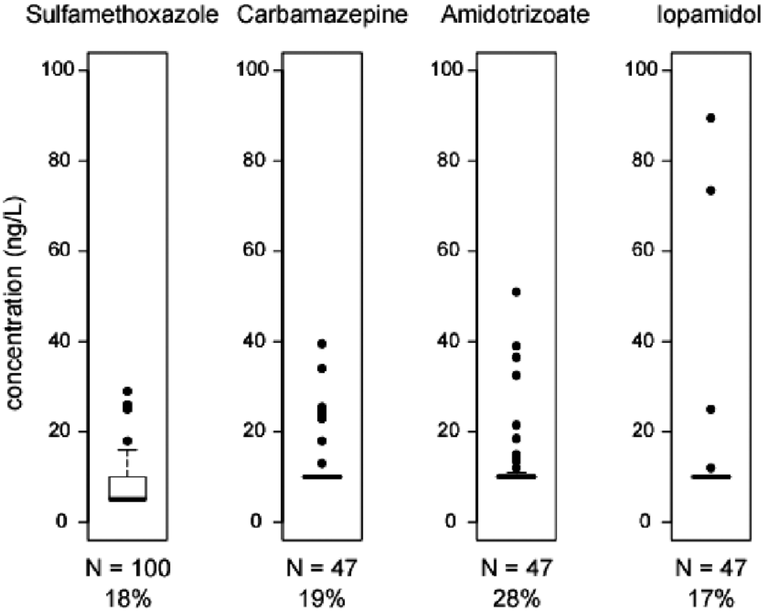


Figure 4. Concentrations of pharmaceuticals found in Swiss groundwater wells. N = number of investigated wells. x% = relative amount of findings above limit of quantification (LOQ). Values below LOQ were set equal to LOQ. (after Hanke et al., 2007), Copyright © 2007 SVGW Switzerland

Using these tracers the distance to a potential contamination source like polluted surface water or diffuse sources can be determined. This needs to be taken into account for the risk assessment of drinking water sources. To current knowledge the trace concentrations of pharmaceuticals in groundwater do not pose a risk for human health. However, following the precautionary principle, discussions are ongoing if drinking water quality limits should be introduced.

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PHARMACEUTICALS AND PERSONAL CARE PRODUCTS (PPCP) IN CANADIAN URBAN WATERS: A MANAGEMENT PERSPECTIVE

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Abstract. A management perspective on pharmaceuticals and personal care products (PPCPs) in Canadian urban waters is presented. The issues of PPCPs occurrence, effects, and means of control have been studied intensively during the past 10 years, but the information available is not yet sufficient to develop risk assessment/management strategies at this time. The management strategies receiving most attention include PPCP emission controls by pharmaceutical return programs, education of medical professionals to reduce prescription rates, incentives for green drug manufacturing, improving treatment technologies for drinking water and wastewaters, and introducing risk assessment regulations. Further research is needed on both effects and risk mitigation by the above listed measures.

Keywords: Human pharmaceuticals; personal care products; risk assessment; environmental effects; risk management; wastewater treatment; water treatment

1. Introduction

Pharmaceuticals and personal care products (PPCPs) have been detected in the environment since the early 1970s, but received full attention much later, only during the last ten years or so (Holtz 2006). This can be largely attributed to the continuing concerns about PPCP effects on human and ecosystem health, and to the advances in analytical instruments, particularly the liquid chromatographs combined with mass spectrometry, making it possible to identify polar organic

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pollutants, including pharmaceuticals, at low levels in various liquid media and solid matrices (Ternes and Joss 2006).

Much of the research completed addressed the sources of PPCPs and their pathways in the environment (Halling-Sorenson et al. 1998; Kolpin et al. 2002; Metcalfe et al. 2003a, 2003b), the means of controlling PPCPs in urban wastewaters by treatment (Boyd et al. 2003), and assessments of PPCP environmental effects (Crane et al. 2006; Daughton and Ternes 1999; Flaherty and Dodson 2005; Parrot 2006; Parrot and Blunt 2005; Servos et al. 2002a; Servos 2007). The research studies completed so far have produced most valuable information on PPCPs, but as yet do not allow a full risk assessment and formulation of risk management strategies (Daughton 2004b). The main purpose of the paper that follows is to overview PPCP issues in Canadian urban waters and examine progress in developing risk management strategies.

2. Sources and Pathways of PPCPs in Urban Waters

The pharmaceutical group meant for human consumption contains 2,000 to 3,000 substances, with many others used in the veterinary medicine, but not addressed here. Human pharmaceuticals can be further classified according to their purpose, with the highest usage groups including antiphlogistics, antibiotics, antidiabetics, antiepileptics, beta blockers, antihistamines, calcium antagonists, psychotropics, muscle relaxants, diuretics, decongestants, and antigout medications. The total annual consumption of pharmaceuticals by the urban population was estimated at about 100,000 t worldwide, which would indicate an average consumption per capita per year of about 15 g/ca/y (Kummerer, 2004b). However, in developed countries the consumption of active pharmaceutical ingredients is about an order of magnitude higher, with a large share contributed by non-prescription drugs, whose sales may exceed those of prescription drugs by an order of magnitude. Canadian data indicate annual sales of few selected analgesics as 800 t/y of paracetamol, 500 t/y of aspirin, and 200 t/y of ibuprofen, indicating per capita consumptions of 25, 16, and 6 g/ca/y respectively (Metcalfe et al. 2004). German data indicate the use of antibiotics of about 5 g/ca/y (Kummerer 2004a), with indications of growing use.

Ingested pharmaceuticals are excreted with urine and faeces, to a various extent, either as active substances or metabolites. Furthermore, as shown by Moffat et al. (2004) about 70% of excreted compounds are in urine and 30% in faeces. Besides human excretions, additional PPCP sources include disposed pharmaceuticals and related waste from the manufacturing process. Total loads from the aforementioned sources are discharged into municipal sewer systems; additional pharmaceutical may be released into the environment through septic tanks (Holtz 2006).

The other products of environmental interest are personal care products containing synthetic musks, which are frequently used as fragrance ingredients in cosmetics, perfumes, shampoos, detergents, fabric softeners, household cleaning products and others. The global annual use of synthetic musks was estimated by Heberer (2002a; 1996 data) around 8,000 t/y. These chemicals follow a similar pathway as pharmaceuticals (Yang and Metcalfe 2006); typically they enter domestic wastewater through grey water from baths and laundry, or dumping of unused materials, and are discharged into municipal sewers.

Following the discharge into municipal sewer systems, PPCPs follow various pathways, depending on the type of sewerage and its condition (Ternes and Joss 2006). In separate sewer systems, municipal sewage is conveyed by sanitary sewers to the wastewater treatment plant (WWTP), with a low risk of untreated sewage escaping into the environment due to sanitary sewer overflows (occurring in hydraulically overloaded sewers with large inflows of extraneous water in wet-weather), or due to WWTP bypasses caused by excessive hydraulic loads threatening the plant operation. Both conditions indicate operational problems that should be corrected. The situation is different in combined sewer systems, which are designed to intercept and convey to the WWTP some multiple of the dry weather flow, but discharge flows in excess of this setting into the nearby receiving waters as combined sewer overflows (CSOs)(Marsalek et al. 1993). Depending on local circumstances, CSOs may convey several percent of municipal sewage directly into the environment with low or no treatment.

Other possible pathways for PPCPs include sewage exfiltration from leaky overloaded sewers and from septic tank drainage beds; such discharges impact on groundwater aquifers.

At sewage treatment plants, incoming flows are subject to various levels of treatment, starting with primary treatment, followed in most cases by secondary treatment and in some cases by even more advanced levels of treatment. However, WWTPs are designed for certain flows reflecting more or less dry weather conditions, and when design flows are exceeded during wet weather, some fraction of the total flow bypasses the facilities providing higher levels of treatment. In the treatment process, PPCPs are subject to some attenuation by such processes as sorption onto sludge, stripping (from the water phase into the gas phase during aeration), and biological transformations. Other removal processes also apply in modern treatment plants processes, including ozonation (Hua et al. 2006) and membrane filtration.

Treated wastewater effluents are discharged into receiving waters and sludge residue (also referred to as biosolids – representing treated and stabilised sludge) needs to be further processed and disposed of. Treated effluents are generally discharged into surface waters, where they may cause environmental effects depending on the effluent characteristics (discharge, chemical and biological composition) as well as on the receiving water body characteristics (the type, magnitude, and hydraulic conditions including mixing). On-land sludge disposal may lead to sludge liquid seepage into the ground and entry into groundwater, particularly when transported by infiltrating rainwater. Consequently, sludge disposal on agricultural land is causing concerns about the associated effects and has been banned in a number of European countries (Ternes and Joss 2006).

Once released into the environment, PPCPs become a part of the urban water cycle and may get into sources of drinking water (Daughton 2004a; Heberer 2002b). Furthermore, PPCPs (and particularly highly bioactive pharmaceuticals) may affect target as well as non-target organisms, and this is the primary concern about PPCPs – their potential effects on wildlife (confirmed, for example, by the studies reviewed by Crane et al. 2006) and on humans (so far not proven; Schwab et al. 2005; Webb et al. 2003). The PPCPs effects are discussed in the following section.

3. PPCPs Effects on Wildlife and Human Health

A large number of studies addressing environmental risks from exposure to PPCPs have been published, particularly for pharmaceuticals (Servos et al. 2002a). Crane et al. (2006) suggested that the most likely exposure of aquatic wildlife is from WWTP discharges, and such an exposure would be continuous, at low concentrations, and best assessed by chronic toxicity testing. They reviewed a large number of studies indicating that the best evidence of effects was developed for natural and synthetic steroids, particularly the oral contraceptive 17α-ethinyloestradiol (Parrot and Blunt 2005; Servos 2007; Servos et al. 2005), followed by antimicrobial substances. The data for other pharmaceuticals is rather limited, with most testing done on micro-organisms, particularly in the case antibiotics, where the major concern is the development of antimicrobial resistance and its implications for public health as well as the aquatic ecosystem structure and functions (Holtz 2006; Ternes and Joss 2006).

Concerning the test organisms used, a great deal of information was produced for algae and Cyanobacteria were found particularly sensitive to antibiotics and thus recommended for future testing (Crane et al. 2006). Other tests were conducted with invertebrates and indicated that low concentrations of ethinyloestradiol (in the order of 1 ng l^{-1}) are environmentally relevant, but antimicrobials exerted relatively low effects. Sediments were found to serve as sinks for contaminants, including pharmaceuticals, and may provide a continuous chronic exposure of sediment-dwelling organisms, including invertebrates. There is hardly any evidence of direct adverse effects of antibiotics on vertebrates, but poorly soluble pharmaceuticals may bioaccumulate in their tissues and thereby expose higher organisms. Crane et al. (2006) concluded that there is enough data to indicate concerns about pharmaceuticals in the environment, but much work focusing on testing a representative range of aquatic organisms to a range of model substances remains to be done.

The data on environmental effects of personal care products are much less plentiful (Heberer 2002a). Several papers were published on synthetic musks, which were found to compromise a cellular defence mechanism that normally prevents toxins from entering cells (Luckenbach and Epel 2005). In general it is agreed that most synthetic musks have minimal direct effects on human and environmental health, but concerns are raised by their bioaccumulation and possible effects at those higher levels (Ternes and Joss 2006). In WWTPs, musks will generally adsorb to sludge (Lishman et al. 2007; Moffat et al. 2004).

Three major types of human exposure to PPCPs have been identified: (a) drinking water, (b) consumption of fish containing PPCPs and their derivatives, and (c) dermal contact during bathing/showering/swimming. In general, pharmaceuticals are well tested with respect to mammalian and human toxicity, but estimates of chemical intake levels from exposure to PPCPs in the environment are not adequately known to evaluate potential risks to humans. For pharmaceuticals, Schwab et al. (2005) and Webb et al. (2003) concluded that the potential human health risk from exposure to various drugs in the environment appears to be low. Furthermore, to date, the detected drug concentrations and the corresponding daily intakes through drinking water are much lower than therapeutic dosages. It has been argued, however, that potentially, there may be non-target, unintended effects at sub-therapeutic doses, unknown additive or synergistic effects due to exposure to chemical mixtures, and the effects caused by continual long-term exposure to low concentrations (Schwab et al. 2005; Ternes and Joss 2006; Webb et al. 2003). Finally, the potential presence of PPCPs in media such as drinking water may result in exposure to human population groups for which the pharmaceuticals are not intended or approved.

4. Current Canadian Research Directions on PPCPs in Urban Waters

The first paper on PPCPs in the Canadian environment was published more than 20 years ago (referenced in Metcalfe et al. 2003a), but only during the last 10 years, the volume of research increased significantly. A major milestone was the first (national) workshop on this topic held in 2002 (Servos et al. 2002b). The workshop provided a forum to review both Canadian and international research in this field and set priorities for future Canadian research. The workshop concluded that there were needs to clearly define the scope of the PPCP issue within the Canadian context, collect data on exposure and effects of PPCPs in the Canadian environment, collaborate with international colleagues, support the development of a Canadian regulatory framework, implement a national science program to address risk assessment and risk management of PPCPs in the Canadian environment, develop and implement best management practices and risk management options, and develop a national communication strategy (Servos et al. 2002b).

To implement a national science agenda, it was further recommended to create a broad multidisciplinary research initiative; establish priority concerns by reviewing sources, distribution, and use patterns of PPCPs; their likely environmental fate, potency mechanism of action, and assessment methods; implement a data collection program for assessing exposure to PPCPs in Canada (wastewater and drinking water, groundwater, surface water and agricultural soils); establish a network within the international community to share information and development of standardised tests; engage other levels (sectors) of government to address agricultural practices and urban water management across the nation; and, implement a risk communication strategy. Following the first workshop, many new studies were initiated and recently reviewed at the two following national workshops in 2004 and 2007. Highlights of the Canadian research on PPCPs follow and represent mostly information extracted from presentations at those workshops (Servos et al. 2002; Parrot 2006; Servos 2007).

Occurrence of PPCPs: a database on use and diversity of PPCPs in Canada has been established by Health Canada, indicating an expanding diversity of PPCPs, increased use and changing patterns due to aging population, increasing drug specificity, and ability to detect these substances due to improved analytical methodologies. Data were collected mostly on occurrence of PPCPs in surface waters and treated effluents. At the same time, an improved understanding of wastewater treatment options and their efficiencies was obtained, with liquid train removals of PPCPs ranging from low removals (~10%) by primary treatment, intermediate removals (~50%) by secondary treatment, and high removals (up to 99% for some substances) by advanced treatment. The majority of PPCP contaminants ends in sludge sent to digesters and best removals are achieved by extended residence times (>10 days). Specific studies of surface waters and wastewater treatment plants were conducted in several provinces, including BC, Alberta (Sosiak and Hebben 2005), Ontario (Metcalfe et al. 2003a; Metcalfe et al. 2003b; Ternes et al. 1999), Quebec and Atlantic provinces. Typical treatment technologies addressed included conventional activated sludge, extended aeration activated sludge, lagoons, oxidation ditches, ultrafiltration and nanofiltration membranes, ozonation, and various stages of aerobic digestion of municipal wastewater sludge (e.g., Lishman et al. 2007; Smyth et al. 2007; Citulski and Farahbakhsh 2007). Thus, a general assessment of principal sources of common PPCPs and approximate levels of removal by various treatment processes is available.

The second part of the PPCP issue, environmental effects, is even more challenging and is currently studied at a number of Canadian research laboratories. There is a community of researchers regularly sharing information and updating research priorities. At a workshop in March 2006, this community identified the following six priorities (Parrot 2006): (a) establishing an electronic forum for exchange of information (references), (b) sharing information on, or resources for, analytical methods (labelled standards, instrumentation, labour, reference standards), (c) developing chemical analyses for tissues/biota, (d) sharing information on endpoints – data gaps, biomarkers of effects, (e) Analytical method development for metabolites, and (f) conducting detailed integrated studies at selected Canadian sites (multitrophic).

With respect to environmental effects (Parrot 2006), much work focused on agriculture and veterinary pharmaceuticals. Antibiotic resistance of *Escherichia coli* is used in microbial source tracking, e.g., on swimming beaches. Effects of triclosan (an antibacterial, with annual usage of 250–500 in the US) were studied in biofilms, observing that it increased a relative proportion of bacteria in biofilms. Effects of WWTP effluents on bacterial production indicated large reduction in bacterial production immediately downstream of WWTP.

Other studies are underway concerning PPCPs in WWTPs, and WWTP effluent or PPCP effects on various organisms: clams and mussels from WWTP impacted sites were more susceptible to temperature increases; studies of pharmaceuticals metabolism in fish showed effects on gene expression in fish; effects of selected PPCPs on Hyalella azteca over multiple generations reduced young production by 30% over five generations; in studies of fish lifecycle exposure to PPCPs and WWTP effluents fathead minnows hatched and grew well in 10–100% effluents, but male minnows had decreased secondary sex characteristics and female minnows exhibited reduced egg production (Parrot et al. 2007); and, snapping turtle body weight was reduced by exposure to the WWTP effluent. Other studies will address wild fish, caged fish and birds.

Future challenges were identified by Parrot (2006) as: prioritisation of PPCPs – for analyses, monitoring, and effects (so far, only 135 PPCP methods have been developed vs. 3,000 pharmaceuticals in use), matrix problems (interference, determining free vs. bound PPCPs, concentrations in sludge, etc.), mixture effects (comparing effects of MWWEs vs. pure PPCPs), collaboration of chemists with biologists; limitations on available analytical methods (only for about 135 compounds); how to interpret monitoring data where effects data are missing; addressing compounds, which may exert effects on biota at concentrations below detection limits; seasonal variation in WWTP performance (winter vs. summer), or PPCP use (e.g., DEET, cold medications); and, monitoring prioritisation – where to monitor first, how often.

5. Management Considerations

Environmental issues undergo a life cycle, which starts with the first stage, observation, followed by investigation, analysis, advocacy and argument, decisions and actions, and finally, feedback and revision (Holtz 2006). In this context, the issue of PPCPs fits the second phase, investigation, though some decisions and actions have been already implemented, but more information is needed for proper assessment and development of risk management strategies.

A standard risk assessment approach to environmental contaminants usually combines four steps: hazard identification, dose response, exposure assessment and risk characterization. Such information then serves for developing risk management plans comprising systematic application of management policies, procedures and practices serving risk mitigation by emission and exposure control, and risk monitoring. Even though the PPCP issue is not mature enough to undertake this risk assessment/management approach, it is useful to use this framework for examining the ongoing activities in this field in Canada (Doerr-MacEwen and Haight 2006).

5.1. PPCP REGULATORY EMISSION CONTROLS

Government regulatory action was taken on a number of individual substances, particularly all new human and veterinary pharmaceutical products, which are regulated under the Canadian Food and Drugs Act (Health Canada 2002). Since Sept. 2001, PPCPs require an environmental risks assessment under the Canadian Environmental Protection Act (1999). In the absence of specific guidelines, the evaluation of human and veterinary products is based on the assessment of chemicals in these drugs. Even the earlier regulations addressed many toxic, persistent and biocumulative substances, which may mimic endocrine disrupters (EDSs). Much of the ongoing research focuses on risks associated with two classes of substances, antibiotics and endocrine disruptors (Holtz 2006). No references were found to bans of human pharmaceuticals, but more regulation is expected with respect to veterinary pharmaceuticals. For example, Canada has banned recombinant Bovine Growth Hormone (rBGH), as did European Union and some other countries (Holtz 2006).

5.2. VOLUNTARY PPCP EMISSION CONTROLS

Efforts are underway to reduce and better target the use of pharmaceuticals, and prevent the dumping of left-over supplies, mostly by education programs and residual drug collection program (Doerr-MacEwen and Haight 2006; Government of British Columbia 1997). More attention is paid to good stewardship in the pharmaceutical industry by ensuring that waste from the manufacturing process is duly pretreated before discharge into public sewers. Such efforts are strengthened by sewer use bylaws specifying which materials and substances may be discharged into public sewers.

Other source controls include promoting/marketing organically grown agricultural products, reducing the use of chemicals, and alternative and organic cleaners and personal care products, including soaps, shampoos and deodorants (Holtz 2006).

5.3. EXPOSURE CONTROL BY SEWAGE AND WATER TREATMENT

Recognising the pathways of PPCPs in the environment, one way of reducing their discharges into the environment and the associated effects is by improved treatment of sewage and sludge residue. So far, the research into these activities has been conducted in Canada without much coordination, which is to be expected during the investigation phase of the PPCP issue. Past experience indicates (e.g., removal of phosphorus from municipal effluents in the Great Lakes Basin in the late 1970s and early 1980s) that coordinated research of treatment technology is generally driven by regulations prescribing effluent limits for targeted contaminants.

In the early research in this field, observations of PPCPs focused on municipal WWTP influents/effluents and allowed to estimate PPCPs attenuations by various whole treatment processes (e.g., Boyd et al. 2003; Holtz 2006; Lishman et al. 2006; Melcalfe et al. 2003a; Servos et al. 2005; Sosiak and Hebben 2005). The reported findings in Canada were similar to those obtained elsewhere (Ternes and Joss 2006): practically no PPCP removal by primary treatment (~10%), 40–50% removals by secondary treatment, and high removals (≥90%) by advanced treatment, including ozonation (Hua et al. 2006), advanced oxidation processes (if there is no risk of formation of toxic byproducts) and membrane technologies (Terner and Joss 2006). In drinking water treatment, tight and loose nanofiltration (Makdissy et al. 2007) and activated carbon (Ternes and Joss 2006) are particularly promising processes. At this stage of research, all these processes appear feasible, but further testing is needed.

Recognising that most of the PPCP load is sequestered in sludge (Moffat et al. 2004), attention needs to be paid to sludge processing as well, particularly where it is disposed of on agricultural land. Studies indicate advantages of extended sludge digestion for PPCPs removals (Lishman et al. 2007; Smyth et al. 2007).

Controls of PPCPs in WWTP effluents reduce exposure of wildlife, and where the same water body may be used for water supply, also to humans. With respect to drinking water, the multi-barrier approach is practiced starting with source protection and continuing with treatment and protection of water quality in the distribution system. Conventional processes (often sand filtration, followed by disinfection) are not designed for PPCP removal, but their modifications are possible by inclusion of such processes as ozonation, activated carbon and nanofiltration, which were all found effective in removal of pharmaceuticals (Ternes and Joss 2006).

5.4. OVERVIEW OF MANAGEMENT ACTIONS ON PPCPS

A compilation of expert stakeholder views on the management of PPCPs has been published recently (Doerr-MacEwen and Haight 2006) and reflects to a fair extent the Canadian situation (half of the respondents were Canadian experts from academia, government and industry). The survey asked the participants to rank the seven selected groups of surface water and groundwater contaminants with respect to the need of management actions, which for PPCPs included eight management options: source/emission controls – educating medical professionals to reduce prescription rates, pharmaceutical return programs, and incentives for green drug manufacturing; exposure controls by wastewater treatment – advanced wastewater treatment, requesting all municipalities to employ secondary or higher treatment, separate treatment of hospital wastewater, and optimisation of wastewater treatment plants; and, finally, risk assessment reguations. The survey findings offer an intriguing perspective on the PPCPs issue. In terms of management action priorities, PPCPs were ranked the fourth and fifth by the European and North American participants, respectively. Both groups ranked more highly nutrients, pesticides and metals, and North Americans also pathogens. The two lower ranked contaminant groups included organic solvents and road salts.

With respect to management actions, the highest priority was assigned to advanced wastewater treatment (which besides PPCP control would produce other benefits as well), followed by five intermediately ranked measures (reduced prescriptions, pharmaceutical return programs, three wastewater treatment options – requesting secondary of better treatment, separate treatment for hospitals, optimisation of WWTPs), and the lowest priorities were assigned to green drug manufacturing and risk assessment regulation (Doerr-MacEwen and Haight 2006).

6. Concluding Observations

PPCPs remain in the forefront of Canadian environmental and human health concerns, particularly in urban areas. PPCPs represent a relatively young issue, still at the investigation stage of the overall life-cycle. Many related issues are currently studied, particularly with respect to sources, occurrence, and transport of PPCPs, their environmental effects, and the means of control at the sources and along their environmental pathways, particularly at wastewater and water treatment plants. Even though the available Canadian data are insufficient for risk assessment and management actions, such data were adequate for taking a number of steps towards managing PPCPs, and further information will be forthcoming from the ongoing Canadian research as well as through the international collaboration. The current trends indicate future actions in three major directions: emission/source controls and regulations, improvements in urban infrastructure to enhance collection and treatment of municipal wastewaters, and conducting education and communication programs informing the public about PPCPs challenges and the ongoing risk management activities.

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VIRUSES IN GROUND WATER

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Abstract. Waterborne disease outbreaks are often associated with non-porous media aquifers, such as fractured bedrock (metamorphic rock) or karst (limestone) aquifers e.g. South Bass Island Ohio USA (Fong et al., 2007). In these aquifers, ground water flow is fast and direct with little opportunity for inactivation or attachment to the aquifer matrix. In addition, coarse, glacial flood, gravel-cobble aquifers also appear to have fast and direct ground water flow. In the United States, public water supplies may be either ground water or ground water under the direct influence of surface water, as determined by the State. For ground water (only) wells, fifteen public water supply wells in the United State representing several aquifer types are found to be enteric virus positive using BGM cell culture methods. Eight of these wells are located in fractured bedrock, karst or gravel-cobble aquifers and were enteric virus positive using BGM cell culture methods.

Keywords: Enteric virus, enterovirus, reovirus, BGM cell culture, ground water, public water supply well, karst, fractured bedrock, gravel, cobble, Ground Water Rule, US EPA

1. Introduction and Background

Public health authorities, in both developed and undeveloped countries, rely on the use of sanitary setback distances between human (and animal) waste disposal sites and drinking water wells to protect human health. Unfortunately, most authorities do not vary setback distances based on hydrogeologic setting despite the knowledge that fecal contamination can have very differing subsurface

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mobility depending on aquifer type (Taylor et al., 2004). The purpose of this paper is to describe some of the data that documents the variable hazard from viruses (and bacteria) pathogenic to humans as a function of aquifer type.

Viruses (as used herein) include all enteric viruses pathogenic to humans as long as they are shed via the gut. This includes enteric viruses such as most adenoviruses serotypes that may primarily infect organs other than the gut but are shed via the gut. Viruses that infect only bacteria are identified specifically as bacteriophage or coliphage. Enteric virus contamination is recognized only through cell culture methods that identify infectious virions. Analyses using molecular methods are not considered herein because these methods are incapable of discriminating infectious from non-infectious agents.

Public water supplies may transmit fecal contamination if they are subject to one or more of the following risk factors: 1) sensitive aquifers; 2) aquifers in which viruses may travel faster and further than bacteria (e.g. alluvial or coastal plain sand aquifers; 3) shallow unconfined aquifers; 4) aquifers with thin or absent soil cover; 5) wells previously identified as having been fecally contaminated; and 6) high population density combined with on-site wastewater treatment systems, particularly those in aquifers with restricted geographic extent, such as barrier island sand aquifers. Other risk factors also may allow or facilitate fecal contamination transmission to PWS wells.

This paper emphasizes identifying important risk factors at PWS wells where 4-log virus inactivation requirement, as required by the Ground Water Rule (GWR) (USEPA, 2006) is not achieved. However, the risk factors apply to all wells because any PWS well may cause waterborne disease when there is any interruption in treatment. However, because waterborne disease outbreaks are not random, but rather are associated with (some) sensitive aquifers (e.g. the recent large Walkerton, Ontario and South Bass Island, Ohio outbreaks both occurred in the Upper Silurian Bass Island Formation), identifying sensitive aquifers is very important.

1.1. AQUIFER SENSITIVITY

The GWR (USEPA, 2006) recommends that aquifer type, which is usually well-correlated with lithology, be established in order to determine if a specific aquifer is sensitive. The GWR suggests that all limestone aquifers, igneous and metamorphic aquifers, and gravel aquifers be regarded as sensitive. This is because limestone is the lithology most likely to be karst; igneous and metamorphic aquifers are likely to be highly fractured; and gravel aquifers are likely to have direct flow paths and rapid ground water velocities due to the shape and large size of their pores. Pumping wells increase the natural flow velocities in sensitive aquifers to a greater degree than they would in a fine-grained, unconsolidated aquifer, for example. States may designate additional sensitive aquifer types if they feel it is necessary to do so to protect public health (e.g. a state may designate sand and gravel aquifers as sensitive).

1.1.1. Karst Aquifer

Karst is defined as a type of geologic terrane within which flowing ground water has dissolved significant portions of the area=s soluble (usually carbonate) rocks (Fetter 2001). Where karst regions occur, infiltrating precipitation and ground water create a permeability structure characterized by numerous and often large, interconnected conduits. Through time, these conduits continue to enlarge, creating unique surface and subsurface drainage networks and characteristic surface landforms. Ground water velocities are usually rapid, and flow paths very direct in karst environments, especially in the vicinity of pumping wells. Microbial pathogens released into karst aquifers from sources such as septic systems or livestock operations are likely to reach drinking water consumers in an infective state. For example, the Walkerton, Ontario *E. coli* outbreak in May, 2000 is believed to have been caused by fecal pollution of a karst aquifer system (Worthington et al., 2002). Table 1 summarizes information about well-known waterborne disease outbreaks that have been reported in karst geologic settings in North America (USEPA, 2002c).

Waterborne disease outbreaks are not randomly distributed. Rather they are more likely to occur in some aquifers, especially karst limestone aquifers. The two outbreaks in New Braun, TX, the outbreak in Georgetown, TX and the outbreak in Brushy Creek, TX all resulted from contaminated wells located in the Edwards Aquifer, a sensitive karst limestone aquifer. Similarly, the outbreaks in South Bass Island, OH, Walkerton, Ontario and Drummond Island, MI all resulted from contaminated wells located in the Upper Silurian Bass Island Formation, a sensitive karst limestone aquifer.

The outbreak in Cabool, Missouri is commonly attributed to replacement of water meters without disinfection follow-up and by broken water mains (e.g. Gelderich et al., 1992). However the outbreak data show that several bloody diarrhea cases preceeded the water main breaks. It is most likely that outbreak was due to intermittent *E. coli* O157:H7 contamination of karst limestone ground water, similar to events in Walkerton Ontario a decade later.

Karst regions are typically characterized by the following: underground drainage networks with solution openings that range in size from enlarged fractures to large caves; closed surface depressions, known as sinkholes, where the dissolution of the underlying bedrock has caused the collapse of overlying rock and sediment; and discontinuous surface water drainage networks that are

TABLE 1. Waterborne Disease Outbreaks Reported in Karst Hydrogeologic Settings in North America

Location	Reference	Number Illnesses/Agent
Richmond Heights, FL, USA	Weissman et al., 1976	1,200 cases/*Shigella*
Cabool, MO, USA	Swerdlow et al., 1992; Gelderich et al., 1992	243 cases/*E. coli* O157:H7; 4 deaths
Georgetown, TX, USA	Hejkal et al., 1982	8,000 cases/Coxsackievirus; 36 cases/Hepatitis A Virus (HAV)
Braun Station, TX, USA (two separate outbreaks)	D=Antonio et al., 1985	251 cases/Norwalk virus; 2000 cases/*Cryptosporidium*
Henderson County, IL, USA	Parsonnet et al., 1989	72 cases/unknown
Lancaster, PA, USA	Bowen and McCarthy 1983	49 cases/HAV
Racine, MO, USA	MO Department of Health, unpublished report 1992	28 cases/HAV
Walkerton, Ontario, Canada	Golder Associates 2000; Health Canada 2000	1,346 cases/*E. coli* O157:H7 (+ *Campylobacter*); 6 deaths
Reading, PA, USA	Moore et al., 1993	551 cases/*Cryptosporidium* (not recognized as GWUDI until after the outbreak)
Brushy Creek, TX, USA	Bergmire-Sweat et al., 1999; Lee et al., 2001	1,300 – 1,500 cases/*Cryptosporidium* (not recognized as GWUDI until after the outbreak)
South Bass Island, OH, USA	Ohio EPA, 2005; CDC, 2005; O'Reilly et al., 2007; Fong et al., 2007	1,450 cases of Norovirus, *Campylobacter*, *Salmonella*
Drummond Island, MI, USA	Ground Water Education in Michigan, 1992; Chippewa County Health Department, unpublished report, 1992	39 cases/unknown
Buttermilk Falls spring, Meade County, KY, USA	Bergeisen et al., 1985	73 cases/HAV

related to the unique subsurface hydrology (Winter et al., 1998). In other mature karst landscapes, characterized by relatively pure limestone in areas of high precipitation, caves and caverns are formed in the subsurface. Conduits in carbonates and gypsum can be quite large with some exceeding 100 feet in diameter (i.e., caves) and several miles in length. Mammoth Cave, Kentucky has a mapped length of more than 340 miles of interconnected conduits distributed over five horizontal levels. Ground water velocities have been measured there at more than 1,000 feet per hour (USEPA, 1997).

Indeed, it is the rapid ground water velocities in karst aquifers that necessitate their characterization as sensitive aquifers. In the karst region of Slovenia, an indicator of fecal contamination injected into a karst aquifer reportedly traveled approximately 24 miles in less than 4 months (Bricelj, 1999). Using conservative ground water tracers, ground water velocities measured in karst aquifers are as high as approximately 0.3 miles per hour (USEPA, 1997). In Florida, ground water velocities surrounding a well have been measured at several hundred feet per hour (USEPA, 1997). In a confined karst aquifer in Germany which was breached by monitoring wells, ground water traveled approximately 650 feet in less than 4 days (Orth et al., 1997). In the Edwards Aquifer, Texas, Slade et al. (1986) reported that dye traveled 200 feet in 10 minutes. This data all indicates that ground water flows extremely rapidly through karst aquifers. Worthington et al. (2002) compares tracer test ground water travel times with predicted capture zone model travel times using the porous media assumption for ground water flow to the PWS wells at Walkerton, Ontario. The measured travel time is substantially faster than the predicted travel time.

Well-developed karst systems may have underground streams because of the large size of interconnected openings in the rock. Underground streams can have flow rates as great as those of surface streams. It is also not unusual in karst terrains for surface streams of considerable size to disappear into solution cavities (swallow holes) intersecting a streambed, creating a discontinuous surface drainage system. These same streams may reappear at the surface at other locations (Winter et al., 1998). Seeps and springs are thus common in karst regions.

Sinkholes in karst regions can play a particularly devastating role in the potential for microbial contamination of ground water supplies. For example, sewage treatment lagoons have been known to leak and eventually collapse over sinkholes. This phenomenon has been documented in West Plain, Missouri in 1978 (Craun, 1984); in Lewiston, Minnesota in 1991; and in Altura, Minnesota in 1974 and 1976 (Jannik et al., 1991). In Missouri, 759 illnesses resulted from the contamination of domestic wells due to this 1978 sinkhole collapse (Craun, 1984).

Even in the absence of sinkhole collapse, the potential for rapid infiltration of fecal contamination through overlying soils into karst aquifers is great. Residual soils, formed by bedrock dissolution, are characteristic of well-developed karst regions. These soils are typically clay-rich, but can have great variation in thickness and hydraulic conductivity. Soil macropores transmit water rapidly, and are caused by channels formed by decayed roots, insect and animal burrows, dessication cracks, soil failure surfaces, and soil piping (EPA, 1997). Rapid flow in the overlying soil may also occur via vertical fissures, even when there is substantial residual soil cover (Smart and Frederich 1986, cited in EPA 1997). Where a thin mantle of glacial till or outwash deposits are present, infiltration velocities may also be high (Crowther 1989, cited in EPA 1997).

The actual transport of fecal bacteria within karst aquifers has been studied at a variety of localities (Malard et al., 1994; Orth et al., 1997; Tranter et al., 1997; Gunn et al., 1997). Malard et al. (1994) suggested that both fractures (discussed in section 2.1.2) and karstification contribute to rapid bacterial transport in limestone. For this reason, Malard et al. (1994) consider the risk of bacterial contamination greater in limestone than in any other type of aquifer.

It is important to note that concentrations of bacteria within karst environments often vary significantly with rainfall. Personne et al. (1998) found that high aquifer water levels, induced by high rainfall, correlated with high bacteria levels in the aquifer. The water level in one Edwards Aquifer well (582 feet deep with a water table 240 feet deep) began rising within 1 hour after a rainfall event (Slade et al., 1986). Mahler et al. (2000) studied fecal coliform and enterococci bacteria near a wastewater irrigation site, and found the presence of bacteria in ground water directly followed rainfall events. Mahler=s data suggests that small sampling intervals of 3 to 4 hours are necessary to describe the breakthrough of bacteria at a monitoring well screened in a karst aquifer.

The potential for rapid transport of bacteria and viruses through karst aquifers necessitates that they be monitored carefully for contamination. Bacteria can rapidly percolate into the unsaturated zone of karst aquifers, as well as be further transported to the saturated zone during periods of intensive rainfall. In fact, Malard et al. (1994) found high occurrence rates for bacteria in a karst aquifer as long as a year after surface pollution had essentially ceased. This data demonstrates that sensitive aquifers can be contaminated even when surface pollution sources are difficult to identify. Furthermore, research shows that surface water and ground water drainage divides generally do not coincide in karst regions due to complex patterns of surface water and ground water flow. For example, a stream may disappear in one surface water basin and reappear in another basin. This situation makes it even more difficult to successfully inventory sources of fecal contamination in the recharge area of a karst well (Winter et al., 1998). Such situations are part of the motivation behind the focus on monitoring sensitive aquifers, rather than merely looking for potential sources of bacterial contamination. In summary, bacterial contamination of karst aquifers is both fairly likely and highly unpredictable, although correlations with rainfall events are common.

1.1.2. Fractured Bedrock Aquifers

Any solid block of igneous or metamorphic rock that is surrounded by fractures is considered essentially impermeable. Thus, all flow is forced to take place within the fractures. A detailed understanding of flow in a fractured bedrock aquifer requires knowledge of fracture widths, orientations, the degree to which individual fractures are mineral-filled, and the degree of fracture interconnection and spacing (Freeze and Cherry, 1979). Most fracture widths are smaller than one millimeter (mm), and a fracture=s capability to transmit ground water (i.e., hydraulic conductivity) is roughly proportional to the cube of the fracture width (National Research Council, 1990). Thus, small changes in fracture width result in very large changes in hydraulic conductivity. For example, a 1 mm fracture can transmit 1000 times more water than a 0.1 mm fracture, provided that other factors are constant (e.g. hydraulic gradient).

Freeze and Cherry (1979) report void space as high as 10 percent of total volume in igneous and metamorphic rock. Other data presented in Freeze and Cherry (1979) suggest that the first 200 feet beneath the ground surface produces the highest water yields to wells because fractures at shallow depths are wider, more numerous, and more interconnected. Nevertheless, municipalities sometimes derive high volumes of water from wells located in fault zones that extend to greater depths.

Tracer tests have been used in several studies to estimate ground water flow rates in fractured bedrock. Malard et al. (1994) report that dye traveled approximately 140 feet in a fractured bedrock aquifer in 2 hours. Becker et al. (1998) reports that water traveled approximately 118 feet in about 30 minutes. Ground water velocities in fractured bedrock aquifers are comparable to velocities in karst aquifers. Thus, fractured bedrock aquifers are vulnerable to contamination by waterborne pathogens. Table 2 (from USEPA, 2002c), summarizes some of the most recent cases of waterborne disease outbreaks due to contamination of wells screened in fractured bedrock aquifers in North America.

TABLE 2. Waterborne Disease Outbreaks Reported inFractured Bedrock Aquifers in North America

Location	Reference	Number Illnesses/ Agent
Couer d=Alene, ID, USA	Rice et al., 1999	117/*Arcobacter butzleri*
Island Park, ID, USA	CDC, 1996	82 cases/*Shigella*
Big Horn Lodge, WY, USA	Anderson et al., 2003	35/Norovirus
Northern AZ, USA	Lawson et al., 1991	900 cases/Norovirus
Atlantic City, WY, USA	Parsionikar et al., 2003	84/Norovirus

1.1.3. Gravel Aquifers

Gravel aquifers, as defined here, are unconsolidated water-bearing deposits of well-sorted pebbles, cobbles, and boulders. Gravel aquifers consist primarily of coarse grains larger than approximately 4 mm or approximately 0.16 inches in diameter, although they may have minor amounts of smaller diameter material as well. Gravel aquifers are often limited in area and are generally produced by high energy events such as catastrophic glacial outburst floods or flash-floods at the periphery of mountainous terrain. They can also sometimes be found at fault-basin boundaries or in glacio-fluvial deposits such as crevasse fillings, eskers, kame terraces, and outwash/valley trains. Typically, these are small, relatively localized aquifers.

2. Virus Occurrence in Public Water Supply Wells

Outbreaks occur as a result of a treatment failure, inadequate treatment or as the result of source water fecal contamination in untreated wells. This paper focuses on virus occurrence and outbreaks in untreated PWS wells in the United States. However, it is often difficult for researchers to obtain consent to sample untreated wells for viruses. Thus, most virus occurrence data reported here were obtained from samples collected prior to treatment in treated wells. If well treatment data are available, untreated wells with virus occurrence are noted.

In the US, PWS wells are classified as either ground water or ground water under the direct influence (GWUDI) of surface water because the ground water is closely connected to surface water. Surface water systems are at risk due to occurrence of *Cryptosporidium* (and *Giardia*) an organism highly resistant to inactivation by chlorination. Thus, in the US, GWUDI wells are often required to have conventional filtration or UV inactivation to protect against *Cryptosporidium* (or are able to demonstrate 2-log Cryptosporidium removal by bank filtration).

Ground water PWS wells are regulated by the Total Coliform Rule (TCR) and the Ground Water Rule. GWUDI wells are regulated by the TCR and the surface water treatment rules (e.g. Long-Term 2 Surface Water Treatment Rule [LT2SWTR]). This paper focuses only on virus occurrence and outbreaks in PWS wells regulated by the TCR and GWR. It is sometimes the case that PWS are retrospectively recognized as GWUDI wells, often after recognition of a cryptosporidiosis or giardiasis outbreak associated with well water (e.g. South Bass Island, OH; Brushy Creek, TX). In these retrospective misclassification examples, any virus occurrence or viral illness data are herein considered to be ground water rather than GWUDI PWS systems because the PWS wells were operating as ground water systems at the time of the outbreak.

Virus occurrence data are limited. High quality virus-positive samples using cell culture methods are available, in the absence of an outbreak, from only 15 PWS wells (Pedley et al., 2006). With such a small sample, it is difficult to confirm suspected risk factors based on infectious enteric virus occurrence. Thus, the conclusions herein are provisional, subject to additional data collection.

Cell culture methods, although capable of identifying infectious viruses, have very limited capability to discriminate among the fecal viruses. All cell cultures reported herein used Buffalo (African) Green Monkey (BGM) kidney cells as the host monolayer. Continuous lines of BGM cells are optimized to recover poliovirus but also favor recovery of many (but not all) of the enteroviruses. For example, some coxsackie A viruses are not recoverable using BGM cells. Also, BGM cells favor recovery of reoviruses. Although most reoviruses have not been shown to cause illness in humans, at least one reovirus serotype (Type 3) is a known human pathogen (Tyler et al., 2004).

In the US (USEPA, 2006), about 114 million people receive ground water from PWS wells. The total number of wells is unknown but the wells are operated by 147,000 PWS systems, each regulated by the TCR and GWR. Most of the population receives treated water but 20 million (18%) consume untreated ground water (USEPA, 2006).

For the population consuming untreated ground water, few data are available to evaluate risk factors associated with their PWS wells. In an unpublished analysis based on available PWS well latitude and longitude data (of unknown quality) and a digital karst limestone map of the United States (Tobin and Weary, 2006), Anzollin (unpublished personal communication, 2006) estimates that about 45,000 PWS wells (29,000 systems) in the US are located in karst limestone terrane and these wells serve a population of about 48 million people.

It is reasonable to assume that eighteen percent of that population (about 8 million people) receive untreated ground water from PWS wells in karst limestone terrane. At present, similar data and analyses are not available for PWS wells fractured bedrock aquifers.

2.1. VIRUSES IN KARST LIMESTONE PWS WELLS

As listed in Table 1, numerous outbreaks have resulted due to fecal (both viral and bacterial) contamination of PWS wells in karst limestone aquifers. Some wells were completely untreated, others were inadequately treated. Because viral outbreaks have occurred in untreated ground water systems in the United States, it is expected that enteric viruses would be identified in raw source ground water from PWS wells, in the absence of an outbreak. Examples of viral outbreaks in untreated ground water supply wells include outbreaks in Ohio, Missouri, and Illinois.

In the South Bass Island, Ohio PWS outbreak, the karst limestone aquifer was contaminated by norovirus via septic tanks and land disposal of septage. Untreated PWS wells (prior to the outbreak) were determined to be positive for fecal bacteria, coliphage and adenovirus (by PCR) (Fong et al., 2007). Other untreated groundwater PWS wells in karst limestone where outbreaks occurred include Racine, Missouri (Missouri Dept. of Health, 1992), Henderson County, Illinois (Parsonnet et al., 1989), Drummond Island, Chippewa County, Michigan (Chippewa County Health Department, Unpublished Report, 1991, GEM, 1992). One large norovirus outbreak in Switzerland (La Newuveville, Bern Canton) also occurred in an untreated karst limestone ground water system (Hafliger et al., 2000, Maurer and Sturchler, 2000; Hrudey and Hrudey, 2004).

Infectious enteric viruses have been identified in four karst limestone PWS wells in the United States. Available data indicate that all four wells were treated before distribution and no health effects are known. At S_'s Market well, in Juniata County, Pennsylvania, Lindsey et al. (2002) identified enteric virus contamination with a measured concentration of 52 PFU/100 liters. These viruses were subsequently shown to be reovirus (Pedley et al., 2006). In a Centre County Pennsylvania fraternal organization building well, Lindsey et al. (2002) identified enteric virus concentration of 18 PFU/100 liters. As described in Pedley et al. (2006), these viruses were identified using serotyping to be echovirus Type 13 and Type 20 and poliovirus Type 3. Because poliovirus Type 3 was used as a laboratory control, it is likely that the poliovirus occurrence was an artifact. In Ash Grove Well #3, Greene County, Missouri, Davis and Witt (2000) report the presence of a non-polio enterovirus with a concentration of 2.1 MPN/100 liters. Poliovirus overgrowth occurred in this sample so additional analysis was undertaken to ensure the presence of non-polio enteroviruses (Jim Vaughan, personal communication to Philip Berger). In Tennesseee well W-1, Johnson (2005) identified (presumed) enterovirus at a concentration of 7 MPN/100 liters.

2.1.1. Indicators of Viruses in Karst Limestone PWS wells

It is well established (e.g. Lieberman et al., 2003) that no single bacterium or bacteriophage indicates (with high likelihood) enteric virus occurrence, although many of these organisms are indicators of fecal contamination. For virus occurrence in karst limestone wells, two of the four wells (Ash Grove #3 and W-1) were enteric virus positive but negative for any bacterial or coliphage indicator organism. However, it is impossible to determine whether additional sampling at these two wells might, in the future, identify coliform bacteria or another indicator when viruses and their indicators are both intermittently present. In contrast, the other two wells (S_'s Market and the fraternal organization) were both positive for a suite of indicators, including *E. coli*, *Clostridium perfringens* spores, enterococci, somatic and male-specific coliphage. Given the small number of karst limestone wells with enteric virus occurrence, it is impossible to make conclusions about the likelihood of enteric virus and fecal indicator co-occurrence and the optimum indicator organism.

Ground water turbidity is sometimes proposed as an indicator for pathogen occurrence or removal efficiency. Unlike surface water, interpreting turbidity measurements in ground water supplies is problematic because pumping wells can create turbidity as a result of on/off pump cycling. Most importantly, pathogen occurrence data collected during and after the South Bass Island, OH outbreak (Fong et al., 2007) shows no relationship between occurrence and turbidity. The wells sampled are located in the karst limestone Bass Island Formation. At the time of the outbreak, the wells were regulated as ground water rather than as surface water (GWUDI). The airport well was positive for TC, *E. coli*, enterococci, coliphage, *Arcobacter*, and human adenovirus (by PCR). Field turbidity at the time of sampling was 4.14 NTU. In contrast, the Skyway Lounge well was positive for the same organisms but the field turbidity was 0.25 NTU.

2.2. VIRUSES IN FRACTURED BEDROCK PWS WELLS

Outbreaks associated with PWS wells in fractured bedrock aquifers are listed in Table 2. Of these outbreaks, only the outbreak at Big Horn Lodge, WY (Anderson et al., 2003) occurred due to virus occurrence in an untreated PWS well. Viruses have been found in three PWS wells drilled into fractured bedrock aquifers. Of these three wells, at least one (in North Carolina) and possibly two wells were untreated. However, no health effects were observed as the result of virus contamination at an untreated well.

At a PWS well in a Chester County, Pennsylvania campground, Lindsey et al. (2002) identified enteric virus with a concentration of 0.21 PFU/100 L. These viruses were subsequently shown to be coxsackievirus type B5 (Pedley et al., 2006). At a subdivision PWS well in Speedwell, North Carolina, echovirus type 11 was recovered at a concentration of 212 MPN/100 L (Lieberman et al., 2002; Dahling, 2002). At a trailer park in Mountain Home, Idaho, coxsackievirus type B4 was recovered at a concentration of 9.5 MPN/100 L (Lieberman et al., 2002; Dahling, 2002). Poliovirus type 1 was used as the laboratory control by Dahling (2002).

2.2.1. Viruses at the PWS Well in Speedwell, North Carolina

The PWS well in Speedwell, North Carolina is located at the foot of a steep incline. About six residences, each with individual septic tanks, are located uphill from the PWS well. The well was untreated at the time of sampling but had a history of total and fecal coliform occurrence. The well was protected by a concrete pad poured around the surface casing but the well was located in a small topographic depression.

The PWS well was constructed in 1987, drilled to 550 feet total depth, with surface casing installed to 57 feet depth. The uppermost 20 feet was grouted with concrete. The well has a measured yield of 15 gallons per minute.The PWS well is constructed in Precambrian gneiss, metagreywacke, schist and amphibolite. The soils (Figure 1) are mapped as the Cowee and Evard soils which are clay loam, loam and sandy loam with 5–30% clay and thick saprolite formation. Measured soil permeability is reported to be 0.6 to 2.0 inches per hour (Goldston et al., 1948).

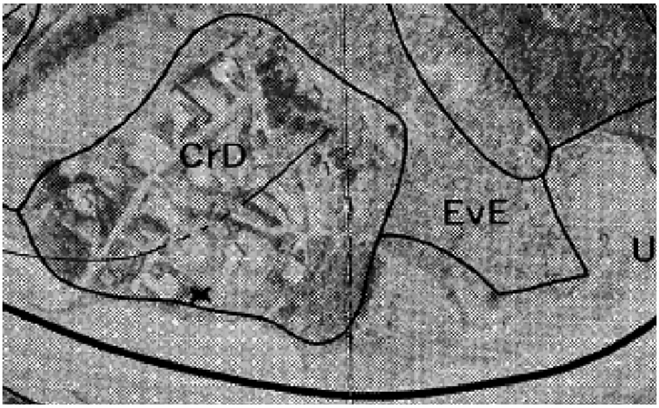

Figure 1. Aerial photograph showing soil mapping units for the subdivision at Speedwell, North Carolina (Goldston et al., 1948)

The PWS well was sampled monthly between March, 1993 and February, 1994. Only one sample, collected on June 22, 1993 was virus positive (at a concentration of 212 MPN/100 L). Weekly rainfall amounts for June, 1993 were measured at Cullowhee, North Carolina, about 3 miles from the well location. Precipitation was 1.08 inches for June 1–7, 2.06 inches for June 8–14, 1.08 inches for June 15–21, and 1.18 inches for June 21–28. Average precipitation in Cullowohee in June is 4.5 inches so the precipitation was slightly higher than normal.

Of the twelve monthly samples, 2 samples were positive for Total Coliform but negative for *E. coli*. One sample was positive for enterococci and one sample was positive for male-specific coliphage. All monthly samples were negative for *Clostridium perfringens* spores, somatic coliphage and *Bacteroides* bacteriophage. Most importantly, the June 23, 2003 sample was positive for echovirus type 11 and negative for all fecal or other indicators. No health effects were identified due to echovirus type 11 occurrence at high concentration.

2.3. VIRUSES IN COARSE GRAVEL GLACIO-FLUVATILE PWS WELLS

Only one or possibly two PWS wells have even been sampled for viruses in coarse gravel glacio-fluvatile deposits. One site was negative for enteric virus (DeBorde and Ward, 1995). The other site, in Milton-Freewater, Oregon (Figure 2) was sampled monthly for a year between December, 1992 and November, 1993.

Four samples (February 9, March 9, May 11, and August 10) were enteric virus positive with concentrations ranging between 10 and 20 MPN/100L (20, 15, 11 and 10 respectively) (Lieberman et al., 2002; Dahling, 2002). In the February sample the viruses were unidentified. The March sample recovered reovirus, the May sample recovered coxsackievirus type A7, coxsackievirus type B1, echovirus type 15 and echovirus type 24. The August sample recovered coxsackeivirus type B1 and echovirus type 15 (Dahling, 2002).

The Milton-Freewater PWS well was constructed in 1962 to serve a motel located in the alluvial valley adjacent to the Walla Walla river. The well is 96 feet deep with (probably) a bentonite slurry grout seal. This well and others in the valley have a history of Total and Fecal Coliform occurrence. Geologic investigations by the Oregon Department of Health (D. Nelson, personal communication to Philip Berger) suggest that the valley has coarse gravel at least to 165 feet depth, is located in a region where river water naturally discharges to ground water but may have discontinuous, partial confining layers.

In addition to the enteric virus occurrence data, the Milton-Freewater PWS well had multiple occurrences of fecal indicators (Lieberman et al., 2002;

Figure 2. Coarse glacio-fluvatile gravel deposits in Umatilla, County, Oregon (Johnson and Makinson, 1988)

Dahling, 2002). All twelve monthly samples were Total coliform positive and half were *E. coli* positive. Five samples were positive for enterococci and nine samples were somatic coliphage positive. Three samples were positive for male-specific coliphage and one sample each was positive for Clostridium *perfringens* spores or *Bacteroides* bacteriophage.

In keeping with the gross fecal contamination at the Milton-Freewater PWS well, enteric virus positive samples were also positive for fecal indicator or total coliform organisms (Lieberman et al., 2002; Dahling, 2002). The February positive sample was also positive for Total Coliform. The March positive sample was also positive for Total coliform, somatic and male-specific coliphage. The May positive sample was also positive for *E. coli,* enterococci, and somatic coliphage. The August positive sample was also positive for *E. coli*, enterococci, somatic coliphage and *Clostridium perfringens* spores. Oregon.

2.4. VIRUSES IN (OTHER) POROUS MEDIA PWS WELLS

Enteric virus has been recovered from two PWS wells in glacial outwash deposits (interbedded sand, gravel and clay) in Southern Michigan (Francy et al.,

2004) and one PWS well in unconsolidated deposits in Bradford County, Pennsylvania (Lindsey et al., 2002). The viruses recovered in Michigan were not serotyped. The Bradford County Pennsylvania well viruses were identified as reovirus. Enteric viruses were also recovered in two of eight samples from a PWS well in a sand and gravel aquifer in Wisconsin (Wisconsin Department of Health, unpublished data, 2000). Banks et al. (2001) report enteric virus in a PWS well in a coastal plain aquifer in Wicomico County, Maryland that was subsequently determined to be rotavirus.

2.5. VIRUSES IN KARST WELLS DESIGNATED (BY THE STATE) TO BE GROUND WATER UNDER THE DIRECT INFLUENCE OF SURFACE WATER

Three Alabama karst wells sampled monthly for one year (Lieberman et al., 2002; Dahling, 2002) are regulated by the State as if they are surface, rather than ground water. These wells are regulated by the Long Term 2 Surface Water Treatment Rule rather than by the Ground Water Rule. As ground water under the direct influence of surface water, they may be required to have coagulation and filtration in addition to disinfection. Because of the close connection between surface water and ground water in these wells, it is not surprising that multiple samples were enteric virus positive. For one well, seven of twelve samples were virus positive. The other two wells each were enteric virus positive in four of twelve samples. As discussed above, a greater hazard results when karst wells are miss-classified as ground water rather than as ground water under the direct influence of surface water because ground water receives less treatment than surface water. Ground water supplies, even in karst limestone, are not required to disinfect unless fecal contamination is identified. Although rare (perhaps not more than 10% of wells or samples), it is possible that enteric viruses can be present in the absence of fecal indicator organisms.

In the absence of treatment, public health protection relies upon pathogen natural attenuation processes such as straining, wedging (microstraining), attachment or inactivation. The efficiency of natural attenuation processes is summarized in Schijven et al. (2002) and Berger (2003).

3. Conclusions

Waterborne disease outbreaks in untreated (and inadequately treated) PWS wells tapping karst limestone and fractured bedrock continue to be recognized. Also, enteric viruses have been recovered from treated (but also untreated) PWS wells from these same aquifers. Because ground water flow is fast and direct with little opportunity for pathogen attenuation in karst limestone and fractured bedrock aquifers, PWS and residential wells in these aquifers should be surveilled with extra vigilance. Treatment and supplemental monitoring should be carefully considered as part of a multibarrier approach to protecting public health.

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ECOHYDROLOGY OF DOJRAN LAKE

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Abstract. In the Republic of Macedonia there are three natural lakes: Ohrid, Prespa and Dojran. Dojran Lake is the smallest one but not less significant as a water resource, natural wealth and scenic beauty. The last 15 years this place of natural heritage is threatened because the lake's water level decreased seriously. The lake watershed and the lake itself are shared by Macedonia and Greece. Since 1988 the lake surface area dropped from 42 km^2 to 31 km^2. This water declination together with the simultaneous deterioration of the water quality resulted with serious ecological impacts. How much the present state of this natural lake is under the impact of hydrology and climate, and how much this is due to some other, not clearly identified causes, should be main goals in future water management in both countries that share the lake and the watershed. A complete environmental assessment can not be made without serious analyzes of the basic hydrological, meteorological and water management data. The intention of the authors is to emphasize the vulnerability of the lake and its biodiversity and to initiate urgent and strong support of the international community in cooperation in water quantity and water quality management between both countries that share the lake and its watershed.

Keywords: hydrology, biodiversity, precipitation, evaporation, water level, water management, restoration

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1. Introduction

Most of the civilizations have been created near water and developed upon its variation in space and time. Many civilizations and rare spaces of flora and fauna have disappeared because of water catastrophes. Such catastrophes in the past can be explained mainly by the inexperience on water behavior and low level of technology development. Today's civilization has knowledge and new technologies to solve the problems regarding water and environment. Eco-hydrology as a new discipline gives a hand to other disciplines, such as biology, geography, forestry, agriculture, ecology, legislation, and to public, politicians, journalists and others (*Bonacci*, 2003). Interdisciplinary approach in use and protection of waters today is needed more than ever. The necessity of interstate cooperation regarding transboundary waters also can be pointed out. In the Republic of Macedonia almost all waters are transboundary. Up to today the activities related to ecohydrology mainly have been focused on the natural lakes.

In the last 15 years Dojran Lake as a place of natural heritage is threatened because the lake's water level decreased seriously. The lake watershed and the lake itself are shared by Macedonia and Greece. Recharge of the lake is from direct runoff, small rivers and groundwater. Since 1988 the lake surface dropped from 42 km^2 to 31 km^2, and more significantly the water volume decreased from 262 million m^3 to only 80 million m^3 in 2000.

This water declination together with the simultaneous deterioration of the water quality resulted with serious ecological impacts. Biodiversity diminished and the reduction of plankton led to a reduction of fish portion. Also the number of birds decreased dramatically. The attack on the ecosystem had a harmful impact on the economy in the region. Tourism had been the most important sector, but it completely stopped, and in year 2000 were only tenth of the level in the eighties.

On the Macedonian side various efforts were initiated to improve the quantity and quality of this water resource. A sewage collector system along the lake shore has been constructed. Also, the previous groundwater extraction for irrigation has been strongly reduced and the irrigated areas were converted to rain-fed farmland and to drip irrigation system.

2. Watershed Characteristics

Dojran Lake is a tectonic lake situated in the Balkan Peninsula in southeastern part of Macedonia at an average altitude of 148 m asl. The watershed and the lake itself are shared by two countries, Greece and Macedonia. The watershed of the lake belongs to the river basin of Vardar that gravitates towards Aegean See. The map of Dojran Lake watershed is shown in Figure 1.

The lake was formed in a karstified basin created by combination of Tertiary volcanic and tectonic activity. The sediments of the lake watershed are composed of mineral-rich ancient alluvial and limestone sediments. A minor part of the watershed on Macedonian side is composed of diluvia clay sediments. These areas are the only arable lands in the area, still with low agricultural quality. The northern and eastern belts of the watershed are rocky and covered with low forests and weeds. The agriculture is not well developed.

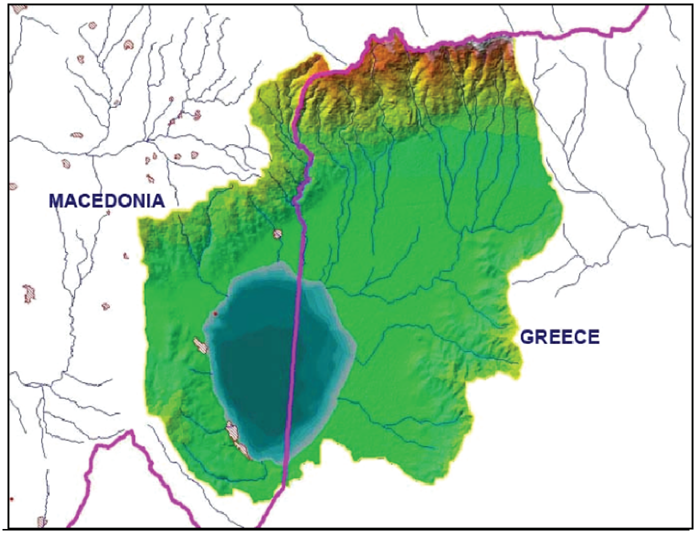


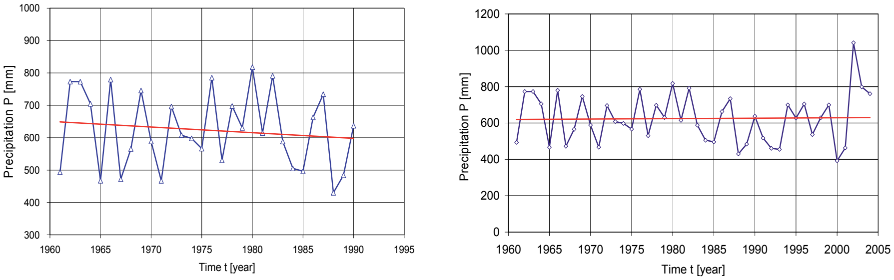
Figure 1. Map of the Dojran Lake watershed

The geographic longitude of the lake is N41°23’ and the latitude is E22°45’. The average altitude of the watershed is 362.9 m asl. Only a small part of about 50 km^2 or 18% is located at altitude higher of 500 m asl. Total watershed area is 271.8 km^2 out of which 92.1 km^2 or 32% belongs to Macedonia. Water surface area of the lake at normal elevation (147.34 m asl) is 42.2 km^2 out of which 27.1 km^2 or 63.6% belongs to Macedonia. The volume of the lake at normal water level is 262 million m^3 which corresponds to the average depth of 6.5 m (maximum depth 10.4 m). The maximum length of the lake is 8.9 km and the maximum width is 7.1 km. Dojran Lake doesn’t have surface outflow and the only outflow is by the evaporation from the lake water surface.

2.1. CLIMATIC-METEOROLOGICAL CHARACTERISTICS

Dojran Lake valley together with Gevgelija – Valandovo valley is one of the warmest in this part of the Balkan. The precipitation and temperature regime has been analyzed for the period 1961–2004 with data from hydrometeorological station at Nov Dojran. Precipitation and temperature regime mainly are under the Mediterranean influence from Aegean See. This influence causes the maximum precipitation in cold part of the year (November-December, 28% of the annual sum) and minimum precipitation in summer months (July-August, 17% of the annual sum). The average annual precipitation sum for the observed period is 624.7 mm and their range is from minimum 392.2 mm in 2000 to maximum 1041.5 mm in 2002.

The long-term annual precipitation sums with linear trend lines for two periods 1961–1990 and 1961–2004 are shown in Figure 2. It is obvious that for the first period the trend line has a declining trend with the equation $P = -1.7529 \cdot t + 4086.3$, while for the second extended period the trend line has a rising trend with the equation $P = 0.2263 \cdot t + 176.01$. This rapid change of the pluvial regime is due to extreme value 1041.5 mm registered in 2002. These graphs show relatively uniform distribution of the precipitation for the first period with maximum in December. The station Nov Dojran (180 m asl) is representative only for the pluvial regime on the lake surface, but is not representative for pluvial analysis of the entire watershed (mean 363 m asl., up to 1877 m asl.).



a) b)

Figure 2. Long-term annual precipitation sums with trend lines: a) 1961–1990, b) 1961–2004

The long-term monthly air temperatures for the period 1961–2004 are presented in Figure 3. Relative humidity in Dojran Lake valley in summer period is 60% and in winter months up to 80%. The highest frequency of 319% has the wind from northwest direction, while the average annual calm is 525%. The winds are frequent 47.5% of the year with the average speed between 1.4 and 3.8 m/s. The most frequent are north-west winds.

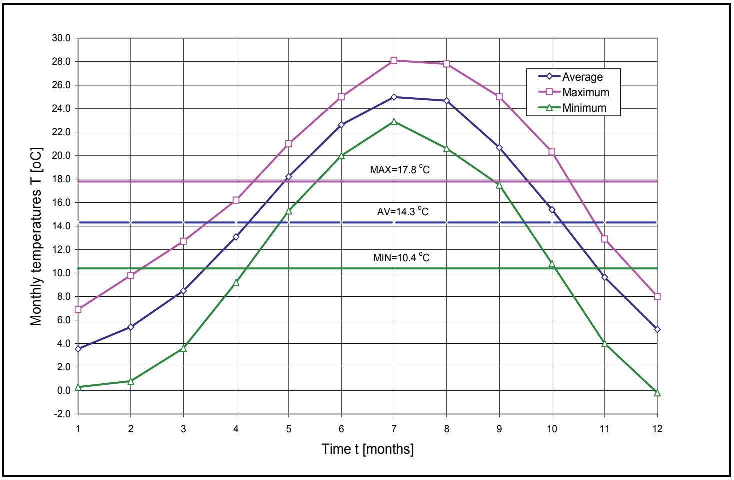


Figure 3. Long-term characteristic monthly air temperatures

TABLE 1. Evaporation from lake water surface

Months	[1961–1990]				[1961–2004]			
	T	Penman	Rohwer	Meyer	T	Penman	Rohwer	Meyer
		E	E	E		E	E	E
	[^{o}C]	[mm]	[mm]	[mm]	[^{o}C]	[mm]	[mm]	[mm]
January	0.6	33.03	74.52	61.92	3.5	20.16	46.40	38.55
February	1.9	27.86	39.91	34.97	5.4	32.11	51.09	44.76
March	4.6	46.84	49.01	43.47	8.5	54.13	64.11	56.86
April	8.6	74.64	71.20	66.95	13.1	86.36	96.11	90.38
May	13.1	110.23	96.71	91.90	18.2	127.68	134.02	127.36
June	16.9	139.18	152.47	143.37	22.6	161.97	217.30	204.34
July	19.1	161.76	217.19	195.07	25.0	187.98	311.30	279.60
August	18.7	136.27	178.45	169.58	24.7	160.57	257.41	244.61
September	16.0	88.22	127.45	125.15	20.7	102.11	171.21	168.12
October	11.4	48.52	77.44	72.76	15.4	56.13	100.91	94.45
November	6.7	24.28	52.06	46.10	9.6	27.42	63.38	56.12
December	2.4	16.40	42.85	35.61	5.2	18.73	52.30	43.47
Sum		907.22	1179.56	1086.85		1035.35	1565.54	1448.62

The average annual sunshine is 2440 hours or 6.6 hours daily. The maximum sunshine is in July with 330 hours or 10.6 hours daily and the minimum is in January with 90 hours or 3.0 hours daily. The computed evaporation from lake water surface by the formulas of Penman, Rohwer and Meyer are presented in

Table 1. The computed annual evaporation varies from 907 mm (Penman) to 1179 mm (Rohwer). Maximum monthly evaporation has been obtained for July. These results show that within the observed period the computed annual evaporation sum (1179.56 mm) is almost twice of the annual precipitation sum.

For the period 1961–2004 the average values of the monthly temperatures have increased rapidly, for example in January from 0.6°C to 3.5°C, and in July from 19.1°C to 25°C, which leads to the increase of the evaporation annual sum for 15–35%. For the extended period the computed evaporation sum (1565.54 mm) has increased to 2.5 times of the observed average annual precipitation sum (624.7 mm).

3. Water Level Analysis

The analyses of water levels in Dojran Lake is carried out with the observed data at water gauge station at Nov Dojran. The average monthly data on maximum, average and minimum water levels for the period 1952–2004 are presented in Figure 4. The average long-term water level is 145.38 m asl that is about 2 m below the normal water level. It is obvious that very strong water level decreasing trend of Dojran Lake has started in 1988. Therefore, the total data series can be divided into the following two time sub-sets: 1) 1952–1987 and 2) 1988–2004.

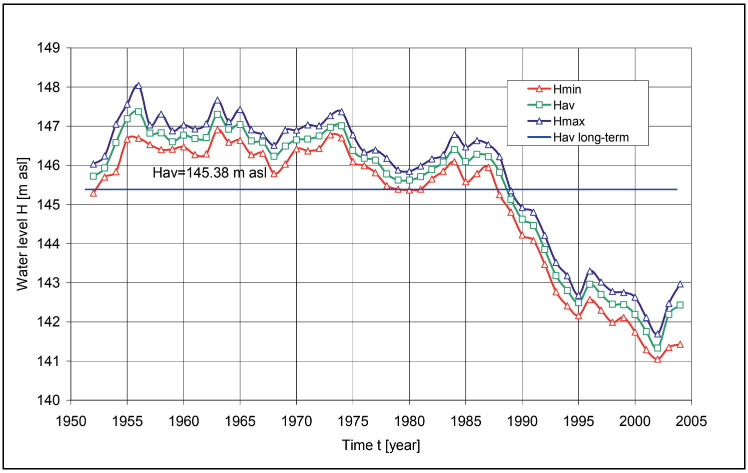


Figure 4. Characteristic water levels in Dojran Lake

The amplitude of observed maximum water levels for the first time sub-set is 148.06–145.85=2.21 m which defines the average water level decrease of 6.31 cm annually. For the first time sub-set pretty regular water level oscillations can be noted with maximum and minimum values appearing every 5 years. The amplitude of observed maximum water levels for the first time sub-set is 148.06–145.85=2.21 m which defines the average water level decrease of 6.31 cm annually. For the first time sub-set pretty regular water level oscillations can be noted with maximum and minimum values appearing every 5 years.

For the second time sub-sets the amplitude of observed maximum water levels is 146.79–141.69=5.10 m which results the average water level decrease of 34.0 cm annually. This decreasing trend is alarming most of all because the causes have not been recognized clearly yet. It is most probable that drastic water level decrease within 1988–2002 might be a result of uncontrolled anthropogenic activities and partly due to the long draught period. The anthropogenic activities are mainly connected to water use in agricultural sector.

The amplitude of average water level oscillations in 2000 is 142.59–141.75=0.84 m, in 2001 is 142.08–141.32=0.76 m, in 2002 is 141.56–141.08=0.48 m, and in 2004 it is 142.44–141.90=0.54 m. These results show decreasing of the average monthly water level amplitudes. The exception is 2002 most probably due to the improved hydrological condition regarding the precipitation sum increase as shown in Figure 2, decrease of the water use from the lake, and partly due to the additional water transfer from Gjavato wells into the lake. The increase of rainfalls can be referred to the start of wet period in 2002 that lasts even today. This effect is not completely natural, and therefore can not be taken as a normal long-term monthly water level oscillation.

4. Water Quality

The most comprehensive analysis on water quality was performed in 2003 (*Smith&Petkovski*). The lake waters are characterized by a rather high alkalinity (pH values between 9.2 and 9.6) and elevated Carbonate and Magnesium hardness (total hardness about 330 mg/l as $CaCo_3$). Thus, the water is chemically well buffered. Still, there are a number of toxic substances, which are near or even beyond toxic levels. Ammonia (NH_3) is with 0.3 mg/l that is already 50% above the chronic toxicity level endangering the life of fish and other aquatic organisms. Lead is exceeding standard levels only at the shoreline, 0.030 mg/l measured against 0.014 mg/l chronic toxicity level. Other substances (chemical oxygen demand, electrical conductivity, iron, dissolved oxygen, phosphorus) are not toxic as such, but their concentrations may have indirect adverse effects on the lake ecosystem. Measured iron values are above the accepted level of 1 mg/l. Phosphorus concentrations are above standard values for lakes and reservoirs, thus indicate a highly eutrophic system. The level of total suspended solids is 37–142 mg/l that is 2–9 times the value of 15 mg/l considered as dangerous. Other measured chemical parameters did not appear to cause any problems. This refers to elements like Arsenic, Boron, Cadmium, Chromium, Copper, Manganese, Sulphide and Zinc.

5. Flora and Fauna

Because of its geotectonic location and climate characteristics, Dojran Lake and its watershed have very rich biodiversity. No special data on vegetation is available on Macedonian side, except that the forests are in rather poor state. On the Greek side the Aquatic Forest of Mouria is rather rare forest and is declared as natural monument. This forest together with a small part of the lake has been proposed for inclusion in EU NATURA 2000 network. In the forest has been recognized habitat of extraordinary importance (number of plant taxa is 46). The condition of the habitat (mixed oak, elm and ash) is considered as unsatisfactory.

Fauna is also very rich in the lake and its watershed. On the Macedonian side fauna has been examined as follows: dragonflies 42 species, stoneflies 42 species, mosquitoes 51 species, amphibian 9 species, reptiles 23 species, birds 87 species out of which 17 species are water birds, and mammals 53 species. On the Greek side studies on fauna are limited to “Aquatic Forest of Mouria”. According to this study three species of amphibians and three species of reptiles have been found. Birds found in the Greek part of the lake include at least 36 species. Two species, Pygmy Cormorant and Dalmatian Pelican, are recognized as endangered species worldwide.

6. Brief Problem Definition and Undertaken Activities

Main economy in the region is tourism and fishery. At present these activities are almost non-existent due to the environmental catastrophe that lasts over ten years. The lake and its biodiversity are influenced by uncontrolled human activities and climate. The result is rapid and large water level decrease. Since 1988 the lake is facing the extreme water level and water volume decrease. From 262 million m^3 in 1988 the volume has decreased to only 80 million m^3 in 2000. According to the biologists over 140 species of flora and fauna have disappeared.

In 2000–2001 the Ministry of Environment and Physical Planning of the Republic of Macedonia have funded and realized the project “Feasibility Study on Dojran Lake Salvation”. Up to now, only the financial resources of the Macedonian Government have been mobilized on monitoring and water recharge from the wells system in Gjavato. The constructed system includes:

two-stage pumping from the wells in Gjavato, pipeline (L=19.3 km) with total pumping head of over 200 m and maximum capacity of 1000 l/s.

Currently the European Agency for Reconstruction is contracting authority of the project titled: Improvement of Management of Transboundary Water Resources. Some of the specific objectives related to Dojran Lake are: a) identification of the reason for lowering of Dojran Lake and potential measures to recover lake levels and improve water quality, b) establishment of regular monitoring system and exchange of monitoring information on all measured components of the water balance of Vardar and Dojran Lake between Macedonia and Greece, c) planning the management monitoring programme, including specific measures to recover Dojran Lake water levels.

6.1. PROBLEM SOLUTION

Besides the hydrological balance disturbance Dojran Lake has faced the environmental catastrophe as well, evidenced by recession of the shoreline accompanied by a complete loss of the litoral zone and its related biological communities (*Petkovski&Smith*, 2001). Litoral zooplankton community has reduction from 94 taxa in 1988 to only 28 taxa in 2001, but this community steel has genetic potential to be restored.

Dojran Lake and its basin need design and implementation of restoration and protection measures. For successful implementation of designed measures, development of a Management Plan is a necessity. Current monitoring is referring only to water level observation and meteorological parameters with rain gauge stations that are not in sufficient number and low elevated. Water quality monitoring is non-systematic, and water use monitoring does not exist.

The Management Plan has to be based on a reliable water balance that cannot be done with limited and incomplete data. Crucial parameter in Dojran Lake water balance is evaporation which is visible from the fact that when the lake surface area is 30 million m^2 and the annual evaporation amounts at least 30 million m^3.

The question which needs a reliable and scientific answer is: Can the disturbed natural balance of the lake be restored and put in state as before 1988? From hydrological aspect the answer is pretty certain. However, various and harmonized activities and measures should be undertaken by both countries that share the lake and its watershed. On the other side the answer on the question: how much the damages over the entire ecosystem can be restored, is very difficult because the scale consideration of the damages up to now has not been specifically defined, and accordingly restoration measures designed.

7. Conclusions

In the last decade Dojran Lake is facing the ecological catastrophe due to a rapid water level and volume decrease. The basic economy in the region, tourism and fishery, has stopped almost completely.

In this region the average yearly long-term precipitation sum is something over 600 mm. It is very important to establish rainfall measurements on higher altitudes in the lake watershed enabling more realistic rainfall-runoff regime. The temperature regime is the warmest in the country that results with very high evaporation from water surface (almost twice the annual precipitation sum). For reliable evaporation estimation direct measurements from water surface are necessary.

The authors would like to stress out the necessity of more intensive cooperation between the authorized institutions in both countries that share the lake basin and the lake itself. The international community and the financial mechanisms should help both countries in improvement of hydrological, meteorological, water quality, water use and environmental monitoring in the lake basin that will lead to better environment. If this will not be done in a very near future no doubt Dojran Lake will reach the point of no return.

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POLYCHLORINATED BIPHENYLS IN THE URBAN ENVIRONMENT OF BELARUS: SOURCES, POLLUTION, PROBLEMS OF MONITORING

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Abstract. In the paper environmental problems connected with such dangerous chemicals as polychlorinated biphenyls (PCBs) are discussed. Sources of PCBs in Belarus, location of the main part of PCBs in cities and towns, as well as specificity of PCB discharges into environment are shown. The content of PCBs in urban soil of different functional zones is given. High level of soil pollution by PCBs in places of PCB-containing equipment installation and storage is revealed. The peculiarities of hot spots formation and spreading of PCBs beyond the places of PCB leakage are established. Pollution of bottom sediments of some aquatic ecosystems by PCBs is identified. The problems and perspectives of PCB monitoring in urban environment are discussed.

Keywords: polychlorinated biphenyls; urban environment; soil pollution; bottom sediments; monitoring

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1. Introduction

Eenvironmental pollution by polychlorinated biphenyls (PCBs) is one of the most pertinent global ecological problems. Synthesized in 1930s for industrial purposes, PCBs were not considered dangerous chemicals for many years. Moreover, PCBs and PCB-containing products were produced and utilized with little restrictions or control in many countries. Only decades later evidence of their long-term adverse effect on human health and ecosystems was revealed, which resulted in the process of gradual introduction of restrictions and prohibitions on the use of PCBs. Nevertheless, PCB pollution remains one of the most critical environmental problems, since at present most of the previously produced PCBs are still either used or stored. The primary source of PCB discharges into the environment is PCB-containing electrical equipment (Berdowski et al., 1999; Guidelines for the identification…, 1999; AMAP, 2000; Breivik et al., 2002).

Wide application of PCBs, a variety of PCB discharges into environment (with leakages, emissions, products and waste), and PCBs' properties resulted in the fact that PCBs can be found virtually everywhere, including background territories. As xenobiotics (substances that are foreign to the natural environment), PCBs are present in all natural components including air, precipitation, waters, bottom sediments, soils, plants and animals, and human body (Toxicological profile…, 2000; Regionally-based assessment…, 2002; Ockenden et al., 2003; Dioxins & PCBs…, 2004). Characteristic features of PCBs' behavior in the environment include their very slow decomposition, ability to long distance distribution and bioaccumulation in fatty tissues of exposed animals and humans. Therefore, even with low PCB concentration in the environment there is a danger of PCBs accumulation on the top of the food chain – in human body.

PCBs have been used for over 40 years in Belarus. Yet, similarly to other post-Soviet Union countries, PCB pollution is a poorly studied problem for Belarus. The usage of PCBs is currently unregulated by Belarusian law. Moreover, there is a lack of specially designated storage facilities for the damaged equipment; and a system for PCB collection and disposal in an ecologically sound manner is not established yet. The research of PCB pollution began in Belarus only in the late 1990s. Today a variety of research initiatives in the field are under way, primarily due to Belarus' accession to the Stockholm Convention on Persistent Organic Pollutants. For example, in 2003–2006 several projects on PCB inventory and environmental pollution assessment were implemented (Kukharchyk et al., 2005; Suboch et al., 2005; Kukharchyk, 2006; The National plan…, 2006).

This article discusses peculiarities of the environmental pollution by PCBs in Belarusian cities, and analyses problems and prospects of PCB monitoring.

2. Methods and Objects

Experimental research was conducted in several cities, including Minsk, the capital and largest industrial city, and Lida, where for the last 30 years PCBs were used in the production of paint and varnish. Primary attention was paid to the study of pollution in soils and bottom sediments, because, on the one hand, they are deponents of PCBs, and on the other hand, they are secondary sources of PCBs re-emission and contamination of other environments.

Soil was sampled from different functional city zones as well from places of PCB use and storage of PCB-containing equipment. The total of 250 soil samples and 20 samples of bottom sediments were examined.

The sum of PCBs as well as individual PCB congeners (PCB-28, PCB-52, PCB-101, PCB-118, PCB-153, PCB-138 and PCB-180) was detected by gas chromatography with electron-capture detection and chromatography mass spectrometry (Suboch et al., 2005). Quantitative analysis was performed using five-point calibration with standard solutions.

3. Results and Discussion

3.1. PCB SOURCES

The following factors are determinative of the environmental situation in Belarus: the use of PCB-containing equipment; and the use of PCBs as raw materials in the production of paint and varnish.

3.1.1. The Use of PCB-containing Equipment

According to the results of the inventory (Kukharchyk et al., 2005; National plan, 2006), the total of roughly 1.5 thousand tons of PCBs were revealed in Belarus, 55 per cent of which is concentrated in power transformers, and 44 percent – in power capacitors. It was established that PCB-containing equipment is used at over 760 industrial enterprises which are located in 140 cities (Figure 1).

Most PCBs are concentrated at enterprises of large cities and industrial centers. For example, nearly 90 per cent of the total volume of PCBs in Belarus is concentrated in 23 cities and towns, where 53% of the total population lives. The largest volume of PCBs was revealed in three cities (Bobruisk, Minsk, Novopolotsk) amounting to 44.4 per cent of the total volume of PCBs in the country.

By now a significant share of PCB-containing electrical equipment has been phased out of operation or reserved. According to the inventory, this category of equipment includes 27 per cent of PCB-containing capacitors and 14 per cent of transformers. The uninstalled equipment is frequently stored on unprepared grounds on enterprise territory. The condition of power capacitors and transformers in many cases was evaluated as unsatisfactory, due to the destruction of their frames and PCB leakages as a result.

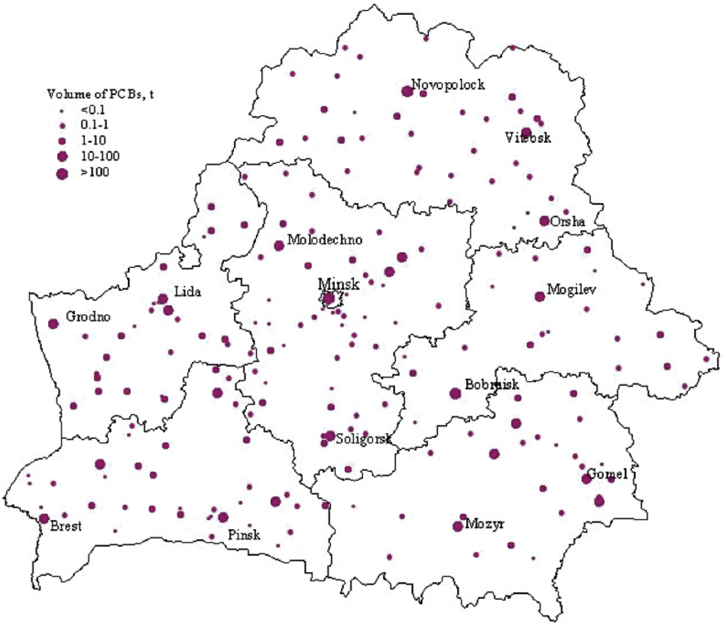

Figure 1. Rating of Belarusian cities by PCB volume

According to calculations, roughly 1.5 tons of PCBs are annually discharged into the environment from leaking power transformers and capacitors (Kukharchyk, Kakareka, 2006). For the purposes of comparison it must be noted that every year only 5 to 10 kg of PCBs are emitted into the atmosphere from thermal sources (fuel and waste combustion; steel production).

It must be emphasized that under the Stockholm Convention, PCB-containing equipment can be used until 2025. Therefore, identification of owners of PCB-containing equipment and regulation of its use and condition, as well as timely prevention of PCB leakage from damaged equipment become extremely important aspects of PCB management.

3.1.2. The Use of PCBs in the Production of Paint and Varnish

During 1968–1998 one of the enterprises in the city of Lida, Grodno region, was using sovol (pentachlorobiphenyl) as plasticizer to produce paint and varnish.

The total of 5 thousand tons of sovol was used (Kakareka et al., 2003). Most of it was transported out of the country with ready products, but some portion has been dispersed in the city through products, sewer waters, atmospheric emissions and wastes. According to the calculations (Kukharchyk, 2006), over the time of its use, nearly 130 tons of sovol leaked into the environment. The most significant discharge of PCBs happened between 1975 and 1985 when the leakages could amount to 3.3–10 tons annually.

3.2. PCB CONTENT IN URBAN SOILS

The results obtained in the process of the study reveal a wide scale of PCB levels in urban soils – ranging from levels below method sensitivity to several milligrams per kilogram of soil (Table 1).

TABLE 1. PCB content in soils of urban landscapes, mg/kg

Compounds	Residential areas (15)*		Green zones (7)		Near industrial enterprises (17)		At industrial site of JSC Lakokraska (13)	
	avg.	max	avg.	max	avg.	max	avg.	max
PCB-28	0.009	0.035	0.068	0.415	0.563	4.9	0.17	0.38
PCB-52	0.008	0.020	0.060	0.162	0.202	1.23	0.95	2.67
PCB-101	0.002	0.007	0.004	0.026	0.074	0.67	2.49	6.78
PCB-118	0.003	0.014	0.004	0.023	0.045	0.50	3.66	10.71
PCB-153	0.002	0.011	0.001	0.004	0.013	0.10	2.25	7.69
PCB-138	0.002	0.012	0.001	0.004	0.031	0.28	3.43	9.58
PCB-180	0.001	0.002	0	0	0	0	0.3	0.96
Sum of 7 congeners	0.032	0.059	0.137	0.635	0.928	7.69	13.25	38.45

*– the number of soil samples is given in the brackets

Higher level of PCB concentration in residential areas and green zones (parks, public gardens) and in the vicinity of industrial enterprises can be primarily explained by the existence of local sources of PCB distribution (discharge into the atmosphere; dispersal of waste, including residual ashes and construction litter). Among individual PCB compounds analyzed in the course of the research, both low-chlorinated and high-chlorinated compounds were identified. This finding proves the multitude of PCB sources. It is well established that the predominant PCB compound in soils of background territories is low-chlorinated (PCB-28). This is the most volatile PCB compound, which is transported through air for long distances.

The level of PCBs in industrial landscapes is determined by the sources of PCB emission. Predictably, high levels of PCBs were revealed on the territory of paint and varnish producing enterprise "Lakokraska", where the sum of 7 isomers reaches 38.45 mg per kg, and the sum of PCBs makes up to 96.6 mg per kg. It was found out, that the enterprise soil is contaminated 30 cm deep.

PCB compounds are dominated by penta- and hexachlorobiphenyls, 53 per cent and 28 per cent respectively, which is clearly indicative of such source of PCB discharge as sovol (Figure 2).

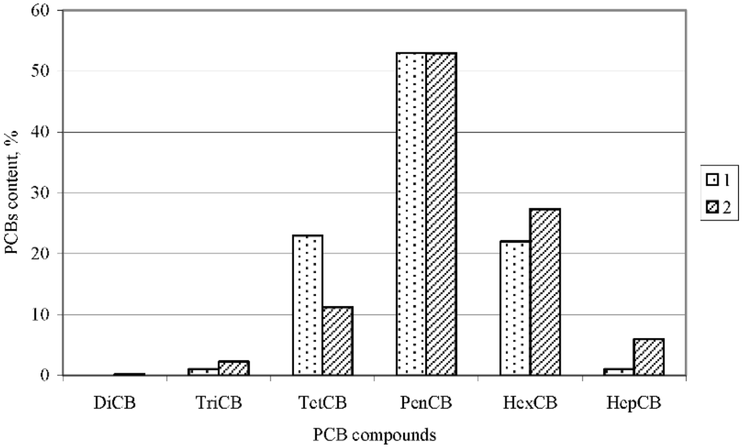

Figure 2. PCB compounds structure: 1 – in sovol, 2 – in soil of industrial site

The research shows that the highest level of soil pollution is found in places of PCB-containing equipment usage and storage (Table 2).

TABLE 2. Content of PCB sum in soils in impact zones of PCB-containing equipment installation or storage, mg/kg

Sampling site, number of samples	Average	Maximum
Places of PCB-containing capacitors installation, 120	12000	82000
Places of PCB-containing capacitors storage (on the ground or on concrete), 16	7130	92000
Places of PCB-containing transformers storage, 4	78000	105000
At distance 1–3 m from PCB-containing capacitors banks, 37	7.03	102
At distance 10–150 m from PCB-containing capacitors banks and storage, 24	0.9	23
Background territories (more than 1 km from sources), 30	0.035	0.165

At the same time, landscapes with extreme levels of PCBs are localized and determined by leakages from damaged equipment. More often that not, the most polluted landscapes are small in size (around 0.05 square meters). Moreover, much wider pollution spots are created in places of emergency leaks (up to 1 square meter and wider). Overall, in roughly 60 per cent of industrial objects assessed during the research, the area of extreme levels of pollution (around 500 mg per kg) was less than 1 square meter; in 20 per cent of the industrial objects the area of extremely polluted soils reached 1 to 5 square meters; and only is single cases did the polluted territory have much larger area.

Basically, those are the so-called "hot spots", in relation to which cleaning and remediation measures should be taken. Thus, according to the Stockholm Convention, substrates with more than 50 mg per kg are subject to ecologically sound management (Stockholm convention…, 2001). The Environmental Protection Agency of the USA equates 500 mg per kg to PCB-containing materials and makes them subject to utilization (40 CFR…, 2002).

The objects researched differ significantly in the level of soil pollution and the depth of PCB penetration. Extreme levels of pollution are found in the upper soil levels – up to 10 cm. However, in cases of easily identifiable spots of PCB spills, a high level of PCB pollution can be found at the depth of 0.5–1 meters.

The danger of PCB leakages depends upon the spread of PCBs beyond the spots of PCB-containing equipment use or storage. This, in turn, may lead to the contamination of nearby territories and other environmental components, including the contamination of ground and surface waters. Due to leakages of liquid from the equipment, new (secondary) sources of PCB pollution are formed, the impact zone of which is practically unlimited because of PCBs' ability to mix with aerial and water flows and spread far beyond their locations of production and use by inclusion into the biological circle. This means that, by definition, local application of PCB-containing equipment (several square meters) becomes not only a source of local anomalies, but a source of regional and, in future, global pollution.

3.3. PCB CONTENT IN BOTTOM SEDIMENTS

Bottom sediments are an indicator of the state of aquatic ecosystems, as well as of catchment's area, from the runoff of which the discharge of pollutants is possible. According to the results of the research, the sum of 7 PCB isomers in bottom sediments of sampled rivers and basins (reservoirs) of Belarus varies from levels below the method detection limit to 23.2 mg per kg. The data in the table 3 confirms pollution of bottom sediments of the majority of basins and rivers examined. Extreme levels of PCBs were detected in bottom sediments of Lidskoe reservoir (city of Lida, Grodno region), which may be explained by the location of an industrial facility of paint and stain producing enterprise “Lakokraska”, where sovol was used on the catchment’s area.

The level of PCBs in bottom sediments of basins and watercourses, remote from PCB impact sources, does not exceed 0.065 mg per kg of dry matter. Congeners of trichlorobiphenyls (firstly PCB-28) are predominant.

TABLE 3. PCB content in bottom sediments, mg/kg

Sampling site, number of samples	Sum of 7 PCB congeners
River and reservoirs of background territories, 5	nd–0.065
River and reservoirs of urbanized territories	
Minsk city, 7	0.023–0.828
Lida town, 3	0.598–23.2

nd – below the detection limit

4. Problems and Perspectives of PCB Monitoring

Control of PCB levels in the environment is one of the necessary preconditions for minimization of its adverse effect on human health and for the performance of international obligations under the Stockholm Convention on Persistent Organic Pollutants. At this point, the problem of environmental pollution by PCBs in Belarus is acknowledged, but the data collected is still insufficient in order to fully realize the extent of contamination.

Systematic monitoring of PCB levels in the environment requires adequate chemical analysis infrastructure as well as regulatory and methodological frameworks. Currently, there are only two chemical analysis laboratories in Belarus accredited to measure PCB levels in soils, wastes and waters. Both laboratories are located in Minsk, and one of them requires significant modernization of equipment. Moreover, the quality of measurements and method sensitivity need to be improved. For example, the condition of available equipment does not allow for large-scale detection of PCBs in surface and ground waters due to low sensitivity of methods used. Besides, the improvement of water sampling method is necessary. Further advancement of research is also impeded by a lack of qualified professionals in the field of detection of organochlorines compounds. In most cases, the procedures of preparing samples, cleaning the extract and its separation are performed manually, which reduces the productivity of the laboratories (The National plan…, 2006).

At this time, methods of PCB detection in soils belong to the most advanced ones. It is however necessary to continue identification of highly polluted territories, because the soil is an important deponent of PCBs and is the most probable source of PCB supply into waters, animal and human food. It is necessary to implement thorough research at the locations of PCB sources, and to determine a network for systematic monitoring of PCB levels in urban soil. Lida, Minsk, Bobruisk and Novopolotsk are Belarusian cities which require primary attention and assessment. It is also recommended to implement monitoring of surface waters and bottom sediments in these cities.

Overall, the research has shown that in Belarus priority should be given to research (including monitoring), aimed at identification of places, which have critical levels of pollution and are most probable sources of pollution of drinking water and food products.

5. Conclusion

Polychlorinated biphenyls present a serious danger to the health of Belarusian people. Over the last years intensive research has allowed to receive, in short time, fairly accurate data on the sources and quantity of PCBs, and the owners of PCB-containing equipment. The research has also made possible to comprehend possible levels of environmental pollution by dangerous chemicals. However, the ecologically sound management of PCBs and the reduction of adverse effect of PCBs on human health remains a difficult and enduring task, which requires significant financial resources for the creation of the necessary infrastructure, improvement of the legal system, training of staff, development of PCB monitoring equipment as well as increasing public awareness of the PCB problem.

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PHYTOTOXICITY ASSESSMENT OF EFFLUENT WATERS, SURFACE WATER AND SEDIMENTS

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Abstract. Bioassays are valuable tools for environmental risk assessment, because they respond to bioavailable fraction of pollutants in water, sediments and soil. The phytotoxicity of water and sediments from Ignalina NPP area, Lithuania, industrial areas in Lithuania and Sweden, and a municipal landfill, and its potential impacts on receiving water was determined by *Lepidium sativum*, *Spirodela polyrrhiza* and *Tradescantia* clone 02. It was found that phytotoxicity of water and sediments from receiving water bodies fluctuated from non-toxic to extremely toxic. The results indicate that vascular plants sensitive tools for the toxicity determination in solid and liquid environment that can be successfully included in bioassays for the environmental risk assessment.

Keywords: vascular plants, phytotoxicity, *Lepidium sativum*, *Spirodela polyrrhiza*, *Tradescantia* clone 02, toxicity assessment, effluent, receiving water

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1. Introduction

Anthropogenic release of chemical substances into the environment can disturb health and stability of ecosystems. It is difficult to measure the environmental quality of water discharges from heterogeneous industrial landscapes, e.g. power plants, landfills or industrial recycling areas. For example, at a scrap metal processing plant, various emissions disperse metal pollution over its territory, that may get into storm water runoff and then into receiving water bodies (Karlavičienė et al., 2005). Assessment of the quality of water, sediments and soil using physical and chemical methods has limitations: a) they do not reflect the transformation of hazardous substances, their interaction and bioavailability; b) they do not allow assessment of the multi-component nature of pollutant and the integrated toxic impact on organisms; and c) the concentration of hazardous compounds does not always indicate the toxic impact of substances on organisms (Wundram et al., 1997; Marčiulionienė et al., 2002). The use of bioassays in environmental studies to evaluate toxicity of contaminants in water, soil, sediments and food offer some improvement. Bioassays estimate the combined effects of all components present (Wang et al., 2001; Blinova, 2004; Montvydienė and Marčiulionienė, 2004; Loureiro et al., 2006). A bioassays battery is widely used to assess the potential adverse effects of existing or new chemical substances and to evaluate the impact of these substances on various spheres of ecosystems in which they may get into (79/831/EEC, Johnson et al., 2004; Kazlauskienė et al., 2004). Usually it is recommended that species representing different trophic levels be included in the battery (Johnson et al., 2004; Selivanovskaya and Latypova, 2004). In most cases bacteria, algae, crustaceans and fish are used. However, the use of vascular plants, which are important component of most ecosystems, is rather limited (Barbero et al., 2001; Ferrara et al., 2003; Selivanovskaya and Latypova, 2004; Loureiro et al., 2006). Vascular plants do tend to be used in crop pesticides toxicity testing and when metaliferous mine spoils or contaminated agricultural land tested for quality (OECD 2003 draft version; Loureiro et al., 2006).

It is the argued in the present paper that there are benefits in using vascular plants bioassays in aquatic systems, compared with bioassays of animals and algae. For example, seeds of *L. sativum* are very sensitive to the environmental impact during seed germination and the early root growth period (Ferrara et al., 2003; Montvydienė and Marčiulionienė, 2004). The turions of *S. polyrrhiza* at the initial stage of first leafy stem development are very sensitive to all kinds of influence, and changes in meristematic tissue are immediately reflected to the plant propagation (Marčiulionienė et al., 2002). The appearance of somatic mutations in *Tradescantia* stamen hair cells allows forecasting the influence of present impact to the development and viability of new generations (Marčiulionienė et al., 2004, 2006).

The objective of the article is to discuss the advantages and disadvantages of phytoxicity tests in accordance with investigations of phytotoxicity of various waters and sludge; and experimentally to evaluate the possible applications of vascular plants *Lepidium sativum*, *Spirodela polyrrhiza* and *Tradescantia* clone 02 in the environmental pollution assessment.

2. Materials and Methods

2.1. SAMPLES AND SAMPLING AREAS

Ecotoxicity testing was carried out on liquid (industrial storm water (ISW) runoff, industrial waste water (IWW), cooling water (CW), process water (PW), municipal waste water (WW), leachate (L) and recipient water (RW)) and solid faze samples (sediments (SE) and bottom sediments of recipient (BSE)) taken from four industrial areas (Ignalina Nuclear Power Plant (Ignalina NPP) (Lithuania), tannery Lithuania), municipal landfill (Lithuania) and scrap metal processing plant (SMPP)) (Sweden) and three recipients (Lake Drūkšiai, reclamation ditches nearby landfill and small stream nearby SMPP).

The main pollutants at SMPP were: heavy metals, PCB's, and PAH's; in the leachate – heavy metals, PCBs, PAHs, fenols, surfactants, nutrients, and chlorides (Kaunelienė and Mačiulytė, 2003); in IWW of tannery – sulphides and chromium salts (Cooman et al., 2003).

The pollutants of interest at the Ignalina NPP were heavy metals, petroleum hydrocarbons, diluted non-organic acids and bases. The municipal WW contained heavy metals, radionuclides, weak organic acids, heavy metals, nutrients, surfactants and were discharged into the lake Drūkšiai (Marčiulionė et al., 1992). This lake serves as a cooler for INPP. Like the Chernobyl NPP, Ignalina NPP was equipped with RBMK–1500 type reactors. The first block was decommissioning in 2005, the second must be closed in 2009. When both reactors were functioning the lake was impacted not only by a thermal pollution, but also by IWW (Marčiulionienė et al., 1992).

2.2. BIOASSAYS

Two-day seed germination and root growth test with *Lepidium sativum* L. (*Brassicaceae*) and fourteen-day growth inhibition test with *Spirodela polyrrhiza* (L.) Schleid. (*Lemnaceae*) were conducted using the modified methods of Magone (1989). Thirty-day experiments with *Tradescantia* clone 02

(*Commelinaceae*) were performed applying the modified method of Osipova and Shevchenko (1984). The bioassays of *L. sativum*, *S. polyrrhiza* and *Tradescantia* clone 02 had been widely described in our previous report (Montvydienė and Marčiulionienė, 2004; Marčiulionienė et al., 2004). The experimental set of each testing scheme consisted of 3 or 5 control samples and 3 or 5 replicates of the test sample. In determining whether the results were statistically different from the control the set of two-intake comparison tests of *Statgrahics plus Version 2.1.* program when $p<0.05$ was applied. The EC_{50} values (i.e. toxicant concentrations that induce 50% growth inhibition of *L. sativum* as percentage of control, in a 2-day experiment) were estimated by linear regression analysis of root length and logarithm of toxicant concentration.

The level of toxic impact on *L. sativum* and *S. polyrrhiza* was assessed by the method suggested by Wang (1992). Based on inhibition of root growth of *L. sativum* and growth rate of *S. polyrrhiza* of 100–60%, 61–40%, 41–20% and lower than 19%, the toxic impact was classified as very strong (VS), strong (ST), moderate (M) and slight (SL), respectively. The tested sample was non-toxic (NE) if the inhibition of growth did not statistically differ from the control, and was extremely toxic (E) if the seed of *L. sativum* did not germinate or plants of *S. polyrrhiza* died. A slight genotoxic effect (SL) on the *Tradescantia* clone 02 stamen hair (SH) system is observed when the number of somatic mutations does not exceed 1%, and non-viable SH are not observed. The moderate effect (M) is observed when the number of somatic mutations is between 1–4% and non-viable SH did not exceed 40%. Strong genotoxic effect (ST) is characterized by the number of somatic mutations exceeding 4%, and viability of SH cells is less than 40%.

3. Results

3.1. IGNALINA NPP

The phytotoxicity testing was carried out in the period of 1993–2000, but data obtained in 1998 and 2000 only are presented here (Table 1). In Ignalina NPP WW, the number of germinated seeds of *L. sativum* in most cases did not differ from the control ($p<0.05$), but inhibition of root growth indicated the impact as moderate or non-toxic (Table 1).

The toxicity of Lake Drūkšiai water (Table 1) on all three plants changed subjected to the pollution level of Ignalina NPP WW, distance from the pollution resource, wind direction, water flow and mixing of water masses; and varied from moderate to non-toxic.

TABLE 1. Toxic effects of various waters as: (i) inhibition of root growth of *Lepidium sativum* (mean, %±SE); (ii) inhibition of growth rate of *Spirodela polyrrhiza* (mean, %±SE), and (iii) genotoxic effects in accordance with number of somatic mutations and non-viable stamen hair of *Tradescantia* clone 02 (mean, %±SE)

Sample and sampling site		*L. sativum*		*S. polyrrhiza*		*Tradescantia*		
		Toxic effect	Growth inhibition, %	Toxic effect	Growth inhibition, %	Genotoxic effect	Somatic mutations, %	Lethality, %
Ignalina NPP (Lithuania) (1998, 2000)								
ISW&PW	ISW and PW system	NE	4.4±0.3	NE	1.9±0.1	ST	7.2±0.6	10.7±0.9
		M	30.7±1.5	NE	0.9±0.08	M	3.6±0.4	15.5±1.3
CW	CW channel	NE	6.5±0.4	NE	3.6±0.2	ST	9.7±0.9	13.8±1.2
		ST	43±0.8	SL	10.9±0.7	ST	8.1±0.71	26.2±2.8
WW	WWTP discharge point	NE	4.5±0.1	NE	0.1±0.02	ST	38.3±4.4	13.9±1.2
		M	30.9±1.6	NE	5.1±0.3	ST	6.5±0.6	24.9±2.4
RW	Lake Drūkšiai, ISW impact zone	NE	2.8±1.6	NE	0.1±0.01	M	6.5±0.5	8.3±0.7
		M	32.4±1.3	NE	7.1±0.4	M	8.1±0.8	17.5±1.2
RW	Lake Drūkšiai, WWTP impact zone	NE	7.9±0.7	NE	2.4±0.2	SL	5.9±0.7	1.7±0.2
		M	38.7±0.8	NE	6.1±0.4	M	4.7±0.4	20±1.9
Tannery (Lithuania) (1996)								
IWW	IWWTP inflow	E	100	E	100	E	0	100
IWW	IWWTP discharge point	E	81.6±6.5	M	51.4±3.7	S	11.3±1.1	18.4±2.3
Municipal landfill (Lithuania) (2002)								
L	Raw leachate well	E	100	–		–		
RW	Reclamation ditch No. 1	E	100	–		–		
RW	Reclamation ditch No. 2	ST	64.3±0.9	–		–		
L	Storage pond	M	31.2±4.0	–		–		
L	Discharge point	M	25.8±3.2	–		–		

ISW & PW – industrial storm water & process water, CW – cooling water, WW – municipal waste water, WWTP – waste water treatment plant, RW – recipient water, IWW – industrial waste water, L – leachate, lethality – non-viable stamen hair of *Tradescantia* (hair contains less than 12 cells); NE – no toxic effect; SL – slight toxic effect; M – moderate toxic effect; ST – strong toxic effect; E – extreme toxic effect; "–" not investigated.

The rather intensive growth of *S. polyrrhiza* in the industrial WW and lake water could be stipulated by rather large amount of nitrogen and phosphorus which is discharged into these waters from Ignalina NPP and municipal waste water treatment plant (Marčiulionienė et al., 1992).

TABLE 2. Toxic effects of various sediments: (i) in accordance with inhibition of root growth of *Lepidium sativum* (mean, %±SE), and (ii) genotoxic effects in accordance with number of somatic mutations and non-viable stamen hair of *Tradescantia* clone 02 (mean, %±SE)

Sample and sampling site		*L. sativum*		*Tradescantia*		
		Toxic effect	Growth inhibition, %	Genotoxic effect	Somatic mutations, %	Lethality, %
Ignalina NPP (Lithuania) (1998, 2000)						
SE	ISW & PW system	SS	–15±0.2	ST	44.9±5.4	12.2±1.1
		NE	5.6±0.2	ST	7.1±0.6	29.1±2.5
SE	CW channel	SL	20.2±1.3	ST	–	–
		M	32.2±1.4	ST	6.3±0.5	25.4±2.3
SE	WWTP,	ST	43.2±2.4	ST	38.6±4.9	29.7±3.3
	discharge point	ST	43.7±3.6	ST	11.6±1.1	27.7±2.5
BSE	Lake Drūkšiai,	NE	3.7±0.2	ST	44.5±3.8	7.4±0.9
	ISW impact zone	M	30.9±2.8	ST	11.6±1.1	18.6±1.5
BSE	Lake Drūkšiai,	SL	16.2±0.7	–	–	–
	WWTP impact zone	ST	43.8±3.3	ST	15.7±1.4	21.5±1.9
Municipal landfill (Lithuania) (2002)						
SE	Raw leachate well	E	100	–		
BSE	Reclamation ditch No.1	VS	31.4±1.5	–		
SE	Storage pond	SL	87.2±2.2	–		
SE	Discharge point	E	100	–		

SE – sediments, BSE – bottom sediments of recipients, ISW – industrial storm water, CW – cooling water, WWTP – waste water treatment plant, lethality – non-viable stamen hair of *Tradescantia* (hair contains less than 12 cells); NE – no toxic effect; SL – slight toxic effect; M – moderate toxic effect; ST – strong toxic effect; VS – very strong toxic effect; E – extreme toxic effect; SS – slight stimulation; "–" not investigated.

In most cases the seed germination of *L. sativum* in the sediments from industrial WW channels of Ignalina NPP and from Lake Drūkšiai during the testing period did not significantly differ from the control ($p<0.05$). Meanwhile toxicity of these sediments to root growth of *L. sativum* varied from strong to slightly toxic or non-toxic (Table 2).

These sediments were strongly genotoxic to *Tradescantia* clone 02 (Table 2). This could be conditioned by the low water stream in the industrial WW channels and absorptive characteristics of channels and lake sediments which is compounded of sand mixing with aleurite-pelite silt. Hence, the obtained results revealed that the sediments in the industrial WW channels and Lake Drūkšiai might become a secondary source pollution of Lake Drūkšiai. In addition, these data identified sediments as more informative for the assessment of watersheds pollution than water.

3.2. TANNERY

Toxicity was assessed from both raw and treated IW of the tannery. It was found that the untreated WW was extremely toxic to *L. sativum*, *S. polyrrhiza* and *Tradescantia* clone 02 (Table 1). The same toxicity level was determined to *Tradescantia* clone 02 after treatment. The treated WW was very strongly toxic to *L. sativum* and moderately toxic to *S. polyrrhiza*. It can be concluded that sensitivity of *L. sativum* and *S. polyrrhiza* to the impact of substances present in tannery waste water differs. Previous investigations have demonstrated, that *L. sativum* is more sensitive to organic substances (Kazlauskienė et al., 2004), while *S. polyrrhiza* is more sensitive to the impact of heavy metals (Montvydienė and Marčiulionienė, 2004).

3.3. MUNICIPAL LANDFILL

It was found that untreated leachate water from a municipal landfill, water from reclamation ditches, and oxidation pond were toxic to *L. sativum*, however, the level of their toxicity differed (Table 1). Leachate water from the landfill and reclamation ditch (No. 1), closest to the leachate tank was extremely toxic. The 50% effective concentrations (EC50) for root growth of *L. sativum* of these samples were determined only after their 8 and 5 times dilution with distilled water, respectively. The sediments of leachate tank and reclamation ditches (No. 1) can be attributed to samples of extremely toxic and very strongly toxic to *L. sativum*, respectively, while water and sediments from the pond, which is used for recreation demands, were moderate toxic (Table 1, 2).

3.4. SCRAP METAL PROCESSING PLANT

Screening investigation of the phytotoxicity of various samples from scrap metal processing plant (SMPP), Sweden, demonstrated that SW from SMPP did not reduce seed germination of *L. sativum* in comparison with control, but in accordance with root growth inhibition tested SW can be attributed to the WW of slight toxicity (Table 3). It was found that water and sediments from the small stream which flow through the territory of SMPP (before storm water input) was slightly toxic and non-toxic, respectively, to *L. sativum* (Table 3).

TABLE 3. Toxic effects of various water and sediment samples at the scrap metal processing plant (SMPP, Sweden) in accordance with inhibition of root growth of *Lepidium sativum* (mean, %±SE)

Sampling point*	Water		Sediments	
Storm water at SMPP	SL	21.3±2.7	ST	44.4±3.8
Stream, upstream from SMPP industrial area	SL	13.4±2.9	NE	3.5±0.6
Stream, storm water input at SMPP industrial area	M	30.7±1.9	E	100
Stream, 60 m downstream from discharge point	M	34.4±3.8	–	–

*Sampling points are indicated in Karlavičienė et al., 2005; NE – no toxic effect; SL – slight toxic effect; M – moderate toxic effect; ST – strong toxic effect; E – extreme toxic effect; "–" not investigated.

However, the toxicity results of water and sediments from the stream after SW input were confounded, because they were strong and very strong toxic, respectively, to tested plant (Table 3). These results are rather difficult to interpret; maybe they are concerned with the different chemical forms of substances and combined effects of all compounds present in tested water and sediments.

3.5. DISCUSSION

The results showed that chemical substances with such toxic features in water maybe carried over rather distantly, because toxic effects of stream water 60 m down of SW input on *L. sativum* was similar in compare with effect caused by water from SW input site (Table 3). The SW from impervious surfaces of plant territory is collected in sedimentation tank. The storm water sludge was taken just before the annual removal of sediments. Depending on the impact to *L. sativum* this sludge can be attributed to sludge of strong toxicity (Table 3). Such toxicity maybe related with rather high concentrations of Cd, Cu, Pb, Zn, and Cr, which exceeded 3–70 times the limits specified in Directive 86/278/EEC (Karlavičienė et al., 2005). The effective concentration (EC50) for root growth of L. sativum of tested sludge was determined after 5 times dilution with distilled water. Investigations showed that SW from SMPP can be potentially hazardous to environment not only due to impact of heavy metals, but also due to their combined effects with oil, benzene, toluene, and etc. which can be contained in scrap metal.

The investigations clearly demonstrated that *L. sativum* and *Tradescantia* can be successfully used in the toxicity assessment of liquid or solid environmental component polluted in different degree. *S. polyrrhiza* can be successfully used in the testing of various liquid samples (included coloured and turbid). However, due to abundance of nitrogen and phosphorus, the growth of this plant become more intensive and can conceal effects of other pollutants and, consequently, can to twist the view of real situation in particular degree. *L. sativum* can be used as screening tests and as acute tests (seed germination and root growth), because of its simplicity, cheapness, and short duration; *S. polyrrhiza* is rather valuable as chronic tests (plant growth, various physiological parameters, and morphological alterations). *Tradescantia* is very sensitive test which can determine genotoxicity of tested sample when other tests do not indicate toxic effects. *L. sativum* and *S. polyrrhiza* demonstrated rather different sensitivity to tested samples of effluents, water and sediments, however, due to different duration of test, the time of plant contact with tested samples differ, consequently, distinguishing what test is more sensitive is not correct. However, it can be concluded that phytotoxicity tests have some advantages and are the same valuable as physical/chemical tools, because phytotoxicity test can help to characterise the sample, especially in cases when effluents, surface water, and sediments might be toxic, despite of the fact that it is lightly polluted. Hence, *L. sativum*, *S. polyrrhiza* and *Tradescantia* clone 02 can be successfully included in bioassays battery's applied in the environmental pollution assessment.

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MONITORING AND MODELLING PESTICIDE DYNAMICS IN SURFACE WATER

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Abstract. Pesticides occur frequently in surface water. We used a combination of monitoring and modelling to assess the fate of pesticides at the catchment-scale. We continuously (sampling interval of eight hours) monitored eight pesticides (atrazine, carbendazim, chloridazon, diuron, isoproturon, lenacil and simazine) in surface water of two Belgian catchments. The surface water showed hourly variations in pesticide concentrations, temporarily exceeding ecotoxicological thresholds. We used the SWAT model to predict hydrology and pesticide fluxes from agricultural land to the river at the catchment scale. In addition, we used an extended version of the RWQM1 model to calculate in-river transformation of pesticides. The models adequately reconstructed the highly dynamic behaviour of the pesticides in the river. The simulations further demonstrated the importance of point sources due to poor agricultural practices and the effectiveness of measures to reduce pesticide inputs into surface water.

Keywords: catchment; modeling; monitoring; pesticides; RWQM1; surface water; SWAT

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1. Introduction

Pesticides are useful to society thanks to their ability to exterminate disease-causing organisms and control insects, weeds and other pests. At the same time, pesticides may be harmful to humans, animals and the environment because of their ecotoxicity, their potential bio-accumulating properties or their anticipated hormone disrupting effects. To gain insight in the processes determining the fate of pesticides in river systems, monitoring and modelling are necessary tools.

Pesticides enter river systems via diffuse sources. As diffuse input pathways run-off, drainflow, drift, atmospheric deposition and groundwater flow can be distinguished. Based on modeling, Bach et al. (2001) showed that surface runoff is expected to be a major source of diffuse pesticide input in Germany. Non-point source input via preferential flow in soil is important in tile-drained structured soils (Leu et al., 2004) and spray-drift is rather specific for orchard regions (Bach et al., 2001). From field measurements, Kreuger (1998) found that inputs by drift or direct spraying were less important.

Pesticides can enter river systems as point sources, i.e., at punctual locations along the river. Examples of point sources of pesticides are sewage treatment plants, sewer overflows and direct inputs due to bad management practices of farmers. The contribution of point sources to pesticide pollution in river systems was demonstrated to be very important in several catchments in Europe. In different catchments in Germany (Neumann et al., 2002) with varying catchment sizes between 7 and 1940 km^2, in Switzerland (Gerecke et al., 2002; Leu et al., 2004), in Sweden (Kreuger, 1998), in the UK (Mason, 2003) and in Belgium (Beernaerts et al., 2005), it was shown that the load of pesticides in rivers could be attributed for 30 up to 90% to point sources.

In view of the risk assessment of pesticides under the EU Plant Protection Products Directive (91/414/EEC) and in view of the river basin management plans in the EU Water Framework Directive (2000/60/EC), a clear need exists to realistically predict surface water concentrations of pesticides. To this purpose, both monitoring and modelling pesticide fate at the appropriate temporal and spatial scales is necessary. In the next paragraphs, we will demonstrate this with a few cases of pesticide pollution in Belgian rivers.

2. Pesticide Monitoring

To date, very few studies looked at the short-term dynamics of pesticides in river water (Kreuger, 1998; Neumann et al., 2002; Leu et al., 2004; Beernaerts et al., 2005). Besides the temporal variation of pesticide concentrations in river systems, there is also spatial variation. Upstream river stretches in agricultural areas are more likely to be exposed to higher pesticide concentrations (Leu et al., 2004; Konstantinou et al., 2006).

2.1. MONITORING DESIGN

We focused on 6 herbicides and 1 fungicide, that are (or were, in the near past) found in high concentrations in Belgian surface waters (Beernaerts et al., 2005; Flemish Environment Agency, 2007). Two typical rural catchments in Belgium, mainly receiving water from agricultural fields, were sampled. Major crops grown were corn, sugar beat, winter wheat and orchards.

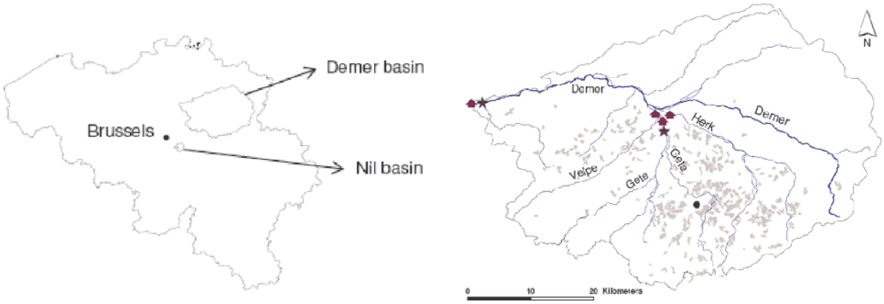

Figure 1. Geographical location of the sampling stations

In the 32 km^2 Nil basin (Figure 1a), an intensive monitoring campaign was conducted between March 15th and June 15th 2004. Two refrigerated sampling stations took 50 ml river water samples every 15 minutes and collected the water in a composite sample every 8 hours along the river: one upstream and one at the outlet of the catchment. During rainfall events, the frequency was increased and each composite sample then represented 6 hours. In the 2100 km^2 Demer basin, a similar campaign was set up in 2005 from May 15th till July 1st. On four locations in the Demer basin (Figure 1b), sampling stations were placed. The pesticides were analyzed using LC-MS/MS after extraction over an on-line SPE (solid phase extraction) unit and after detection in multiple reaction monitoring mode (MRM) using positive ion electrospray.

Daily rainfall data for the meteorological stations in Chastre-Blanmont and Sint-Truiden were obtained from the Royal Meteorological Institute (RMI) and hourly discharge data were made available by DGRNE (Direction Génerale des Ressources Naturelle et de l'Environnement) for the Nil and by the HIC (Hydrological Information Centre) for the Demer.

2.2. MONITORING RESULTS

The measured pesticide concentrations for the Nil (small scale, tens of km^2) and Demer (larger scale, hundreds to thousands of km^2) catchment are represented in Figure 2.

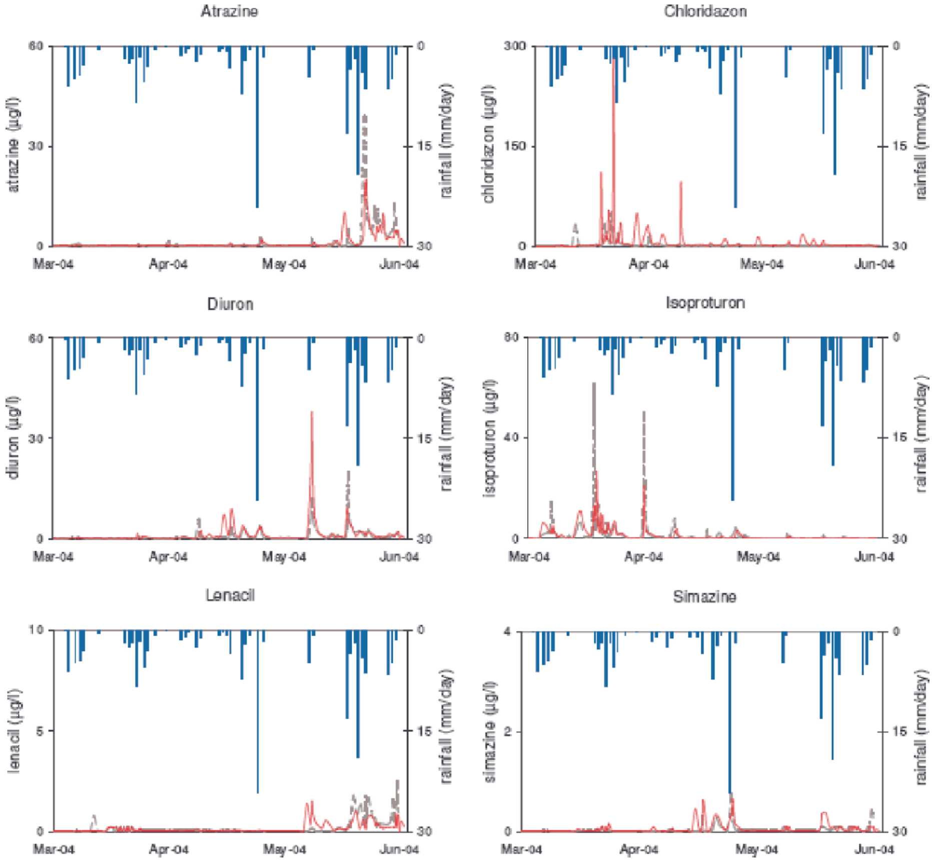

Figure 2. Subdaily pesticide concentrations in (a) the Nil, a small-scale catchment (tens of km^2) and (b) the Demer, a larger-scale catchment (thousands of km^2). In the Demer, the solid line represents the concentrations at the outlet, whereas the broken lines refer to pesticide concentrations in the upstream tributaries

The results show extremely dynamic pesticide concentrations in surface water. The concentration fluctuations are the largest in the small-scale catchment. High pesticide concentrations could be found in the river after application and rainfall, and are mainly attributed to runoff. Even larger peaks were observed in the absence of rain immediately after application. We attribute these peaks to direct input of pesticides to the water system due to the clean-up of spray equipment, leaking tools, processing of spray waste, and application on paved surfaces. In Figure 2 such an event can be seen for chloridazon around the 15th of April: there is a period without rain, but still high chloridazon concentrations were observed. It can be shown that 30 to 95% of the total annual pesticide load passing in the small catchment could be attributed to point sources.

Similar to small-scale catchments, the pesticide concentrations show a highly variable course in the larger-scale catchments. Nevertheless, the maximum concentrations for all observed pesticides at all monitoring stations in the larger-scale catchment are lower than those measured in the small-scale catchment, except for simazine. The importance of point sources can be assessed for pesticides that were applied during the monitoring campaign, i.e., atrazine, carbendazim, diuron, lenacil and simazine. High concentration peaks originating from point sources are clearly visible for atrazine around mid June. The results also clearly show an effect of dilution along the larger-scale catchment: the concentration peaks are higher and more narrow in the upstream tributaries as compared to those seen downstream, which are more suppressed and spread out due to dilution and dispersion.

In summary, high-frequent monitoring reveals that pesticide concentrations in surface water show an extremely dynamic behaviour, which can be explained to a certain extent by rainfall/runoff characteristics of the catchment, but to a large extent also by point sources. This causes pesticide concentrations in surface water in the application period to follow a random pattern. This random behaviour determines the design of monitoring programmes of pesticides in surface water. Given the large variability in pesticide concentrations during application, a sufficient number of samples needs to be taken in order to estimate the true water quality status with an acceptable certainty. For example, atrazine showed a coefficient of variation of 92% based on the high-frequent monitoring in the Demer catchment in June 2005. A total number of 34 samples needs to be taken to state with a confidence of 95% that the true mean water quality for that period lies between 346 and 620 μg/L, or an accuracy of 28% (relative to the mean). The selection of the desired level of accuracy depends on the measurement accuracy. If one wants 20% accuracy, a number of 67 samples would be needed. When there is no clear trend in the concentrations, time-series of pesticide concentrations during application over multiple years may be used to determine the true water quality.

3. Pesticide Modelling at the Catchment Scale

A whole range of models exist that predict pesticide concentrations in river systems. They range from rather simple screening tools to complex catchment or watershed models. Watershed models are useful for analyzing long-term effects of hydrological changes and water management practices, e.g., AnnAGNPS (Bingner and Theurer, 2001), HSPF (Donigian et al., 1993) and the Soil and Water Assessment Tool SWAT (Arnold and Fohrer, 2005). SWAT is a model for continuous simulations in predominantly agricultural watersheds and HSPF is suited for mixed agricultural and urban watersheds. MIKE SHE (Refsgaard and Storm, 1995) is both a single-event and long-term continuous simulation model. MIKE SHE is suitable for small areas or watersheds for studies of hydrology and non-point-source pollution (Borah and Bera, 2003). The new generation of models includes fully-coupled watershed models. Three fully-coupled numerical models are currently available, namely InHM (Loague et al., 2004), MOD-HMS (Panday and Huyakorn, 2004), and HydroGeoSphere (Sudicky et al., 2005). The main distinguishing feature of these models is that they fully couple the surface and subsurface hydrologic domains by simultaneously solving one system of non-linear discrete equations describing flow and transport in both flow regimes.

3.1. MODELLING SETUP

We selected the SWAT model to calculate pesticide fluxes from agricultural land to the river in the small Nil catchment. SWAT simulates pesticide movement into the stream network via surface runoff (in solution and sorbed to sediment transported by the runoff), and via percolation in the soil profile and transport through the aquifer. The movement of the pesticide is controlled by its solubility, degradation half-life, and soil organic carbon adsorption coefficient. Pesticides on plant foliage and in the soil degrade exponentially according to the appropriate half-life. Pesticide transport by water and sediment is calculated for each runoff event and pesticide leaching is estimated for each soil layer when percolation occurs.

We used an extended version of the RWQM No. 1 model (Reichert et al., 2001) as implemented in the WEST modeling and simulation software (MOSTforWATER NV, Kortrijk, Belgium) to model in-river transformation processes from one location in the river to a downstream location. The advantage of using RWQM No. 1 instead of SWAT for modelling pesticide processes in the river lies in the fact that it has closed elemental mass balances and that it explicitly considers microbial biomass as a state variable. A better accounting of biological activities will also affect the way the environmental conditions in the river change (e.g., pH, dissolved oxygen concentration) which may influence the fate of the pesticide in the water column. Another advantage of RWQM No. 1 lies in its capability to study the fate and behaviour of different pesticides at the same time while the SWAT model can only route one pesticide at a time. With the RWQM1 model very small time steps can be used (e.g., minutes) compared to the SWAT model which uses daily or hourly (ESWAT) time steps. For modeling sedimentation and resuspension processes, and follow the fast pesticide concentration dynamics, this an important advantage.

3.2. MODELLING RESULTS

3.2.1. Pesticide Fluxes to the River

The first step in watershed modelling of chemicals is to get hydrology well simulated. Figure 3 shows the calibrated model results for discharge at the outlet of the small Nil catchment. The model is specifically calibrated for the spring period, since most herbicides were applied and monitored during that period. Generally, a good fit is obtained between observed and modelled discharge. The most sensitive parameter in the model was the curve number, an empirical parameter that accounts for rainfall/runoff properties of the landscape. Since the Nil catchment shows a distinct topography and is not tile-drained, hydrology is dominated by surface runoff properties.

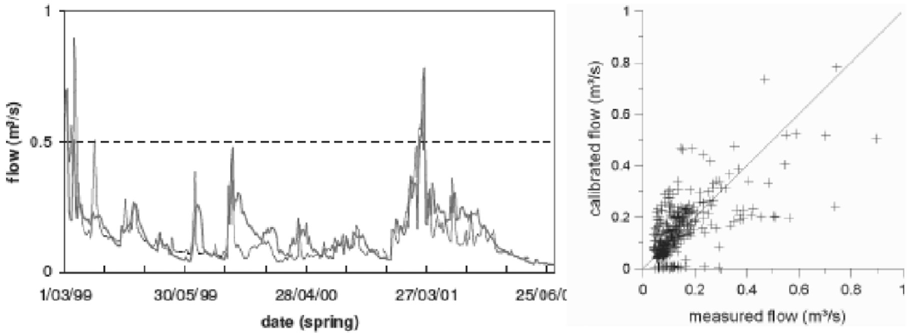

Figure 3. Calibrated model predictions for discharge in the spring period in the small catchment

To account for point sources of pesticides to surface water, adaptations to the original SWAT model were needed. To check model performance, the SWAT model results were compared to the results of the intensive monitoring campaign performed during the years 1998–2002. The results are shown in Figure 4. Calibration was performed for 1998, while 1999 up to 2002 were used to validate model predictions. A relatively good approximation of the pesticide concentrations, e.g., the lower concentrations in 2001, and representation of the concentration pattern was obtained with the model.

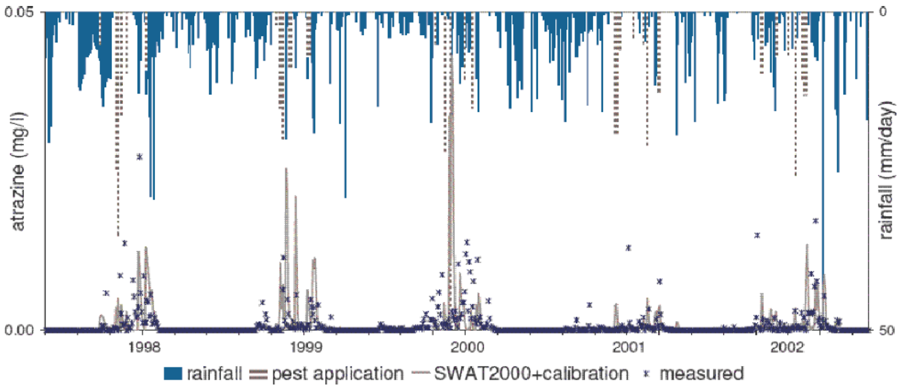

Figure 4. Measured and predicted atrazine concentrations at the catchment outlet after calibration (spring periods of 1998–2002)

The validated SWAT model was subsequently used to quantify the loads resulting from run-off, atmospheric drift, and point sources. The results show that the total atrazine load to the river represents 1.5–2.2% of the amount applied in the catchment (2001 showed 0.3% lost). This is in good agreement with the measured quantities. The model further shows that 9–38% can be attributed to point sources, which underestimates the estimated real load (assumed in dry periods) of 39–54%. This is due to the sensitivity of the model to hydrology: overpredictions of flow lead to underpredictions of pesticide concentrations. A negligible load can be attributed to drift. The validated SWAT model was further used to quantify the effect of agricultural measures on pesticide fluxes to the river, such as residue management, sowing cover crops, buffer strips, strip cropping or contour farming. Preliminary calculations show that strip cropping is more efficient in reducing pesticide loads than buffer strips or residue management. Since the soil processes in SWAT are described empirically, the results are qualitative and can be used for ranking measures, not for quantifying them.

3.2.2. Pesticide Transformation in the River

Predictions of pesticide concentrations at the outlet of the Nil catchment were made using the extended RWQM No.1 model. The measured concentrations in the upper reaches of the river were taken as upper boundary condition for the model. The results are shown in Figure 5.

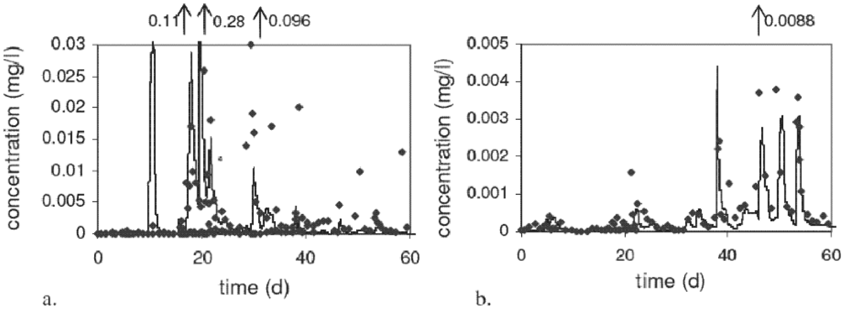

Figure 5. Predicted surface water concentrations of (a) chloridazon and (b) diuron at the outlet of the Nil catchment based on measured concentrations 8 km upstream

The model predicts the concentrations at the outlet extremely well without extensive calibration. In this case, the outlet concentrations are determined to a large extent by the measured concentrations upstream, rather than additional processes or fluxes along the 7-km-river stretch. River processes will become much more important in larger catchments where rural subcatchments deliver pesticides that are further diluted and degraded in the river downstream.

4. Conclusions

Pesticides occur in surface waters in a highly dynamic pattern, resulting from the distinct pesticide applications during the season and from rainfall events. Monitoring programmes of pesticides and other priority chemicals should take this dynamic behaviour into account. Pesticides end up in the rivers due to diffuse sources but to a large extent also due to point sources. This causes pesticides to occur randomly in rivers during the period of application. Given the large temporal variability, a sufficient number of samples needs to be taken to adequately represent water quality.

Catchment models such as SWAT are able to reproduce the dynamics of pesticides in the river. SWAT showed the importance of runoff and point sources and the relative unimportance of drift in a small Belgian catchment. The model also allowed to rank various management options to reduce pesticide loads. Modelling the river system using RWQM1 further showed that in-river processes are relatively unimportant in small catchments.

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METHODS FOR TOXICITY TESTING OF XENOBIOTICS IN WASTEWATER TREATMENT PLANTS AND IN RECEIVING WATER BODIES

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Abstract. This paper focuses on conventional and advanced promising methods for the evaluation of toxicity originated by xenobiotics in WWTPs and surface waters. A concise review about toxicity tests applied to activated sludge and to receiving water bodies was presented. Advantages or limitations of the methods were discussed. Both heterotrophic and nitrifying activity were considered. Experimental results on the application to activated sludge of conventional toxicity tests (based on respirometry and bioluminescence) and advanced methods (based on the direct quantification of viable or dead bacteria by using flow cytometry) were presented in this paper. The advantage of respirometry and flow cytometry is related to the use of bacteria present in WWTPs, without need of using pure bacterial strains different from activated sludge.

Keywords: activated sludge; bioluminescence; flow cytometry; heterotrophic activity; inhibition; nitrification; respirometry; surface water; toxicity; xenobiotics

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1. Introduction

The presence of toxic xenobiotics in the sewerage reaching a wastewater treatment plant (WWTP) may cause (A) a partial inhibition of activated sludge, reducing the rate of biological kinetics and worsening the effluent quality and (B) a further impact on the quality of the receiving water body when refractory xenobiotic compounds are not degraded in the WWTP.

The bacteria inhibition induced by toxic chemicals may be caused by the formation of a stable complex with an enzyme, a receptor site or others, or by physico-chemical changes in pH, redox, etc. Among effects produced by the exposure of microorganisms to harmful chemicals, possible actions are:

- damage or strong permeabilization of cell structure, followed by cell lysis;
- inhibition of cell metabolic activity, such as respiratory activity, intracellular enzyme activity or membrane potential;
- blocking of cell replication.

The effect of toxicants against single environmentally relevant bacteria species such as *Vibrio fischeri* was widely investigated, but many contributes indicate that the correct evaluation of the inhibitory effect should be performed directly against the mixed bacteria populations present in activated sludge or surface waters. Furthermore the same microorganisms present in different natural environments can differ significantly in their physiological status; while mixed populations inside the activated sludge can undergo an acclimatization process, when xenobiotics enter WWTPs habitually.

This paper focuses on the alternatives for measuring toxicity on activated sludge in WWTPs and surface water, comparing advantages and limits of the methods. Some experimental results are described and compared: a simplified method (based on respirometric techniques), an advanced approach (based on flow cytometry) and a conventional bioluminescence bioassay (based on *Vibrio fischeri*). The common xenobiotic compound 3,5-dichlorophenol was tested in the proposed methods.

2. Methods for Toxicity Testing on Activated Sludge in WWTPs

A considerable number of different tests have been proposed in the scientific literature for assessing toxicity on biological treatment systems. A review on toxicity methods was published in 2000 by Water Environment Research Foundation (WERF, Love and Bott, 2000), where the criteria for influent wastewater toxicity monitoring methods and suggested research needs were addressed. Recently Ren (2004) described the most recent research and developments in methods for assessing wastewater toxicity on activated sludge.

The following categories of methods are briefly described:

1. methods based on respirometry: applicable directly to activated sludge, for measuring both heterotrophic and nitrifying respiration rate;

- methods based on bioluminescence: application of bioluminescent bacteria, different from activated sludge;
- methods based on ATP luminescence: cellular ATP content of activated sludge is measured as indicator of bacteria activity;
- methods based on enzyme assays: chromogenic substrates are used to monitor enzymatic reaction in activated sludge;
- methods based on cell counting: applicable to quantify reproductive growing bacteria;
- methods based on flow cytometry: specific properties of bacterial cells (membrane integrity or permeabilisation, membrane potential, …) present in activated sludge can be directly monitored by binding cells with fluorescent probes and quantifying stained bacteria rapidly with flow cytometry;
- methods for evaluating inhibition on nitrification: based mainly on respirometry, titration methods or on ammonia dynamics.

Most part of these methods are aimed to the analysis of specific functions of the whole bacterial communities in activated sludge, by using methods such as oxygen consumption rate (respirometry), ATP luminescence or enzymatic activity. Other approaches are aimed to the analysis at single-cell level by using direct methods, such as conventional plate counts for measuring replication ability of bacterial cells, or the advanced technique of flow cytometry for discriminating specific functions of bacterial cells. The main advantage of this advanced techniques is the application of highly selective methods revealing changes in some specific functions of bacterial cells with high sensitivity.

All bioassays introduced above allow to measure short-term inhibitions, observable in the sample immediately or within few hours. Information about long-time inhibition on WWTPs microorganisms is scarce in the literature.

2.1. METHODS BASED ON RESPIROMETRY

Respirometric techniques have been used widely to test the toxicity effects of different pollutants on activated sludge (*inter alia*, Volskay and Grady, 1990; De Bel *et al.*, 1996). In general a respirometric method is based on the continuous measurement of the microbial consumption of dissolved oxygen (DO) in lab reactors or on-line devices. Respiratory activity inhibited by the presence of a toxic compounds results in a decrease in oxygen consumption rate. Respirometric measurements are considered quite meaningful, since they instantaneously express the response of sludge to any change in its metabolic conditions. The great advantages of respirometry for assessing inhibition effects is the use of bacteria present in activated sludge instead of pure strains coupled with the simplicity of equipment and procedures.

In closed respirometers, the DO utilization rate is expressed through the OUR parameter (Oxygen Uptake Rate), calculated as the slope of the straight line fitting the decrease of DO concentration versus time. Respirometric tests can be carried out by measuring a single OUR and without aeration during the test (single-OUR test), or by measuring an entire respirogram (multi-OUR test) made up of several subsequent OUR and re-aerations.

Single-OUR test is more rapid than multi-OUR and more suitable to test volatile compounds, due to the absence of forced aeration. On the other hand multi-OUR offers the possibility to monitor the respirogram for several hours, evaluating the toxicity during a period as long as the hydraulic retention time in the WWTP reactors. Ricco *et al.* (2004) have proposed to utilise pure oxygen at the beginning of the test for increasing DO concentration over the saturation value. In this way the test duration can be significantly prolonged without the need of providing aeration, as done in multi-OUR test.

ISO 8192 test (ISO, 1995) and the OECD 209 method (OECD, 1987) are proposed as standardized water quality-tests for evaluating inhibition of oxygen consumption in activated sludge.

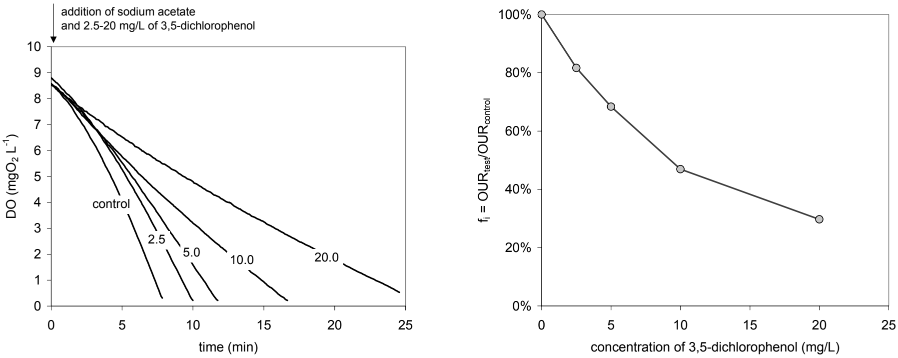
Single-OUR respirometry was compared with multi-OUR respirometry for assessing inhibition of 3,5-dichlorophenol on heterotrophic and nitrifying bacteria in activated sludge, using a series of closed respirometers, made up of a temperature controlled 2-Litres reactor. Aeration and mixing are guaranteed by compressed air and magnetic stirrer. Dissolved oxygen was monitored by an oxymeter (OXI 340, WTW) connected to a data acquisition system. OUR is measured during programmed phases without aeration. The results are described in the following chapters.

2.1.1. Single-OUR Respirometry

For evaluating inhibition of heterotrophic biomass, the following procedure was carried out. The control run (without toxicant) started with the dosage of sodium acetate as readily biodegradable organic carbon source (30 mgCOD/L), while the test run contained sodium acetate and the toxicant (3,5-dichlorophenol). ATU was added in both the runs. OUR value in the test run ($\mathrm{OUR_{test}}$) was compared with OUR value in the control run ($\mathrm{OUR_{control}}$):

$$f_i = \frac{\mathrm{OUR_{test}}}{\mathrm{OUR_{control}}} \cdot 100 \tag{1}$$

where f_i is expressed as percentage and assumes value from 1 (no inhibition) to 0 (total inhibition).



(A)

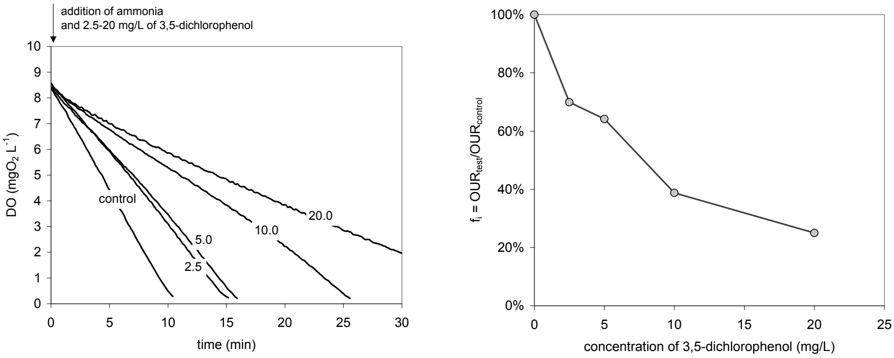
(B)

Figure 1. (A) Dynamic of DO concentration resulting from single-OUR tests carried out at different concentrations of 3,5-dichlorophenol (between 2.5 and 20 mg/L) and (B) f_i curve on heterotrophic biomass in activated sludge

OUR$_{test}$ was calculated as the slope of the straight line of each curves indicated in figure 1A. For example the slope measured of 10 mg/L of 3,5-dichlorophenol is approximately two-fold minor than the control.

Figure 1B shows f_i dependence by 3,5-dichlorophenol concentration.

For investigating inhibition of nitrifying bacteria the same procedure without ATU was applied, replacing reference substrate sodium acetate with ammonia (3 mgN/L). The results obtained testing 3,5-dichlorophenol in the range 2.5-20 mg/L are shown in figure 2.



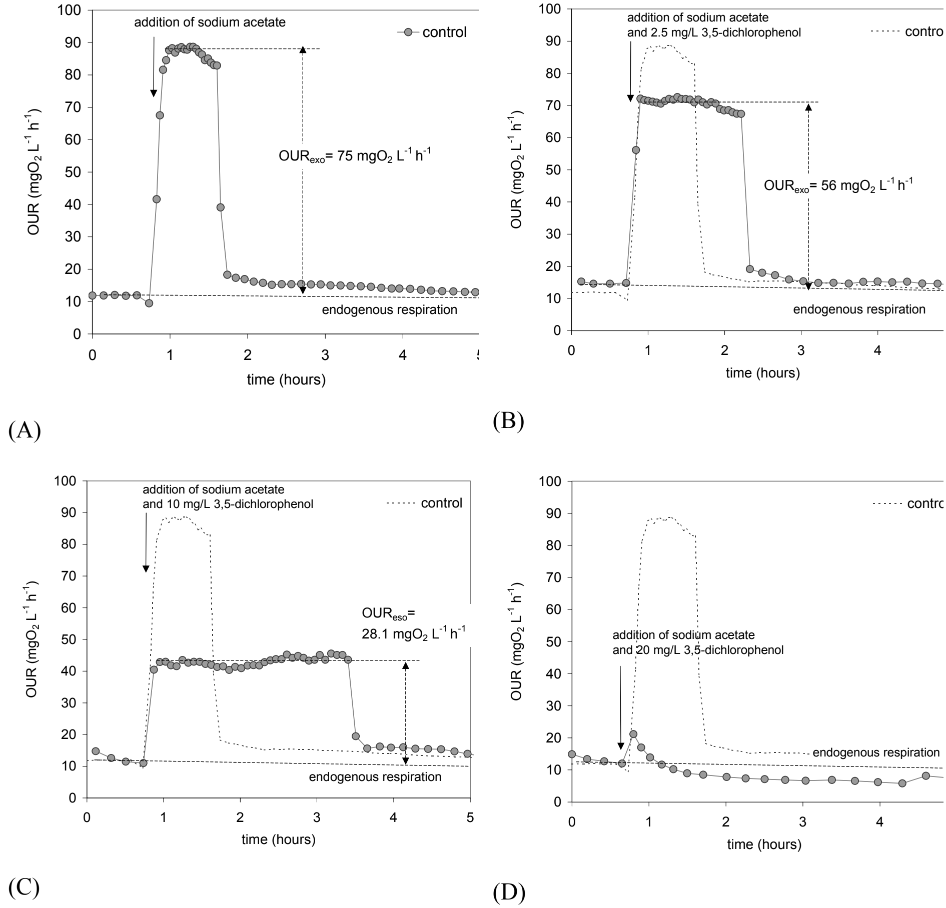
(A)

(B)

Figure 2. (A) Dynamic of DO concentration resulting from single-OUR tests carried out at different concentrations of 3,5-dichlorophenol (between 2.5 and 20 mg/L) and (B) f_i curve of nitrifying biomass in activated sludge

Both heterotrophic biomass and nitrifying bacteria showed a significant inhibition against 3,5-dichlorophenol.

With using single-OUR test for evaluating nitrification rate, it may result difficult to distinguish nitrification oxygen demand from oxygen demand due to oxidation of biodegradable COD. This problem can be overcome by comparing oxygen consumption before and after ATU addition (Gernaey *et al.*, 1997). The contribute of nitrification alone can be calculated as the different between these two values.



(A) (B)

(C) (D)

Figure 3. (A, B, C, D) Respirograms obtained for different concentrations of 3,5-dichlorophenol between 0 and 20 mg/L

2.1.2. Multi-OUR Respirometry

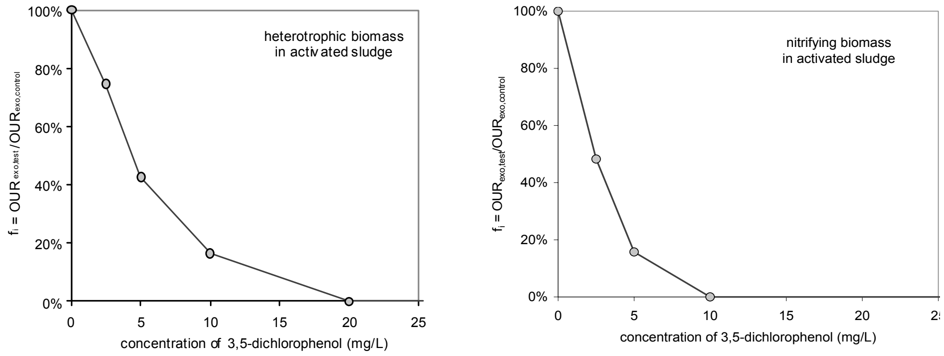
In the case of multi-OUR test the exogenous and the endogenous respiration can be considered separately. With regards to heterotrophic biomass, the control run (without toxicant) was carried out with the dosage of sodium acetate (around 300 mgCOD/L), while the test run contained sodium acetate and 3,5-dichlorophenol. ATU was added in both the runs. When sodium acetate was added to activated sludge an immediate increase of OUR value was observed reaching a quite horizontal plateau. Without toxicant, the maximum exogenous OUR (OUR_{exo}) is equal to 75 mgO_2/L^{-1} h^{-1}, as indicated in figure 3A. With addition of 2.5 mg/L of 3,5-dichlorophenol the horizontal plateau decreased at 56 mgO_2/L^{-1} h^{-1} (figure 3B) and COD oxidation required a longer period.

In figure 3 B-D respirograms obtained for different dosages of 3,5-dichlorophenol together with OUR profile of endogenous respiration before toxicant addition are indicated. Increasing the concentration of 3,5-dichlorophenol the plateau of exogenous respiration (OUR_{exo}) decreased progressively. In figure 3B and C the plateau relative to the maximum exogenous OUR was well defined, while in figure 3D disappearance of the horizontal plateau and reduction of the endogenous respiration were observed at 20 mg/L of 3,5-dichlorophenol.

Inhibition was calculated with the same expression indicated above in Eq. 1:

$$f_i = \frac{OUR_{exo,test}}{OUR_{exo,control}} \cdot 100 \qquad (2)$$

where $OUR_{exo,test}$ and $OUR_{exo,control}$ are the maximum value of exogenous respiration measured in the test run and in the control run respectively.



(A) (B)

Figure 4. (A) f_i curve on heterotrophic biomass in activated sludge; (B) f_i curve on nitrifying biomass in activated sludge

The f_i curve of 3,5-dichlorophenol on heterotrophic biomass in activated sludge, resulting from the respirograms shown in figure 3A-D, is indicated in figure 4A. Multi-OUR test with nitrifying bacteria were carried out similarly to the procedure described above. Respirograms were obtained dosing ammonia (40 mgN/L) as standard substrate for reaching the maximum nitrification rate. Sodium bicarbonate was added to avoid pH decrease. Inhibition was evaluated from each respirogram: the maximum exogenous OUR ($OUR_{exo,test}$) was calculated and compared with the $OUR_{exo,control}$ measured in the test without toxicant. The resulting f_i curve on nitrifying biomass is shown in figure 4B.

The interpretation of the respirograms could be more complicated in presence of toxic wastewaters containing biodegradable COD; in this case the oxygen consumption is related to both oxidation of biodegradable COD and to nitrification.

2.2. METHODS BASED ON BIOLUMINESCENCE

The most common *Vibrio fischeri* bioassay is based on freeze dried cells of this marine organism. The decrease in light emission was used for evaluating the inhibition of the bacterial metabolic activity.

The application of bioluminescent bacteria for monitoring toxicity on activated sludge is controversial, being this method too much sensitive. This greater sensitivity shown by *V. fischeri* might be due to sorption effects within the activated sludge. In fact the sludge matrix may favorite the sorption and immobilisation of chemical pollutants onto and within particulate substances, reducing inhibition when using activated sludge (Dalzell *et al*., 2002). However further work should be carried out to determine whether and when *V. fischeri* may be used as a potential model for evaluating activated sludge susceptibility.

Guitérrez *et al.* (2002) find higher sensitivity to toxicants in the bio-uminescence bioassay with respect to respirometry. Ricco *et al.* (2004) suggested a greater tolerance to toxic compounds observed in respirometric tests with respect to pure culture of marine microbial species (Microtox®) due to heterogeneity and more variable growth environment in activated sludge.

An example of the f_i curve on 3,5-dichlorophenol evaluated with a bioluminescence bioassay (LUMIStox, Lange) is indicated in figure 5 (contact times: 15 and 30 minutes).

2.3. METHODS BASED ON ATP LUMINESCENCE

Adenosine triphosphate (ATP), being present in all living cells, is an indicator of metabolic activity and/or active biomass. The quantification of ATP content was proposed as a toxicant screening test in activated sludge. Toxic compounds affecting bacteria induce changes in cellular ATP content; ATP is rapidly destroyed in dead organisms. Samples of activated sludge are incubated for 30 minutes in presence of the toxicant and then ATP is extracted from cells and quantified in a luminometer (Dalzell *et al.*, 2002; Dalzell and Christofi, 2002).

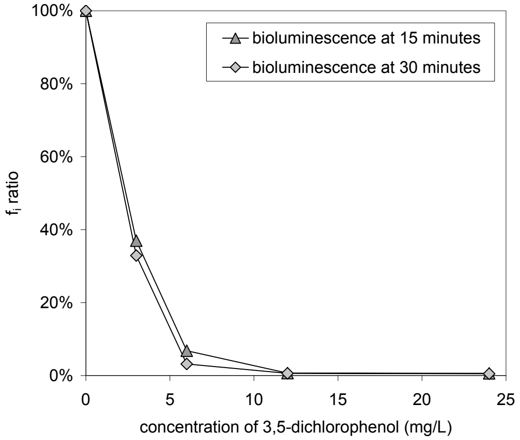


Figure 5. f_i curve determined by bioluminescence bioassay

2.4. METHODS BASED ON ENZYME ASSAYS

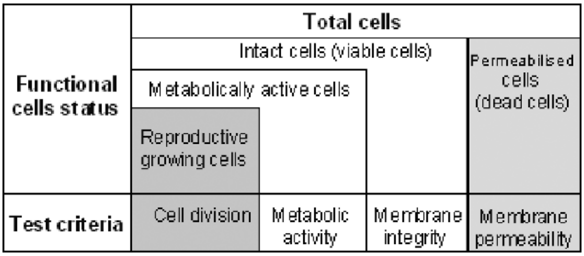
Dalzell *et al.* (2002) investigated inhibition of L-alanine-aminopeptidase, a central metabolic enzyme of the proteolytic pathway of gram-negative bacteria. Activated sludge was exposed to the inhibitor compound together L-alanine-4-nitroanilide hydrochloride, a chromogenic substrate solution. The concentration 4-nitroaniline, resulting from the enzymatic activity is related to the toxic effect.

2.5. METHODS BASED ON CELL COUNTING

Conventional techniques based on CFU counts require a delay of 24 to 48 h after plating. Effect of toxic substances on cell division could be performed detecting changes in colonies enumeration, but few cells are recoverable by standard cultivation methods, considering that a part of cells may be viable despite their inability to form colonies. The dissociation between viability and ability to form colonies was clarified introducing the existence of a "viable-but-not-culturable" state (Nebe-von-Caron *et al.*, 2000). Therefore plate counts are thought to underestimate the total number of viable microorganisms due to the presence of some bacteria in a viable-but-not-culturable state. In wastewater or activated sludge, culturable bacteria are only a small part of total bacteria, significantly less than 5–15% (Wagner *et al.*, 1993; Amann *et al.*, 1995).

2.6. METHODS BASED ON FLOW CYTOMETRY

- The categorisation of physiological states of bacteria (Nebe-von-Caron *et al.*, 2000) is shown in Figure 6.



	Total cells			
Functional cells status	Intact cells (viable cells)			Permeabilised cells (dead cells)
	Metabolically active cells			
	Reproductive growing cells			
Test criteria	Cell division	Metabolic activity	Membrane integrity	Membrane permeability

Figure 6. Categorisation of physiological states of bacteria according to by Nebe-von-Caron *et al.* (2000)

Microbial cell properties indicated in figure 6 can be investigated by means of fluorescent staining dyes specifically designed to bind with peculiar cell components.

Toxic substances, interacting with some cellular properties, modify functional cell status. In the case of cellular membrane damage, cells become permeabilised and therefore are classified as dead. The cell uptake of certain classes of impermeant compounds – fluorescent nucleic acid binding dyes such as propidium iodide, TO-PRO-3 and Sytox Green –indicates cell death. On the contrary, integrity of the membrane to such dyes has been used as the main indicator of viable cells.

The polarisation of cells (reduction of the normal membrane potential) may occur or enzymatic activity may be reduced significantly as effect of toxic compounds. Several fluorescent dyes may be used to evaluate changes in the membrane potential of bacteria: cyanine dyes including DiOC2(3) or oxonol dyes including DiBAC4(3).

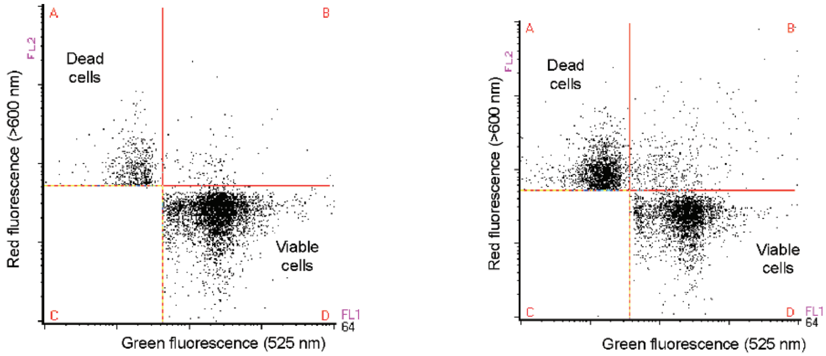
Metabolically active cells can be distinguished on their ability to hydrolyse fluorogenic substrates such as fluorescein diacetate (FDA), or alternatively cFDA, BCECF-AM and others recently developed molecules. FDA enter both viable and dead cells, where it is enzymatically hydrolysed by non-specific esterases with release of fluorescein molecules. Fluorescein is retained into viable cells, resulting in the emission of green fluorescence, while is leached from dead cells. Substances able to inhibit enzymatic activity hydrolyse significantly less amount of FDA (less fluorescence emission).

Toxicants may inhibite cell division, without altering membrane integrity and metabolic activity. To demonstrate cells uptake of fluorescence dyes epifluorescence microscopy or flow cytometry can be used. Observations under microscope require few hours to quantify bacteria in a single sample, while flow cytometry takes few minutes for processing a sample. Flow cytometry, being a cultivation-independent technique, allows to preserve bacteria in a state which does not much differ from that in life.

Flow cytometry has been widely applied for investigating inactivation of pathogens by antibiotics and antibacterial substances by monitoring growth kinetics inhibition. New is the application for investigating environmental bacteria inhibition by toxicants and xenobiotics.

An example of the evaluation of death and viability of bacterial cells in activated sludge after the addition of 3,5-dichlorophenol is described here. In this context the term “viable” is used as synonymous of “integer” cells, that are cells with an integer membrane, discriminated by means of the double staining with SYBR-Green I (SG-I) and propidium iodide (PI), according to the procedure described by Ziglio *et al.* (2002).

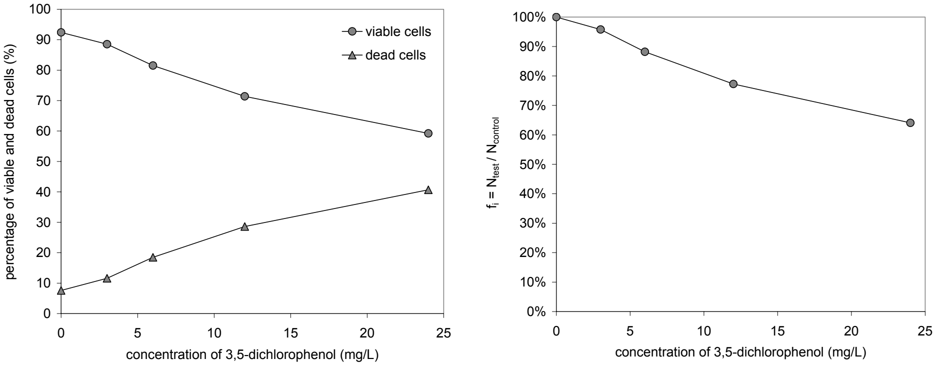
The interpretation of the flow cytometric analysis was performed by means of cytograms, in which green fluorescence was plotted vs. red fluorescence. Viable cells are characterised by a predominant level of green fluorescence (emission wavelength, λ_{em} = 525 nm) due to the staining of SG-I, but without PI emission. On contrary, dead cells exhibit red fluorescence (emission wavelength, λ_{em} > 600 nm), because the simultaneous staining of nucleic acid by SG-I and PI causes the phenomenon of energy transfer. Two examples of cytograms are indicated in figure 7. The cytogram in figure 7A refers to activated sludge without toxicant, while cytogram in figure 7B refers to activated sludge after addition of 24 mg/L of 3,5-dichlorophenol.



(A) No dosage of 3,5-dichlorophenol (control) (B) 24 mg/L of 3,5-dichlorophenol

Figure 7. Cytograms of viable and dead cells in activated sludge: (A) without toxicant; (B) with the addition of 24 mg/L of 3,5-dichlorophenol

In the control test (figure 7A) 92,4% of cells were viable, while the remaining 7.6% represents dead cells. As shown in figure 7B, the percentage of dead cells increased up to 40.7% when 24 mg/L of 3,5-dichlorophenol was added, demonstrating cellular membrane permeabilization. The percentage of viable and dead cells, calculated with respect to the total number of cells (viable + dead) are indicated in figure 8A, as a function of the dosed concentration of 3,5-dichlorophenol. Percentages of viable cells decreased quite linearly with the increasing of 3,5-dichlorophenol dosage, because of the progressive cell death.



(A) (B)

Figure 8. (A) percentage of viable and dead cells as a function of concentration of 3,5-dichlorophenol; (B) f_i curve of 3,5-dichlorophenol on activated sludge

Inhibition was calculated with an expression similar to that indicated in Eq. 1, substituting OUR with the number of viable cells:

$$f_i = \frac{N_{test}}{N_{control}} \cdot 100$$

where N_{test} and $N_{control}$ are the number of viable cells in the test run (with toxicant) and in the control run (without toxicant) respectively. The f_i curve of 3,5-dichlorophenol evaluated by flow cytometry is shown in figure 8B.

2.7. METHODS FOR TESTING INHIBITION OF NITRIFICATION

In general methods for evaluating inhibition of nitrification are based on:

- measurement of the consumption of ammonia and/or production of nitrite and nitrate;
- monitoring of the amount of a base added for maintaining pH around a constant value in the reactor;

- measurement of the oxygen uptake rate associated with the oxidation of ammonia.

The first approach is the most broadly applied method, but is quite time-consuming. Inhibition leads to accumulation of ammonia (and eventually nitrite) and to reduction in nitrate production. A standardised test is the ISO 9509 (ISO 1989). With regards to xenobiotic substances, such as pharmaceuticals, some observations are referred to by Halling-Sørensen (2001).

2.8. COMPARISON OF INHIBITION CURVES OF 3,5-DICHLOROPHENOL MEASURED BY RESPIROMETRY, FLOW CYTOMETRY AND BIOLUMINESCENCE

Figure 8 shows the comparison among the inhibition curves of 3,5-dichlorohenol, obtained by using three different approaches: (1) single-OUR and multi-OUR respirometry, (2) bioluminescence bioassay and (3) analysis of viable cells with flow cytometry. In this figure the percentage of inhibition was calculated as the difference (100-f_i).

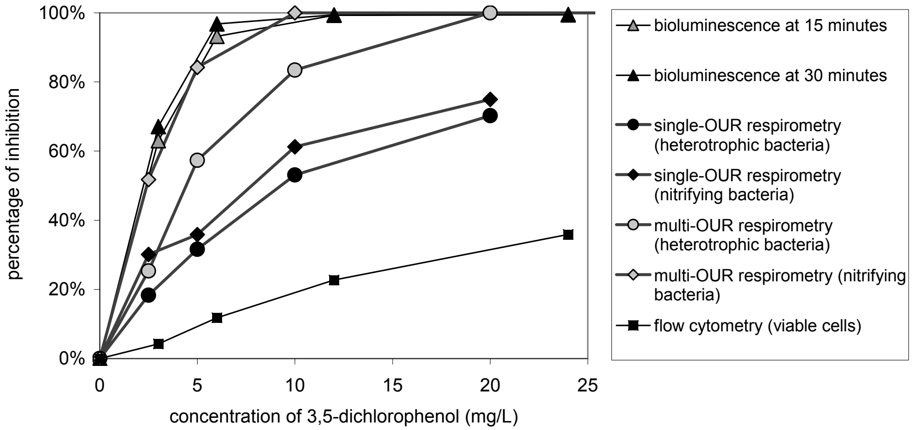


Figure 9. Comparison among inhibition curves determined by single-OUR and multi-OUR respirometry, bioluminescence and flow cytometry

All methods respond to toxicant. Bioluminescence bioassay and respiroetry were more sensitive with respect to the flow cytometric analysis. The addition of 3,5-dichlorophenol affected membrane integrity causing the death of a fraction of cells (30% at 20 mg/L). Sludge respiration was significantly affected by the addition of the toxicant. At 20 mg/L of 3,5-dichlorophenol 70% of cells did not demonstrate respiration activity by using the single-OUR method, whereas total absence of exogenous respiration was observed in multi-OUR test. This measured difference of inhibition between single- and multi-OUR method is related to the different time of exposure to the toxicant, longer in the multi-OUR test. According to the literature *Vibrio fischeri*, used in the bioluminescence bioassay, resulted very sensitive, indicating greater inhibition effects with respect to other methods. Nitrifying bacteria resulted more sensitive to 3,5-dichlorophenol in multi-OUR respirometry and showed percentages of inhibition quite similar to *Vibrio fischeri*.

3. Methods for Toxicity Testing on Surface Waters

Bioassays for evaluating toxic effect produced by effluent wastewaters on receiving water bodies can be distinguished on the basis of: (1) the considered indicator organism considered; (2) the effects on the indicator organism (mortality, reproduction, …); (3) the duration of the test: short-term or long-term for assessing acute or chronic toxicity.

It is impossible to represent an entire ecosystem by one specific indicator species. Therefore, in order to have meaningful results, a battery of bioassays representing locally relevant species from all trophic levels is considered a prerequisite (Devisscher *et al*., 2007).

Methods for evaluating toxicity of effluent wastewater discharged from WWTPs are reviewed by Farré and Barceló (2003), where methods are distinguished on the basis of the used organisms:

- Fish bioassays: the test measures LC50 after 96 hours of exposure. The test is quite laborious and the most used species are rainbow trout and the fathead minnow;
- Invertebrate bioassay: *Daphnia* is the most applied species. Test has a duration of 24–48 hours. EC50 is evaluated by the immobilisation of the daphnids;
- Algae bioassays: measurement of algal growth inhibition; a standard algal toxicity test is ISO 8692 (1989), that uses *Selenastrum capricornutum* as model organism for freshwater algae;
- Bacterial bioassays: the luminescent bacteria *Vibrio fisheri* is the most used species for evaluating toxicity; some observations have been done above.

In the last years several efforts have been directed to the development of biosensors, in which a biologically active element (enzymes, DNA, immobilised microorganisms, …) is coupled with a physico-chemical transducer. The advantages of biosensors is the availability of a complete instrument able to operate on-site and to give fast responses and semicontinuous signals (Devisscher *et al*., 2007).

Recently flow cytometry and the double staining with FDA and Propidium Iodide was proposed as a rapid acute bioassay for inhibition evaluation on marine and freshwater microalgae (Franklin *et al.*, 2001).

4. Conclusions

Three approaches – respirometry, bioassays with flow cytometry and bio-uminecence bioassay – were compared for assessing toxicity of a common xenobiotic, 3,5-dichlorophenol. Good results were observed in toxicity detection by respirometry, a technique that does not require complex apparatus and can be easily applied in the routinely practice of the wastewater treatment plants. Respirometry indicated a strong toxicity both on heterotrophic bacteria and nitrifying bacteria. Furthermore a loss in cellular membrane integrity was observed with flow cytometry, indicating that 3,5-dichlorophenol is permea-ilising a fraction of viable cells. Bioluminescence bioassay, with *Vibrio fischeri* bacteria resulted very sensitive, reporting the highest inhibition effects.

The application of different bioassays may be useful for demonstrating mechanisms of toxicity of xenobiotic substances on activated sludge (or surface waters). In this context flow cytometry appears as a very promising techniques, allowing to test directly bacteria in activated sludge, evaluating in short time important physiological functions of the interested cells.

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CHROMIUM AND ATRAZINE CONTAMINATION OF THE LJUBLJANSKO POLJE AQUIFER

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Abstract. Contamination of the Ljubljansko Polje aquifer with Cr+6 dating to 1986 is considered to be one of the best-investigated groundwater pollutions in Slovenia. The contamination put a halt to water pumping in one of the wells for water supply in the Kleče pumping station, this being the major pumping field of the municipal company for water supply. Chemical analyses of Cr+6 were carried out for almost each groundwater sampling in Ljubljansko Polje aquifer and a large amount of data has been made available. In-depth investigation and pollution modelling was carried out and several papers were published on the subject. Contamination is a good tracer, which gives data on groundwater flow, hydrodynamics dispersion and leaching-out of pollution. The contamination in the most polluted pumping field of Kleče is today below the limit of chemical detection. Nowadays, highest degrees of aquifer pollution are identified south of the Hrastje pumping station. Furthermore, contamination by atrazine is also discussed.

Keywords: Ljubljansko Polje aquifer, Chromium contamination, atrazine

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1. Introduction

The aquifer Ljubljansko Polje is the main source of water supply of the Ljubljana municipality. The aquifer comprises 80 square kilometres in surface. The southern and western parts of the aquifer area are heavily urbanised, Figure 1. The four main water stations of the Ljubljana municipality water supply company JP VO-KA, are the WS Klece, WS Sentvid, WS Hrastje and WS Jarski Prod.

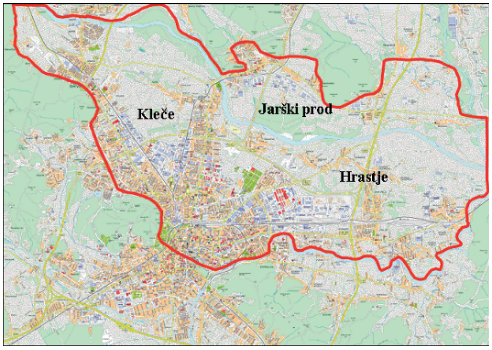

Figure 1. Aquifer Ljubljansko Polje with water stations

The aquifer is more than 100 metres deep on the location of WS Kleče. The matrix consists of coarse gravel coefficient of permeability of 1 cm/s. The main sources of groundwater are infiltration from the Sava River and recharge from precipitation. Mean yearly recharge from precipitation is about 1.5 m^3/s and mean yearly infiltration from the Sava River is about 3 m^3/s. Municipality water supply takes 1.2 m^3/s of water. The quality of groundwater reaches the standards for drinking water and it is used without any treatment. Water consumption has decreased in Ljubljana over the past fifteen years. This has been achieved through water saving programs, such as improved efficiency of household appliances or the decrease in the amount of water leached from pipes in water distribution networks through better maintenance.

Groundwater contamination in Ljubljansko Polje by way of hexavalent chromium was the first major contamination of the water source that called for extensive remedy measures and caused a temporary halt of water pumping from one of the wells of the WS Kleče. Only the WS Klece and WS Hrastje were polluted by hexavalent chromium. This has so far been the only instance of contamination that endangered the aquifer of Ljubljansko Polje to an extent that the contamination interfered with its proper functioning. The contamination was identified at the beginning of 1986, research and reorganisation measures were carried out between 1986 and 1990.

Hexavalent chromium makes an almost ideal indicator for water movement, owing to the unchanged ability of its characteristics. Additionally, underground it does not bind to the matrix or it is absorbed mostly at the surface. As a consequence of the contamination, chemical analyses of chromium levels in its oxidation form +6 have become a necessary part of groundwater monitoring and in analyses of drinking water quality. Therefore, a large amount of data on chromium levels at different observation points for the period after 1986 has been made available. The level of hexavalent chromium is an indispensable non-natural indicator for making assumptions regarding underground water movements and dynamics of pollution movements, and their dispersion under conditions present in the Ljubljansko Polje groundwater. However, it needs to be stressed that the level of determining the chromium concentration in analyses was higher than today, since the lower levels of determination in laboratories were more than 10 times higher than the lowest level of determination achieved in laboratories by using the modified standard methods nowadays. The concentrations identified today are often on the border of the limit of detection of the modified standard methods (in the majority of Slovene laboratories this being 5 µg/l). The research carried out in the JP VO-KA laboratory with the modified standard method showed a determination level of 3 µg/l. Expert literature shows a decrease in the level of determination amounting to levels lower than 0.2 µg/l.

2. General Characteristics of Chromium

Chromium was found by Louis Nicolas Vauquelin in 1797. Its name is derived from Greek, *hroma* meaning ‘colour’, since its different compounds are usually very colourful.

Chromium is a polyvalent element, found naturally in the air, soil, water and lithosphere. The most important natural chromium ore is the mineral chromite $FeCr_2O_4$. Oxidation states ranging from 2+ to 6+ are characteristic of chromium, however only the oxidation states 3+ and 6+ represent the chromium form used practically. Divalent chromium is relatively unstable, quickly oxidating into the trivalent chromium. In nature, trivalent chromium is the most stable state of chromium in nature and therefore most commonly found and its salts – mostly oxides – that are generally insoluble in water in the pH range of 4–11. Hexavalent chromic salts are less stable, more soluble and biologically active. The oxidation potential for transforming the trivalent chromium into the hexavalent one is high, and the probability of transformation into a higher oxidation form is reduced. So far, the research has shown that the hexavalent is not the prevailing natural chromium form, with few exceptions. The need for reducing the hexavalent chromium into the trivalent increases with a falling pH. The hexavalent chromium form, which is usually linked to oxygen atoms is a strong oxidant. In the presence of organic elements in water, a reduction to the trivalent form is made possible.

The trivalent chromium is the chromium form found in plants, food and is of vital importance (in traces, in low levels). According to research, the food that we eat contains the value of 0.5 ppm of the trivalent chromium. An estimated daily intake ranges from 0.03 to 0.1 mg of the trivalent chromium, the necessary dosage amounting to 0.01–0.04 mg of chromium tied in the form of organic particles and between 0.1 to 0.3 mg of chromium in inorganic form.

Despite the wide range of chromium in the soil and plants, it is rarely found in natural water above the concentration of the natural background, amounting to 1 μg/l. High concentrations are indicators of anthropogenic pollution.

A widely used method for determining the hexavalent chromium in water is the spectrophometric method, which applies the diphenilcarbazide according to modified methods. In reactions with the diphenylcarbazide it forms a red/violet colour complex. The reaction is highly sensitive and specific for chromium and the substances possibly causing disturbances are present in the drinking water in negligible quantities. The absorption is measured at a wavelength of 540 nm.

The elementary form of chromium does not show any tendency of migration from the surface through soil layers. Experiments have shown that a major part is withheld in the first few centimeters of soil. The chromium compounds in riverbeds are present as sediments, partially as suspended matter, and are then adsorbed onto the river sediments.

3. Toxicity of Chromium

Chromic chemicals are used in different industries, i.e. in leather industry for skin tannage, in electroplating for coatings, in chemical industry for making pigments. Hexavalent chromium (Cr6+) is far more mobile than the trivalent (Cr3+) chromium. The trivalent chromium is immersed into poorly soluble substances that are inaccessible to organisms (Kozuh et al. 2000).

Chromium is one of the elements essential to life, however in increased concentrations in the environment these elements prove toxic. The trivalent chromium is the form that has a biological function in terms of digesting sugar and fat.

The primary route of human exposure is through inhalation, ingestion and dermal contact. Inhalation is the most common form of exposure in several work environments. In day-to-day life, the exposure to chromium occurs through food and water intake as well as through inhalation. The main route of chromium excretion is via kidneys into urine, and via bile duct into faeces. Irrespective of the manner of intake, Cr3+ is absorbed to a far lesser degree than Cr6+. The absorption of Cr6+ is smaller, if the chromium intake occurs through mouth cavity, and thus the risk is not magnified. However, Cr6+ is highly toxic when entering through dermal contact and through respiratory tract, respectively. Chromium has the potential to cause skin infections/ulceration, nasal tissue damage and upper respiratory lesions, even lung cancer. Further on, contact dermatitis and hypersensitive reactions have been observed (Shrivastava 2002). The whole intake of Cr6+ is reduced into Cr3+ before penetrating into the circulation of blood. Damaged immune system due to Cr6+ and Cr3+ has also been examined thoroughly. Cr5+ and Cr6+ cause apoptosis, i.e. human lymphocyte death. Citotoxic and genotoxic effects of chromium have also been well examined. Both types of injury occur when Cr6+ reduces into Cr3+. In the reduction process reactive free radicals are formed, causing great cell damage. Genotoxicity of chromium Cr6+ results in direct damage of DNA. Cr3+ does not penetrate into cells, on the other hand, Cr6+ penetrates through plasmalemma with anion transmitters. Cr6+ does not react with macromolecules such as DNA, RNA, proteins, and lipids. However, Cr3+ and intermediate Cr5+ form covalent bonds with macromolecules. Cr6+ compounds are 10–100-times more toxic than Cr3+ compounds. Generally, the hexavalent chromium is far more toxic due to its oxidation potential and fast penetration through cell membranes into cell interior (Katz SA. 1993).

4. Contamination and Remedy Measures

Contamination was identified at the end of 1985 while testing the neutralisation devices when acquiring the occupancy permit in the local industrial zone. The waste water sample contained 175 μg/l of Cr(+6). Since chromium was not used in the described technological procedure, an analysis of drinking water was made at the starting stage of the technological procedure. The analysis showed a concentration of 150 μg/l, exceeding the permitted value (50 μg/l). Investigations into water quality in the vicinity of the Klece reservoir (Fig. 1) showed chromium contamination. Further analysis of water sampled from the rest of the wells and piezometers in Ljubljansko Polje revealed that chromium concentrations were not above the determination level.

The major potential pollutants included emissions from galvanisation plants at the pumping station drainage area, investigated as early as in January 1986. It was established that chromium concentrations were in excess of the acceptance criteria by 100 times and that the piping system was damaged. The Vizmarje galvanisation plant was dealt with separately situated west of the well of the Sentvid railway station. The authorities had investigated into its inadequate functioning before. Examination of emissions into the sewage system had revealed that the system was badly damaged, causing the flow of wastewater into the aquifer. The galvanisation plant was shut down immediately and the entire complex removed.

Beside the reorganisation of galvanisation plants, the remedial measures included cleansing and pumping from the Sentvid railway station and pumping into the sewage system water from the contaminated well in the Klece pumping station. The nearby wells were excluded from the system temporarily.

Concern over chromium pollution and preparation for a new central purification plant have called for a more intensive control over polluters connected to the JP VO-KA sewage system. A special care was given to the monitoring of potential Cr (+6) polluters, due to a continuous presence of smaller traces of Cr (+6) of the Kleče pumping station.

5. Analysis of Observation and Research Data

Pollution is distributed over the area and depth of the streamline. Sampling is done in the well, serving as the influent part of the perforated piping system. If the well is in contact only with surface groundwater, then the pollution possibly misses the well, however during the pumping the sample reads a mean concentration of the polluter with regard to pumping quality and distribution of the polluter in the streamline. In respective pumping stations, the concentration depends on water pumping distribution from individual wells, i.e. groundwater streamlines in the pumping station prior to sampling and in-between. The polluter quantity changes, depending on the direction course of the groundwater in a longer period of time prior to sampling and hydrologic boundary conditions. An analysis of changes in polluter concentrations provides valuable information on aquifer characteristics and groundwater movement, i.e. the polluter can be used for tracing purposes. The available data on chromium concentration were taken into account, from 1986 onwards, as well as oscillation in the groundwater level in the Klece and Hrastje pumping stations.

Analyses of groundwater streamlines for extremely dry and humid periods show relatively small deviations in pace directions. Changes with regard to streamlines vary to a negligible degree even in extremely dry and humid periods, Figure 2 (Brilly 1988). In dry seasons, the streamlines in the Klece pumping area are directed southeast-east towards the Sava River, and in humid periods from the Sava southwards. In the Hrastje pumping station area the streamlines in dry seasons are directed westwards and in humid seasons towards northwest, that is in the Sava River direction.

Hydrologic data on groundwater levels in the Klece pumping station (Figure 3) reveal that pollution first came about at the time of longer period of groundwater level decline, July 1986–January 1987, followed by a period of higher groundwater levels until the end of 1987 and then a moderate period in 1988 that ended with a severe drought. The following years gained in humidity, especially in 1994 and 1997. At times, a higher degree of chromium outside the pumping stations is identified, namely in the industrial wells.

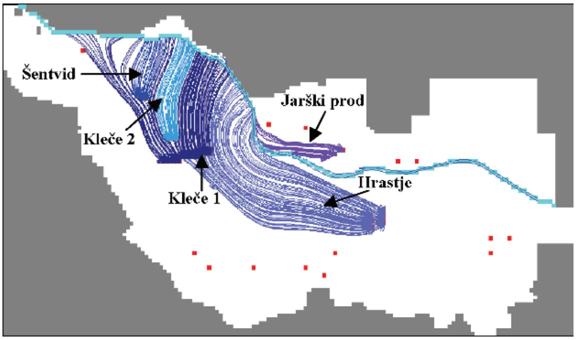

Figure 2. Catchment areas of the Ljubljansko Polje pumping stations

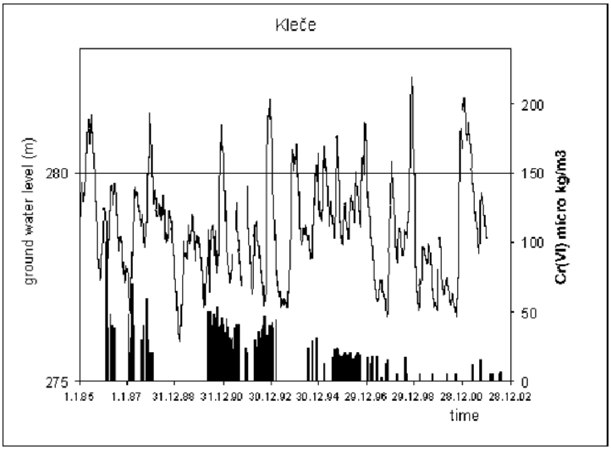

Figure 3. Water level and contamination with Cr (+6) at Klece

Chromium concentration in the Klece pumping facility wells was examined as early as in the very beginning of groundwater contamination with chromium (Figure 3). Due to successful remedy activities of the major polluter, Cr (+6) concentrations were reduced (Brilly 1990). First, pollutant traces were identified in the wells at the easternmost edge of the Klece I pumping station. After remedial measures the concentration decreased quickly, achieving the values acceptable in water supply. Spreading of pollution of the pumping station to other wells was identified at the other wells in the next years.

In the Hrastje pumping station, the hexavalent chromium was identified in one well in 1987, and in July 1994 the contamination was identified in all wells of the western part of Hrastje. Later, traces of chromium above the limit of detection were identified in the south wells only. In the northern part of the pumping facility with water outlet from the Sava, the chromium traces were rarely above the limit of detection. A secondary maximum in data occurred in 1994. Typically, pollution is on the increase with water level decline, and vice versa, Figure 4. Characteristically for the values today is a gradual increase of Cr (+6) concentration with its emergence in dry periods.

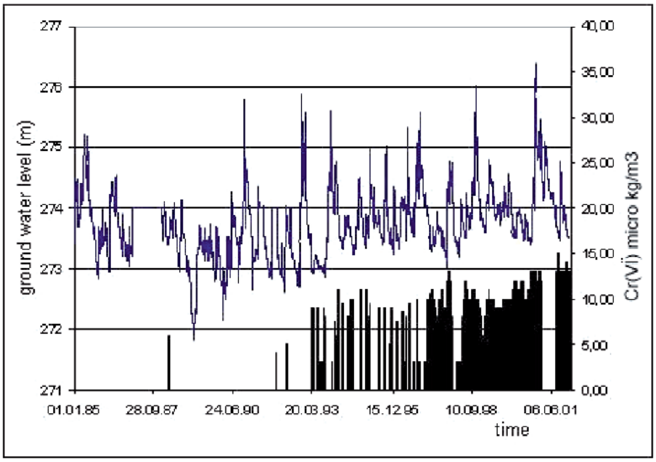

Figure 4. Water level and Cr (+6) contamination at the Hrastje pumping station

Space distribution of Cr+6 contamination today covers the central part of the Ljubljansko Polje aquifer, Figure 5. The area width is between 100 m and 2.0 km with an area of 20 km^2. The site of outflow into the Sava River is not known since there was no monitoring carried out downstream of the safe belt areas.

6. Atrazine Contamination

Atrazine is a herbicide widely used because it is economical and effectively reduces crop losses due to weed interference. It is frequently used on corn, soybeans, sorghum, sugar cane, pineapple, pine trees, other crops and as a non-specific herbicide on industrial sites. It is of particular concern to water supplies due to its popularity, relatively long half life (60 to 100 days) and because it is not strongly absorbed by soil. Atrazine is very often detected in groundwater as

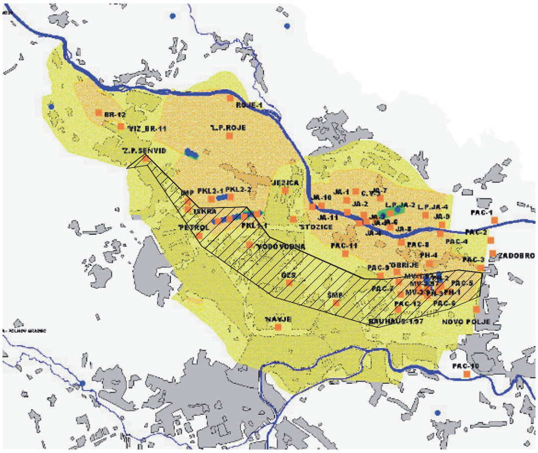

Figure 5. Area of Cr (+6) contamination

a result of agricultural activity. Agriculture was highly recommended in the protected zones of the Ljubljana aquifer but the improper use of herbicides contaminated the groundwater. The contamination was identified twenty years ago. As in other countries of the EU, atrazine was banned in Slovenia, and the concentration of atrazine has slowly dropped. From the contaminated wells the pumping for water consumption stopped. In 2003 the use of water from pumping station Hrastje was minimized as much as possible, only some wells were still used for a few hours per day. This is also the reason why the data stopped to scatter, Fig. 6. The concentration slowly dropped and today the water is of quality good enough for consumption.

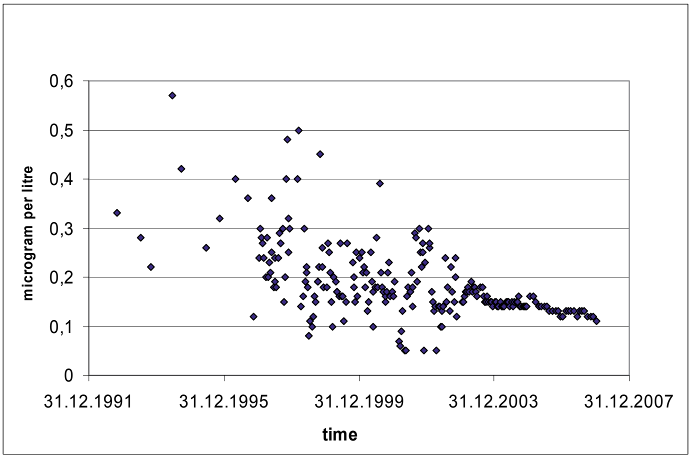

Figure 6. Atrazine content in the water of the Hrastje pumping station

7. Conclusion

The total concentration of chromium in any of the sampling sites in Ljubljansko Polje does not exceed the value of 50 μg/l, this being the permissible level according to the Regulations on health suitability of potable water. Temporary concentrations of the hexavalent chromium in the Kale pumping station are gradually declining and it is expected that they will sink below the lower limit of detection in all wells of the reservoir.

Noticeably, the Hrastje pumping station exhibits a trend of mild increase in the Cr+6 concentration, spreading from the south northwards. The most likely cause is the pollution cloud from the vicinity of the Hrastje pumping station, moving towards the WS Hrastje and resulting from to pumping works and changes in the flow courses – the groundwater level at the Hrastje pumping station area having been raised.

On-site and laboratory analyses of Cr+6 pollution have given valuable data and information on hydrodynamic features of geological formations of Ljubljansko Polje. These measurements have provided grounds for working out ground water models and will continue to do so in the future.

The groundwater regime at Ljubljansko Polje is highly specific and several phenomena, such as pollution trends and groundwater level movements, can be considered only on the basis of several years of monitoring.

The high quality of groundwater of Ljubljansko Polje results from the hydrological conditions (humid climate) and of an aquifer composed of coarse gravel from which the contamination flushes out in 10 to 20 years.

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WASTEWATER TREATMENT AND REUSE

COST MODELLING IN WASTE WATER TREATMENT PROCESSES: AN EMPIRICAL ANALYSIS FOR SPAIN

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Abstract. The reuse of resources obtained from regenerating wastewater is an absolute must both from a social and also environmental and health viewpoint. For any water reuse project to be viable, water treatment processes must be optimised. In this sense, extensive knowledge of the structure of costs associated to each of the treatment technologies available is necessary. This research applies cost modelling methodology by adjusting a series of representative functions and an empirical analysis is undertaken for a sample of wastewater treatment plants in Spain.

Keywords: cost modelling, water reuse; effluent destination; wastewater treatment plants; cost structure; cost function, scale economies

1. Introduction

It is obvious that water reuse is beneficial, not only because it enables water resources to be recovered, but also because it reduces environmental impacts. However, it is also equally true that economic variables such as costs and the price of treated water condition its use, particularly in comparison to other available resources. In this sense, an in-depth analysis of the local water market

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is required in order to establish a profitability threshold in technical and economic terms that makes water reuse an attractive option in certain sectors including agriculture, industry and aquifer recharging. This analysis should bear in mind both the costs involved in the various water supply alternatives (Onkal and Demir, 2006) and the type of crop, profit margins, social stance with respect to the environment, irrigation methods and guaranteeing supply, among other aspects.

Any given analysis of the potential of water reuse in a particular region and for a series of specific uses requires an extensive knowledge of cost structure (Asano, 1991, 1998; Mancini Sipala and Vagliasindi, 2003; Hidalgo and Irusta, 2004). Once the necessary quality parameters have been defined, existing alternatives (mainly conventional resources and desalinising) should be studied. It is important to know the structure of the costs linked to alternative water resources. When calculating the structure, not only technical costs should be taken into consideration, but also the value of externalities and opportunity costs (Seguí, 2004). Once the structure of costs is know, price fixing mechanisms are studied in order to assess the possibilities of regenerated water demand. In this sense, the role of the various incentives for using regenerated water could be assessed (Renzetti, 2003).

It would also be advisable to use a methodology based on cost optimising in order to assess the potential of water reuse as an alternative to conventional resources in each type of possible use in a particular region (Oron and Mehrez, 1996; Brimberg, Mehrez and Oron, 1994, 1995; Friedman et al., 1984). Distribution and transport costs for each use should also be included. Each destination will have a specific cost structure. When it comes to analysing the potential of the existing resources from treatment plants in a given region, we must assess, in the first place, the resources available to be reused, in the second place potentially available resources, that is, those which could be obtained from plants that already exist, but after implementing treatment systems by carrying out the necessary investment and in the third place the resources that could be obtained from new built plants (Angelakis et al., 1999). In all cases, the cost per cubic meter of regenerated water on the way out of the plant would have to be taken into account, together with the costs stemming from transport via piping to the final destination (Richard, 1998). The quality of the water used must obviously be in accordance with its final use.

In this context, we aim to carry out an analysis of the processes of treatment of wastewater by means the obtaining of cost functions. On try to know in detail the performance of the plants as well as the existence of possible differences .at cost level according to the destination of the effluent. This exhaustive knowledge of the costs associated to the treatment and the water reuse is considered as a basic requirement when valuing the true potentiality of the regenerated water in any territory.

2. Empirical Application

This research proposes a waste water treatment cost model as a basic tool for assessing the potential of water reuse as an alternative source of water resources. To this aim, information from a sample of 339 treatment plants located in Spain (Valencia Region) has been used.

According to Table 1, most plants (61 per cent) produce less than 250,000m^3/ year. However, the largest facilities, that is, those which produce more than 5,000,000m^3/year, treat the majority (69.23 per cent) of the waste water considered in the sample.

TABLE 1. Sample Description (339 Plants)

Size (m^3/year)	Number of Plants	%	Total Amount of Water Treated (m^3)	%
Below 50,000	73	21.53	2,150,091	0.46
50,001 – 100,000	62	18.29	4,400,190	0.94
100,001 – 250,000	71	20.94	11,149,781	2.39
250,001 – 500,000	44	12.98	15,409,301	3.30
500,001 – 1,000,000	28	8.26	19,994,506	4.29
1,000,001 – 5,000,000	38	11.21	90,420,798	19.39
Over 5,000,000	23	6.78	322,855,057	69.23
Total Sample	339	100.00	466,379,724	100.00

Despite the type of treatment applied in all the plants under analysis is not very different, the cost of this process varies considerably depending on which size group the plant belongs to. As can be observed in Table 2, the average cost of treatment per cubic meter is 0.669 euros for the smallest plants (below 50,000m^3/year), compared to 0.085 euros/m^3 in the largest plants (over 5,000,000 m^3/year). Clearly, this fact reveals the presence of economies of scale in the treatment process. On analysing the cost structure in more detail, we can see how personnel costs figure prominently in all size groups and particularly in the smallest plants (Table 3). This item represents almost 41% of the total cost per cubic meter in the sample as a whole.

TABLE 2. Breakdown of Costs per Cubic Meter (€/m^3) by Plant Size

Size Groups (m^3/year)	Personnel	Energy	Maintenance	Waste	Other	Total
Below 50,000	0.369	0.095	0.069	0.024	0.112	0.669
50,001 – 100,000	0.229	0.067	0.042	0.021	0.059	0.418
100,001 – 250,000	0.139	0.053	0.028	0.021	0.034	0.275
250,001 – 500,000	0.108	0.047	0.025	0.021	0.022	0.223
500,001 – 1,000,000	0.094	0.041	0.018	0.023	0.026	0.202
1,000,001 – 5,000,000	0.064	0.038	0.013	0.022	0.019	0.156
Over 5,000,000	0.030	0.016	0.010	0.015	0.013	0.085
Total Sample	0.048	0.024	0.013	0.018	0.016	0.119

TABLE 3. Costs per Cubic Meter by Plant Size in Percentages

Size Groups (m^3/year)	Personnel %	Energy %	Maintenance %	Waste %	Other %	Total %
Below 50,000	55.13	14.27	10.26	3.56	16.78	100.00
50,001 – 100,000	54.74	15.99	10.02	5.07	14.18	100.00
100,001 – 250,000	50.49	19.33	10.23	7.60	12.36	100.00
250,001 – 500,000	48.37	21.21	11.11	9.64	9.67	100.00
500,001 – 1,000,000	46.60	20.35	8.84	11.51	12.70	100.00
1,000,001 – 5,000,000	40.80	24.10	8.40	14.38	12.32	100.00
Over 5,000,000	35.84	18.82	12.06	18.20	15.07	100.00
Total Sample	40.61	20.24	10.62	14.80	13.72	100.00

Once the cost structure associated to the plants in the sample is obtained, we will attempt to model them in order to increase the possibilities of both interpreting and predicting these costs. We aim to express treatment costs as a function of the amount of water treated. Using the various curve estimation models in the literature as a basis (Gonzalez-Serrano et al., 2006; Friedler and Pisanty, 2006; Chen and Chang, 2002; Nishikawa, 1998; Oron and Mehrez, 1996; William, 1996), we find the potential function is the best fit. The cost curve is as follows:

$$C = \alpha Q^{\beta} \tag{1}$$

where C is Total cost of treatment (€/year); Q is the Amount of waste water treated (m^3/day), while α, β are parameters.

Concretely, the cost model obtained for our sample of plants is showed below:

$$C = 916.862 * Q^{0.659} \tag{2}$$

This formulation is in same way that other empirical applications existing in the literature, for example, Gonzalez-Serrano et al. (2006) and Friedler and Pisanty (2006).

The modelling of the treatment costs not only allows us to know the outstanding paper of the scale economies in this context but also the influence of the different treatment types. Also, the calculation of these cost functions allows comparing from a cost point of view the water reuse in relation to other water sources into a wider model of water supply in a geographical area.

Our following objective is the comparison of the wastewater plants in cost terms taking account the effluent destination. With this aim the plants in the sample are grouped depending on whether effluent are channelled to reuse or not. The cost structure for the two groups is showed in Table 4. The group of plants that allocates its effluent to reuse comprises 36 facilities with an average cost of 0.123 euros/cubic meter. On the other hand, the group of plants whose effluent is not reused is made up of 303 facilities with an average cost of 0.118 euros/cubic meter. Just as we expected, the cost of the treatment for an effluent to be reused is bigger than other options. However, it is necessary to highlight the scarce difference among the structure of costs of both groups such as one can observe in Tables 4 and 5 and Figure 1. Surely the existence of scale economies associated to the biggest size in the plants whose effluent is reused could contribute to explain this fact. It is also significant that *personnel cost* represents a bigger relative weight in the case of the plants whose effluent is not reused.

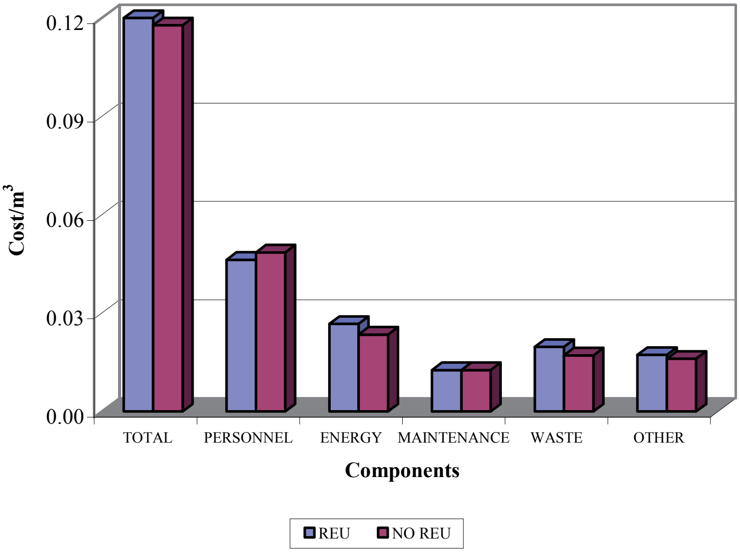

Figure 1. Cost by Components

TABLE 4. Total Cost (€/m3) by Effluent Destination

Effluent Destination	Personnel	Energy	Maintenance	Waste	Other	Total
Reuse	0.046	0.027	0.013	0.020	0.017	0.123
No Reuse	0.049	0.023	0.013	0.017	0.016	0.118

TABLE 5. Cost Structure by Effluent Destination in Percentages

Effluent Destination	Personnel %	Energy %	Maintenance %	Waste %	Other %	Total %
Reuse	37.78	21.80	10.29	16.06	14.07	100.00
No Reuse	41.20	19.92	10.69	14.54	13.65	100.00

Now we aim to carry out a new cost modelling trying to build a function for each one of the previously established groups according to the destination of the effluent. The obtained cost functions are:

$$\text{Reuse: } C = 707.815 * Q^{0.698} \tag{3}$$

$$\text{No Reuse: } C = 949.395 * Q^{0.653} \tag{4}$$

It is important to highlight the fact that the parameter β is bigger in the representative cost function of the group of plants whose effluent is reused in relation to the other group of plants. Hence the plants whose effluent is channelled to reuse require more costs by cubic meter treated, especially from a certain plant size (see Figure 2).

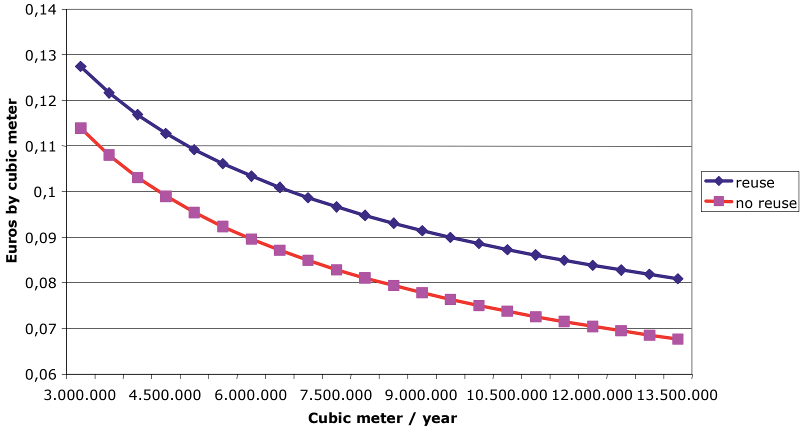

Figure 2. Total Cost by Effluent Destination

An extension of this work would be the calculation of cost functions for each treatment type and simultaneously to incorporate a bigger number of explanatory variables in the model. The availability of detailed statistical information is fundamental to guarantee the progress of this kind of research.

3. Remarks

The modelling exercise provides valuable information in a simple way in order to optimize the management of available water resources in those regions where they are lacking. Apart from how efficient waste water treatment systems are, it is also important to value the potential of the water reuse market, particularly in agriculture, by comparing the various cost structures associated to the conventional alternatives. Users' position, their economic power and interest in treated water distribution systems must also be taken into account. It is also worth studying demand in order to assess the possibilities of treated water usage accordingly.

In order to carry out a comparative analysis of the costs associated to each alternative, the following aspects must be taken into account: energy consumption for pumping and distributing water, well maintenance and piping for conventional resources and energy, personnel costs, maintenance, chemical products and analysis in the case of treated water. In the case of treated water, we must also take into account that the structure of costs varies depending on the size of the plant. As a result, determining a profitability threshold would also give us the minimal size of a plant at which competitive treated water use is guaranteed.

The aim of this work has been to contribute to increase the knowledge of the wastewater treatment costs through the use of modelling methodologies. Using cost functions you can approach with detail and scientific rigor the true potentiality of the water reuse to palliate in a reasonable way the water imbalances in a geographical area.

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REVIEW ON THE ASSESSMENT OF THE REMOVAL EFFICIENCY OF WASTEWATER TREATMENT PLANTS FOR SELECTED XENOBIOTICS

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Abstract. Wastewater treatment plants (WWTPs) represent a significant source for the input of micro pollutants as endocrine disruptors (EDs) or pharmaceutically active compounds (PhACs) into the aquatic environment. Those xenobiotics show effects to aquatic life at very low concentration e.g. by interfering with their hormone system. As a consequence investigations on the removal potential of various traditional as well as new waste water treatment technologies are undertaken in order to identify appropriate removal of xenobiotics from the urban water cycle. Beside laboratory experiments with synthetic wastewater and addition of a known concentration of the substance of interest, full scale treatment plants representing a broad range of layouts and concepts as well as a broad range of substances analyzed are investigated. In that context removal rates are calculated by comparing inflow and effluent concentration. This paper deals with a review on aspects that have to be kept in mind when assessing the removal potential of full scale wastewater treatment plants in order to avoid systematic errors and to come up with reliable results that can be compared to other plant configurations or operation types. After theoretical considerations an example for a mass balance of a complex waste water treatment plant is given to show a procedure suitable to reveal reliable information on the behavior of xenobiotics during wastewater treatment.

Keywords: xenobiotics removal; wastewater treatment; mass balance

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1. Introduction

Although the aim of wastewater treatment worldwide always was focused to protect the environment from the adverse effects of waste water discharges in general, up to recent time main emphasis was put on traditionally observed problems in the receiving waters as oxygen depletion and eutrophication (e.g. EU 1991). Appropriate wastewater treatment plants therefore were developed and built to prevent that kind of pollution implementing different treatment technology strategies as well as different evaluation procedures in regard to the necessary requirements for the treatment efficiency. Fulfilling those requirements (more or less) area-wide led – and with ongoing implementation still leads – to an increasing enhancement of water quality in the receiving waters. But during the last years intensified public, scientific and political focus was put on micro pollutants like endocrine disruptors (EDs), pharmaceutically active compounds (PhACs), chemicals used in industry and agriculture and as well personal care products that can be found in surface as well as in ground waters in very low but nevertheless relevant concentrations. Those substances are primary “unknown” to nature and therefore referred as Xenobiotics and additionally, due to their low environmental concentrations observed as micro-pollutants.

The effluent of wastewater treatment plants showed to be a significant source for those substances to enter the aquatic environment via the urban water cycle and studies on the concentrations of endocrine disruptors and PhACs in the effluent of wastewater treatment plants already were undertaken some years ago (e.g. Ternes 1998, Ternes et al., 1998, Heberer 2002a). Despite most of the substances not readily degradable, they are removed from the sewage with different efficiency depending on the layout of the waste water treatment plant and their adsorption behavior to activated sludge (Heberer 2002a, Clara et al., 2003c). In most of the studies only inflow and effluent concentrations are compared to calculate removal rates for the investigated substances and hardly any specification on the investigated wastewater treatment plant can be found that would allow an engineer to evaluate the applied concept or that would make efficiencies really comparable. As the efficiency of wastewater treatment plants is stipulated by legal requirements on national and international level (EU 1991) in regard to the sensitivity of the receiving water, tremendous differences in the removal are to be expected depending on the application of primary, secondary and tertiary treatment. Prior to the demand for implementation of advanced treatment technologies, existing and well established technologies have to be evaluated. In this paper some general considerations on the basic requirements for data comparison is dealt with.

2. Wastewater Treatment

2.1. GENERAL ASPECTS

The initial goal of waste water treatment historically was a focus on hygienic aspects to avoid epidemics and protect drinking water resources from contamination by wastewater. Although this goal still remains valid nowadays, additional important protective aspects as the general environmental protection of waters (running waters and lakes, ground waters, estuaries and the sea) were added by time. During time waste water treatment faced new requirements that lead to new concepts and plant layouts to tackle those challenges. An initial purpose of wastewater treatment was the reduction of the discharged organic load to prevent oxygen deficiencies in receiving waters. As a next step the removal of ammonia, phosphorous and nitrate were implemented by introducing nitrification, denitrification and P-precipitation. As a consequent step forward, the topic of xenobiotic micro pollutants is in discussion right now. Figure 1 (from Ternes & Joss 2006) summarizes the historical development of the activated sludge process that is used most commonly in biological waste water treatment and that proved to fulfill the removal efficiencies as required.

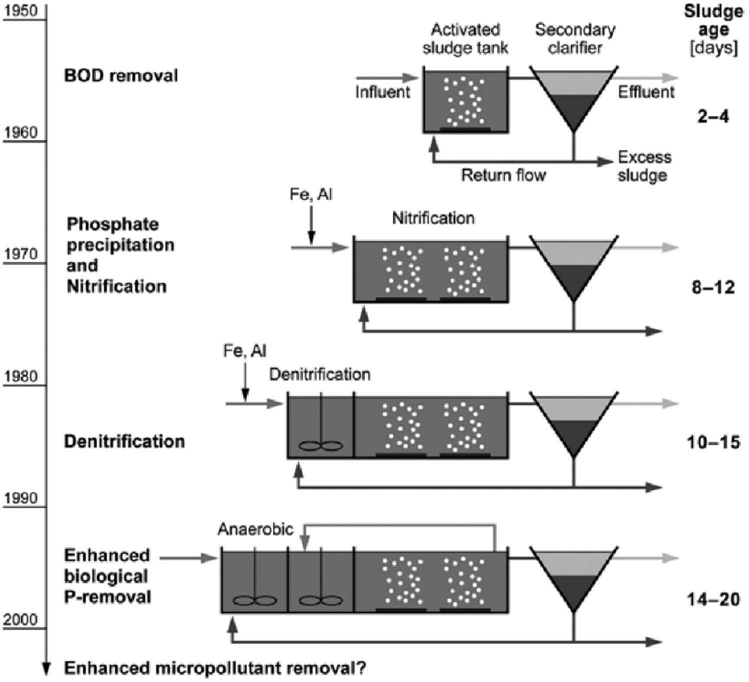

Figure 1. Overview on the development of wastewater treatment systems in time (in: Ternes & Joss, 2006)

During the last decades the traditional concept of the activated sludge process was modified at several edges resulting in a broad variety of possible process layouts and concepts. This implements for example multiple stage plants, SBR systems and membrane bioreactors that all have their advantages and disadvantages. Nevertheless those systems follow the same biological laws and principles. And all those modifications implement the same removal mechanisms making them basically comparable in regard to the removal efficiency for xenobiotics if some basic but crucial information is provided to characterize the system.

2.2. MECHANISMS OF REMOVAL DURING BIOLOGICAL WASTE WATER TREATMENT

The following processes are relevant for the removal of xenobiotics during biological waste water treatment:

- Adsorption to primary and secondary sludge
- Stripping to aeration gas
- Biological modification and degradation
- Unspecific chemical variation due to pH, Redox and equilibrium reactions

2.2.1. Adsorption Processes

Adsorption of substances to particulate matter – depending on the substance characteristics – is an important removal mechanism in municipal wastewater treatment. In waste water treatment the most important particles available as absorbent is coming from the activated sludge itself. Whereas primary sludge is introduced via the sewerage the secondary sludge is produced during wastewater treatment by bacterial growth, adsorption of various matter and precipitation products. Adsorption is a relevant process for substances with:

- low solubility in water indicated by an octanol/water distribution coefficient log $P_{OW} > 4,0$ (Rogers 1996)
- low polarity
- low volatility.

Under equilibrium conditions the concentration of a substance adsorbed on sludge (C_{SS}) is proportional to the concentration in solution (C_w) applying the content of suspended matter (SS) and the distribution coefficient K_d (Ternes & Joss 2006)

$$C_{SS} = K_d \times SS \times C_w \tag{1}$$

C_{SS} concentration sorbed onto sludge, per unit reactor volume [μg L^{-1}]
K_d solid-water distribution coefficient [L kg^{-1}]
SS suspended solids concentration in raw wastewater or production of suspended solids in primary and/or secondary treatment per L of wastewater [kg L^{-1}]
C_w dissolved concentration [μg L^{-1}]

Assuming equilibrium conditions SS is not the total content of suspended substances but the amount of sludge produced in the system, as only this newly produced sludge is available as adsorbent and the sludge already in the system for the duration of the sludge age is supposed to be saturated and therefore not available for sorption of newly introduced substances. This implements that activated sludge systems with a low sludge age and therefore high specific excess sludge production have a higher adsorption potential compared to low loaded systems with high sludge age and a low specific sludge production per COD inflow.

K_d is different for different sludges! Depending on the organic matter content and the chemical composition of the sludge this very much influences the behavior of the adsorbent. This is why primary sludge usually shows much higher K_d values compared to secondary sludge.

2.2.2. *Stripping to Air*

Stripping of xenobiotics due to the substance transfer into the air bubbles introduced during the aeration process can be important for low molecular weight substances with low solubility in water. The amount stripped into the gas phase depends on the

- Amount of gas introduces (aeration system)
- solubility in water
- liquid-gas partitioning coefficient or Henry coefficient K_H.

According to Langford und Lester (2003) stripping is relevant for substances with a $K_H > 10^{-3}$ whereas Rogers (1996) gives more precise criteria with:

- High stripping potential: $K_H > 10$ and $K_H/P_{OW} > 1\times10^{-4}$
- Low stripping potential: $K_H < 10$ and $K_H/P_{OW} < 1\times10^{-4}$

The concentration of the stripped substance (C_G) can be calculated by the concentration dissolved in water (CW) and the Henry coefficient (K_H) by:

$$C_G = K_H \times C_W \tag{2}$$

K_H Henry or air water partitioning coefficient [–]
C_w soluble concentration of trace pollutant [μg L^{-1}]
C_G concentration of trace pollutant in air [μg L^{-1}]

By multiplication of C_G with the amount of air (q_{Air} in m^3 air per m^3 wastewater) applied the amount of the substance stripped can be calculated as a part of the substance mass balance.

2.2.3. Biological Transformation and Degradation

Beside adsorption processes the biological transformation of xenobiotics is the most important removal pathway for xenobiotic substances. Biologically induced modifications of the considered substance implement various degrees of change:

- Removal or change of a chemical side group (deglucoronisation, desulfatisation, shortening of ethoxyl chains, …)
- Partial degradation (degradation of chemical groups, break down of aromatic structures, …)
- Full mineralization.

All those different degrees of biological modification have in common, that the parent substance is "removed", meaning that it can not be found by chemical analysis. Even a slight modification of the parent substance results in the suggestion of a "full removal" representing an unsatisfying condition. This aspect even leads to observations in literature, that certain substances (e.g. hormones like estradiol) are "produced" within the wastewater treatment plant. This observation is due to the fact that e.g. estradiol is excreted by humans as a conjugate to make it better soluble and therefore excretable. Within the sewerage parts of the conjugated hormones are cleaved setting free the unconjugated hormone that is available for chemical analysis resulting in the measured "inflow" concentration. During wastewater treatment additional deconjugation occurs. If the amount of deconjugation exceeds the amount of adsorption + stripping + biological transformation of the target substance, the effluent concentrations are observed to be higher compared to the inflow concentrations. As for most of the substances no conjugation is assumed and unconjugated forms are analyzed chemically the "real" inflow quantity of the substance is not known in most cases.

The different degrees of biological modification can be associated to two different pathways linked to microbial growth:

- Substrate growth
- Co-metabolism.

During substrate growth the substance is mineralized and used as carbon and/or energy source. During cometabolism growth a primary substrate occurs and the enzyme system for usage of the primary substrate is used for transformation of the xenobiotic too as a result of affinity and substrate specific of the enzyme.

In waste water treatment the system parameter "sludge age" or "sludge retention time" (SRT) is of central importance in relation to biological removal processes. The SRT is related to the growth rate of microorganisms, as only organisms, which are able to reproduce themselves during this time can be detained and enriched in the system. According to this definition, high SRTs allow the enrichment of slowly growing bacteria and consequently the establishment of a more diverse biocoenosis with broader physiological capabilities compared to STPs with a low SRT. The correlation between treatment efficiency (e.g. carbon removal, nitrification) and SRT is based on this principle (ATV-DVWK, 2000), and can be described by Monod kinetics. According to Monod kinetics the achievable effluent concentration of a certain compound is dependent on the selected/operated SRT and independent of the influent concentration.

The application of a Monod type kinetic presumes that the substrate of concern is the limiting factor for microorganisms' growth. This means, that the chemical must be sufficiently easy to metabolize and it also must be available in sufficient amounts to result in significant energy and/or biomass recovery (Schwarzenbach et al., 1993). If a compound is only present in trace levels, the degradation of these substances does not result in any significant change of cell numbers. These chemicals are usually transformed in a cometabolism and the concentration variation rates correspond to a mixed substrate growth as mentioned earlier. Assuming a constant relation between the production rate of new cells and the disappearance rate of a certain chemical (yield, Y), the Monod approach corresponds to Michaelis-Menten kinetics. The enzyme based Michaelis-Menten kinetics seems more suitable to describe changes in the concentrations of micropollutants as degradation or transformation rates and not cellular growth are usually measured in wastewater treatment.

As the two models are linked and show the same hyperbolic form, no statements can be given whether enzyme chemistry or microbial growth determines the rate of chemical degradation (Schwarzenbach et al., 1993). However, if a micropollutant is biodegradable and this degradation can be described by the mentioned kinetics, even in the low concentration range and in case of a mixed substrate growth (cometabolism) a specific SRT can be associated to the substance. The relevant kinetic parameters maximum growth rate μ_{max} and half saturation constant K_s are those describing the dependency of bacterial growth on a primary substrate. According to these observations a critical value for the SRT should be identifiable. At SRTs operated below this critical value, no removal due to biodegradation is to be expected and if a substance is not adsorbed to sludge, effluent concentrations in the range of influent concentrations are probable. In STPs operated at higher SRTs than the critical value nearly a complete removal related to the specific substance will occur. If the loading is very constant over the time a distinct threshold marks the critical SRT, whereas strongly varying effluent concentrations are observed within a certain SRT range at unsteady influent conditions. The dependency of the effluent concentration on the SRT is schematically illustrated in Figure 2.

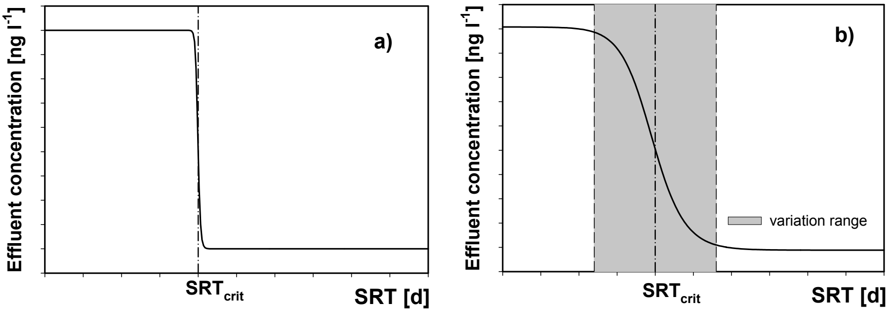

Figure 2. Dependency (schematic) of STP effluent concentrations on the SRT for (a) constant and (b) varying influent conditions

According to these statements, the achievable effluent concentrations of substances degraded following Michaelis-Menten kinetics are not related to influent concentrations but depend only on the operated SRT, whereas treatment efficiencies in percent depend notably on influent concentrations. This implicates that as soon as a SRT required for removal is reached, the effluent concentration is stable whereas influent concentrations can show a significant change on a daily, weekly or seasonal level. Due to this changes in the influent calculated removal rates relating influent and effluent concentrations can change significantly.

For comparing the removal rates at different treatment plants based on the activated sludge process a comparable total sludge retention time is required. Actual SRT e.g. can be derived from COD mass balance and related to 20°C ($SRT_{20°C}$) implementing the temperature (T) in the bioreactor and a correction coefficient (f_P=1,072) for the temperature.

$$SRT_{20°C} = SRT_{\mathrm{T}} \times 1.072^{(\mathrm{T}-20)} \tag{3}$$

2.3. SAMPLING

Sampling for investigation on the removal of xenobiotics in full scale waste water treatment plant is a challenge. Even in recent literature grab samples from inflow and effluent are taken, filtered samples are analyzed and differences expressed in percentage of removal. Information derived by this procedure is not useful to describe removal pattern or removal potentials of treatment technologies. At the best this procedure can be used in steady state laboratory plants with constant inflow situations. For full scale plants several aspects have to be taken into consideration that opposes this simplified approach.

- Daily, weekly and seasonal inflow pattern in regard to wastewater flow, organic load and inflow concentrations
- Hydraulic retention time between inflow and effluent
- Different K_D values for solids in inflow and effluent
- Changes occurring during sample storage for daily composite samples
- Stormwater events
- Recovery and accuracy of chemical analysis.

Figure 3 and Figure 4 show weekly fluctuations of selected xenobiotics in the inflow and the effluent of a WWTP. In order to demonstrate the fluctuations, data were normalized to the mean value of the week. Data represent mean values from 4 sampling periods in May, July (time of summer vacations), October and December (week of Christmas holidays) in order to investigate on yearly fluctuations too (see Table 1).

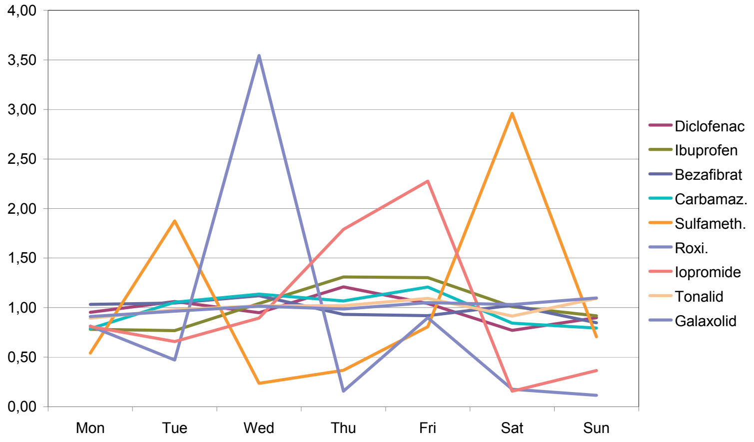

Figure 3. weekly fluctuations in the inflow concentration of selected xenobiotics as a mean of 4 sampling periods over a year normalized to mean value of the week = 1

Comparing inflow concentrations in Figure 3 and effluent concentrations in Figure 4 it can be seen, that effluent concentrations show a more homogenous picture compared to the inflow situation. In the effluent only for few substances a slight weekly pattern can be observed, whereas in the inflow the weekly dynamics is obvious for most parameters. A comparison even reveals the hydraulic flow time of ~3 days that can be observed at this plant by comparing occurance of peak concentrations for Iopromide, Sulfamethoxazole and Galaxolide in the inflow and effluent.

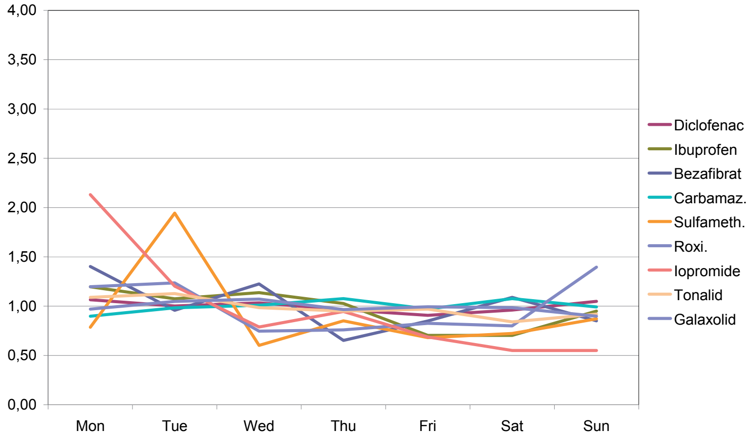

Figure 4. weekly fluctuations in the effluent concentration of selected xenobiotics as a mean of 4 sampling periods over a year normalized to mean value of the week = 1

Beside weekly fluctuations a seasonal variation of inflow concentrations can be observed too resulting from different use and consumption data over theyear. Results normalized to the mean concentration over the year are summarized in Table 1. Whereas some parameters show a +/– constant concentration over the year for other parameters tremendous fluctuations can be observed. Analytical errors are not responsible for this behaviour, as each month data represents the mean of 7–10 daily composite samples used for calculation of a mean concentration and outliers are considered.

Figure 5 illustrates removal data from Table 1. Even a distinct yearly fluctuation can be observed e.g. for Ibuprofen concentrations over the year, removal stays constant at a high level all over the year. For other parameters a fluctuation in the removal rate of 20% can be observed, whereas e.g. Sulfamethoxazole shows a variation between –80 and +60%. This example additionally demonstrates the necessity of considering metabolites and conjugates that can retransform to the parents substance and therefore interferes with removal calculations.

Those aspects considering sampling make it difficult or at least expensive to reveal reliable information on the removal behaviour and to access relevant full scale data. Sampling strategy, time, interval, storage and location on the one hand are as important as accuracy and precession of chemical analysis on the

TABLE 1. seasonal fluctuations in inflow and effluent concentration as well as removal rate. Inflow and effluent concentrations normalized to mean value over year

inflow

month	Diclofenac	Ibuprofen	Bezafibrat	Carbamaz.	Sulfameth.	Roxi.	Iopromide	Tonalid	Galaxolid
May	0,88	0,73	0,52	1,06	2,92	0,04	0,25	1,16	1,03
Jul	1,12	1,33	0,53	1,04	0,20	0,09	0,16	1,04	1,49
Okt	1,23	0,74	1,00	0,98	0,20	4,47	3,72	0,55	0,28
Dec	0,87	1,21	1,81	0,92	0,20	0,17	0,43	1,13	1,13
Mean	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00

effluent

month	Diclofenac	Ibuprofen	Bezafibrat	Carbamaz.	Sulfameth.	Roxi.	Iopromide	Tonalid	Galaxolid
May	0,96	0,89	0,05	1,05	2,12	0,58	0,83	0,98	0,87
Jul	0,96	0,70	0,05	1,04	0,77	0,49	0,55	1,16	1,16
Okt	1,01	0,70	0,11	0,99	0,43	2,11	1,04	0,92	0,68
Dec	1,05	1,49	3,14	0,92	0,43	0,94	1,42	0,98	1,26
Mean	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00

% Removal

month	Diclofenac	Ibuprofen	Bezafibrat	Carbamaz.	Sulfameth.	Roxi.	Iopromide	Tonalid	Galaxolid
May	52,62	99,14	99,42	6,67	65,54	–64,62	6,25	86,98	85,33
Jul	62,73	99,63	99,50	4,95	–80,00	44,27	0,00	82,80	86,50
Okt	64,35	99,33	99,33	4,38	0,00	95,02	92,05	74,25	57,24
Dec	47,34	99,13	89,88	5,91	0,00	41,06	6,18	86,65	80,60
Mean	56,53	99,29	94,17	5,49	52,55	89,47	71,46	84,60	82,58

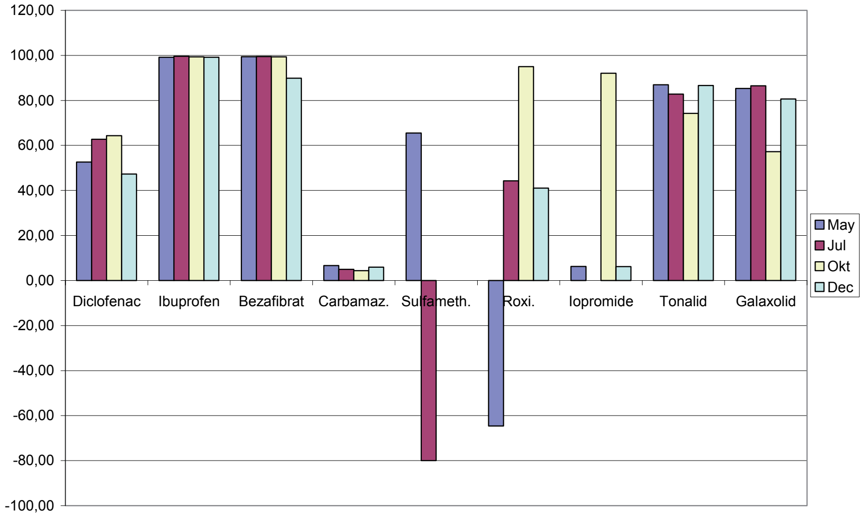

Figure 5. mean calculated removal rates for selected xenobiotics during 4 sampling campaigns (7–10 data each sampling) as difference between inflow and effluent concentrations at a WWTP (% removal data from Table 1)

other hand both are essential for a conclusive picture that represents the information required for environmental risk assessment, plant design and operation or implementation of a legal framework.

2.4. CHARACTERIZATION OF REMOVAL TECHNOLOGY

Beside information on sampling and chemical analysis, a proper characterization of the system investigated is essential. This is valid for laboratory plants and much more for full scale plant in order to have a base that can be used to categorize investigations on the fate of xenobiotics in regard to technologies and their efficiency.

For full scale plants t least size, design capacity, SRT related to 20 or 10°C, F/M ratio and rough plant configuration is required. Plant configuration should implement pretreatment, number of stages for biological treatment, type of biological treatment (biofilter, SBR, MBR) content of suspended solids, information on N and P removal, type of sewerage connected to the plant and an estimation of the relation between municipal and industrial contribution to the inflow load.

3. Determination of Removal Rates

Comparing technologies, plant layouts and processes the term "removal" has to be specified. Is the wastewater treatment plant considered as system border for investigating the behavior of a target substance, removal would mean summing up the amount of substance in the inflow (input to system) and comparing it to the amount in all output compartments (effluent, exhaust air, sludge). This requires a detailed mass flow balance for the treatment plant. If only inflow and effluent concentrations are considered as frequently found in literature, the term "removal" much more relates to the "removal from the aqueous phase" (additionally in most cases only the dissolved part in the liquid phase), meaning that inflow and effluent concentrations are compared implementing all problematic aspects related to sampling. This approach may not express reliable information on substance removal during waste water treatment.

In order to decrease the inaccuracy, mass balances over a longer time period are required. A balance time frame for a period over one sludge age would be ideal but not feasible in most cases, so at least 7–10 days should be considered to compensate for weekly fluctuations in the inflow. Additionally mass balances are useful to perform plausibility checks on measured values and parameters of operation that are very much needed for the calculation of a removal of xenobiotics as e.g. wastewater flow. Phosphorous and COD are proper parameters to perform an initial mass balance to investigate on the sufficiency of the sampling and flow data. Mass balances can be done e.g. according to Nowak et al. (1999) based on corresponding chemical analysis and respiration rates of the sludge. Mass balances also serve for the evaluation of process characteristics like SRT, specific excess sludge production (Q_{ES}) and F/M ratio.

Mass balances can be done for units of different size and complexity. In a simple case only an aeration tank is considered (Figure 6) whereas in a complex case the whole wastewater treatment plant is divided into several process units that are balanced independently (e.g. anaerobic digestion process – see Figure 9) and afterwards combined to an overall mass balance for the whole treatment plant (Figure 10).

$$M_{i,IN} - M_{i,E} - M_{i,ES} = r_i * V_R = \text{Removal}$$

$$M_{i,IN} = Q_{IN} * s_{i,IN} * (1 + X_{SS,IN} * K_{D,i})$$

$$M_{i,ES} = Q_{ES} * s_{i,E} * (1 + X_{BM} * K_{OM,i})$$

$$M_{i,E} = Q_E * s_{i,E} * (1 + X_{SS,E} * K_{D,i})$$

$$X_{SS,E,MBR} = 0$$

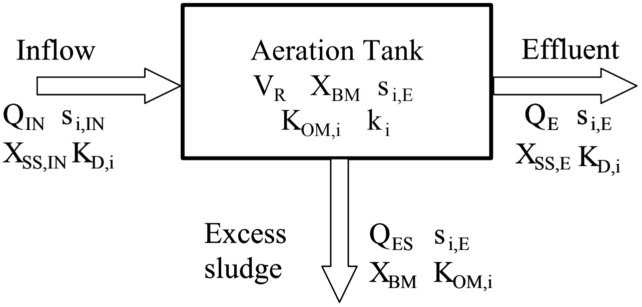

Figure 6. example for a simple mass balance of an aeration tank

After deriving reliable data from the mass balance of phosphorous and COD, loads in the inflow ($M_{i,IN}$), effluent ($M_{i,E}$) and excess sludge ($M_{i,ES}$) can be calculated for the xenobiotic of interest. Mean values of inflow ($s_{i,IN}$) and effluent($s_{i,E}$) concentrations during the 7–10 day sampling period can be used to obtain dissolved concentrations in the filtered samples together with an average flow (Q_{IN}, Q_E) for determination of an average daily load. Measured concentrations in inflow ($s_{i,IN}$) and effluent($s_{i,E}$) should be well above the limit of quantification (LOQ). Results between LOQ and LOD (limit of detection) or even below the LOD should not be used as those inaccuracies lead to large errors in the mass balance and consequently in information in removal rates derived. The portions of the substance adsorbed to activated sludge in the aeration tank (X_{BM}) or the suspended solids in the inflow ($X_{SS,IN}$) and effluent ($X_{SS,E}$) respectively can be measured or calculated applying the substance specific K_{OM} value where the distribution coefficient K_D refers to the organic matter (f_{OM} = VSS/TSS) of the activated sludge. In combination with the mass balance and the concentrations in the filtered sample, $K_{OM/D}$ serves as a basis to calculate removal of the selected substances via adsorption to the excess sludge derived from mass balance and loss due to suspended solids in the effluent (Clara et al., 2003a). $K_{D,i}$ values for the investigated substances can be derived from laboratory scale experiments or from literature.

The total removal of substances within the system border balanced is calculated as:

$$\%\ \text{removal} = 100\ \% - \frac{\text{load in effluent} + \text{load in excess sludge}}{\text{load in inflow}} \times 100\ \%$$

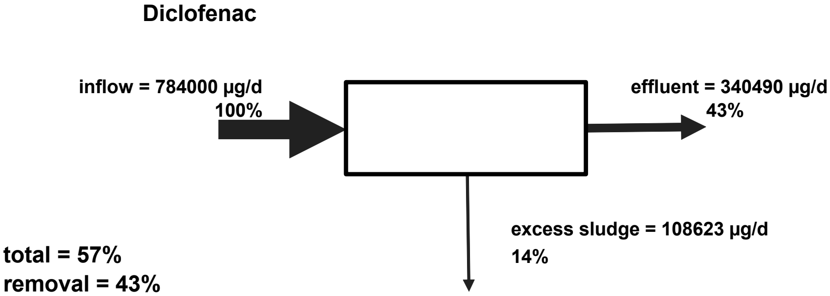

Figure 7. Example for a simple mass balance to determine overall removal rates in an aeration tank according Figure 6

4. Example

A two stage activated sludge plant with a mesophilic anaerobic sludge digestion was sampled over a period of 10 days. The treatment plant is charged from a separated sewer system and designed for a capacity of 167,000 population equivalents (based on 120 g COD/pe/d) with carbon and nitrogen removal. Due to distinct winter tourism in the drainage area, the loading of the plant shows characteristic seasonal fluctuations. A flow scheme of the sewage treatment plant is shown in Figure 8.

The primary treatment consists of screens and aerated grit chamber. The first stage is a highly loaded activated sludge tank operated at a sludge retention time (SRT) of less than one day. The second, low loaded stage (2. stage) is operated at a SRT of about 20 days (related to 10°C). Nitrogen removal is obtained in the second stage via simultaneous nitrification and denitrification. Phosphorus removal is performed by precipitation with aluminium salt.

A small part of the excess sludge abstracted from the first stage is used for the supernatant treatment. The main part of the excess sludge from the first stage and the whole excess sludge from the second stage are pumped to a static thickener from where the digesters are fed. The digested sludge is pumped into a storage-thickener and further dewatered by a filter press. Before discharging the supernatant back into the first stage, it is treated in an additional tank operated as sequenced batch reactor (SBR). The entire digested and dewatered sludge is composted after the treatment.

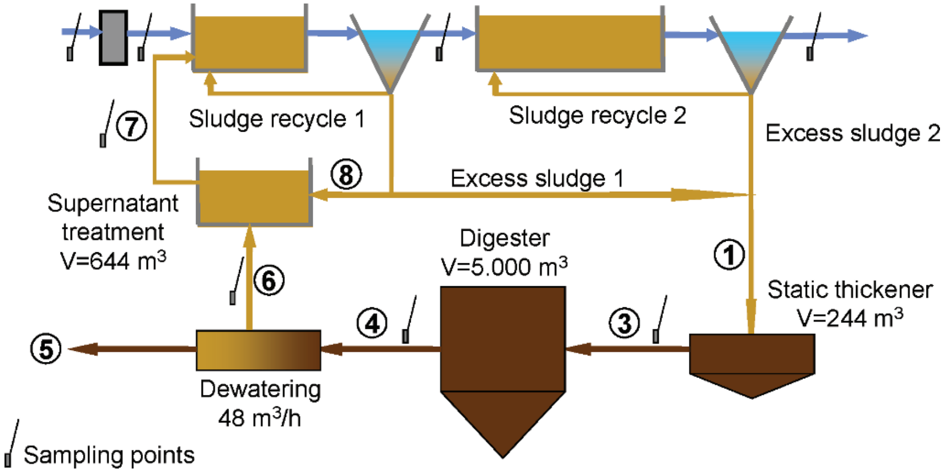

Figure 8. Flow scheme of the investigated two stage sewage treatment plant

Out of the mass balance detailed information on the particular processes can be obtained, as e.g. for the behaviour during anaerobic digestion. Comparing the measured dissolved concentrations it was observed, that the concentrations in the effluent of the digester were significantly higher than in the influent for most of the substances, except for the polycyclic musks (see Table 2). The EDS Bisphenol-A and the PhACs Diclofenac and Carbamazepine show higher dissolved concentrations in the effluent than in the influent of the anaerobic digester. These higher dissolved concentrations in the effluent of the anaerobic digester can be explained by desorption processes. The organic fraction of the sludge (volatile suspended solids VSS) is the relevant adsorbent for the investigated compounds. During the anaerobic sludge stabilization a degradation of the organic matter occurs. In the sampled digester about 50% of the organic matter in the influent is degraded in the reactor (see Table 2). This degradation of organic matter leads to a release of the initially bound substances to the liquid phase. If a certain compound is not degraded under anaerobic conditions, an increase of the dissolved concentrations can be observed in the effluent of the anaerobic treatment step. Figure 9 illustrates the mass balance for the musk fragrance Tonalide as an example. The results for all compounds studied are summarized in Table 2.

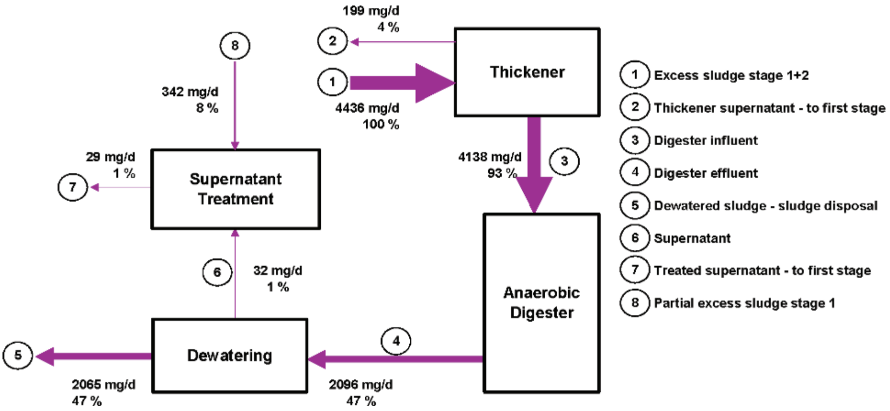

Figure 9. Mass balance for the polycyclic musk Tonalide (AHTN) – system border: sludge treatment of plant Figure 8

TABLE 2. Results of the mass balances for the investigated substances during the different steps of the sludge treatment. Numbers indicate load at positions in Figure 9; numbers for AHTN are data in Figure 9

		Thickener		Anaerobic Digester		Dewatering			Supernatant Treatment	
	Unit	In	Out	In	Out	In	Out		In	Out
		①	②+③	③	④	④	⑤	⑤+⑥	⑥+⑧	⑦
BPA	[mg/d]	28,101	41,110	40,014	40,113	40,113	38,923	40,113	3,013	379
	[%]	100	146	142	143	143	139	143	11	1
DCF	[mg/d]	1,434	1,356	331	575	575	64	575	600	676
	[%]	100	95	23	40	40	4	40	42	47
CBZ	[mg/d]	993	1,018	562	779	779	51	779	797	1,100
	[%]	100	103	57	78	78	5	78	80	111
AHTN	[mg/d]	4,436	4,337	4,138	2,096	2,096	2,065	2,097	374	29
	[%]	100	97	93	47	47	47	48	8	1
HHCB	[mg/d]	14,572	11,419	10,742	3,499	3,499	3,367	3,500	1,193	126
	[%]	100	79	74	24	24	23	24	8	1

Bisphenol-A, Diclofenac and Carbamazepine are not affected during the anaerobic treatment. The total mass flux in the effluent corresponds to the mass flux in the influent, resulting in the conclusion that no degradation of these compounds under anaerobic condition occurs. Bisphenol-A is known to be biodegradable under aerobic conditions (Staples et al., 1998; ERA-BPA, 2002).

During the supernatant treatment BPA and the musk fragrances are removed in notable amounts, whereas the other compounds passed this additional treatment step without any reduction. This corresponds to prior statements, indicating the ready biodegradability of BPA under aerobic conditions. Also the polycyclic musks Tonalide and Galaxolide seem to be biotransformed during the aerobic supernatant treatment, as the effluent load is notably lower than the load in the influent. DCF and CBZ are not degraded and pass the supernatant treatment unaffected. The effluent loads correspond to the masses in the influent.

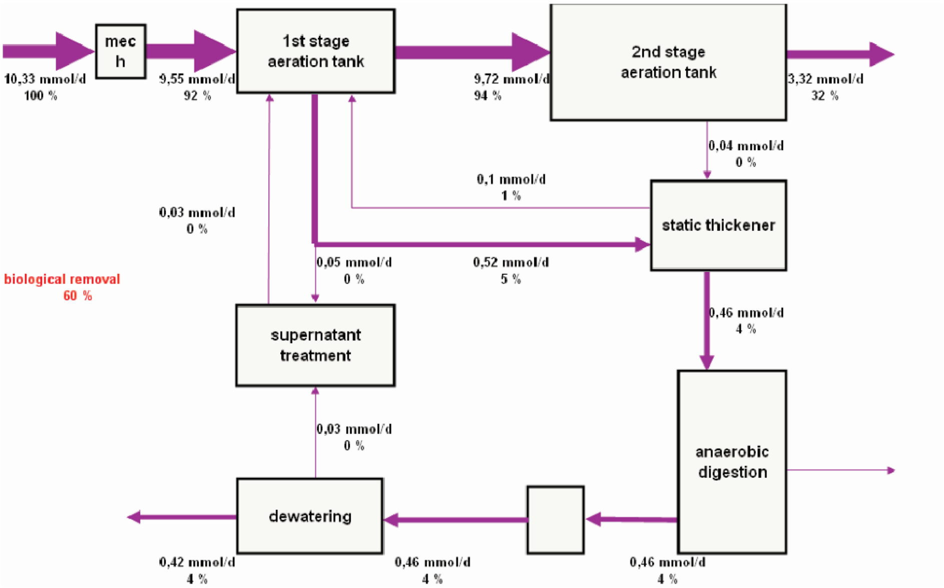

Figure 10. Mass balance fort he WWTP schematized in Figure 8 for the molar sum of natural steroid hormones (Estron, Estradiol and Estriol). Numbers related to inflow load = 100%

Figure 10 summarizes the mass balance for the whole treatment plant investigated based on daily composite samples over 10 days at the sampling sites indicated in Figure 8. The results of the mass balance are related to the total inflow concentration as 100%. Percentages given indicate total loads (dissolved and associated to particles) entering or leaving the unit.

K_d values were analysed for primary sludge as well as sludge from the 1st and 2nd stage and for anaerobic digestion once by analyzing dissolved and total concentrations. For the other 9 sampling days only filtered samples were analyzed and adsorbed fractions calculated to save resources.

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POSTER SECTION

AQUEOUS PHOTOCATALYSIS, NATURAL ORGANIC MATTER CHARACTERIZATION AND REMOVAL: A CASE STUDY OF THE PHOTACATALYTIC OXIDATION OF FULVIC ACID

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Abstract. Natural organic matter (NOM) is a complex mixture of organic compounds that occurs ubiquitously in both surface and ground waters. Its presence in water supplies not only contributes to aesthetic problems such as taste, odor and color, but also to operational and regulatory issues which include increased chemical usage, increased sludge production and membrane fouling. The variability in the amount and nature of natural organic matter is a significant factor in controlling the reactivity of aquatic humic substances with chlorine during water treatment processes. Hence, the potential for the formation of carcinogenic disinfection byproducts necessitates the removal of organics prior to chlorination stage in search for alternative advanced oxidation technologies to ensure compliance with drinking water quality standards. Humic substances (HS) represent the major fraction of naturally occurring organic substances comprised of carbon rich polydisperse polyelectrolytes. During recent years a significant interest has been devoted to the photocatalytic treatment of HS as model compounds of NOM. This paper addresses some basic issues related to the photocatalytic treatment of a model fulvic acid in relation to the relevant UV-vis and fluorescence spectroscopic properties. The oxidative removal of fulvic acid is evaluated by pseudo first order as well as Langmuir Hinshelwood kinetic models.

Keywords: Natural organic matter, fulvic acid, photocatalytic oxidation, UV-vis spectroscopy, fluorescence spectroscopy

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1. Introduction

Humic substances (HS); mainly humic and fulvic acids are the major fraction of naturally occurring organic substances. They are comprised of highly functionalized carbon rich polydisperse polyelectrolytes. Their ambiguous structures combine both hydrophobic and hydrophilic regions that result in the solubility enhancement modifying the toxic behaviour of various pollutants and impacting the transport of dangerous compounds in the aquatic system. More importantly, HS are well known precursors of carcinogenic and mutagenic trihalomethanes generated in conventional water treatment procedures, including chlorination (Rook, 1974; Singer, 1999). In this respect, it is necessary to remove these organics prior to chlorination stage in search for alternative advanced oxidation technologies to ensure compliance with drinking water quality standards.

During recent years, a significant interest has been devoted to the TiO_2 mediated photocatalytic oxidation of humic acids as model compounds of NOM (Bekbolet, 1996; Uyguner and Bekbolet, 2005a; Uyguner and Bekbolet, 2005b). Owing to the formation of hydroxyl radicals (•OH), photocatalytic oxidation exerts a powerful oxidizing power in the reaction mixture, and thus can mineralize a myriad of undesirable organic matters to CO_2, H_2O and inorganic constituents. Some basic issues related to photocatalytic degradation kinetics of model humic substances supplied from commercial sources and the effect of solution matrix as specified by the presence of some common anions and cations on the photocatalytic removal of a model humic acid was investigated in detail (Bekbolet et al., 1998; Uyguner and Bekbolet, 2005a; Uyguner and Bekbolet, 2005b). However, only a limited number of research has been conducted on the removal of fulvic acids that are the water soluble portion of humic substances (Uyguner and Bekbolet, 2005). One of the recent studies in literature explains the removal of a commercial fulvic acid with an integrated approach incorporating photocatalytic oxidation with ultrafiltration for the effective separation of TiO_2 particles from its aqueous suspension (Fu et al., 2006).

Complementary to previous studies of humic acids and their photocatalytic oxidation properties, the objective of this work is to investigate the photocatalytic degradation of a standard fulvic acid solution focusing on the spectroscopic methods using UV-vis and fluorescence spectroscopy.

2. Materials and Methods

Suwannee River Fulvic Acid (IHSS FA) standard material purchased from the International Humic Substance Society was used as the model humic substance. A stock solution of 1000 mg L^{-1} was prepared by dissolving fulvic acid in distilled deionized water and diluting it to a solution of 50 mg L^{-1} resulting in a dissolved organic carbon (DOC) content of 20.6 mg L^{-1}.

Photocatalytic oxidation of fulvic acid (50 mg L^{-1}) was carried out in the presence of TiO_2 Degussa P-25 (0.25 mg mL^{-1}) in a continuously mixed batch reactor using a 125 W BLF lamp as the light source (Uyguner and Bekbolet, 2005b). Prior to molecular size fractionation, partial oxidation of fulvic acid was carried out up to the extent that UV_{254} absorbance value was removed by approximately 50%.

Molecular size fractionation of raw and photocatalytically treated fulvic acid was performed by Amicon 8050 ultrafiltration stirred cell system through a sequence of membranes which are of 100 kDa, 30 kDa, 10 kDa and 3 kDa nominal molecular size (Uyguner and Bekbolet, 2005b).

2.1. PARAMETERS USED FOR THE CHARACTERISATION OF FULVIC ACID

UV-vis absorbance values of the samples were determined using a Perkin Elmer λ 35 Spectrophotometer. Absorbance values at 436 nm ($Color_{436}$), 400 nm ($Color_{400}$), 365 nm (UV_{365}), 300 nm (UV_{300}), 280 nm (UV_{280}), and 254 nm (UV_{254}) were recorded for the evaluation of UV-vis parameters as absorbance ratios such as E_{254}/E_{365} (UV_{254}/UV_{365}), and E_{254}/E_{436} ($UV_{254}/Color_{436}$). Specific UV absorbance ($SUVA_{254}$, cm^{-1} mg^{-1} L) was used to represent DOC (mg L^{-1}) normalized aromatic moieties (UV_{254}). Dissolved organic carbon measurements of fulvic acid were performed on a Shimadzu TOCV CSH analyzer.

Fluorescence spectra in synchronous scan mode were recorded on a Perkin Elmer LS 55 luminescence spectrometer in the excitation wavelength range of 300–650 nm using the bandwidth of 18 nm between the excitation and emission monochromators (Senesi, 1990). The emission spectra were scanned over the range of 400–600 nm at a constant excitation wavelength of 350 nm (Senesi, 1990; Hautala et al., 2000).

3. Results and Discussion

3.1. PHOTOCATALYTIC DEGRADATION OF FULVIC ACID

Photocatalytically oxidized fulvic acid displayed the basic UV-vis spectroscopic structural pattern of native fulvic acid irrespective of the irradiation time. In a similar manner, DOC removal also followed an exponential decay as could be modelled by pseudo-first order reaction kinetics:

$$\text{Rate} = -dA/dt = k\,A \quad (1)$$

where, A is the absorbance of the specified UV-vis parameter of fulvic acid (m^{-1}) or DOC content (mg L^{-1}), t is the irradiation time (min), and k is the pseudo-first-order decay rate constant (min^{-1}).

The evaluation of the kinetic data for a variety of humic and fulvic acids from aquatic and terrestrial sources were discussed in a recent study where the half life value for the removal of IHSS FA (50 mg L^{-1}) in terms of DOC was reported to be one third of that of UV_{254} (Uyguner and Bekbolet, 2005b). As a complementary approach, confronting the photocatalyst effect, kinetics under different loading conditions were also assessed revealing that both of the rate and rate constants increase with increasing TiO_2 amount.

TABLE 1. Pseudo first order model parameters of photocatalytic removal of 50 mg L^{-1} IHSS FA in the presence of different TiO_2 loadings

	0.10 mg mL^{-1} TiO_2		0.25 mg mL^{-1} TiO_2		1.00 mg mL^{-1} TiO_2	
	k min^{-1}	Rate $m^{-1}min^{-1}$	k min^{-1}	Rate $m^{-1}min^{-1}$	k min^{-1}	Rate $m^{-1}min^{-1}$
$Color_{436}$	3.98×10^{-3}	0.0203	7.22×10^{-3}	0.0368	2.58×10^{-2}	0.132
$Color_{400}$	3.96×10^{-3}	0.0388	6.71×10^{-3}	0.0658	2.24×10^{-2}	0.219
UV_{365}	4.13×10^{-3}	0.0795	6.46×10^{-3}	0.125	2.00×10^{-2}	0.388
UV_{300}	3.28×10^{-3}	0.176	4.87×10^{-3}	0.259	1.55×10^{-2}	0.825
UV_{280}	2.70×10^{-3}	0.185	4.02×10^{-3}	0.275	1.33×10^{-2}	0.910
UV_{254}	2.65×10^{-3}	0.241	3.76×10^{-3}	0.342	1.22×10^{-2}	1.11

Increasing the TiO_2 loading from 0.1 mg mL^{-1} to 1.0 mg mL^{-1} by ten fold has the effect of increasing the rate by approximately five fold. In view of the generally presented optimum loading of 1.0 mg mL^{-1} of TiO_2, the pseudo first order degradation rate constants for the specified UV-vis parameters range from 1.22×10^{-2} min^{-1} to 2.58×10^{-2} min^{-1}. However, different results were reported in literature, as depicted by Fu et al., (2006), 0.50 g L^{-1} of a nano-structured TiO_2/silica gel photocatalyst was found to be the optimum concentration for the photocatalytic removal of a fulvic acid. It was explained that increasing the catalyst concentration had the effect of decreasing the degradation rate of fulvic acid. Considering the use of different photocatalyst, reactor, and fulvic acid of various origins, it is plausible to achieve diverse results. Taking into account the comprehensive network of reactions occuring during the photocatalytic process, a complex kinetic model comprising all the dependent parameters on the degradation rate was developed (Minero, 1999). However, the most widely applied kinetic models of photocatalytic decomposition of organic compounds are based on Langmuir-Hinshelwood (L-H) equation which is a modified form of pseudo first order reaction kinetics (Equation 2). According to

L-H mechanism, the reaction rate is proportional to the surface coverage assigned for the reactant.

$$R_{LH} = k_{LH}\, K_{LH}\, A/(1+K_{LH}\, A) \qquad (2)$$

where R_{LH} (m^{-1} min^{-1}) is the rate of the reaction, k_{LH} (min^{-1}) is the reaction rate constant, K_{LH} (m), the adsorption coefficient of the reactant onto TiO_2 under irradiation conditions and A (m^{-1}) the initial value of the specified UV-vis parameters or DOC content (mg L^{-1}) of fulvic acid. The linear transformation of the L-H type relationship, by plotting the reciprocal of the initial rate against the reciprocal of the initial substrate concentration allows the values of the kinetic parameters k_{LH} and K_{LH} to be determined from the intercept and the slope of the straight line as presented in Table 2.

TABLE 2. Langmuir Hinshelwood kinetic parameters of fulvic acid (IHSS FA: 20–50 mg L^{-1}, TiO_2: 0.25 mg mL^{-1})

Kinetic parameters	$Color_{436}$	$Color_{400}$	UV_{365}	UV_{300}	UV_{280}	UV_{254}
k_{LH}, min^{-1}	0.0089	0.0209	0.0513	0.0991	0.131	0.189
K_{LH}, m	0.822	0.487	0.470	0.102	0.0701	0.0523
R_{LH}, $m^{-1}min^{-1}$	0.00742	0.0178	0.0469	0.0857	0.112	0.161

The effect of the model parameters on the overall rate equation is expressed by the L-H rates following the same increasing trend of the L-H rate constants. Both of the constants increase in the order of $Color_{436}$, $Color_{400}$, UV_{365}, UV_{300}, UV_{280} and UV_{254} revealing that UV absorbing centers may be removed more selectively than the color forming moieties. On the other hand, the adsorption coefficients, K_{LH}, in the range of 0.822 to 0.0523 display a decreasing trend with respect to decreasing absorbance values. The respective removal rates of fulvic acid are found to be relatively lower than the removal rates of humic acids that have longer chain fatty acid moieties and higher hydrophobicity (Uyguner and Bekbolet, 2005a).

3.2. UV-VIS SPECTROSCOPIC ANALYSIS

UV-vis spectroscopy was utilized as an effective tool for the characterization of humic substances either in terms of spectral changes in a defined wavelength domain or by specific absorbance values measured at certain wavelengths.

It was reported by several researchers that the quotient E_{250}/E_{365}, which is a property of aquatic humic substances, increases as the aromaticity and molecular size decreases (Peuravuori and Pihlaja, 1997). The higher E_{250}/E_{365} ratio of IHSS FA is in agreement with its lower aromatic content and lower molecular size as opposed to other humic substances recently studied (Uyguner, 2005). The ratio of E_{254}/E_{436} gives a good impression about the intensity of the UV absorbing functional groups compared to the colored ones. E_{254}/E_{436} values in the range of 4–11 were reported for terrestrial dissolved organic matter which has a greater organic matter content associated with the presence of tannin like or humic like substances derived from plants and soil organic matter (Battin, 1998). In all cases, the highest ratio was achieved for IHSS FA compared to the other humic acids. Accordingly the UV-vis parameters of treated fulvic acid as a function of irradiation time were presented in Table 3.

TABLE 3. UV-vis parameters of fulvic acid as a function of photocatalytic irradiation time (IHSS FA: 50 mg L^{-1}, TiO_2: 0.25 mg mL^{-1})

time, min	E_{254}/E_{365}	E_{254}/E_{436}	$SUVA_{254}$
0	4.80	18.17	4.42
30	5.07	18.88	5.96
60	5.59	21.63	5.94
90	5.99	23.96	3.94
IHSS FA raw	4.70	17.86	4.42

Changes in the spectroscopic ratios and $SUVA_{254}$ values were reported for fulvic acid after 0, 30, 60 and 90 min of irradiation time which approximately correspond to 6%, 38%, 47% and 52% removal of DOC, respectively (Table 3). Prior to photocatalysis, preadsorption of fulvic acid could be assessed by the initial introduction of titanium dioxide to the solution (t = 0 min) in the absence of light. However, this process does not indicate any significant difference in the respective absorbance ratio values as presented in Table 3. Dahlen et al. (1996) reported that E_{254}/E_{365} ratio increased from 4.5 to 4.9 while the dissolved organic carbon content of fulvic acid decreased by 20% after UV-vis irradiation. In a recent study related to the photocatalytic degradation of humic acid the specified absorbance ratio increased from 2.7 to 3.4 after 30 min with a subsequent reduction of DOC by 48% (Uyguner and Bekbolet, 2005b). Similarly, the photocatalytic oxidation of fulvic acid after 30 min resulted in a 8% increase of E_{254}/E_{365} ratio.

Initial work on the characterization of different humic substances of different origins revealed $SUVA_{254}$ results ranging from 7.0 to 9.5 m^{-1} mg^{-1} L for humic acids (Uyguner, 2005). These values are much higher than $SUVA_{254}$ value obtained for fulvic acid (4.4 m^{-1} mg^{-1} L). Considerably lower values attained for fulvic acid clearly indicate more hydrophilic character with respect to humic acids. Taking into account the chemical interpretation of the absorbance values, the use of some spectroscopic ratios was also launched in literature for the assessment of the structural diversity of the complex humic moieties (Hautala et al. 2000). On the other hand, the interpretation of the UV-vis absorption intensities during photocatalytic oxidation in correlation to the removal of organic carbon revealed a substantial increase of $SUVA_{254}$ value by 35% after 30 min and a relavant decrease of 11% after 90 min of irradiation.

3.3. MOLECULAR SIZE DISTRIBUTION PROFILES OF FULVIC ACID

Aiming at focusing on a comparative basis, the parameters linked to molecular size of fulvic acid were measured by UV-vis spectroscopy after molecular size fractionation in the range of 0.45 μm to 3 kDa for both raw and partially oxidized fulvic acid (Figure 1 and Figure 2).

The fast removal of both of the UV-absorbing moieties and color forming groups during photocatalytic oxidation as evaluated in terms of molecular size fractions via ultrafiltration process is noticeable.

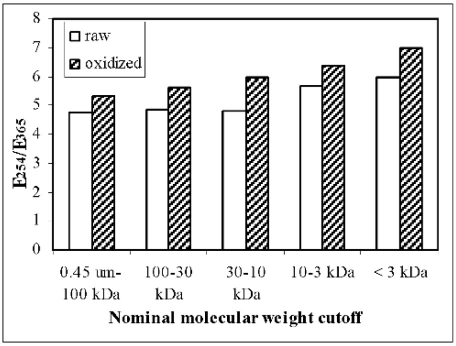

Figure 1. Comparison of E_{254}/E_{365} ratio of raw and treated fulvic acid

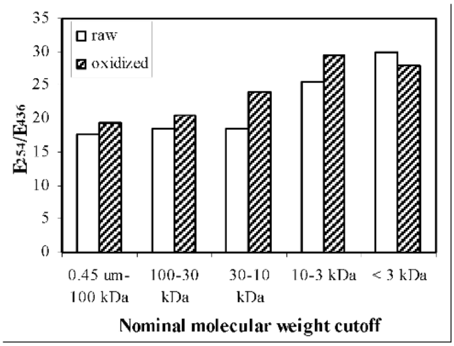

Figure 2. Comparison of E_{254}/E_{436} ratio of raw and treated fulvic acid

As previously reported, the UV-vis spectra of the molecular size fractions of humic substances exhibit a similar declining pattern, the absorbance values of which also gradually decrease with the molecular size fractions (Uyguner and Bekbolet, 2005a, Alberts et al., 2002). The differences of the absorbance ratios of each size fraction indicate diverse reactivities. As a general trend, the absorbance ratios of the fractionated fulvic acids also increase with decreasing molecular size. Such a pattern suggests a shift in the UV-vis absorbance towards higher wavelengths with increasing molecular sizes as reported by Duarte et al. (2003).

3.4. FLUORESCENCE SPECTROSCOPIC ANALYSIS

The synchronous scan fluorescence spectra of raw and partially oxidized fulvic acid with respect to their decreasing size fractions are presented in Figure 3 and Figure 4.

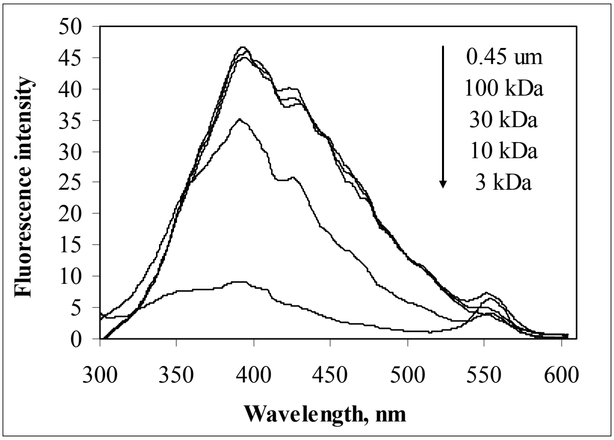

Figure 3. Synchronous scan spectra of the molecular size fractions of raw IHSS FA

As could be seen from Figure 3, raw IHSS FA has a sharp peak around 395 nm. The fluorescence intensity exhibits the same emission maxima and the same fluorescence intensity up to 30 kDa fraction. For the lower size fractions of 10 kDa and 3 kDa, a rapid decline of the fluorescence intensity is observed.

As a general trend, oxidation leads to a shift of the fluorescence intensity to lower wavelengths (Figure 4). After partial oxidation, in addition to the

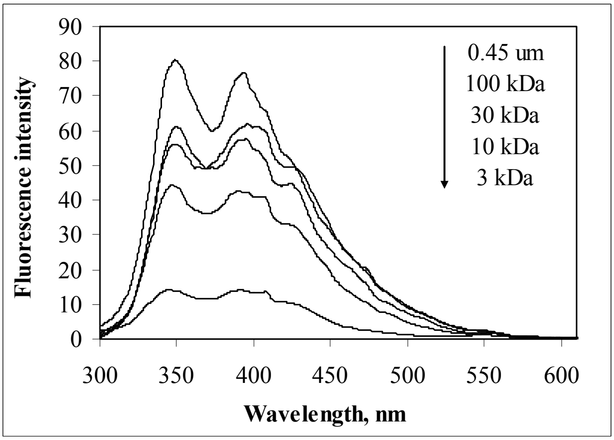

Figure 4. Synchronous scan spectra of the molecular size fractions of oxidized IHSS FA

presence of peak maxima at 400 nm, the formation of another peak around 350 nm is observed. The fluorescence intensity decreases up to 10 kDa keeping the twin peak shape of the spectra.

The comparison of the two spectra shows that the fluorescence intensities of each size fraction significantly increase after photocatalytic oxidation with a blue shift of the spectra. It is noted that all fractions of fulvic acid play a significant role in the radical initiated photocatalytic oxidation process.

4. Conclusions

The photocatalytic degradation of fulvic acid was investigated focusing on the kinetics of degradation based on the use of model equations. The spectroscopic changes induced during the photocatalytic oxidation process were evaluated by UV-vis and fluorescence spectroscopy. The declining trend of the specified UV-vis parameters, the related changes in the fluorescence spectra, decrease of TOC content during degradation, indicated the oxidative degradation of fulvic acid by photocatalytic oxidation.

Moreover, based on the comparison between the synchronous scan fluorescence spectra of the molecular size fractions of raw and oxidized fulvic acid, it could be concluded that oxidative cleavage of the molecule leads to a blue shift of the spectra which is indicative to the formation of new fluorophores. Hence, molecular size specific distribution of the absorbance ratios could be assed for the oxidized fractions of aquatic humic substances.

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CHEMICAL AND ECOLOGICAL PROBLEMS OF SMALL RESERVOIRS AT DESIGNING OF WASTEWATER TREATMENT INSTALLATIONS

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Abstract. On the basis of the analysis of chemical parameters of quality of natural waters of small reservoirs we showed unacceptability of their use as waste waterways. One of the options to solve this problem is to dispose such drains in reservoirs with the greater diluting ability at simultaneous simplification of wastewater cleaning technology.

Keywords: small reservoirs, waste water, ecosystem degradation, quality of natural and waste waters

1. Introduction

The water resource is an integral part of social, economic and ecological spheres of society. Quantitative sufficiency and qualitative characteristics of water determine the level of life-support, condition of health and gene pool of mankind. Unfortunately, anthropogenic overload of the water ecosystems results in both quantitative and qualitative exhaust in many regions of Ukraine.

Such processes have irreversible character in many reservoirs. First of all, anthropogenic influence is observed in small rivers, brooks and other small water objects. It is mainly caused by wastewaters disposal having quantitative and qualitative structure, which significantly exceeds the assimilation ability of reservoirs. It is necessary to note, that wastewater pollution of reservoirs is

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regulated by the Ukrainian legislation. However, it is put into practice only in average and large water objects while small reservoirs are often practically unattainable. Unofficially such water objects are considered as minor[1], to which it is not necessary to apply all requirements of the state nature protection legislation.

Real dilution ability of the water reservoirs is almost ignored at designing of the wastewater treatment equipment.

In most cases such reservoirs are used as waste waterways to bigger water objects with greater assimilation ability. It leads to catastrophic ecological degradation of brooks, small rivers and their transformation into drain channels. In the local water use practice such examples are not single.

2. Experiment and Discussion

We investigated consequences of very polluted waste water disposal into a brook to understand the problem and to find its appropriate solutions. The brook is influenced by the meat-treatment plant, which is located in Rosokchach village of Ternopil region (Ukraine). This enterprise is engaged in the meat processing (8 tons per day) and meat-products manufacturing (2 tons per day). This enterprise uses water in slaughter shop, to wash the sausage and canning shops equipment, to feed the steam-force equipment and for sanitary and drinking needs of the personnel.

Thus, the enterprise releases 108380 m^3/year of waste waters. They are polluted with blood, dung, fats, proteins, organic and inorganic nitrogen compounds (urea, ammonia). Existing waste water cleaning complex consists only of mechanical fat-catcher.

Qualitative parameters of the cleaned wastewaters at the release of drains into the brook are given in Table 1.

As it is seen from the Table 1, pollution level of initial wastewaters with BOD_5 is 792,8 mg/l and considerably exceeds maximal allowable qualitative parameters of wastewaters to be disposed of to natural reservoirs. This maximal level should not exceed 15–25 mg/l.

The cleaned wastewaters in such a way are disposed of into the brook with a small feed debit. Further wastewaters of this brook get to the Seret river, where they are being finally assimilated.

The scheme of our research of the wastewater influence on the brook and the Seret river is shown in Fig. 1. The water analyses tests were carried out according to methods[2].

TABLE 1. Quality of the enterprise waste water

№	Pollutant	Pollutant concentration, mg/l	№	Pollutant	Pollutant concentration, mg/l
1	COD	2848,2 ± 13,6	8	Chlorides, Cl^-	492 ± 8
2	BOD5	792,8 ± 9,5	9	Sulphates, SO_4^{2-}	57,0 ± 1,3
3	Suspened substances	96,7 ± 5,4	10	Dry rest	2463 ± 26
4	Ammonium cation, NH_4^+	28,3 ± 1,0	11	Fats	92,8 ± 6,4
5	Nitrites, NO_2^-	0,99 ± 0,17	12	Phenols	0,06 ± 0,01
6	Nitrates, NO_3^-	15,6 ± 2,1	13	Synthetic active substances	0,11 ± 0,03
7	Phosphates, PO_4^{3-}	8,13 ± 0,55	14	Iron (sum)	0,98 ± 0,05

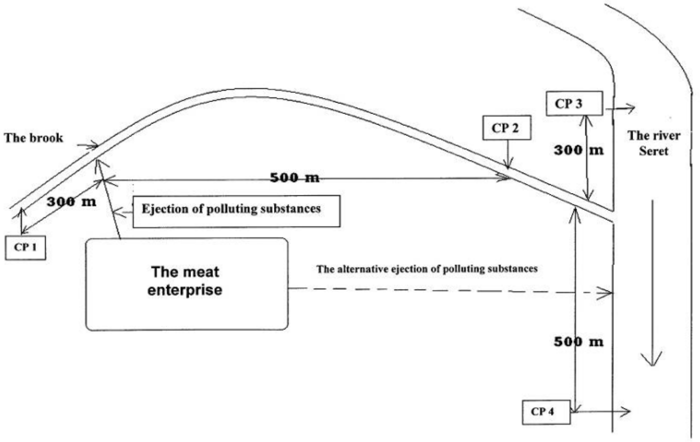

Figure 1. The scheme of the definition of waste water influence of the enterprise on the brook and the Seret river

The brook water analysis was taken at two points. Check point 1 was situated upstream from the dispose point and checkpoint 2 was situated downstream. Another two check points were situated at the river of Seret. Check point 3 was situated upstream from the point of the junction with the brook. Check point 4 was situated downstream from the junction point. The upstream checkpoints (1 and 3) were used to get levels of background concentration of the pollutants. Then the data from the downstream check points were compared to background levels.

The brook water quality parameters are shown in Table 2, and Table 3 shows same parameters for the river of Seret.

As it is seen from Table 2, the background water quality in the brook meets the requirements of high class water use (fishfarming category).

TABLE 2. Water's qualitive in the brook

No.	Pollutant	Concentration, mg/l		
		Background quality of the brook water (check point 1)	The brook water quality at check point 2 (downstream of the waste-water disposal)	Maximal allowable concentration levels for the fishfarming reservoirs.
1	COD	9,6 ± 0,5	105,8 ± 6,5	15
2	BOD_5	1,83 ± 0,15	36,7 ± 2,9	2,24
3	Suspended Substances	5,3 ± 0,7	26,14 ± 1,97	+0,25 to background
4	Ammonium cation, NH_4^+	Absent	11,02 ± 0,76	0,39
5	Nitrites, NO_2^-	0,13 ± 0,01	20,78 ± 0,99	0,08
6	Nitrates, NO_3^-	5,5 ± 0,5	13,5 ± 0,8	40
7	Phosphates, PO_4^{3-}	0,18 ± 0,02	5,4 ± 0,3	3,12
8	Chlorides, Cl^-	38 ± 3.01	281 ± 6	300
9	Sulfates, SO_4^{2-}	52 ± 2.0	52 ± 4	100
10	Solid-residue	453 ± 6.0	843 ± 11	1000
11	Fats	None	16,7 ± 1,3	
12	Phenols	None	0,012 ± 0,002	0,001
13	Synthetic active substances	None	0,08 ± 0,01	0,1
14	Iron (overall)	0,17±0,01	0,52 ± 0,05	0,1

However, BOD_5 at check point 2 becomes almost twenty times greater than the maximal allowable level (MAL) and concentration of the suspended substances becomes almost five times greater than its MAL. Therefore, the brook water does not meet any standard regulating sanitary and hygienic condition of the water objects. It transforms into the enterprise waste waterway to the Seret river.

Comparative analysis of the water quality at check points 3 and 4 allows ascertaining an influence of the consolidated influence of the brook and the enterprise on the water quality of Seret. For example, BOD_5 is increased by 20% at the check point 4.

Thus, the existing level of the enterprise wastewater disposal practically destroys the brook ecosystem and negatively influences the Seret river.

TABLE 3. The Seret-river water quality

№	Pollutant	Pollutant concentration, mg/l	
		The river water quality at check point 3	The river water quality at check point 4
1	COD	28,42 ± 0,62	32,8 ± 0,4
2	BOD_5	3,24 ± 0,22	3,68 ± 0,06
3	Suspended substances	41,57 ± 4,42	43,7 ± 0,4
4	Ammonium nitrogen NH_4^+	2,18 ± 0,07	2,86 ± 0,08
5	Nitrites, NO_2^-	0,12 ± 0,02	0,13 ± 0,02
6	Nitrates, NO_3^-	12,05 ± 0,68	13,06 ± 0,56
7	Phosphates, PO_4^{3-}	0,92 ± 0,06	0,93 ± 0,09
8	Chlorides, Cl^-	52,6 ± 5,9	80,7 ± 1,5
9	Sulfates, SO_4^{2-}	44,07 ± 7,63	45,8 ± 0,7
10	Solid-sediment	549 ± 31	568,4 ± 6,7
11	Fats	None	5,2 ± 0,6
12	Phenols	0,005±0,001	0,006 ± 0,002
13	Synthetic active substances	0,06±0,01	0,06 ± 0,01
14	Iron (overall)	0,506±0,011	0,53 ± 0,05

A project of the wastewater treatment equipment has been designed since such a high level of the wastewater disposal is inadmissible. Projected of the water treatment complex includes a stage of the biological cleaning and another stage of advanced purification.

The scheme of the projected water treatment complex is following. The waste waters initially flow in one of settlers equipped with an arc-sieve to separate large impurities. Then the wastewater is pumped to the inlet chamber and then to the settler-floatator. The settler-floatator is a combined machine, which initially sediments larger impurities, then the rest of coarse-dispersed suspended substances can be removed by the pressured flotation with recirculation of the working fluid. The treated wastewater after the settler floatator is used as the working fluid in the beginning of the water treatment cycle and later it is substituted with the clarified wastewater from the secondary settler of the second biological purification stage. Air is pumped through the the working zone using an air ejector. Saturation of the liquid occurs in the pressured head tank. Floatation sediments are removed from the surface of the floatator-settler to a radial tray using a radial scraper. Further wastewaters pass through two stages of the biological cleaning. The first stage airtank is intended to remove of main part of the pollution.

The airtank – settler of the second stage of cleaning has similar design and is intended to achieve complete biological cleaning of wastewater and separation of the slime mixture. Air tank has been equipped with the vertical cylindrical separator, which divides the airtank into central, sedimental, and peripheral airation zones. Thus, the second stage airtank works in a low-loading on the active silts mode. This mode guaranties stabilization of superfluous silt. Both airtanks are equipped with effective airators to supply the air into the silt by the jets of the working liquid. Silt mixture from the bottom part of the airtank is used as the working fluid.

Nozzles of the jet airators are established in such a way to ensure rotation of the silt mixture in the aeration zone. This design gives us a possibility to ensure suspended free floating active silt. The jet airation pumps of the first stage airtank feed its jet airators. The jet airation pumps of the second stage airtank-settler feed its airators and one airator of the fisrt stage airtank. This scheme ensures silt mixture circulation between the first and second stage airtanks.

Existing project of the water treatment proposes the polystirole foam filtration for the advanced purification of the wastewaters. The filtrate and the washing liquid are accumulated behind the filter.

Then the wastewaters should be disinfected using the solution of NaClO, which is directly dozed into the contact reservoir.

The stabilized superfluous active silt, collected from the airtank of the second stage should be piped back to the inlet chamber of the water treatment equipment. Biocoagulation of impurities by the superfluous active silt allows essential increase the wastewater cleaning efficacy.

Then the superfluous active silt should be precipitated together with other coarse-dispersed suspended particles in the settler-flotator. Then the superfluous active silt sediment and the flotation slurry should be dehydrated at the silt platforms. Finally the cleaned wastewaters should be drained to the brook.

Thus, the plannning firm has proposed the modern domestically produced water treatment complex including biological cleaning and advanced purification stages. Projected technical parameters of the drain water are shown in the column 2 of Table 4.

However, ecological legislation requires to determine if the project ensures allowable parameters of the wastewater to be drained to the brook. We aimed next stage of our research to find answer to this question.

TABLE 4. Comparison of effectiveness of the water treatment equipment and requirements of MAL

Pollutants	Pollutant concentrations, mg/l		
	Quality data of wastewaters, which can be achieved on the projected water treatment equipment using the advanced purification	Permissible quality of the cleaned wastewaters drained to the brook (calculated)	Wastewaters quality parameters, which can be achieved on the projected water treatment equipment without advanced purification
1	2	3	4
COD	30	34,7	80
BOD_5	6	3,74	15
Suspened substances	6	6,16	15

The computer calculation by the Rodziller's method[3] was used to determine normal level of the projected cleaned water drain to the check point 2. The following parameters were used as initial data:

1. The brook's hydrological characteristics (Table 5);
2. Parameters of the background quality of the brook water at the check point 1 (Table 2);
3. Projected parameters of the wastewater quality (Table 4, column 2).

Table 5. Hydrological parameters of the brook and Seret

Parameters	Units of measurements	Parameter level		
		The brook	Seret	
			Winter	Summer
Minimal use of 95% flow providing	m^3/sec	0,012–0,018	0,77	0,58
Average width	m	1,2	15	15
Average depth	m	0,2	1,1	0,66
Average speed of flow	m/sec	0,1–0,2	0,24–0,4	0,2–0,3
Winding factor		1,08	1,087	

Results of our calculations are shown in Table 4, col. 3. As seen, the projected water treatment equipment can ensure necessary level of cleaning by COD and suspended substances content. However, the calculated level of BOD is much lesser than the projected level. Thus, we can conclude that the projected water treatment equipment can not completely remove negative influence of the enterprise wastewater on the brook.

It means that assimilating capability of the brook was not considered during designing of the water treatment equipment.

To relieve this problem we propose to establish direct drain channel of the wastewater to the river of Seret. This channel should be only 500–600 m long.

We calculated consequences of draining wastewater to the river. Following data were used for such calculation:

4. Hydrological characteristics of Seret (Table 5);

- Background quality of Seret water at the check point 3 (Table 3);
- Quality parameters for the cleaned wastewater (cleaning without advanced purification stage, Table 4, column 4).

Analysis of the calculation results proves that such a direct drain of the wastewater directly to Seret ensures needful quality parameters even without advanced purification stage. It is only needful to lay a wastewater collecting pipe from the water treatment outlet to Seret.

This solution ensures:

a) Significant simplification of the water treatment technology;
b) Avoiding of extra expense to construction and maintenance of the advanced purification complex;
c) Preservation of the brook and its ecosystem in their natural state.

3. Conclusion

It is needful to avoid draining of wastewater to small natural reservoirs to preserve their ecosystems. Existing schemes of wastewater drain to such reservoirs should be substituted with bypassing of wastewater to greater water objects with higher assimilation grade.

We propose to solve this problem through some restrictive legislative measures protecting small reservoirs from unassimilated drains.

We also propose to ensure at least tenfold dilution of the wastewater comparing to the river flow. This measure should protect the river's ecosystem from degradation caused by excessive content of the water pollutant.

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FACTS, CONTRADICTIONS AND POSSIBLE IMPROVEMENT ACTIONS FOR HAZARDOUS WASTEWATER MANAGEMENT – A CASE STUDY

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Abstract. Pollution caused by direct discharge of waste leaching in tanning industry is a major contamination for sites (soil and groundwater) in Romania. Next to Nitrogen-based organics, organic and inorganic sulphides and Chromium are some of the most hazardous contaminants discharged and historically present on tannery sites. As the industrial branch enters the IPPC (Integrated Pollution Prevention Control) Directive, the strategies of local businesses consisted in reducing production capacity, rather than implement adequate reduction or treatment measures. An analysis is carried out for water consumption/wastewater discharge in the spirit of Cleaner Production principles and some environmental indicators are measured for one important branch unit and benchmarked against EU references. The study is completed with cost analysis. Improvement actions are identified and the effects, in terms of environmental performance, of their implementation are quantified.

Keywords: tanning industry, toxic effluents, water/wastewater management, cleaner production, TECHNOBAT

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1. Introduction

Three major aspects are considered for water management in an industrial process:

1. Water consumption, as consumption of a limited natural resource. Within the sustainable development concept water is similarly quantified and monitored as the other raw materials. This is a distinct category when describing the “material intensity” of a product/service, as F. Hinterberger synthesized in 2004. When the “chemically tanned leather” is described, the reported value of “water intensity”, according M. Ritthof (2002), is 515 t/t for the entire Life Cycle.
2. Pollution that is generated along the technological processes and that is discharged as effluents and
3. Costs related to water uptake completed with wastewater treatment costs and discharge fees and penalties. These costs are not usually accurately accounted and the unit management aren’t either aware of their real values or that they add to the production cost following an arbitrary allocation key (Environmental Management Accounting – EMA, technical module developed within the UNIDO Regional Project, Transfer of Environmentally Sound Technology – TEST in Danube River Basin, 2003).

The analysis was based on real data that were limited to those available at the unit level and calculations were made for evaluating the effects of measures that were implemented at pilot level.

The study was carried out as part of a national R&D project supported by the Ministry of Education and Research and the main reason for involving the unit was to raise awareness of its management and for better substantiating decisions related to water/wastewater management.

2. Unit Water supply

Two categories of raw water, industrial and drinking, are supplied from the municipal net. Figure 1 synthesizes values for the water consumption along two-year period:

3. Other Services Related to Water Management

If the water consumed is paid at the real uptake value, the unit has been contracting, on annual basis, services that are paid regardless those services are satisfactorily provided or not:

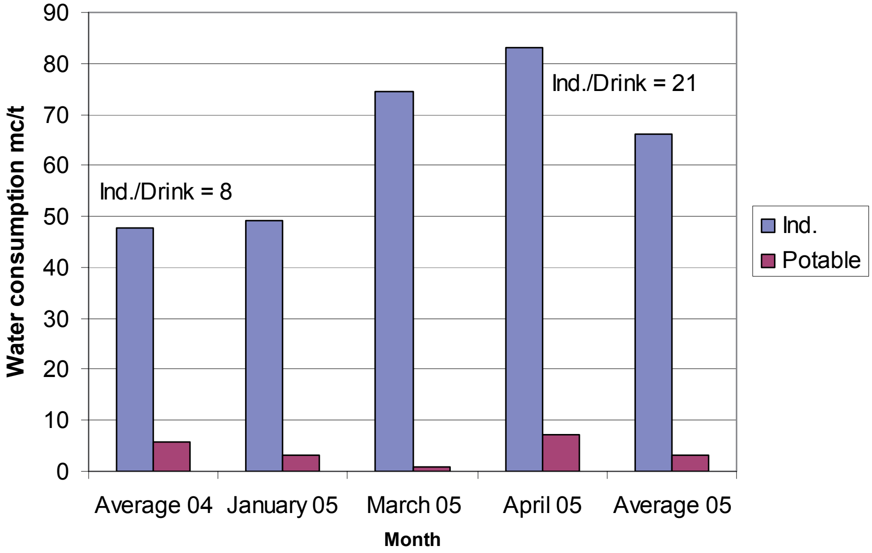

Figure 1. Specific water consumption, mc/t raw hide

1. Sewerage use related to industrial effluent, at about 49% industrial water uptake;
2. Sewerage use for domestic effluent, at about 22% drinking water uptake;
3. Sewerage use for storm water, for a fix rainfall value (500 l/m^2.year);
4. Effluent re-pumping to the municipal wastewater plant (negative slope);
5. Additional tax, based on empiric calculation enforced by water/wastewater operator.

All these mandatory services have a considerably formal character that facilitates avoiding the real problems and responsibility for the unit water/ wastewater management, which are:

1. Obsolescence and non-functionality of the local wastewater treatment facility;
2. Internal pumping of local effluents towards the unit wastewater facility (negative slope) and
3. Distribution of drinking water (about 7% from the total uptake) to other businesses on site for industrial use.

Two important remarks are to be made:

1. The total water uptake at higher values (monthly average) was noticed for those months when the production operated capacity situated at low values and
2. The reduction of drinking water uptake (2005 vs. 2004), as one feedback to our preliminary analysis, had, as negative effect, the significant increase in industrial water uptake (to be noted in Figure 1).

4. Effluent Discharge

The unit total effluent, which is not measured, has three components:

1. The industrial effluent, calculate at 85% flow of the industrial water uptake (according the technological process procedure);
2. The domestic effluent, at the same flow as the drinking water uptake and
3. The rainfall effluent, at constant value, calculated as multi-annual average of the geographic area.

As mentioned in chapter 3, the water consumption was not rigorously function of the production obtained. This was a piece of evidence that the water management is not an important element in the unit strategy. As a direct consequence, the continuously positive trend in water consumption was reflected in the structure of discharged effluent. Figure 2 and Figure 3 offer a comparison between 2004 and 2005 average values.

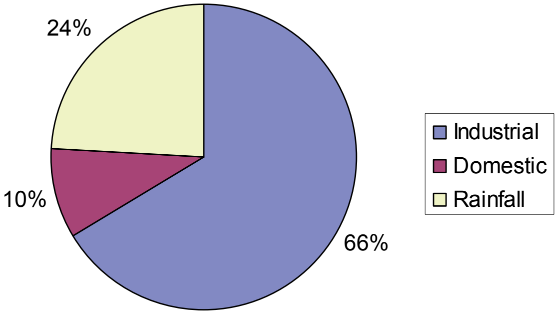

Figure 2. Structure of Total Effluent, average – 2004

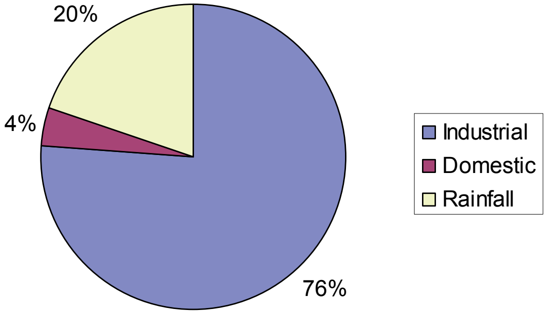

Figure 3. Structure of Total Effluent, average – 2005

This negative tendency was to be found in the costs the unit had to pay for water uptake and services (Figure 4).

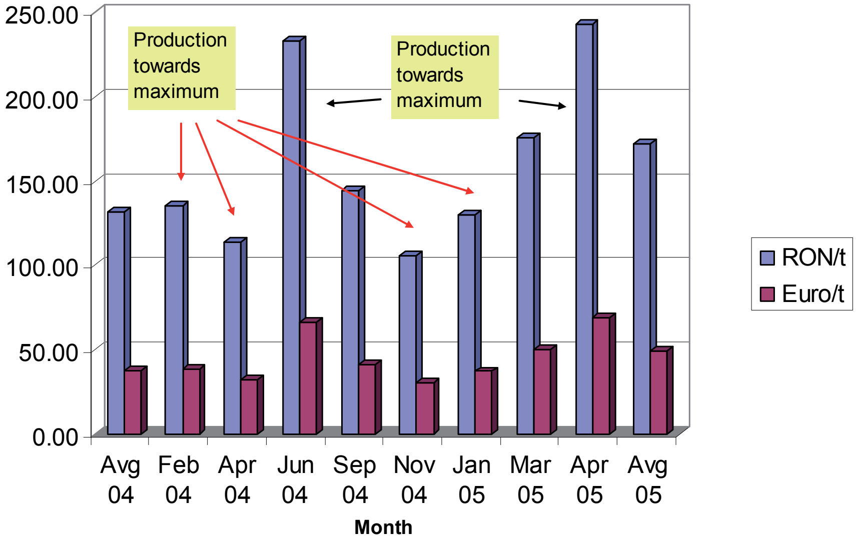

Figure 4. Water related costs in relation with real production (base: rawhide)

A deeper analysis (according the UNIDO methodology, which was mentioned before) of the water-related costs revealed some interesting aspects:

1. About 0.7 Euro/mc is paid for water uptake and usage. This costs are to be found in an increase of leather production costs with Euro50/t;
2. About half of the price is due to the negative slope of the unit location (10% internal pumping and more than 40% re-pumping to the Municipal Wastewater Facility);
3. No treatment costs are emphasized as no real treatment is provided.

A general picture is offered by Figure 5.

Compared with reliable reference data (presented by J. Ludvik, in a thorough analysis, which was carried for UNIDO, in 2000), the main characteristics of the unit effluent situate as follows:

- a monthly, daily respectively, effluent at values up to 1000% higher than those practiced in EU;
- no xenobiotics are either enforced or monitored. For the calculated concentration of Sulphides the unit condition is illustrated in Figure 6:

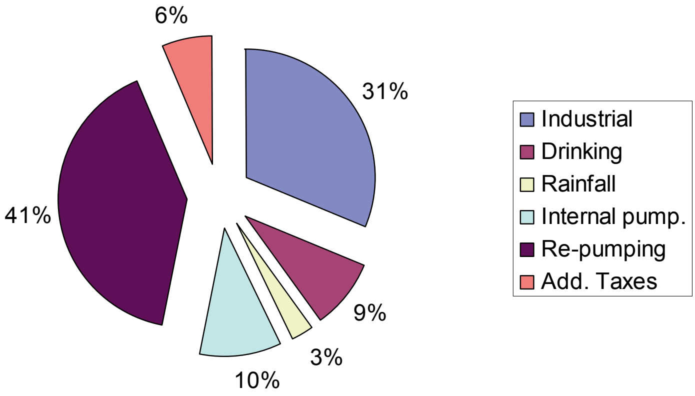

Figure 5. Cost Structure for water management, average – 2005

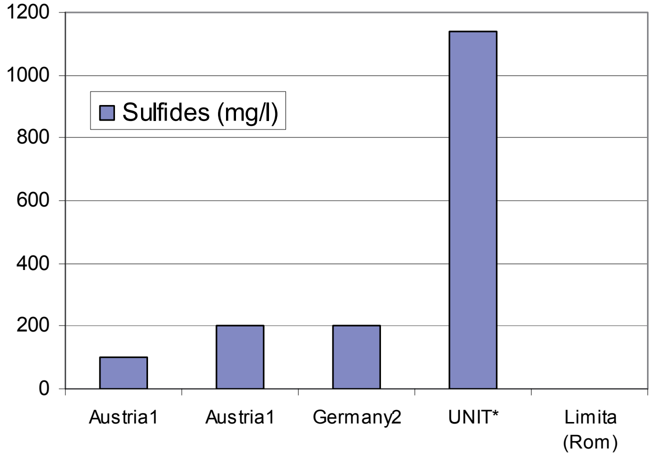

Figure 6. Sulfide content in the total effluent before treatment – mg/l

- the measured values of organic load (as COD and BOD), as shown in Figure 7 and Figure 8 reflect the same situation;
- UNIT* values refer to the unit final effluent, after passing the treatment facility where no treatment is applied and after which a monthly control is enforced.

Although the 10-fold level of total flow is expected to bring in significant dilution, the measured concentrations still keep higher values at almost similar scale.

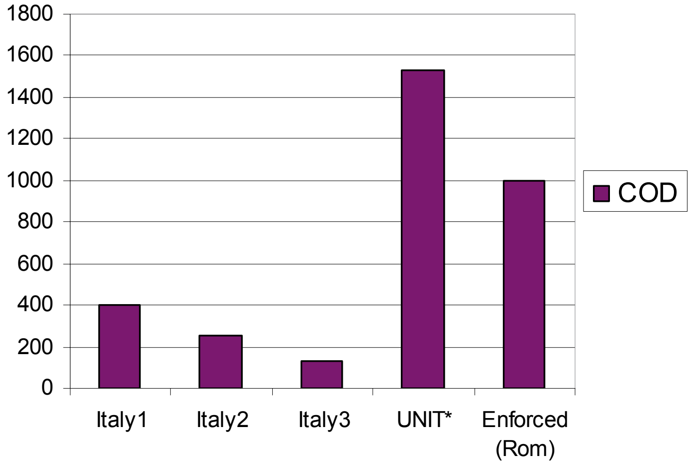

Figure 7. Total Effluent COD, before treatment – mg/l

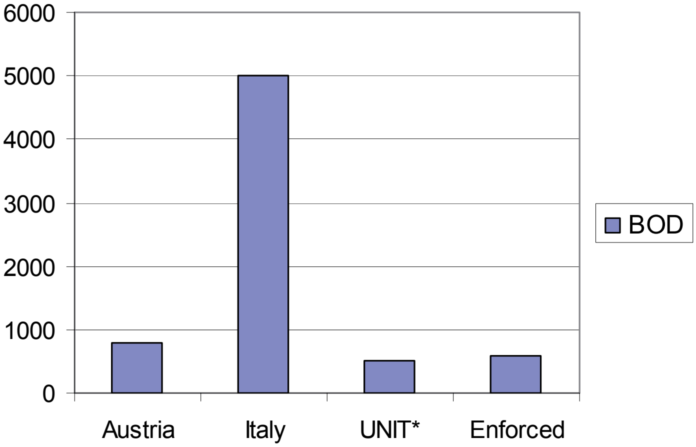

Figure 8. Total Effluent BOD, before treatment – mg/l

5. Improvement Potential

The improvement potential in terms of process relations with the environment is not exploited. The main cause of this lack of interest has to be found in the low prices the unit pays for environmental liabilities, on the one hand and lack of soundness of the enforced limits, on the other hand.

What the research team proposed, through a step-by-step approach, in the spirit of Cleaner Production, consisted in technological up-grade at the most polluting process-stage: hide liming-deliming. The *adopted solution (TEHNOBAT)* was first investigated in a laboratory research work and then replicated at both pilot and industrial level. This consisted in changing the chemistry and the operation procedure, with local hair separation. The main operation parameters before and after TEHNOBAT implementation are presented in Table 1 and they show drastically reduced values for some of the indicators that were monitored. Two characteristics only (Sulphides and BOD) need some more elaboration in order to be within the range of values for the best operated similar processes.

TABLE 1. Comparative characteristics of the local effluent (2005)

No.	Characteristic	MU	Conventional Option I	Conventional Option II	TEHNOBAT	Literature - Conventional
1	Flow	m^3/t	4	3.5	3.15	3; 8
		m^3/discarge	18.64	14.95	13.45	
2	pH	units	11.6; 12	11.5; 12	10; 11	12; 13
3	Suspended Matt.	g/l	27.23	31.64	16.3	
4	Dissolved residue	g/l	40.17	65.72	28.6	
5	Extractable Matt.	g/l	0.41	0.19	0.07	
6	**Sulphides**	**g/l**	**4.28**	**6.70**	**1.49**	**0.6; 1.2; 4**
7	Chlorides	g/l	21.65	47.47	10.48	
8	CaO	g/l	2.70	2.70	0.88	
9	COD	g/l	24.40	46.21	16.10	17; 25; 80
10	**BOD**	**g/l**	**10.80**	**23.53**	**6.87**	**3**
11	N_{total}	g/l	2.52	3.27	2.40	
12	N-NH4	g/l	0.27	0.49	0.33	
13	TKN	g/l	1.95	2.84	2.07	2; 5

Analyzing the results in terms of specific discharges, these are close to, or even better than the best reported ones (Figure 9, 10, 11):

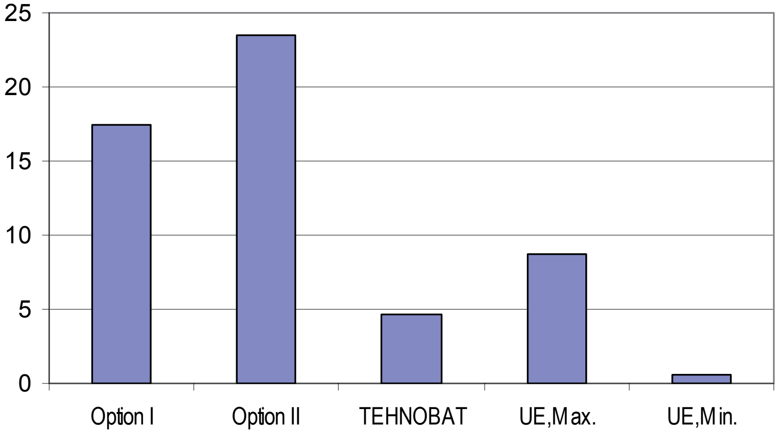

Figure 9. Specific local discharge of Sulphides, kg/t

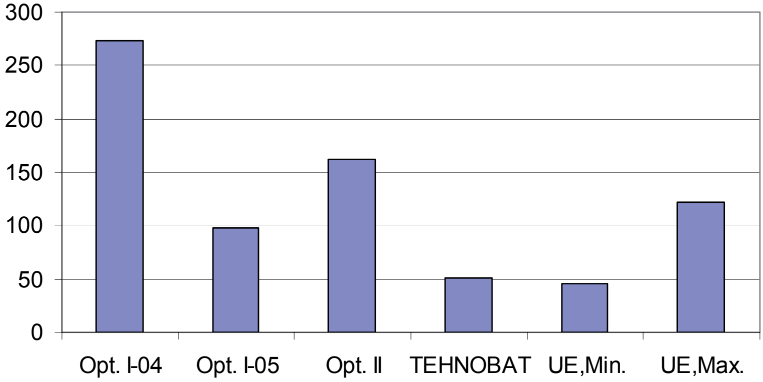

Figure 10. Specific local dischrge of COD, kg/t

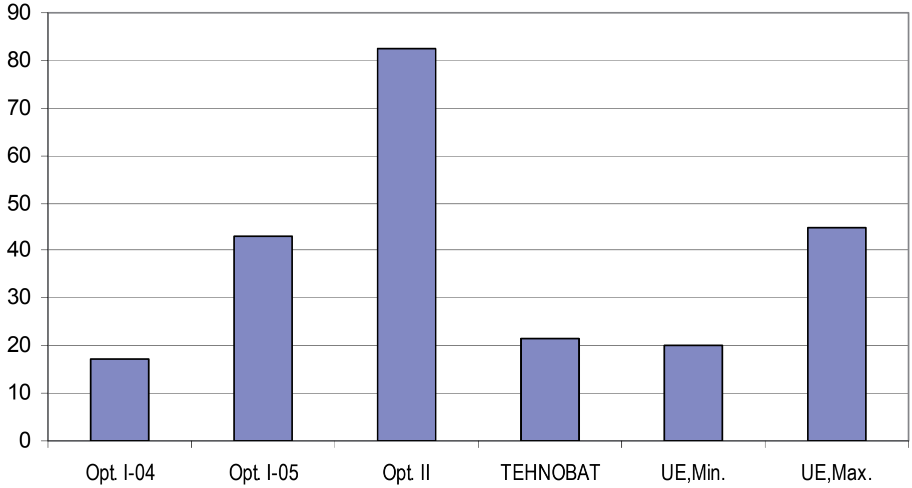

Figure 11. Specific local discharge of BOD, kg/t

Conclusions

The industry of skin and hide tanning followed a continuous decline in Romania, reducing its production to about 10% of the 1998 capacity. Although the other newly adopted environmental laws and regulations are equally stringent, through their production capacity, the local tanning units don't enter the IPPC provisions.

A representative tannery that processes bovine hides (the "unit") agreed to participate for project demonstration.

The analysis regarding water and wastewater management that was conducted at plant level revealed interesting and important results:

- water of drinking quality is being consumed in production processes
- the water uptake doesn't correlate with wastewater discharges and so with fees and penalties paid for
- an immediate measure, consisting in reduction of drinking water consumption, had a rebound effect: the increase of industrial water uptake
- coupled with continuously water price increase, the unit costs related to water management are continually growing.

A research was conducted for process improvement and the most polluting process stage was upgraded: the chemistry and operating procedures were changed at liming-deliming set of processes.

A remark needs to be made regarding the lack of unitary approach within the project working team itself: there seems to be a distorted understanding even at the level of branch experts. They don't fully agree with BREF/BAT style and measure units, on the one hand and they are excessively focused on the main production/product, on the other hand. This project was a good demonstration of the fact that all the technical thinking and education need to be restructured and that "the merely accumulation of specialized knowledge is no longer sufficient (it's doubtful whether it ever was); education and training should focus on advancing problem-solving competence" (as, in 2003, F. Hinterberger and Renata Zacherl underlined in a comprehensive study for the Ministry of Agriculture, Forestry, Environment and Water Management, Austria).

The research work proved that most of the targeted indicators could be brought at comparable values with reference data. With all the positive results demonstrated, a common question remains un-answered: whose task is to take further action and put them in practice? Simply enforcing the law – although here it's not a relevant case – produced already bad consequences through shutting down many units or downsizing others. Avoiding western paths and practices that are presently being fought against seems the most intelligent approach, but the project demonstrated that this is not to be achieved on a short term. "Incremental improvements" for increasing eco-efficiency don't seem to be motivating enough for real implementation commitment. A joint effort of all parties, including the institutional dimension as the 4th pole of sustainability, is more likely to give a solution and the Spangenberg's "prism of sustainability" (stressed in 2007 by Maria Teodorescu and Carmen Gaidau) seems a more appropriate model for the economies under transition, in their striving towards a sustainable path.

ACKNOWLEDGEMENT

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COMPLEX KINETIC INDIXES FOR ESTIMATION OF SURFACE AND WASTE WATER QUALITY

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Abstract. The more effective pathways of pollutants transformation in surface and waste waters are the interreservoir redox processes with participation of intermediate active particles. Among them the most interesting ones for natural water chemistry are the reactive products of a biochemical cycle of oxygen – singlet oxygen and hydroxyl (OH) radical. To determine the particles steady state concentration the methods of the measurements of the initiation rate and the effective interaction rate constant of these particles with natural water components (antioxidizing capacity relative to particle) have been developed. It is shown that the value of antioxidizing capacity relative to OH-radicals is the informative index of the total water pollution, and the value of antioxidizing capacity relative to singlet oxygen is estimation of the specific organic substances contribution. A classification for the aquatic medium purity classes depending on the value of antioxidizing capacity relative to OH-radicals is proposed based on the field data systematization.

Keywords: pollutant transformation; singlet oxygen; hydroxyl radical; antioxidizing capacity

1. Introduction

Currently, natural water participates in anthropogenic and natural water cycles. Anthropogenic cycle is the use of a natural reservoir water for power production, in industry, agriculture, for drinking water supply, household needs,

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etc. A significant part of used water is returned to a reservoir as urban and industrial sewage with a very high content of polluting substances (xenobiotics).

Surface waters experience the greatest anthropogenic pressure. They serve as a natural accumulator of polluting substances (pollutants) released into the atmosphere and lithosphere.

Contribution of various processes to self-purification of natural waters depends on the nature of pollutants. In general, various pollutants participate in aggregate processes of mass transfer and transformations (Skurlatov et al., 1994; Zepp, 1991).

2. Background

Among all the chemical transformations of pollutants in natural waters, photochemical transformations and catalytic processes of oxidation are of the greatest interest. All of these reactions proceed with intermediate formation of free radicals.

The following expression determines the rate of natural water self-purification for a given component (P_i) oxidation by free radical mechanism (Ernestova et al., 1992, 1994):

$$\frac{d[P_i]}{dt} = k_{ef}[R_i]\cdot[P_i] \qquad (1)$$

Here k_{ef} is the effective rate constant of water self-purification from substance P_i due to interacting with active particles R_i, s^{-1}; $[R_i]$ is quasi-stationary concentration of active particles, M.

Several researchers (Ernestova et al., 1994, Skurlatov et al., 1994) used the dye 4-nitrozo-N,N-dimethylaniline (PNDMA) as a model compound to determine transformation rate kinetics of pollutants interacting with active particles. PNDMA is known as a selective acceptor of OH-radicals (Kraljik and Trumbo, 1965) that has a high extinction coefficient ($\varepsilon = 3{,}4\cdot10^4$ $M^{-1}sm^{-1}$ at $\lambda = 440$ nm). The product of its oxidation-reduction (redox) decomposition is a colorless non-reactive compound.

Investigations have been done on how other intermediate particles formed in natural waters impede PNDMA kinetic transformation. These investigations largely dealt with solvate electron (e_{aq}^-), singlet oxygen ($^1O_2$) and superoxide ion-radical (O^{2-}). The use of pulse radiolysis and photolysis methods helped to show that the contribution of e_{aq}^- and O^{2-} to PNDMA kinetic transformation is insignificant, and the contribution of $^1O_2$ is comparable to the one of OH-radicals (Semenova, 1998).

3. Kinetic Indices Measurement Techniques

Direct measurements of the majority of intermediate active particles are practically impossible, since their concentrations in natural waters $[R_i]$ are very low. Indirect kinetic methods are commonly used to determine steady-state concentrations of the particles in natural waters (Ernestova et al., 1992; Semenova, 1998):

$$\left[R_i\right]_s = \frac{W_{i,R_i}}{\Sigma k_{i,R_i}\left[S_{i,R_i}\right]} \tag{2}$$

Here $W_{i,Ri}$ is initiation rate of active particles $[R_i]$ in natural waters, $M.s^{-1}$. Parameter $(\Sigma k_{i,Ri}[S_{i,Ri}])$ is the effective transformation rate interaction constant between pollutants and active particles or antioxidizing capacity of water relative to particle R_i. On one hand, this parameter determines ability of environment to stabilize free radical processes, which is extremely important for a water body. On the other hand, according to Eqs. (1) and (2), its high value due to anthropogenic load decreases efficiency of self-purification of water environment by free radical mechanism.

Initiation rate of OH-radicals in natural water due to photochemical $(W_{i,h\nu})$ and biochemical $(W_{i,bio})$ processes is estimated by the degree of dye PNDMA transformation (decoloration) under sunlight and in the dark (fig. 1). Time of reaction under sunlight is $\Delta\tau_{h\nu} \sim 0{,}5\text{–}1{,}0$ h, and in the dark $\Delta\tau_{(bio)}$ – ~5–24 h. Value $W_{i,h\nu\ (bio)}$, $M\cdot s^{-1}$, can be found from:

$$W_{i,h\nu(bio)} = \frac{\Delta A_{h\nu(bio)}}{l\cdot\varepsilon\cdot\Delta\tau_{h\nu(bio)}\cdot 3{,}6\cdot 10^3} \tag{3}$$

where $\Delta A_{h\nu(bio)}$ is the difference of optical density of natural water solution (NW) in the beginning and in the end of light (dark) experiment; l is the length of a cell, sm; $\varepsilon = 3{,}4\cdot 10^4\ M^{-1}sm^{-1}$ is PNDMA extinction coefficient; $\Delta\tau_{h\nu(bio)}$ is exposition time of NW solution, h.

It was found that $W_{i,h\nu(bio)}$ can vary from 10^{-12} up to 10^{-9} $M.s^{-1}$, on the average making for $W_{i,bio} \sim 3\cdot 10^{-11}\ M\cdot s^{-1}$, and for $W_{i,h\nu} \sim 10^{-10}\ M\cdot s^{-1}$ depending on the water body.

Initiation rate of singlet oxygen (*$W_{i,}O2$*) was calculated using dye PNDMA decoloration rate at water photolysis in the presence of nitroxyl radical 2,2,5,5-tetramethyl-2,5-dihydropyrazine-1,4-dioxide (DPDO) (see fig. 1), an effective acceptor of OH - radicals (Skubnevskaya et al., 1985). Thus estimated $W_{i,O2}$ can vary from 10^{-11} up to $n\cdot 10^{-10}\ M\cdot s^{-1}$ depending on the water body.

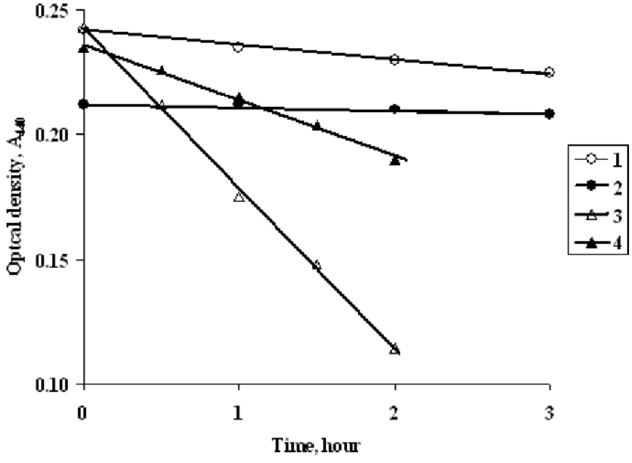

Figure 1. Kinetic of PNDMA decoloration in natural water (Volga) in dark (1, 2) and at photolysis (3, 4): 2 – in the water filtered through membrane filter Ø0,22 μm; 4 – at presence nitroxyl radical DPDO

The method of determination *of antioxidizing capacity of natural water relative to OH-radicals* ($\Sigma k_{i,OH}[S_{iOH}]$) is based on comparison of decoloration rate of dye PNDMA under action of OH-radicals in distilled water (DW) in absence and in presence of natural water (NW). To initiate OH-radicals, photolysis of hydrogen peroxide under sunlight or under artificial sources of UV- radiations was used (GD 52.18.24.83–89, 1990; Semenova, 1998).

Decoloration rate of dye (W_{PNDMA}) in distilled water coincides with the initiation rate of OH-radicals provided that $k_{PNDMA}[PNDMA] > k_{H2O2}[H_2O_2]$. In natural water, the formation of OH-radicals competitevely interacts not only with dye PNDMA but also with natural “traps” of radicals. This slows down decoloration rate of dye cooperate (fig. 2).

Antioxidizing capacity ($\Sigma k_{i,OH}[S_{iOH}]$, s^{-1}) can be estimated using the following expression:

$$\sum k_{i,OH}\left[S_{i,OH}\right]=\left[\frac{\left(\Delta A_{H_2O_2}-\Delta A_O\right)^{\mathrm{DW}}}{\left(\Delta A_{H_2O_2}-\Delta A_O\right)^{\mathrm{NW}}}-1\right]\cdot n\cdot k_{PNDMA}\left[PNDMA\right] \qquad (4)$$

where ${}_{\Delta}A_{H_2O_2}^{DW(NW)}$ and ${}_{\Delta}A_0^{DW(NW)} = 1/m\cdot\Sigma(A_1-A_2)_{H_2O_2(0)}^{DW(NW)}$ is an arithmetic mean difference of solutions DW and NW optical density in the beginning (A_1) and at the end (A_2) of the experiment in the presence ($\Delta A_{H_2O_2}$) and in the absence (A_0) of hydrogen peroxide; n is the dilution degree of solutions; m is the number of tests; $k_{PNDMA} = 1{,}3\cdot10^{10}$ $M^{-1}s^{-1}$ is the bimolecular rate constant interaction of dye with OH-radicals (Pikaev and Kabakchi, 1982); [PNDMA] is the dye concentration, M.

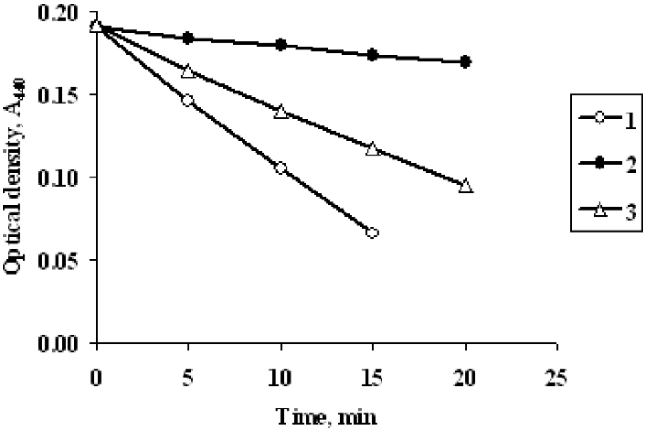

Figure 2. Definition of antioxidizing capacity of water relative to OH-radicals with use artificial light (xenon lamp): 1 – distilled water with additive H_2O_2; 2 – natural water (Protva) without additive H_2O_2; 3 – natural water (Protva) with additive H_2O_2, n=4

The sensitivity of the index $\Sigma k_{i,OH}[S_{iOH}]$ determination method is estimated to be $1 \cdot 10^3$ s^{-1}.

For determination *of natural water antioxidizing capacity relative to singlet oxygen* ($\Sigma k_{i,O2}[S_{i,O2}]$) the above-mentioned method has been modified (Semenova, 1998). Photolysis of dye Bengal rose (BR) was used to initiate $^1O_2$. The dye PNDMA was used as a competitive acceptor of forming $^1O_2$. However, in this case it was necessary to take into account the possibility of suppression of $^1O_2$ formation by water k_d (Haag and Hoigne, 1986). $\Sigma k_{i,O2}[S_{i,O2}]$ can be found from:

$$\sum k_{i,O2}\left[S_{i,O2}\right] = \left[\frac{\left(\Delta A_{BR} - \Delta A_O\right)^{DW}}{\left(\Delta A_{BR} - \Delta A_O\right)^{NW}} - 1\right] \cdot n \cdot k_d \tag{5}$$

where $_{\Delta}A_{BR}{}^{DW(NW)}$ and $_{\Delta}A_0{}^{DW(NW)} = 1/m \cdot \Sigma(A_1 - A_2)_{BR(0)}{}^{DW(NW)}$ is an arithmetic mean difference of solutions DW and NW optical density in the beginning (A_1) and at the end (A_2) of the experiment in the presence (A_{BR}) and in the absence (A_0) of Bengal rose; n is the dilution degree of solutions; m is the number of tests; $k_d = 2 \cdot 10^5$ $M^{-1}s^{-1}$ is the rate constant of $^1O_2$ quenching by water.

Dimension and physical meaning of the antioxidizing capacity parameter allow to interpret it as an effective destruction rate constant of OH-radicals (or lifetime of OH-radicals) in natural water. Therefore, by substituting typical values for fresh waters $W_{i,OH} \sim 3.10^{-11}$ $M \cdot s^{-1}$ and $\Sigma k_{i,OH}[S_{iOH}]$, $\sim 10^5$ s^{-1}, we obtain an independent average estimation of *OH-radicals stationary concentration* $[OH]_s \sim 3.10^{-16}$ M.

The knowledge of the interaction rate constant between a pollutant and OH-radicals ($k_{i,OH}$) makes it possible to estimate the effective rate constant of its radical transformation in natural water (k_r):

$$k_r = k_{i,OH} \cdot [OH]_s \tag{6}$$

At typical values $k_{i\,OH} \sim 10^9\, M^{-1}s^{-1}$ and $[OH]_s \sim 3 \cdot 10^{-16}$ M, characteristic time of pollutant transformation by OH-radicals can be several months to several days. When OH-radicals are initiated photochemically $[OH]_s$ can reach up to 10^{-14} M. In this case period of pollutant transformation can be as short as one day.

4. Estimation of Natural Waters Pollution

Measured kinetic indices $W_{i,Ri}$ and $\Sigma k_{i,OH}[S_{i,OH}]$ are also independent integral indicators of natural water quality. Thus, in addition to estimation of natural water reactive ability for self-purification due to OH-radicals formation, the value of natural water antioxidizing capacity ($\Sigma k_{i,OH}[S_{iOH}]$) let us estimate the total water pollution degree by nonspecific organic compounds. Indeed, assuming that $k_{i,OH} \sim 10^9\ M^{-1}s^{-1}$, we obtain an estimate of the effective concentration of such compounds:

$$[S_{i,OH}] \approx 10^9 \cdot \sum k_{i,OH} [S_{i,OH}] \tag{7}$$

This expression allows to classify natural water quality according to the measured values of $\Sigma k_{i,OH}[S_{i,OH}]$ based on existing water quality standards (GD 52.18.24.83-89, 1990):

- at $\Sigma k_{i,OH}[S_{i,OH}] < 3 \cdot 10^4\ s^{-1}$ water is classified as pure;
- at $3 \cdot 10^4 < \Sigma k_{i,OH}[S_{i,OH}] < 3 \cdot 10^5\ s^{-1}$ water is classified as polluted with signs of ecological damage;
- at $\Sigma k_{i,OH}[S_{i,OH}] > 3 \cdot 10^5\ s^{-1}$ the water body ecology is damaged, water is very polluted.

In addition, because this kinetic index $\Sigma k_{i,OH}[S_{i,OH}]$ describes total pollution of the aquatic system and strongly correlate with its biological quality (Semenova, 1998) its measurements can be easily applied to practical waste water control.

The value of natural water antioxidizing capacity relative to singlet oxygen is also useful for estimation of natural water pollution. It is known, that the constant of physical quenching of $^1O_2$ due to the interaction with dissolved oxygen is equal to $2\cdot10^5$ $M^{-1}s^{-1}$. Therefore, one can adopt the value of ~ 60 s^{-1} of the quantity $\Sigma k_{i,O2}$ $[S_{i,O2}]$ as the criterion of very pure water that is water where dissolved oxygen is the only acceptor of singlet oxygen. However field data show (see table), that $\Sigma k_{i,O2}[S_{i,O2}]$ can be significantly higher. Judging from the value of $\Sigma k_{i,O2}[S_{i,O2}]$ the concentration of specific acceptors of singlet oxygen in natural waters can reach 10^{-4} M.

TABLE 1. Antioxidizing capacity of water in relation to OH-radicals and singlet oxygen

Sampling station	$\Sigma k_{i,OH}[S_{i,OH}]$ s^{-1}	$\Sigma k_{i,O2}[S_{i,O2}]$ s^{-1}
river Protva, Obninsk	$1{,}6 \cdot 10^5$	$3{,}4 \cdot 10^4$
river Ugra	$2{,}0 \cdot 10^4$	$< 10^3$
river Ufa	$7{,}9 \cdot 10^4$	$4{,}8 \cdot 10^4$
river Volga, Volgograd	$9{,}1 \cdot 10^4$	$3{,}3 \cdot 10^4$
river Volga, V.Lebyazh'e	$1{,}0 \cdot 10^5$	$1{,}0 \cdot 10^4$
river Volga, Astrahan	$1{,}25 \cdot 10^5$	$3{,}7 \cdot 10^4$
river Ahtuba	$1{,}7 \cdot 10^5$	$6{,}0 \cdot 10^3$
river Bereket	$8{,}0 \cdot 10^4$	$< 10^3$
river Buzan	$3{,}0 \cdot 10^5$	$1{,}5 \cdot 10^4$

Such a high concentration $[S_{i,O2}]$ can be dew to increased contents of the toxic pollutants that are highly reactive with $^1O_2$, such as polycyclic hydrocarbons, furans, and amines (Monrol, 1977; Wikinson and Brummer, 1981).

Another interesting quantity is the ratio of antioxidizing capacity of natural water relative to various active particles. In pure water even under condition of equality $[S_{i,OH}]$ and$[S_{i,O2}]$

$$\frac{\sum k_{i,O2}\left[S_{i.O2}\right]}{\sum k_{i,OH}\left[S_{i,OH}\right]}\langle 0.1 \tag{8}$$

Field data confirm that (see table) with the increase of anthropogenic load:

$$\lim \frac{\sum k_{i,O2}\left[S_{i,O2}\right]}{\sum k_{i,OH}\left[S_{i,OH}\right]} \rightarrow 1 \tag{9}$$

It means that processes of water self-pollution in response to anthropogenic load and technogenic pollution can significantly influence water quality.

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CONTINUALLY MEASURED ORP AND PH SIGNAL FOR CONTROL OF NITROGEN REMOVAL

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Abstract. The use of pH and ORP as control parameters for the denitrification process in activation with intermittent aeration (simultaneous nitrification – denitrification) at municipal wastewater treatment plants is compared and discussed. The termination of denitrification was identified either by both signals or ORP and pH independently. In addition, the signals were used for control of the whole activation process and for the improvement of its efficiency.

Keywords: nitrogen removal; denitrification; regulation and control; ORP and pH measurement

1. Introduction

A biological nitrogen removal from the waste water depends on the creation of optimal conditions for nitrification and denitrification. Both of these biochemical processes require specific conditions. In particular, concerning the requirements for the presence of the oxidation agent they are contradictory. Nitrification requires dissolved oxygen, while denitrification ceases in the presence of oxygen.

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It is therefore obvious that optimal nitrogen removal will depend on the exact set up of oxic and anoxic conditions, especially in the case of activation with simultaneous nitrification – denitrification in one reactor (activation with intermittent aeration). Operationally proved processes are (Drtil et al., 1999):

- set up of oxic and anoxic periods by a timer
- set up of oxic and anoxic periods according to continuously measured NH_4-N and NO_3-N concentrations
- set up of anoxic periods according to continuously measured ORP or ORP and pH signal
- set up of oxic periods according to current respiration rate.

ORP regulation is based on the fact, that the ORP value is decreasing during the denitrification process, while after its completion the ORP record shows a break and the decrease rate speeds up (Ermel, 1983; Charpentier et al., 1989; Moriyama, 1990). pH regulation is similar: after completion of denitrification connected with production of OH^- increase of pH is stopped or slows down (Drtil et al., 1998; Drtil et al., 1995; Al-Ghusain et al., 1994; Al-Ghusain et al., 1995; Chang et al., 1996). These breaks were recommended to be appropriate for the aeration equipment control, i.e. after the completion of denitrification an aeration equipment starts to work creating thus oxic conditions necessary for nitrification. However it was proved, that ORP or pH signal did not show a break indicating NO_3-N removal in all cases. Results from detailed laboratory research described in (Drtil et al., 1999; Drtil et al., 1998) have shown that the higher the organic substrate concentration was in the activation, the higher was the denitrification rate and the more significant the pH break was. Exactly the contrary was valid for the relation of ORP signal and the actual substrate concentration. As a result, the optimal regulation system should simultaneously record both signals, while the end of denitrification could be indicated by both signals together, or at least by one of them. ORP and pH signals significantly depend on the waste water composition, which quality might differ day to day. As the regulation is not based on the evaluation of absolute values of these parameters but on their time course, both signals were recommended for regulation of denitrification in the waste water treatment processes.

Termination of nitrification and its identification is not so explicit. Set up of oxic period either by a timer or according to current respiration rates or stabilized ORP signal were described or recommended (Drtil et al., 1999; Drtil et al., 1998).

Independent monitoring of ORP or pH was used at several waste water treatment plants (WWTP) or in laboratory models. In this paper, verification of both signals common measurement at full scale municipal WWTP with simultaneous nitrification- denitrification is described.

2. Methods and Objects

The ORP and pH signals were measured at municipal WWTP Vitkov (Czech Republic).The decisive parameters of the WWTP and the activation were as follows:

- inflow: daily average 20 l s^{-1}; BOD_5 = 230 mg dm^{-3}; Suspended solids SS = 156 mg dm^{-3}; Ntotal = 40 mg dm^{-3}; T = 15°C
- effluent: BOD_5 = 10 mg dm^{-3}; SS = 16 mg dm^{-3}; Ntotal = 7 mg dm^{-3}; NH_4-N = 2 mg dm^{-3}
- mechanical pretreatment: fine screens and grit chamber
- activation: completely mixed reactor with intermittent aeration (aerators and mixer in the same reactor); volume = 700 m^3; hydraulic retention time = 0,4 d; volumetric loading Bv = 0,575 kg $m^{-3}.d^{-1}$ (kg BOD_5); sludge retention time SRT = 20 days.

ORP and pH probes were installed directly in activation reactor and both signals were measured under oxic and anoxic conditions. Platinum electrode (with a silver/silver chloride reference electrode) was used for the ORP measurement and glass electrode for the pH measurement. Oxic (t_N) and anoxic (t_D) periods in activation were adjusted by a timer:

- phase I.: automatically adjusted, t_D = 130 min, t_N = 180 min
- phase II.: automatically adjusted, t_D = 300 min, t_N = 240 min
- phase III.: periods manually adjusted according to current nitrogen concentration, t_D = 30 and more min, t_N = 60 and more min.

The whole experiment took 2 weeks in August 2006.

3. Results and Discussion

3.1. IDENTIFICATION OF DENITRIFICATION TERMINATION

Termination of denitrification (NO_3-N removed) was indicated by both signals. Typical breaks, which were confirmed by laboratory analyses of NO_3-N (NO_3-N = 0 mg dm^{-3}) are in Fig. 1–5. It was proved that common measurement of ORP and pH is legitimate.

Complete removal of NO_3-N during the whole 2 weeks experiment was identified 18 times. Indication was registered as follows:

- only ORP break: 1 x; ORP and pH breaks: 9 x; ORP break and not sharp pH break: 6 x; only pH break: 1 x; no pH and ORP break: 1 x.

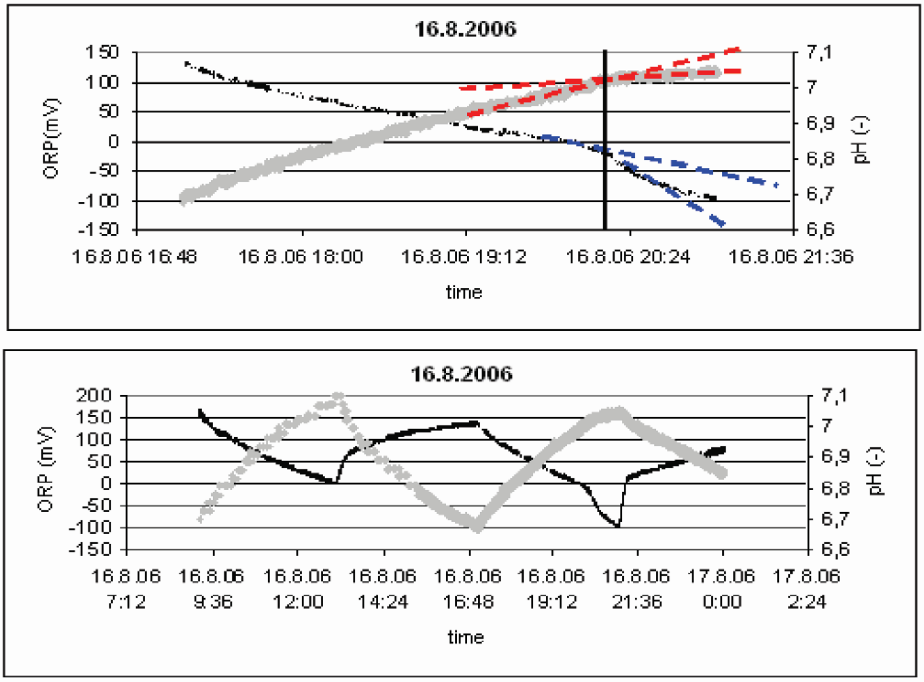

Figure 1. Example of identification of NO_3-N removal by ORP (black) and pH (gray) signal (slopes in break points are highlighted by dashed lines). Oxic and anoxic periods were adjusted by a timer – phase I. (start of oxic period/aeration is connected with ORP increase; start of anoxic period/mixing is connected with ORP decrease). At 13:00 NO3-N were not removed (denitrification incomplete) – no breaks. At ca. 20:00 NO3-N were removed (denitrification completed) – ORP and pH breaks.

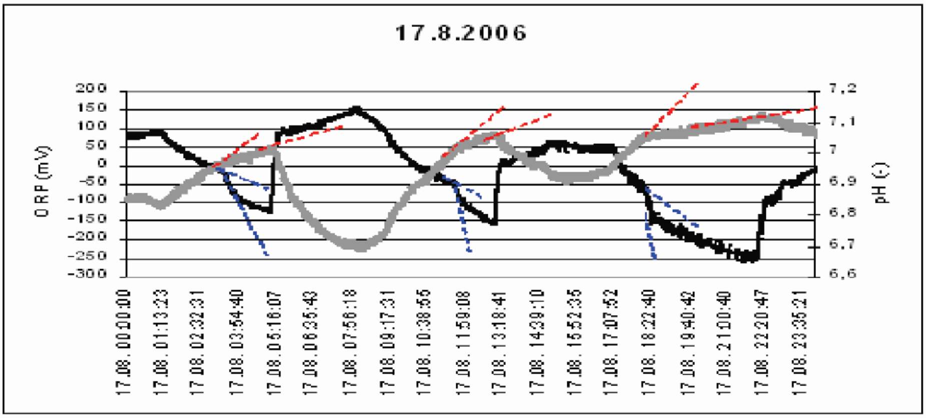

Figure 2. Next examples of NO_3-N removal identification by ORP (black) and pH (gray) signals (slopes in break points are highlighted by dashed lines). Start of oxic period/aeration is connected with ORP increase; start of anoxic period / mixing is connected with ORP decrease.

ORP signals and the breaks were more sharp. Breaks in pH depend on the neutralisation capacity of the wastewater and on the intensity of mixing and CO_2 stripping (Drtil et al., 1995; Pitter, 1999). At WWTP Vitkov increase of pH during denitrification was only 0,1 – 0,3. Anyway, the pH breaks were detectable.

Only in one case the removal of NO_3-N was identified just by pH (Fig. 4). This result corresponds with the conclusions described in (Drtil et al., 1999; Drtil et al., 1998). In laboratory models feeded with synthetic and sewage wastewater it was proved, that NO_3-N removal was detectable by only ORP, only pH or by ORP and pH. Removal of NO_3-N was indicated by pH in a case of highly loaded system, i.e. rate of denitrification was high. Under low loaded conditions or during endogenous denitrification removal of NO_3-N was indicated just by ORP. At WWTP Vitkov is a completely mixed activation, with continuous inflow. Concentration of organic substrate in activation is very low (BOD_5 is on the same level as in the effluent and the denitrification rates are low). Under such conditions the dominance of ORP breaks is logical.

From the long-term records of the measured signals it can be concluded that in a case that ORP and pH signal did not show a break (Fig. 3), we can adjust an ORP value which indicates that denitrification is completed and the system is already under anaerobic conditions. This value should be measured for a given

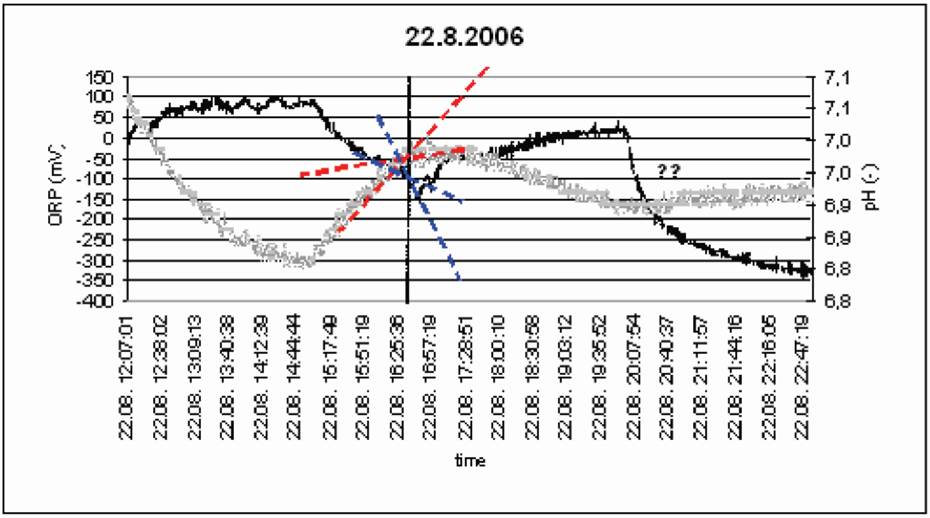

Figure 3. Example of a not explicit identification of NO_3-N removal: at 16:30 breaks on both signals; at 20:10 no break on ORP (black) and pH (gray) (possible explanation: in the evening was the loading of WWTP very high, denitrification rate was also too high and signals didn't respond to change of anoxic to anaerobic conditions). At 20:10 the removal of NO_3-N is detectable only from intensive decrease of ORP to less than – 100 mV.

activation and wastewater (absolute ORP value is influenced by all ions in wastewater, not only by nitrogen ions; Pitter, 1999). From the measurements realised at WWTP Vitkov it follows, that ORP approx. – 80 mV is a limit value when anoxic conditions are changed for anaerobic. Absolute values of ORP when denitrification was completed were as follows (in mV): –20; –10; –10; –50; –50; –70; – 60; – 80; – 30; –50; – 40; –40; –50; –60; –40.

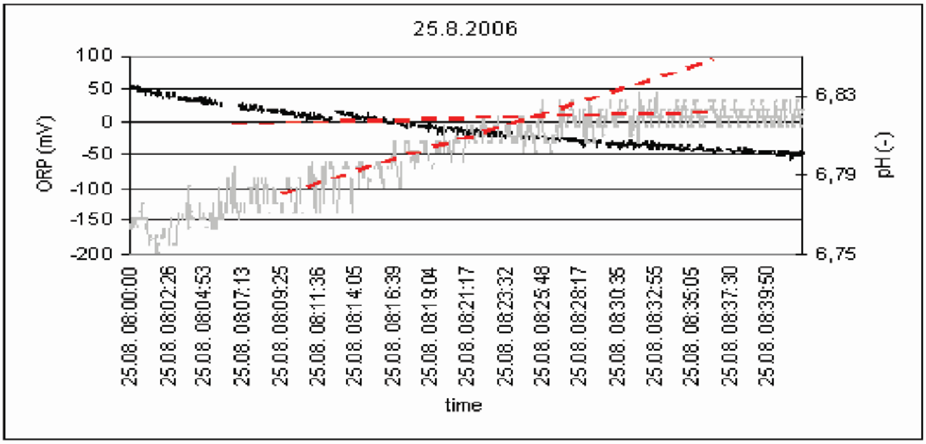

Figure 4. Example of pH (gray) identification of NO_3-N removal (8:00 is a typical hour for “morning” peak in loading; rate of denitrification was high).

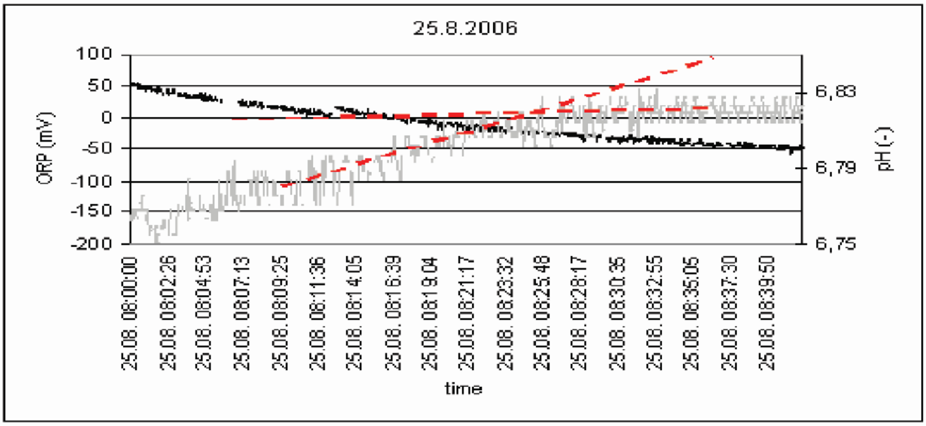

Figure 5. ORP (black) and pH (gray) signal measured on 25/08/2007 – summary record indicating denitrification termination. At 00:29 a.m., 04:34 a.m., 10:11 a.m.: ORP and pH breaks are detectable; at 08:30 a.m. (morning peak loading): break only on pH signal.

A fact that NO_3-N removal can be indicated by ORP and pH signals in a completely different way is confirmed on Fig. 5. Introduced is a half day record of ORP and pH. Even the breaks on ORP and pH differ, still these signals can be used for identification of NO_3-N removal.

3.2. IDENTIFICATION OF NITRIFICATION TERMINATION

Termination of nitrification (NH_4-N is completely removed) was not indicated. Explanation is simple: in activation with continuous inflow NH_4-N can not be removed to 0 mg dm^{-3}. Nitrification is a Monod type reaction and at certain concentration (at WWTP Vitkov these concentrations were approx. 1 mg dm^{-3}) the nitrification rate is lowered to a value which is the same as the rate of NH_4-N inflow (mg NH_4-N $dm^{-3}.h^{-1}$). In such an activation nitrification never terminates.

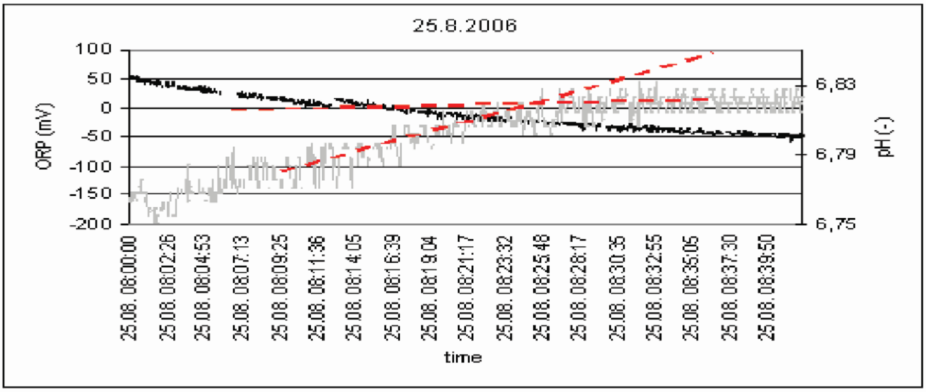

Figure 6. Influence of O_2 and ORP on nitrification. Only after the O_2 concentration and ORP (black) were increased (O_2 to 5–6 mg/l and ORP to –80 mV) (approx at 15:30), nitrification started and pH (gray) started to fall down.

Anyway, common measurement of ORP and pH signals was useful for a control of nitrification:

– similarly as for denitrification, we can adjust an ORP value which indicates that NH_4-N concentratrion is so low that longer aeration has no sence. These values measured for a wastewater in Vitkov were:

- from +50 till +100 mV in a case when denitrification was complete and during anoxic periods NO_3-N was removed to 0 mg dm^{-3}
- from +100 till +200 mV in a case when denitrification was incomplete, during anoxic periods NO_3-N was not removed to 0 mg dm^{-3} and overall concentrations of NO_3-N during nitrification periods were higher

– nitrification was always connected with decrease of pH. This fact was used in a situation which happened from 18/08 till 21/08/2006 (Fig. 6). During these days activation was overloaded and, in addition, ratio between anoxic and oxic periods (phase II.- see Experimental) was too high. Under anoxic conditions accumulation of NH_4-N in activation was too intensive (during anoxic period NH_4-N just inflows to the reactor and is not nitrified). As a result ORP gradually decreased to less than –200 mV under anoxic conditions and during oxic periods ORP increased to not more than –100 mV. Under these conditions nitrification did not start during oxic period even concentration of dissolved oxygen was 2–3 mg dm^{-3}. Only after the concentration of oxygen was increased to 5–6 mg dm^{-3}, ORP was increased to more than –80mV and the nitrification started. Such circumstances can be either measured by NH_4-N and NO_3-N analyses, or very simply by recording of pH: start of nitrification is connected with sharp decrease of pH.

3.3. OTHER USE OF CONTINUOUSLY MEASURED ORP AND PH

Common measurement of ORP and pH brought for an operator of the WWTP also other usable results:

- oxic conditions are connected with ORP increase and anoxic with ORP decrease
- in a case of nitrification, pH falls and ORP rises. During denitrification pH rises (but this conclusion is valid only for sewage wastewater; changes in pH values depend on acidobasic balances and on average oxidation number of organic carbon; Drtil et al., 1995; Pitter, 1999)
- gradual increase of pH on long- term record indicates, that denitrification starts to be more intensive than nitrification (it exists a risk that nitrification is less efficient and effluent NH_4-N concetration is growing)
- gradual decrease of pH on long- term record indicates, that nitrification is more intensive than denitrification and there is a risk that effluent NO_3-N concentration is growing
- from a long-term record of pH and ORP signals optimum duration of oxic and anoxic conditions can be adjusted (with a timer).

Attention: monitoring system based on ORP and pH measurement must be treated against short term changes (rapid, few minutes lasting increase or decrease etc.). In addition, attention should be given to the treatment of ORP and pH probes.

4. Conclusion

Continuously measured ORP and pH signals can be used for dynamic control of nitrogen removal and control of activation with simultaneous nitrification – denitrification (activation with intermittent aeration). From the long-term measurements realised at municipal WWTP Vitkov follows:

- termination of denitrification (NO_3-N completely removed) was indicated by breaks on both signals commonly or on ORP or pH signal individually
- breaks on ORP records were detected in much more cases compared to pH breaks. This fact is connected with a hydraulic characteristics of the activation at WWTP Vitkov. In completely mixed reactor with continuous inflow is permanently a low loading with organic substrate and the rates of denitrification are relatively low. Termination of low rate dentrification is identified mostly by breaks on ORP signal
- removal of NO_3-N can be identified not only by ORP and pH breaks, but also by measuring of absolute values of ORP. This value must be verified for a given wastewater and WWTP (in Vitkov removal of NO_3-N was completed at ORP less than –80 mV
- termination of nitrification (NH_4-N completely removed) was not indicated. In completely mixed activation with continuous inflow nitrification does not terminate
- ORP values indicate that NH_4-N concentrations are so low that longer aeration has no sense. These values measured for a wastewater in Vitkov were from +50 till +100 mV (in a case when denitrification was complete and during anoxic periods NO_3-N was removed to 0 mg dm^{-3}) and from +100 till +200 mV (in a case when denitrification was incomplete)
- nitrification was always connected with decrease of pH. This fact was used for a prompt control of the process. After the activation was overloaded and ORP decreased to values less than –100 mV oxygen concentration necessary for the start of nitrification was 5–6 mg dm^{-3}. Corresponding ORP was –80 mV. Start of nitrification was connected with sharp decrease of pH
- from long-term record of ORP and pH signals optimum ratio of nitrification and denitrification periods can be adjusted.

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OPERATION OF DOMESTIC WASTEWATER TREATMENT PLANT WITH SUBMERGED MEMBRANE MODULES

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Abstract. This study was focused on membrane technology and possibility of using membrane processes for wastewater treatment. The main idea was to monitor a starting phase of domestic wastewater treatment plant model. The monitoring of domestic plant model was realized at the municipal wastewater treatment plant (WWTP) Devínska Nová Ves – Bratislava in the period between February 2005 and September 2006. The system was stable without external chemical treatment of membrane modules and the quality permeate was very high. Removal of COD and BOD_5 was in range of 91–98%. The process of nitrification was very successful with the high efficiency (>95%). During the whole experiment WWTP was working without any problem.

Keywords: domestic wastewater treatment plant, immersed membrane bioreactor, membrane processes, wastewater

1. Introduction

Current and impeding legislation on wastewater effluent discharge has led to need for enhanced treatment processes capable of removing high percentages of BOD, suspended solids, nitrogen, phosphorus, bacteria, etc. One of the most

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promising technologies, which could fulfil these requirements, is the membrane filtration process. Combining membrane technology with biological reactors for the treatment of wastewaters has led to the development of membrane bioreactors (MBRs).

A membrane can be thought of as a material through which one type of substance can pass more readily than others, thus presenting the basis of a separation process. The basic membrane separation processes are reverse osmosis, nanofiltration, ultrafiltration, microfiltration, and "classic" particle filtration (Stephenson T. et al., 2000) (Figure 1).

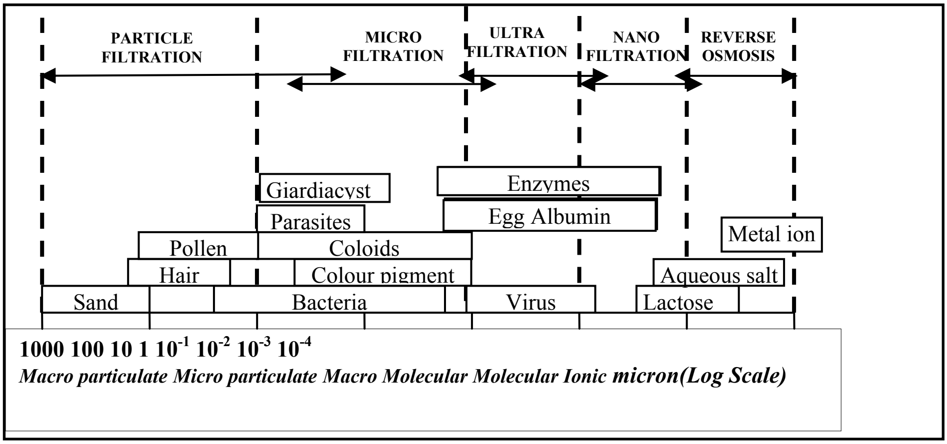

Figure 1. Rejection capability of the different membrane separation processes

Every technology has advantages and disadvantages. Assuming that it is clear the combining of membrane process with biological wastewater treatment process resulted in advantages there were once:

- The permeate from the membrane is free from solids and macro-colloidal material. Typical water products are the most obvious (suspended solids < 5 $mg.l^{-1}$, COD ≈ 25–30 $mg.l^{-1}$, NH_4-N ≈ 0.2 $mg.l^{-1}$). Complete retention of all suspended matter is attainable, including bacteria and/or viruses, such that effluents can be of a quality suitable for discharge to sensitive regions, further purification by dense membrane processes or even recycling;
- MBRs can be operated at low hydraulic retention time (HRT) and long sludge ages without washout of biomass common in activated sludge. The membrane effectively nullifies problems of filamentous growth and degassing sludges, enabling optimal control of the reactor in terms of the residence time of the

micro-organisms. The typical biomass concentration in the MBRs varies in the range of 10 – 15 g.l^{-1};

The purpose of this study was to investigate the long term operation of domestic WWTP with immersed membrane module without backwashing or chemical cleaning. The pilot-scale experiments with MBRs were running from February 2005 till September 2006.

2. Methods and Objects

2.1. DESCRIPTION OF DOMESTIC WASTEWATER TREATMENT PLANT WITH MEMBRANE FILTRATION

A commercially produced domestic WWTP with immersed membrane module (company ASIO Brno, Czech republic) was used for purpose of this study. Tested domestic WWTP with total working volume of 1.55 m^3 was installed at municipal WWTP Bratislava – Devínska Nová Ves (ca 35 000 PE). The wastewater was pumped after passing through fine screens (6 mm) into the pilot plant in amount of 450 – 700 litres per day (discontinuously eight times a day). The first section the pilot plant was primary sedimentation reactor where the particular suspended solids were settled and accumulated on the bottom. The pre-treated wastewater followed to the biological reactor with activated sludge, equipped with immersed membrane modules and fine-bubble aerators. Aerators were used for aeration of activated sludge as well as to aeration cleaning of membrane module. Treated water was pumped through membrane using small (12W) pump.

Technical parameters of used membrane modules are shown in Table 1. Table 2 shows the system operational period. The long term operational period of the MBR consisted of three phases.

TABLE 1. Specifications of the membrane modules

Membrane producer	Martin System AG (Germany)	Zena Membranes (Czech republic)
Module configuration	Flat sheet	Hollow fibre
Material of membrane	Polypropylen	Polypropylen
Pore size [μm]	~ 0.04	less then 0.1
Surface area of membrane module [m^2]	6	4

TABLE 2. Basic experimental conditions

Period	Time period	Inflow rate [l.d^{-1}]	Main phase goal	Used membrane type	HRT in aeration tank [day]
First	Feb 05 – Jul 05	360	Start-up without inoculation sludge	Flat sheet	1.87
Second	Jul 05 – Sep 05	450	Start-up with inoculation sludge, long term operation	Flat sheet	1.6
	Sep 05 – Jan 06	700			1.1
Third	Mar 06 – May 06	480	Parallel operation of two type of membrane	Flat sheet and hollow fibre module	1.6
	May 06 – Oct 06	700			1.1

3. Results and Discussion

3.1. THE FIRST PERIOD (FEBRUARY 2005 – JUNE 2005)

Membrane module siClaro FM611 from Martin Systems was installed into the model of domestic wastewater treatment plant on 14th February 2005 and its operation started. The pilot plant was not inoculated by activated sludge, upon the agreement with membrane producer.

From the start up during the start-up phase we concluded that, clogging of the membrane could be related to sludge inoculation. It is highly probable that microscopic, colloid or high-molecular particles in raw municipal wastewater cause preterm clogging of the membrane. The free moved small particles in activation tank got more quickly into the membrane pores. If the particles were in the environment with higher concentration of sludge, there would be physical or physical-chemical reactions among particles and sludge flocks to cause slower plugging of the membranes or it would be completely reduced. The start-up of the new membrane reactor must be realized together with inoculation of reactor with starting concentration of sludge at about 0.5 – 1 g.l^{-1}.

Besides the technical problems, samples were analyzed during the whole first phase. The values of COD in output were 12.4 – 124.3 mg.l^{-1} (average value is 64.4 mg.l^{-1}) which represent 85% efficiency of the process. The process of nitrification was not present (the values of ammonium nitrogen were approximately 33 mg.l^{-1} in the long term) and the increase of nitrate nitrogen was not significant.

3.2. THE SECOND PERIOD (JULY 2005 – JANUARY 2006)

After the negative experiences from the first phase, the second stage was started with sludge inoculation. Figure 3 shows sludge concentration and flux during the second phase. The start-up concentration of sludge was 0.6 g.l^{-1}. Accumulation of solids and biomass growth during the second period led to almost constant sludge concentration 3.0 – 3.5 g.l^{-1} After two months of relatively stable concentration of sludge in activated sludge tank inflow into reactor was increased from 450 l.day^{-1} to 700 l.day^{-1} (September 05). This increase of inflow caused slowly but continually increases of sludge concentration in the activated sludge tank up to 12–13g.l^{-1}. One of the reasons of increasing sludge concentration in

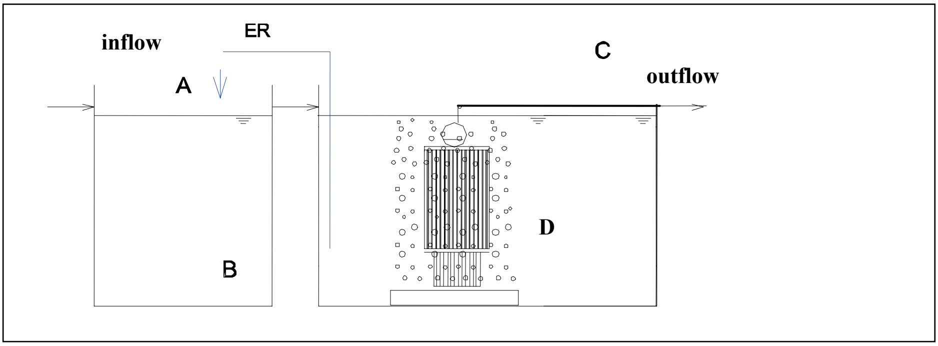

Figure 2. Schematic diagram of treatment system with membrane module: A, B = sedimentation/ separation tank, C = aeration tank with membrane module, D = membrane module, under the module is fine bubbles system to supply O_2 and for partly cleaning, ER = external recycles (for excess sludge)

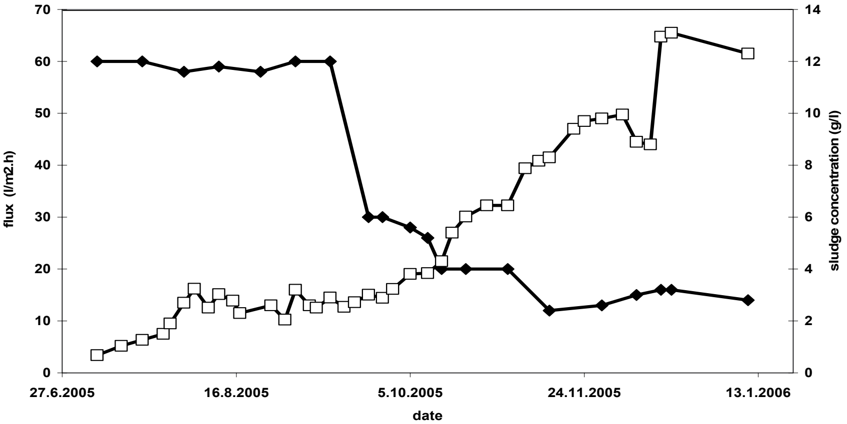

Figure 3. Concentration of activated sludge and flux (flat sheet membrane module) □ concentration of sludge, ■ flux flat sheet

the system was digestion of primary sludge from settling tank. This sludge was accumulated and digested in primary settling tank during summer season and was not removed from the system. The flux showed relatively stable values of 60 l.m^{-2}.h^{-1} and did not change during first two months of operation. Similarly as observed in parameter sludge concentration, the parameter flux highly decreased after the increase of wastewater inflow. This decrease was probably caused by significant fraction of digested primary sludge in activation sludge tank. This sludge had very sticky consistence for membrane filtration. In the next experimental phases digested sludge was regularly drawn from primary settling tank.

The main influent quality parameters, outflow from sedimentation tank and treated wastewater of effluent are summarized in Table 3. Average input values of COD concentration were 787.8 mg.l^{-1} and 45.6 mg.l^{-1} in output, respectively. Efficiency of suspended solids removal was very high – 99.7%. Nitrification ran without any problem. The efficiency of ammonium removal was 97.1%. Removal of nitrogen was not the goal of this study, nevertheless, there was observed relatively high efficiency in parameter N_{tot}. It was caused by denitrification in those parts of activation tank which weren't enough aerated. Considering the high sludge concentrations and long retention times, it can say that denitrification was relatively successful.

TABLE 3. Water qualities of the influent, outflow from sedimentation tank and effluent treated wastewater

	Influent wastewater		Sedimentation tank output		Effluent (flat sheet membrane module)		
Conc. [mg.l^{-1}]	average	scope	average	scope	average	scope	η [%]
COD	787.8	502.7 – 1419	157.6	145.6 – 663.7	45.6	12.4 – 86.9	94.2
BOD$_5$	327.4	227.2 – 420.1	188.5	80.5 – 333.7	5.8	2.8 – 12.2	98.2
MLSS	383.1	60 – 976.7	120.2	83.0 – 203.3	< 3	–	≈100.0
NH$_4$-N	68.6	33.5 – 134.1	77.1	42.3 – 164.3	1.5	0.2 – 14.1	97.1
N$_{total}$	156.7	91.5 – 259.5	158.5	88.5 – 291.2	29.0	2.4 – 46.0	81.4
PO$_4$-P	1.5	0.6 – 2.2	1.4	0.2 – 3.0	1.3	0.2 – 2.1	–

Some quality parameters (COD, BOD) in the effluent were relatively high compared with literature statements (Aprica Studi et al., 2005, H.F. Van Der Roest et al., 2005). As the reason could be take into account the fact that during whole operation of this phase there was not excess sludge withdrawal from the system and soluble parts of decayed sludge were slowly cumulated. These parts could slightly increase some effluent parameters.

3.3. THE THIRD PERIOD (MARCH 2006 – SEPTEMBER 2006)

In the third phase the pilot plant experiment started with sludge inoculation. In the aeration tank were inserted two different membrane modules (flat sheet membrane and hollow fibre membrane). During the third period the concentration of sludge continually increased from 0.6 g.l^{-1} to 12 g.l^{-1}, which is shown in Figure 4. Flux was measured in the both membrane modules. For flat sheet membrane module was start value of permeability 60 l.$m.^{-2}h^{-1}$ and for hollow fibre was 30 l.$m.^{-2}h^{-1}$. After the start-up of operation moderate slump of flux was observed. However in the whole sixth months of operation was observed relatively constant flux on the level of 30–40 l.$m.^{-2}h^{-1}$for flat sheet and 20 l.$m.^{-2}h^{-1}$ for fibre membrane. During the whole third phase there was no cleaning of the flat sheet membrane cleaned neither mechanical nor chemical. At the beginning of August 2006, fibre membrane was cleaned by back-flush of air because of significant decreasing of flux (see Figure 4). At the end of this phase, more quantity of digested primary sludge entered into the activation tank again, which caused significant decrease of flux in both membranes. Afterwards, third phase experiments finished.

In Tables 4 and 5 a water quality of influent, outflow from sedimentation tank and effluent treated wastewater are presented. Average COD of influent was 644.4 mg.l^{-1}. The effluent concentration of COD from flat sheet membrane and hollow fibre membrane was 56.3 mg.l^{-1} and 51.6 mg.l^{-1}, respectively. The effluent COD concentration and the efficiency of organic matter removal were approximately identical in both membranes modules. The NH_4-N of the effluent in both membranes modules were 0.9 – 1.1 mg.l^{-1}. During this phase oxidation of ammonium was stabilized (the effluent concentration of nitrate was over 30 mg.l^{-1} in previous period).

TABLE 4. Water quality of the influent, outflow from sedimentation tank

	Influent Raw municipal waste water		Outflow from sedimentation tank	
Concentration [mg.l^{-1}]	average	scope	average	scope
COD	644.4	247.9 – 1163.9	347.8	156.5 – 617.3
BOD_5	239.4	110.0 – 450.0	88.3	35.0 – 180.0
MLSS	247.5	100.0 – 480.0	104.4	10.0 – 321.4
NH_4-N	67.5	28.8 – 147.6	58.6	28.1 – 102.9
PO_4-P	2.1	0.7 – 4.7	2.6	0.8 – 4.9
N_{total}	149.1	88.8 – 268.2	119.6	75.5 – 177.3

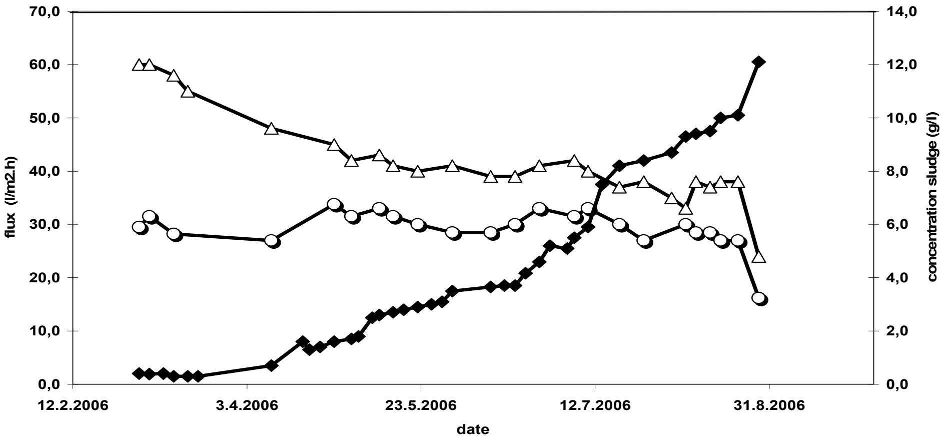

Figure 4. Concentration of activated sludge and flux (flat sheet membrane module and hollow fibre membrane module). ■ concentration of sludge , ○ flux hollow fibre, Δ flux flat sheet

TABLE 5. Water quality of the effluent treated wastewater (flat sheet membrane module and fibre membrane module)

	Effluent (flat sheet membrane module)			Effluent (hollow fibre membrane module)		
Concentration [mg.l^{-1}]	average	scope	η [%]	average	scope	η [%]mg/l
COD	56.3	14.9 – 109.9	91.3	51.6	17.8 – 118.6	91.9
BOD$_5$	3.1	0.8 – 8.4	98.7	4.1	0.8 – 8.8	98.3
MLSS		< 3	≈ 100.0		< 3	≈100.0
NH$_4$-N	0.9	0.1 – 4.5	98.7	1.1	0.3 – 3.6	98.4
PO$_4$-P	2.0	0.3 – 4.8	–	2.1	0.5 – 5.1	–
N$_{total}$	30.8	10.4 – 66.7	79.3	31.9	12.9 – 71.1	78.6

Parallel operation of flat sheet and hollow fibre membrane modules reached quite similar results in effluent quality. According to the output concentrations, the effluent quality from the membranes was very similar. From our point of view, we could confirm that flat sheet membrane in long term view kept relatively higher values of flux which showed its good operation parameters. During the six-months period different requirements on cleaning in both membrane systems were observed. In case of hollow fibre membrane, membrane cleaning was necessary after four months of operation, while the flat sheet one was working whole term without the need of cleaning.

4. Conclusion

On the end this presentation it could be say that, long-term operation of domestic wastewater treatment plant with membrane filtration has been followed into good information and very positive results. The removal of organic matter in this system was stable and at high level (up 90%). Under these conditions, more than 97% of ammonium was removed, and effluent NH_4-N concentration was less then 1,5 $mg.l^{-1}$ long term. Treated water did not contain suspended solids and microbiological quality of the effluent was comparatively similar to quality of drinking water. Total coli forms were not observed on the MBR effluent, as expected because the MBR's membrane should provide complete removal of bacteria by size exclusion. Parameters such as Escherichia coli were 0 KTJ/10 ml sample of effluent from MBR according to other authors with similar membrane models (Chorvátová et al., 2006).

From two years of operation of MBR we could summarize a few important facts that are very useful for next experiments:

- Pilot plant has needed inoculation of activated sludge (during the first stage), because membrane module without inoculation was clogged by suspended solids in short time.
- MBR was in the long-term operation without excess sludge draw-off which is conditional by effective pre-treatment stage (high HRT in the pre-settling tank).
- Testing membrane modules were in operational mode several months without whichever cleaning and their operational parameters (flux) were good enough during this period.
- Effluent parameters were at very good quality level.

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THE COMPARATIVE STUDY OF THE OVERALL EFFECT OF CRUDE OIL ON FISH IN EARLY STAGES OF DEVELOPMENT

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Abstract. The overall toxic impact of crude oil on fish was evaluated in acute and chronic tests by use of rainbow trout (*Oncorhynchus mykiss*) (embryos, larvae and juveniles). Survival, physiological (heart rate, gill ventilation frequency) and haematological parameters of test objects were studied. Crude oil depending on concentration and exposure duration caused a significant increase in larval mortality, whereas embryos were less and juveniles were least sensitive to the impact of oil. Sublethal crude oil concentrations induced significant alterations in cardio-respiratory parameters of embryos and larvae, as well as in respiratory and haematological parameters of juvenile fish.

Keywords: crude oil, toxicity, fish, embryos, larvae, juveniles

1. Introduction

Oil products spilled into the environment have multiple negative effects on aquatic organisms. Direct kills of aquatic organisms (especially of more sensitive juvenile forms) can occur through coating with oil and by asphyxiation (Hoong Gin et al., 2001). In addition, the incorporation of finely dispersed particles of oil and oil products into organisms can negatively affect organs and systems, either directly or as a consequence of bioaccumulation processes (Woodward et al., 1983; Lockhart et al., 1996). Oil globules and oil sheen observed in stomachs of pink salmon fry captured at oiled sites indicated that ingested oil is

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also the route of hydrocarbon contamination. Laboratory studies demonstrated that crude oil-contaminated food at high doses reduced growth and feeding of fish (Carls et al., 1996). The impact of crude oil and oil products on aquatic organisms can vary considerably depending on oil type, concentrations and duration of exposure to these pollutants.

Oil products can be acutely toxic during a short-time exposure and can affect metabolism and reduce growth when exposure is prolonged. Long-term, low-level exposures of pink salmon embryos to artificially weathered oil indicated obvious abnormalities and impact on survival (Heintz et al., 1999). Tests with herring embryos and larvae also demonstrated their extreme sensitivity to oil solutions, probably because oil is sequestered into lipid-rich tissues that are then incorporated into developing fish tissue as lipid reserves are metabolized (Carls et al., 1999). Crude oil and its fractions (polycyclic aromatic hydrocarbons) can cause a variety of effects in early life stages of fish that have been chronically exposed as embryos, including mortality, developmental abnormalities and edemas (Barron et al., 2004; Barron et al., 2003; Rice, 1987). According to Pollino and Holdway (2002), the incidence of abnormalities in the larvae of freshwater rainbow fish continued to increase in developing fish after the completion of a 96-hour exposure, which suggested the possibility of accumulation of waterborne petroleum hydrocarbons (PHC) in the yolk sac. These delayed impacts were also determined for the growth of pink salmon (Heintz et al., 2000).

Scientific data demonstrated that crude oil and oil products do not have the same type of toxic action, as different toxicity mechanisms are participating, depending on main oil fractions, the type of exposure (acute or chronic), the organism's sensitivity and experimental conditions (Baron et al., 2004). Few data concerning the toxicity of crude oil or oil products to local freshwater and marine aquatic organisms are available in Lithuania (Kazlauskiene et al., 2004, Vosyliene et al., 2005).

The aim of the present study was to investigate the overall effect of crude oil on rainbow trout (*Oncorhynchus mykiss*) in all development stages (embryos, larvae, juveniles) depending on crude oil concentration and exposure duration and to study the specificity of oil impact on physiological parameters of fish.

2. Material and Methods

Rainbow trout as "eyed-egg" stage embryos and juvenile fish were obtained from the Zeimena Salmon Hatchery and acclimated under laboratory conditions. Studies were conducted in the Laboratory of Ecology and Physiology of Hydrobionts. The overall effect of crude oil on embryos was studied from the "eyed-egg" stage to beginning of hatching (7–8 days), whereas on larvae from the beginning of hatching to yolk-sac resorption (42–44 days). Short-term (4 days) and long-term (14 days) toxicity tests on juvenile fish were performed. During the tests, the mortality of embryos and larvae, physiological parameters (cardiorespiratory), such as heart rate (HR, counts/min), gill ventilation frequency (GVF, counts/min), disorders of blood circulatory system development and behaviour responses, were recorded (Vosyliene et al., 2003). Gill ventilation frequency (GVF, counts/min) and the "coughing" rate or gill cleaning reflex (CR, counts/min) of adult fish were measured during 3-minute periods for each test fish individually, and the mean value for 10 fish was calculated. Blood was sampled from 10 fish. Erythrocytes (RBC, $10^6 \times mm^3$), haemoglobin concentration (Hb, g/l), haematocrit level (Hct, l/l), leukocyte counts (WBC, $10^3 \times mm^3$) were determined using routine methods (Svobodova, Vykusova, 1991). Giemsa – May Grunwald – 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 lymphocytes, and four stages of neutrophils.

The impact of seven concentrations of crude oil (0.11g/l, 0.22 g/l, 0.43 g/l, 0.87 g/l, 1.73 g/l, 3.46 g/l, 6.93 g/l) was examined. The highest concentration consisted of 0.5 part of 96h LC50 of oil to embryos of rainbow trout (Kazlauskiene, unpubl. data). One hundred embryos were exposed to each concentration of oil and two replications were performed.

Changes in concentrations of petroleum hydrocarbons (PHC) (dissolved and thindispersed fraction, mg/l) in water were measured with an AN-1 analyzer (Vosylienė et al., 2005). Concentration 1.73 g/l consisted of 28.2 mg/l of dissolved and thindispersed fraction of PHC. A decrease in PHC concentrations was observed after 24 h (~ 4.5 times) and after 120 h (~ 7.6 times). Control water and water with oil were changed every day.

Embryos were incubated in a cold and dark room at 10°C. Artesian water of high quality was used for dilution. 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.

Data significance was determined using the programme GraphPAD InStat (USA).

3. Results and Discussion

A slight elevation in embryonic mortality induced by 3.46 and 6.93 g/l concentration of oil was recorded, while 0.43, 0.87, 1.73, 3.46 and 6.93 g/l concentrations of crude oil caused a significant increase in larval mortality (Figure 1). Hatching was found to be the most sensitive stage of development, the majority of exposed embryos partially emerged from the chorion died during the hatching period. The activity of exposed embryos decreased, some embryos were unable to complete hatching. Significant mortality of larvae was registered in groups affected by 0.43, 0.87, 1.73, 3.46 and 6.93 g/l concentrations of crude oil from the beginning of hatching until yolk-sac resorption (Figure 1). The hatching of embryos exposed to crude oil lasted from 9 to 12 days (5–6 days in controls). These data corresponded to the results on sensitivities of pink salmon, Coho salmon (*Oncorhynchus kisutch*) (Moles et al., 1979) and rainbow trout (Pollino and Holdway, 2002) at early life stages. Larval rainbow trout were more sensitive to crude oil exposure, with acute toxicity occurring at concentrations causing sublethal damage in embryos. The difference in sensitivities is most likely due to the chorion protecting embryonic fish (Pollino and Holdway, 2002).

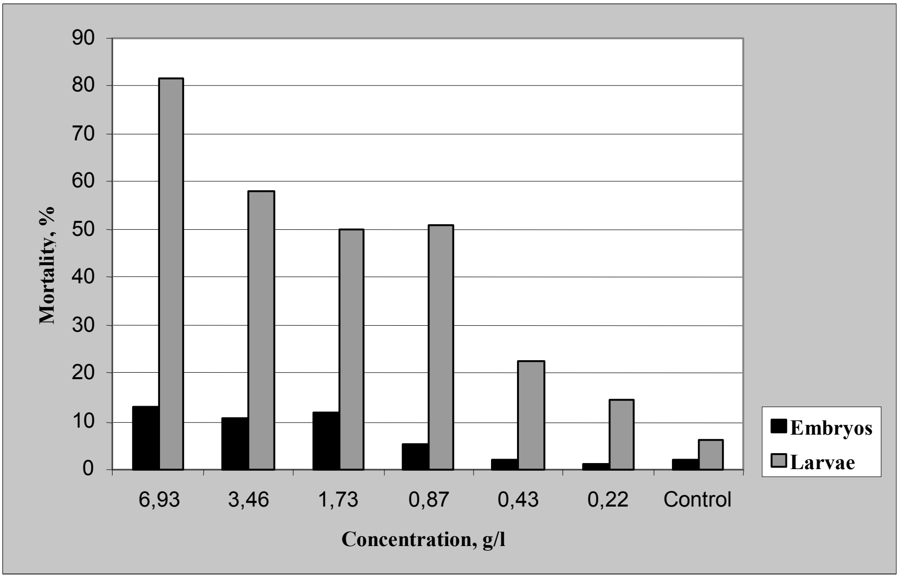

Figure 1. The effect of crude oil on the mortality (%) of embryos and larvae of rainbow trout

Approximately about 20% of embryos and 30% of larvae exposed to 0.87–6.93 g/l concentrations of oil were found to have developmental disorders. In unhatched embryos, or retarded hatching blood clots in various body sites were observed. In addition, reduction in the rate of haemoglobin synthesis and poorly developed eye pigment of embryos and larvae were observed. In some embryos, blood pigmentation did not develop at all. Larvae were smaller, with abnormal yolk sac as compared to controls. They died soon after hatching. According to scientific data (Barron et al., 2003, 2004; Carls et al., 1999; Marty et al., 1997), sublethal effects caused by embryonic exposures to crude oil and polycyclic aromatic hydrocarbons, include edema of the yolk sac, pericardium, hemorrhaging, disruption of cardiac function, craniofacial and spinal deformities, genetic damage, anemia.

The effect of highest concentrations (0.87, 1.73, 3.46 and 6.93 g/l) of crude oil induced a significant decrease in the HR of embryos and larvae (Table 1). No significant changes in the HR of embryos (72.0 ± 1.5 – 72.6 ± 1.6 counts/min, control – 73.7 ± 1.5 counts/min) and larvae (70.6 ± 3.6 –71.6 ± 4.4 counts/min, control – 71.4 ± 3.2 counts/min) were registered after a 10-day exposure to 0.43 and 0.22 g/l of oil (Table 1). The GVF of larvae significantly decreased only in individuals exposed to 3.46 and 6.93 g/l of crude oil (Table 1).

TABLE 1. The HR and GVF of embryos and larvae of rainbow trout depending on the concentration of crude oil (duration of exposure 10 days) (n = 10)

Concentration,	Embryos	Larvae	
g/l	HR, counts/min	HR, counts/min	GVF, counts/min
6.93	64.9 ± 1.4*	47.7 ± 1.0*	74.9 ± 2.3*
3.46	65.7 ± 0.8*	52.3 ± 3.5*	73.1 ± 1.7*
1.73	64.6 ± 1.0*	53.7 ± 1.5*	92.6 ± 2.5
0.87	63.4 ± 1.0*	58.3 ± 4.0*	88.6 ± 2.9
0.43	72.0 ± 1.5	70.6 ± 3.6	96.6 ± 1.4
0.22	72.6 ± 1.6	70.6 ± 4.4	93.7 ± 2.1
Control	73.7 ± 1.5	71.4 ± 3.2	92.0 ± 3.3

* value significantly different from control ($P \leq 0.05$).

The behaviour pattern of exposed larvae also changed, more than 50% of larvae did not make nests, showed a very weak or no response to external stimuli.

The higher sensitivity of larvae to the impact of oil as compared to embryos was confirmed by alterations in physiological parameters. HR changes in larvae induced by the same concentrations of crude oil were more pronounced than in embryos (Table 1). This negative impact was confirmed by more obvious and often observed changes in the blood circulation of larvae. In addition, the HR of larvae in comparison with GVF was a more sensitive parameter to the adverse impact of oil (Table 1). Probably, disorders in the functioning of gills are mostly related to their physical fouling by crude oil. HR disorders might be related to the specific toxicity of PHC, whereas changes in the HR of embryos and larvae were caused by lower concentrations of crude oil. These results are in accordance with data reported by Girling et al. (1992) that products, which are dispersed, but not completely dissolved in water, adversely affect organisms as a result of the combined effects of toxicity and physical fouling. HR disorders occurred in embryos may cause negative consequences to the respiratory process, development and hatching success. It should be emphasized that changes which are frequently detected at the embryonic stage of fish are often seen as different functional disorders at later stages of development (larvae, fry) (Kazakov, 1998). Changes in the yolk blood circulation of larvae (blood concentrated in the yolk-sac, poor blood circulation) can also disturb the normal sequence of physiological processes, inhibit the growth rate of larvae, reduce their biomass and retard development (Kazlauskiene, 2004). Similar results for sturgeons at early stages of development exposed to crude oil (asynchronous development and death of some individuals, embryonic and larval malformations, retarded development, disturbed HR, delayed hatching and increased larvae mortality) were reported by Michailova et al. (2001). Sublethal effects caused by embryonic polycyclic aromatic exposures include hemorrhaging, disruption of cardiac function, reduced growth and development of larvae (Barron et al., 2004).

The exposure of adult fish to crude oil (1.73 and 0.87 g/l) did not affect their survival. The GVF of adult fish significantly ($P<0.05$)decreased from 106.0 ± 1.9 (control) to 70.0 ± 2.0 and 73.0 ± 2.0 counts/min after a 4-day exposure to both concentrations of oil (Table 2), and observed decline of this parameter did not return to control level after a 14-day exposure to oil (Table 2). No significant alterations in CR were found in fish exposed to crude oil. Our previous data demonstrated that this parameter significantly increased after a 1-day of exposure to similar concentration of oil and lowered to the control fish level after 4-day exposure (Vosylienė et al., 2005).

TABLE 2. The effects of crude oil on respiratory parameters of rainbow trout juveniles

Concentration	Parameters	
mg/l	GVF (counts/min)	CR (counts/min)
	4-day exposure	
1.73	70.0 ± 2.0*	2.8 ± 0.2
0.87	73.0 ± 2.0*	2.0 ± 0.3
Control	106.0 ± 1.9	2.3 ± 0.6
	14-day exposure	
1.73	79.0 ± 1.4*	1.4 ± 0.2
0.87	81.0 ± 6.5*	1.8 ± 0.5
Control	96.8 ± 2.5	1.0 ± 0.3

* values significantly different from controls ($P<0.05$).

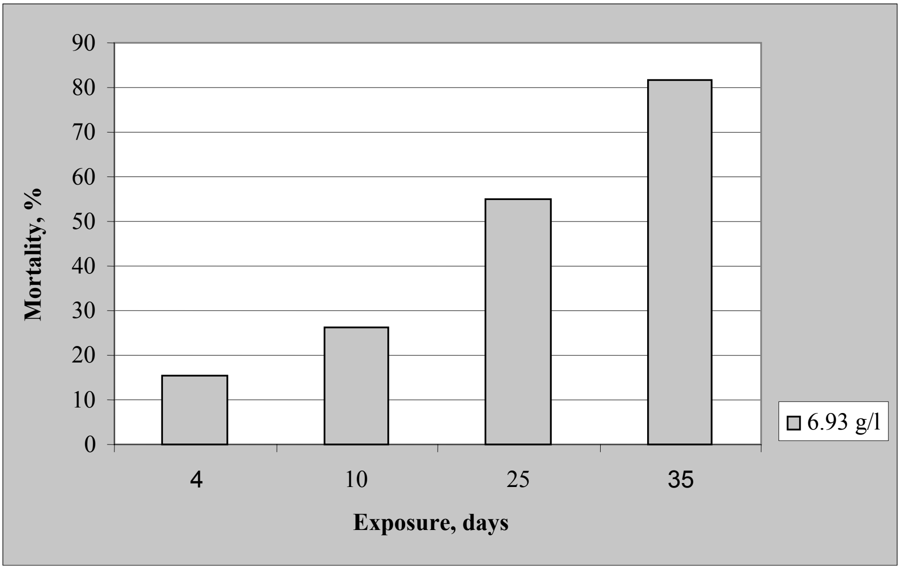

Figure 2. The mortality (%) of rainbow trout larvae depending on the duration of exposure to crude oil

No significant alterations in RBC counts were found in fish exposed to crude oil (Table 3). The red blood system of fish is quite stable and shows considerable compensatory abilities to the sublethal toxic effect of the pollutants (Vosyliene et al., 2005). Haemoglobin concentration was significantly lower in fish exposed to 1.73 g/l of oil after a 4-day exposure and remained significantly decreased after a 14-day exposure to both studied oil concentrations. The

TABLE 3. The effects of crude oil on haematological parameters of rainbow trout juveniles

Concentration	Parameters			
mg/l	RBC ($10^6 \times mm^3$)	Hb (g/l)	Hct l/l	WBC ($10^3 \times mm^3$)
		4-day exposure		
1.73	0.90 ± 0.03	82.0 ± 1.6*	0.40 ± 0.02	15.1 ± 1.8*
0.87	0.97 ± 0.04	88.0 ± 3.3	0.42 ± 0.03	16.1 ± 2.3*
Control	0.95 ± 0.08	92.5 ± 2.6	0.44 ± 0.01	19.1 ± 0.4
		14-day exposure		
1.73	0.93 ± 0.05	66.0 ± 3.7*	0.33 ± 0.02*	13.8 ± 1.5*
0.87	0.95 ± 0.07	76.0 ± 2.1*	0.39 ± 0.02	14.1 ± 2.8*
Control	0.91 ± 0.07	91.0 ± 5.6	0.38 ± 0.01	20.8 ± 0.2

* values significantly different from controls ($P<0.05$).

haematocrit level after 14 days of exposure decreased only in fish exposed to 1.73 g/l concentration of oil. We suggest that, probably, some morphological damages of gills had been occured, which had effect on their functional ability and could impair gas exchange in organism. These alterations in turn could induce disturbances in ionic regulation processes in the fish and cause the decrease in haematocrit level (Table 3).

A significant drop in WBC count was found in fish blood after a 4-day exposure, and a similar, significantly lower WBC count was found after 14-day tests too (Table 3). A decrease in WBC can be induced by oil-induced damage in gills, liver or kidney, and impaired function of these organs. A decrease in WBC count indicates a possible impairment of the immune mechanisms of the intoxicated fish.

Submicroscopic evaluation of blood smears did not demonstrate any considerable changes in erythrocyte counts as compared to controls. This study did not bring evidence of strong destructive effects of oil on rainbow trout erythrocytes. In all samples, lymphocytes predominated, their share did not significantly decrease as compared to controls and made up 91.5–92.5%. A significantly lower percentage of immature (large) lymphocytes was found in the blood of juveniles exposed to both studied concentrations of crude oil both after 4- and 14-day exposures. Neutrophylic granulocytes were much less numerous than lymphocytes. The amount of neutrophils in fish exposed to 0.87 –1.73 g/l of oil was significantly lower as compared to the control value and amounted to 2.0–2.8% after 14 days of exposure. No significant changes in thrombocyte count were observed. Changes in leukocyte count demonstrated adverse effects of long-term exposure to oil on the immune system of fish and indicates a possible impairment of the immune mechanisms of the intoxicated fish. Leukopenia and changes in leukograms might have resulted from toxic action of oil directly on WBC or oil-induced damage of other tissues. On the other hand, pollutants affecting fish may induce chronic stress that can modulate the response of immune system cells (Secombes et al., 1991).

The results demonstrated that crude oil in the concentrations of 0.87–1.73 g/l did not induce the mortality of juvenile rainbow trout. The death of fish beyond early juvenile stages usually requires a heavy exposure to oil. It is unlikely that large numbers of adult fish inhabiting large bodies of water would be killed by the toxic effects of petroleum. Fish kills are usually caused by large amounts of oil moving rapidly into shallow waters or after spills in smaller closed water bodies (Albers, 1995). However, sublethal toxicity of oil and its products induces damages in fish gills, disturbs fish respiration abilities, alters haematological parameters and can lower immune resistance of young fish. These adverse sublethal effects can threaten the wellbeing of organisms and reduce their reproduction.

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EVALUATION OF VILNIUS CITY (LITHUANIA) SNOW POLLUTION TOXICITY BY USE OF FISH BIOTESTS

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Abstract. The aim of the study was to evaluate the toxicity of snow pollutants by use of fish, rainbow trout (embryos, larvae and juveniles). The atmospheric deposition accumulated in snow was evaluated in three areas with different pollution level in Vilnius city (Lithuania). Survival and various physiological parameters of test-objects were recorded during short-term and long-term toxicity tests. Alterations in biological parameters revealed differences in toxic effects of snow melt waters (SMW) depending on the duration of exposure. Significant changes in the survival of larvae were induced by SMW from all study sites.

Keywords: atmospheric deposition; snow; pollutants; toxicity; fish; embryos; larvae; juveniles

1. Introduction

Snow accumulates a variety of xenobiotics from the atmosphere, so it can function as a non-point source of pollution. Snow contaminants include heavy metals (Adll, 2002; Viclander, 1999), petroleum products such as oil and grease products, organic chemicals (Villa et al., 2004; Herbert et al., 2006), deicing salts (Sansalone and Glenn, 2002), soil materials, etc. High concentrations of

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heavy metals were detected in snow samples collected in close proximity to emission sources such as motor-vehicle emissions, combustion of coal and fuel-oil, industrial areas (Adll, 2002). Heavy metal levels in urban snow were several times higher than the background levels. The majority of particulate matter accumulated in snow is not biodegradable and is potentially deleterious to the environment (Sansalone and Glenn, 2002). In addition, pollutants released during spring melt into aquatic ecosystems can affect freshwater chemistry (Thunqvist, 2004), change water quality, and induce threat to biota as are released just at the time when many aquatic animals are most vulnerable. Though scientific data concerning the toxicity of snow accumulated atmospheric deposition is very scarce, its genotoxicity was demonstrated in the Montreal metropolitan area (White et al., 1995). The majority of studies deal with the toxicity of deicing salts to environment (Viskari, et al., 1997; Czerniawska-Kusza, et al., 2004; Vosyliene, et al., 2006). The toxicity of atmospheric deposition was studied using *Tradescantia* stamen-hair assay. The authors considered that urban air pollutants play a significant role in the development of pollution-dependent mutations (Guimarães et al., 2004).

Salmon fish, cool water habitants, are very sensitive to chemicals, especially in early life stages; therefore they are widely used for the evaluation of toxic effects of different origin pollution (Vosyliene et al., 2003, Kazlauskiene et al., 2004). We have selected the rainbow trout in its ontogenesis for the assessment of snow melt water (SMW) toxicity. The aim of the study was to evaluate and compare the toxicity of Vilnius city atmospheric deposition (snow pollutants) by use of fish, rainbow trout (*Oncorhynchus mykiss*) at different stages of development, as test-objects.

2. Materials and Methods

The rainbow trout as eye-egg stage embryos and juvenile fish were obtained from the Zeimena Salmon Hatchery (Lithuania) and acclimated under laboratory conditions. Short-term (96 hours) toxicity tests with eye stage embryos, larvae and juvenile fish, and long-term tests (10–12 days) with eye stage embryos and yolk-sac larvae (38–40 days before yolk-sac resorption) were conducted under semi-static conditions. Mortality observations were made at 24-hour intervals. 200–400 embryos were exposed to SMW in two replications. During the tests, parameters such as heart rate (HR, counts/min) of embryos, and heart rate (HR, counts/min), gill ventilation frequency (GVF, counts/min), and integrated parameter (relative body mass increase, %) of larvae were recorded (Vosyliene et al., 2003). Gill ventilation frequency (GVF, counts/min) and "coughing" rate, or gill-cleaning reflex (CR, counts/min) were measured during 3-minute periods for each test juveniles individually, and the mean value for 10 individuals in each group of fish was calculated. Deep well water of high quality was used for keeping of control fish. The average hardness of water was approximately 284 mg/l as $CaCO_3$, pH ranged from 7.6 to 7.8. Water temperature for embryos was 10°C ± 0.5°C, for juvenile fish 9–10°C; oxygen concentration ranged from 8 to 10 mg/l.

Atmospheric deposition accumulated in snow was evaluated at 3 sites of Vilnius city (samples were taken from the area of 2 m^2) with different levels of pollution: site 1 – residential region in the industrial area of Vilnius city (inside the yard, 30–50 m from the nearest street, behind high buildings); site 2 – residential area in the region of intensive traffic (transport parking place near the supermarket, the sampling place was 1 m from the edge of the parking place); site 3 – non-traffic site in a park, in the outskirts of Vilnius, near the laboratory where toxicological studies were performed. Snow in the sites was allowed to stay unaffected by snow-handling practices at the same place. Two snow falls in February were recorded, after which (in March) snow samples (after exposure of about one month) were taken from the top till the ice crust in all 3 study sites. The samples were collected in plastic bakers and transported to the laboratory. Snow was melted at the temperature of 9–10°C.

Analyses of water were carried out for pH, conductivity, suspended solids, heavy metals (Pb, Cd, Cu, Zn, Ni, V, Cr, Hg), oil products (C_{15}-C_{28}), and benzo(a)pyrene. Pb, Cd, Cu, Zn, Ni, V, Cr concentrations were determined by the atomic absorbtion method with Zeeman spectrophotometer (Sakalys et al., 2004). Hg amount was determined by mercury analyser GARDIS (Institute of Physics). Oil products (C_{15}-C_{28}) by IR spectrophotometer, and concentration of benzo(a)pyrene was analyzed by spectrofluorescent method (Milukaite, 1998). Total concentrations of chemicals in water and suspended solids are analysed and evaluated in this paper.

The significance of all the data obtained was determined by use of Student's t-test with $P \leq 0.01$, $P \leq 0.05$.

3. Results and Discussion

SMW' did not affect the survival of juvenile fish, but a slight increase in the mortality of embryos as compared to controls was registered after a 4-day exposure to SMW' from site 2 and site 3 (88.5%, 85.5%, 93.5% control, respectively). The most expressed total mortality of larvae during a 4-day hatching period was registered for individuals exposed to SMW' from site 1 (55.5% survival). A significant increase in mortality was also registered in larvae exposed to SMW' from site 2 and site 3 (69.5% and 76.1% survival, respectively, compared to 89.2% in controls) (Fig. 1).

SMW’ caused a significant decline in hatching success as compared to controls (0.5%). The majority of exposed larvae partially emerged from chorion died during the hatching period (43.0% in site 1, 36.2% in site 2, 42.1% in site 3). Activity of exposed embryos lowered, some embryos were unable to complete hatching. Marked disorders were noticed in the process of hatching (head first hatching). The hatching of embryos exposed to SMW’ from all sites lasted from 8 to 10 days (5–6 days in controls). Significant mortality of larvae was registered in all groups affected by SMW’ over 4 days after hatching, later no significant alterations in mortality of exposed larvae were recorded till the end of the tests.

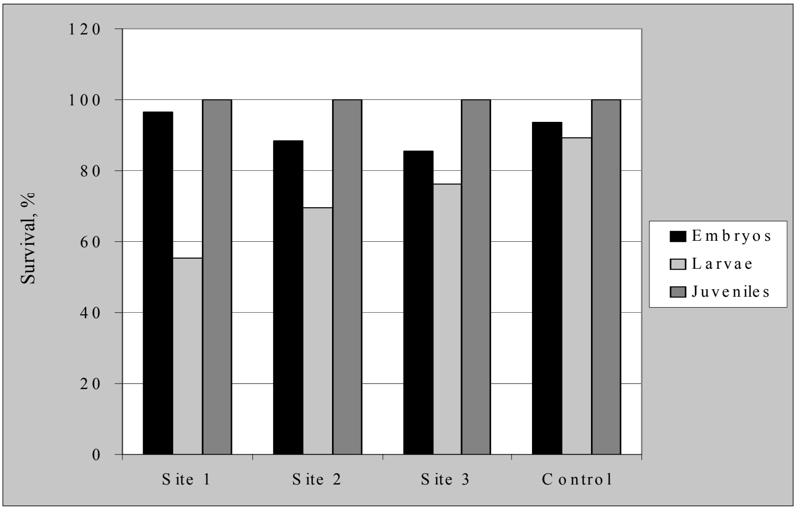

Figure 1. Effect of SMW’ on survival (%) of rainbow trout embryos, larvae and juveniles

No significant changes were found in the heart rate of embryos after 5-day exposure to SMW’ from all study sites (88.6 ± 2.8 – 91.2 ± 4.2 counts/min) as compared to controls (89.2 ± 2.6 counts/min). Also, no significant changes were found in HR of larvae after 10-day exposure to SMW’ from site 1 and site 3, whereas the larvae exposed to SMW from site 2 suffered a significant decrease in HR and GVF (Table 1). A similar significant reduction of GVF was also recorded in larvae exposed to SMW, growth was reduced and was lower than in controls. Relative mass increase of larvae also reduced at the end of the tests (Table 1). The most commonly encountered defects were: gross malformations, yolk-sac alterations, retarded growth and development, and disorders in the behaviour of larvae (larvae were scattered, more than 50% of larvae did not make nests).

TABLE 1. Effect of SMW’ on biological parameters of larvae and juveniles of rainbow trout

Sites	Parameters			
	Relative body mass increase, %	HR (counts/min) 10-day exposure	GVF (counts/min) 10-day exposure	GVF (counts/min) 2-day exposure
		Larvae		Juveniles
1	35.5	92.0 ± 2.8	106.2 ± 4.8	77.6 ± 0.9
2	18.0	82.0 ± 2.4*	78.4 ± 2.4*	73.6 ± 1.5*
3	37.8	89.2 ± 3.8	91.4 ± 2.6*	80.3 ± 1.2
Control	59.7	90.6 ± 2.6	99.2 ± 2.2	79.7 ± 1.6

*Values significantly different from controls ($P < 0.05$).

The GVF of juveniles decreased after 1-day exposure of fish to SMW from site 2, and a significantly ($P < 0.05$) lower value of this parameter (68.0 ± 0.9 count/min) was also registered at the end of tests. Nevertheless, no significant changes were found in GVF of juveniles exposed to SMW’ from sites 1 and 3 after 1-day exposure and at the end of the tests. After 1-day exposure, CR, on the contrary, significantly increased from 1.3 ± 0.1 to 2.7 ± 0.2 and from 1.6 ± 0.1 to 2.9 ± 0.5 counts/min in juveniles exposed to SMW’ from site 1 and site 2, respectively. However, this parameter lowered to the control level after 2-day exposure. No significant alterations in this parameter were found in juveniles exposed to SMW from site 3 and in individuals exposed to SMW’ from all study sites at the end of tests.

The data obtained confirmed that fish at early stages of development are more sensitive to pollutants than older ones. The data obtained in our study are in accordance with literary data concerning toxic effects of copper (Kazlauskiene et al., 2003), oil products (Barron et al., 2003), and benz(a)pyrene on fish at early stages of development (Hose et al., 1982). Larvae are more sensitive to acute and long-term toxic effect of SMW, than embryos and juvenile fish. Our tests performed under experimental conditions revealed that SMW could induce remarkable deleterious changes in various systems of the developing fish organism. Exposure to SMW disturbed cardio-respiratory responses in embryos and larvae. This is consistent with the results obtained with juvenile rainbow trout, confirming that even short-term exposure to SMW pollutants resulted in significant alterations in fish respiratory parameters. The long-term impairment of oxygen supply can lead to the following negative consequences, such as the slowed down embryo development, delayed hatching, and adversely affected growth of larvae.

Alterations in biological parameters of larvae and juvenile fish revealed the differences in toxic effects of SMW’ on fish: survival of larvae mostly depended on the duration of exposure. The most significant effect on the survival of larvae was determined during a long-term test, throughout the test the survival of larvae in SMW from sites 1, 2 and 3 was 33.0%, 52.5% and 42.1%, respectively, compared with 84% in controls. Thus, the SMW from site 1 (residential area) was more toxic than the SMW from site 3 (outskirts of Vilnius) and from site 2 (transport parking).

Physical and chemical analysis of SMW' also revealed differences in some studied parameters: NaCl concentration in SMW from site 2 was 1030 mg/l while in SMW' from sites 1 and 3, respectively, 14.2 and 10.8 mg/l, conductivity of SMW from site 2 was 3800 µS/cm, while from sites 1 and 3, respectively, 102 and 70 µS/cm. SMW' pH ranged from 6.5 to 7.35. Nevertheless, this range was not dangerous for fish life, as e.g. for the protection of aquatic life the pH of water may vary within 6.5–9.0. The measurements of heavy metal concentrations demonstrated that only the amount of copper was by some order of magnitude higher in site 2, compared with MPC of this metal in the fresh water receiver (Executive Order No 625) (Table 2). It should be emphasized that the determined Cu concentration (0.429 mg/l) passes into the ranges of lethal Cu concentrations for fish. Our previous data demonstrated that the 96-hour LC50 (mg/l) of copper for embryos of rainbow trout was 0.9, for larvae 0.4, and for adult fish 0.7 mg/l (Kazlauskiene et al., 2003). We suppose that low mortality of embryos and the absence of mortality in juveniles exposed to SMW in acute toxicity tests might have been related to the form of metals, especially, copper, as the majority of all metals studied could be bound with particulate or dissolved matter. Complexation by dissolved matter may result in high total concentrations of metals in water, and increase or decrease their bioavailability. Our previous data showed that Cu and Zn complexones with DTPA were less toxic to embryos and larvae of rainbow trout than their soluble ions. This effect could be explained by their different bioavailability. The integument of trout embryos is characterized by selective permeability, which increases resistance to substances of high molecular weight (Kazlauskiene, Marciulioniene, 1999).

TABLE 2. Concentrations of heavy metals (µg/l) in SMW' of various sites of Vilnius city

Sites	Metals (µg/l) (soluble form, ions)							
	Pb	**Cd**	**Cu**	**Zn**	**Ni**	**V**	**Cr**	**Hg**
1	2.8	0.35	22.6	39.5	6.34	2.38	0.5	0.25
2	6.2	0.98	429.7	38.2	5.4	4.0	0.7	0.2
3	1.5	0.34	18.6	1.59	5.3	2.08	0.5	0.11
MPC	5	5	10	100	10	–	10	< 1

Concentrations of oil products in SMW' from site 1 (1.32 mg/l), site 2 (5.40 mg/l), and site 3 (2.2 mg/l) exceeded from 26.4 to 108 times the MPC of this substance in the fresh water receiver (0.05 mg/l), and concentrations of benz(a)pyrene were higher approximately from 3 to 15 times than the MPC (0.05 µg/l) of this pollutant in water receivers (Table 3) (Executive Order No 625). Furthermore, it was detected during the experiment that the main part of metals was in soluble phase of SMW, while organic substances were mainly in insoluble phase. It was determined only 5–30% of benzo(a)pyrene in liquid phase and 20–50 times higher concentration of oil products was determined in solid residue. These data allow to suggest possibility of interactions of inorganic and organic pollutants in SMW' as a mixture of various kinds of pollutants. Mixtures of such pollutants can be additive, more-than-additive/synergetic or antagonistic in toxicity to the test-objects studied.

TABLE 3. Total concentrations of oil products (mg/l)* and benzo(a)pyrene (µg/l)** in SMW' of various sites of Vilnius city

Chemicals	MPC	Sites		
		1	2	3
Oil products	0.05 mg/l	3.20	5.40	2.20
Benzo(a)pyrene	0.05 µg/l	0.164	0.76	0.144

* Total concentration of oil products in liquid and solid phase of atmospheric deposition;

** Total concentration of benzo(a)pyrene in liquid and solid phase of atmospheric deposition.

In general, the data obtained show that the rainbow trout in its ontogenesis is a very sensitive and suitable test-object for evaluating the toxicity level of snow polluted with xenobiotics. The results demonstrate that even short-term exposure of fish to xenobiotics mixtures cause considerable alterations in their physiological systems. Such changes in organism may persist even after dilution or removal of toxic xenobiotics from aquatic ecosystems.

ACKNOWLEDGEMENT

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MINIMIZATION OF DANGEROUS POLLUTANTS IN THE NEW SANITATION CONCEPT FOR SEPARATION TREATMENT OF WASTEWATER

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Abstract. Paper deals with development of new sustainable sanitation concept which has significant advantages in ecological and economical aspects compared to the conventional system (centralised). The new sanitation concept is used in the workroom and in the household in south Moravia. The alternatives to conventional wastewater systems (high costs and high water consumption) are therefore becoming more indispensable for future generation.

Keywords: minimization, new sanitation concept, separation treatment; storm water; storage tank; nutrients; water pollutants

1. Introduction

Research projects "Integrated Approach for Stormwater Utilization in Urban Area" and "Minimization of nutrients and waste water emit into surface and underground waters" deal with a new approach for storm and wastewater management in urban areas and their application for decentralized system. The main consideration coming-out from limitation drainage of waste water, disposal, recycling of wastes and economic minimization of nutrients and waste water emit into environment.

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2. Projects

2.1. INTEGRATED APPROACH FOR STORMWATERUTILIZATION IN URBAN AREA

During former intensive construction of sewer networks quick storm water outflow from urban area was preferred. Therefore nowadays most storm water is drained as quickly as possible to receiving body without any useful use. The project has been started in 2005. The methods and approaches which are processed: storm water retention (definition of advantages, overview of suitable measures, assessment of the optimal parameters for retention tanks), storm water use (definition of advantages, technologies for storm water treatment, rainwater quality assessment, methods for optimal parameters assessment for various types of tanks), storm water infiltration (study of legislation, optimal design of infiltration objects). The project is divided into 2 phases.

- **In Phase I. – Pre-study:** we are picked up theoretical approach.
- **In Phase II. – Pilot project:** we are picked up practical approach in existing household. For flushing is used and tested the storm water tank, which are accumulated rain atmospheric precipitation (rooftop, patio of balcony). The surplus of storm water is infiltrated by the help of mechanism of infiltrations into the groundwater. This new concept is combinig a variety of measures (best stormwater management practices) to deal with stormwater runoff. We tested storm water (Table 1) and storm water (Table 2). In the second case we are drawed storm water from dripping-flap, and we compared

TABLE 1. Chemical analyses – atmospheric precipitations

pH	KNK4.5 (mmol/l)	conduktivity (mS/m)	N-NH_4^+ (mg/l)	N-NO3- (mg/l)	S-SO42- (mg/l)	Pb (μg/l)
5,63–7,08	0,1– 0,4	1,4–5,9	0,20–1,47	0,19–1,01	0,13–0,5	1–3,65

TABLE 2. Chemical analyses – first flush

BOD (mg/l)	COD (mg/l)	pH	dissolved substance	N-NH_4^+ (mg/l)	Mg (mg/l)	Ca (mg/l)
5,5–6,00	22,3–24,33	7,2–7,5	31,5–33	0,45–0,51	0,59–1,62	6,8–23,8

KNK4.5 (mmol/l)	Pb (μg/l)	SO42- (mg/l)	conduktivity (mS/m)	Zn (mg/l)	NO3- (mg/l)
0,52–0,60	19,3–17,60	42,7–39,6	7,1–20,30	0,2–2,09	1,35–18,60

the chemical analyses. In the storm water out-flowing from the roof are water pollutants from nature (leaves, excrements of birds) and matters which are rising from roof (burnt tile, sheet and plastic covering, colors etc.). Under the thumb of rain, sun and frost are small amount of roof are loosening, dripping-flaps are corroding and toxics substance are releasing (Cu, Zn, etc.). Current consumption (1 month rainless) was at the beginning rainfall scene so that all matters from first flush were intercepted. Results from monitoring (without Pb) filling-up Notice in Czech Republic No. 252/2004 for drinking water. For using storm water as flushing water is necessary take out matters (blocking up of flushing jet).

2.2. MINIMALIZATION OF NUTRIENTS AND WASTE WATER EMIT INTO SURFACE AND UNDERGROUND WATERS

Project deals with new progress approach and machines for waste water and their application for decentralized system. The main consideration coming-out from limitation dranaige of waste water, disposal, recycling of wastes and economic minimization of nutrients and waste water emit into environment.

Project have been started in March 2006 and comparise sanitation system between centralised (conventional flush-water toilet with botton) and decenralised sanitation concepts (gravidity separation toilet, waterless urinal). The project is divided into 3 phases.

In Phase I. – Pre-study: we are picked up theoretical approach, collection information about the various projects and compared cost between a conventional and new sanitation concept. Conventional sanitation concept – conventional flush-water toilets, one sewer system, normal gravidity sewer system for the area transporting wastewater to the existing WWTP. Separation sanitation concept – waterless urinal+gravidity separation toilet with separate outlet for urine and feaces, collection and storage of the urine, transport to the utilization tank, grey water are transported in gravidity sewer system, treatment in a package WWTP.

In Phase II. – Case-study in workroom: we are testing decentralised sanitation cocept in existing workroom. In the sanitation concept is used waterless urinal, urine is collecting in utilization tank (Figure 1). The urine (dilution with minimum of water) is taken off at regular intervals (twice per month). The values indicators of measurement are logged and evaluating. (COD, BOD, Ca, suspended solid, dissolved substance, pH, P_{total}, N_{total}, $N\text{-}NH_4$, bacteria: Proteus vulgaris, Entercoccus, Klebsiella pneumoniae, Streptococcus alfa, Escherichia coli, etc.). The urine is accumulated in urine tank 6 month. We are setting – up information for urine stripping (reuse nutrients, minimization of dangerous pollutants).

In Phase III. – Pilot project: will be tested new sanitation concept in existing household. The area has conventional sanitation concept. In the new sanitation concept is used separation toilet and waterless urinal. Our type of toilet is based on two, well separated bowls. One for faeces – has a bulge which prevents an overflow of the flushing water infected with bacteria and viruses to the front, second for urine. The storm water treatment is used for flushing.

The segregation of domestic wastewater at the source into three separate flows gives:

- Grey water – all remaining household wastewater (laundry, kitchen, bath) which is not faecally contamined. By reusing domestic grey water for the purposes of toilet flushing, garden watering, there is potential to reduce potable water usage.
- Brown water – water from separated toilet with special bowl for faeces – has gross faecal contamination.
- Yellow water-water closet, bidet and bidette waste, separation toilets, waterless urinals – has faecal contamination.

Grey water is treated in natural pond system and utilized; black water is treated in membrane package WWTP, yellow water is accumulated in urine tank (chemical, bacterial analyses). Economy of centralized and decentralized systems is compared and advantages and disadvantages of both systems are discussed.

Figure 1. Urine tank

3. Results and Discussion

Our results from projects will be important for next development in the decentralized sanitation in the Czech Republic. The main consideration coming-out from limitation drainage of waste water, disposal, recycling of wastes and economic minimization of nutrients and water pollutants emit into environment.

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POLLUTION OF GROUND SOURCES OF DRINKING WATER WITH TECHNOGENIC TRITIUM

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Abstract. Problems of fresh groundwater pollution with technogenic tritium are considered with Obninsk (Russia) for illustration. The paper deals with engineering and geological reasons of groundwater pollution with tritium near Obninsk. Tritium concentrations in municipal water intakes and springs are by 20–100 and 10,000 times, respectively, higher as compared to the background value in Russia as a whole. The highest concentrations are observed near radioactive waste repositories. Tritium migration over the water bearing horizons and tritium dispersal within the anomaly are studied. Health risk assessment for Obninsk population has been performed. The risk of stochastic effects of exposure in chronic tritium intake amounted to $1 \cdot 10^{-7}$.

Keywords: radioactive waste repositories, tritium, migration, drinking water, health risk

1. Introduction

A lot of radiation-dangerous objects (RDO) available in the world and the economic activity have generated some pressing problems for human health and the environment. Obninsk was founded on the basis of a large town-forming

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object (State Scientific Centre of the Russian Federation the “Institute of Physics and Power Engineering” (IPPE) of the Federal Agency for Nuclear Power Engineering). Developments of nuclear technologies, the available centers of utilization, reprocessing and disposal of radioactive materials and wastes have governed the need for studying technogenic radionuclide behavior and migration in our region. A particular emphasis should be placed on the problem of environmental pollution with tritium.

Tritium (T or ^3H) is a superheavy radioactive isotope of hydrogen, the half-live of which is 12.26 years. In disintegration this isotope emits β-particles of the maximum energy 18.6 keV (the mean β-particle energy is 5.8 keV). Tritium is a part of tritium water (HTO, T_2O), it exits as a gas (HT, T_2) and also is a part of organic and inorganic compounds that contain hydrogen, among them compounds forming biological tissues where tritium usually replaces the atoms of ordinary hydrogen.

Natural tritium is formed mainly in the upper atmosphere and its content in the atmospheric air is 1 atom per 10^{14} atoms of tritium and 1 atom per 10^{18} atoms of hydrogen in water, i.e. $8.65 \cdot 10^{-2}$ Bq/l. The total reserves of natural tritium in the world are in the equilibrium for a long time and amount to $(8–25) \cdot 10^{17}$ Bq (1.5–2 kg) (Egorov, 2003) About 99% of the total amount of natural tritium are contained in water and involved into its natural circulation. Prior to nuclear testing the mean tritium concentration in fresh water basins was 0.2–0.9 Bq/l (Larin, 2003)

The ingress of artificial (“technogenic”) tritium into the Earth’s atmosphere has begun with the ground thermonuclear explosions (1954–1962). The total tritium activity produced by nuclear explosions is estimated to be $2.4 \cdot 10^{20}$ Bq as shown by UN Scientific Committee on Nuclear Radiation Effects (1978). In nuclear power plant operation tritium enters the environment in a form of gaseous releases and liquid wastes.

The above sources of natural and anthropogenic tritium have formed background levels of this radionuclide in Russia and the adjacent water area. According to long data, tritium content in the seas surrounding Russia varies within 4–10 Bq/l with a pronounced downward tendency. Background levels of Russian river pollution with tritium are 2–7 Bq/l, the averaged Russian values being within 4 Bq/l (Makhon’ko, 1998).

2. Sources of Technogenic Tritium Near Obninsk

In 1995 when testing groundwater sources of the Protva left bank where all Obninsk enterprises are placed, the SPA “Typhoon” employees had found that the higher tritium content was observed at all outlets of groundwater sources in the sanitary zone of Obninsk water intakes, including those upstream of the town and NPP (Makhon'ko, 1996). Maximum tritium concentrations up to 46.9 kBq/l refer to water in the first above floodplain terrace of Protva near the new IPPE radioactive waste (RAW) repository (Makhon'ko, 1996). For comparison, according to the Russian RSS-99 (Radiation safety standards RSS-99, 1999) the intervention levels for inorganic tritium compounds are 7700 Bq/l and for organically bounded tritium 3300 Bq/l.

In addition to the above IPPE repository, the source of tritium water in Obninsk region may be spent tritium targets found in the RAW repository, the fast neutron reactor BN-10, another decommissioned reactors, the RAW repository of the All-Russian Research Institute of Physics and Chemistry, soil anomalies formed as a result of pipe-line leakages and air releases, discharged water and purification fallout, old dumping sites and technological accidental discharges (Silin, 2005).

3. Materials and Methods

Monitoring of tritium dispersal at the IPPE industrial site and near Obninsk had been performed by analyzing tritium content in the reference wells of the RAW repository, water and snow in the IPPE area and adjacent territories and water from four Obninsk water intakes.

Water from the wells under control was taken with a special sampler. Snow at each selected site was sampled to the total depth of snow into plastic packs. Then snow was melted at a room temperature and this water was placed into tight vessels. Samples were analyzed after filtration and distillation.

Results of water sample measurements were obtained by Moscow Physics and Engineering Institute's laboratory and by the external monitoring laboratory of Smolensk NPP with the help of a precision liquid-scintillation beta-spectrometer Gardian 1414-03 (Wallac Oy, Finland). The spectra measured were analyzed using the programme Wallac Spectrum Analysis. Measurement error did not exceed 10%.

4. Identification of Drinking Water Pollution with Tritium in Obninsk Water Intakes

The industrial complex of radiation-dangerous objects has a pronounced impact on natural resources in the basin and fresh water hydrosphere, in particular. Considering congestion of enterprises, it is difficult to assess the role of each source in groundwater pollution. Besides, a piezometric depression exceeding 200 km^2 in area with degradation of the level up to 42 m and a general slope to the opposite natural runoff (towards the centre of Moscow artesian groundwater basin) has been formed along the chain of water intakes in the industrial water bearing horizon. This piezometric depression has changed the hydrodynamics and the geochemistry of groundwater that adversely affected the water quality. As a result, the chemical composition now is governed by a space-deterministic combination of natural and technogenic factors and processes.

Scattering of radioisotopes under these conditions proceeds according to their chemical properties and geochemical peculiarities of the environment. Tritium possesses the highest mobility in groundwater and can be used as a tracer for migration processes because it is practically not held in geochemical barriers. Figure 1 presents a map of the territory surveyed with the isolated aureoles of anomalous tritium concentrations.

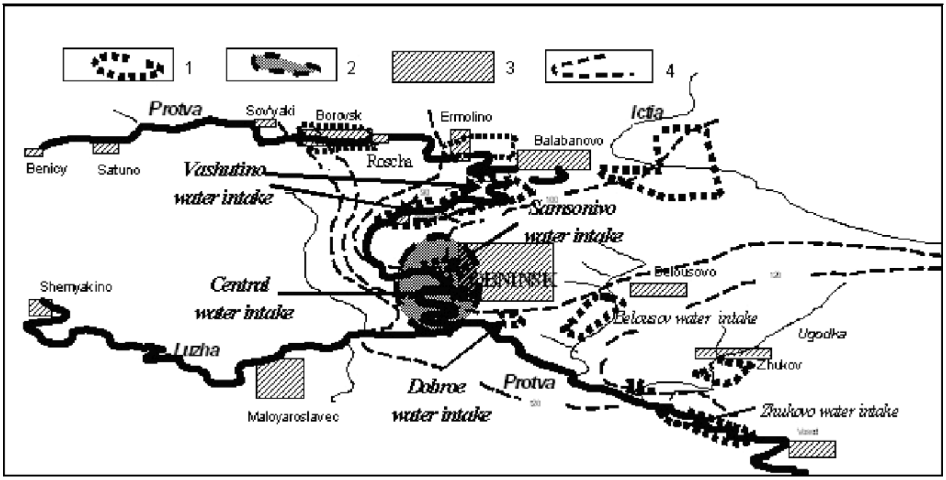

Figure 1. Surveyed territory of the Oka-Tarusa water bearing horizon: 1 – large grouped water intakes; 2 – territory with the anomalous tritium content in water; 3 – settlements (Obninsk and its neighbourhoods); 4 – hydroisopiezes of the level of horizon in service

Trial calculations of tritium migration and the RAW repository have been done from a mathematical model of an isothermal nonstationary two-phase flow of constant density developed by Zinin A.I and Zinina G.A. (Drozhko E.G., 1997). According to this model, tritium is discharged through the Quaternary deposits. In this case a part of tritium passes below the river bottom in the foot of alluvial deposits and then leaks into the Oka-Tarusa water bearing horizon where it is entrained in the inversion flow towards Vashutino water intake, i.e. the centre of a depression funnel. Another part of the aureole is discharged into a river downstream (Figure 2).

The calculated balance of tritium received from the source in a simulated period is the following: 75% of tritium decay when moving in groundwater, 25% of tritium is discharged into the Protva river, mainly, through the Quaternary deposits and only an insignificant amount of it (0.005%) reaches Obninsk water intakes.

Tritium discharge into the Central and Samsonovo water intakes begins simultaneously, in 20 years from the commencement of tritium leaching out of the disposal site. Then the discharge increases and is leveled off by 70–80 years of the time period simulated.

Higher tritium concentrations in some water samples are found in all Obninsk groundwater intakes, however, the statistically reliable limits of tritium anomalies are revealed only in the Central and Camsonovo water intakes. The expected reason for this anomaly is tritium migration out of the disposal site through the Quaternary sand layer simultaneously in two water bearing horizons of the industrial site: in Protvino horizon (C_1 pr) during seasonal filling and Oka-Tarusa one (C_1ok-tr) (Figure 2). The hydraulic relationship between horizons is realized through lithological windows and possibly near the water wells. In this case the rates of tritium migration from sourves to water intakes rise by some orders of magnitude. The uncertainty in data interpretation is explained by poorly studied hydrodynamics and hydrochemistry of the industrial site.

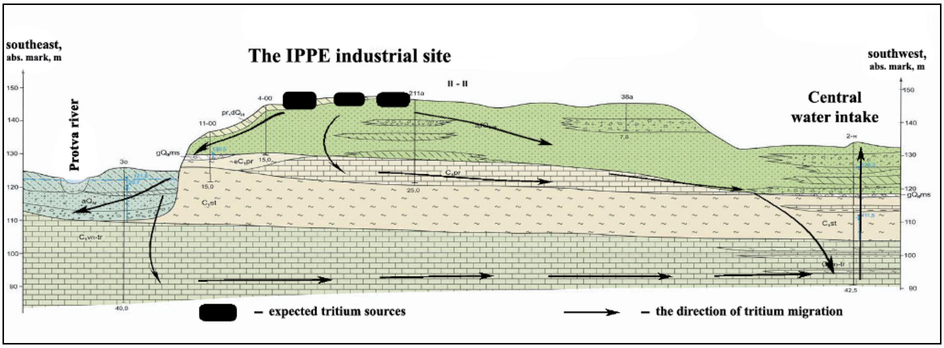

Figure 2. The scheme of groundwater pollution with tritium the geologic-hydrologic section

5. Analyzed Tritium Content in Obninsk Groundwater

Table 1 presents data on tritium content in snow and water of nine springs and water sources of Obninsk and its neighbourhoods.

TABLE 1. Results of ^{3}H measurement in water samples (March 2005)

Sampling site	Specific activity of ^{3}H, Bq/l
Springs, Obninsk neighbourhoods	1 ÷ 24
Springs near the IPPE industrial site	6290 ÷ 37 000
Observation well №5 (the IPPE industrial site)	6720
Snow (the IPPE industrial site)	9 ÷ 168
Snow (Obninsk, out of the IPPE industrial site)	<1 ÷ 4
Central water intake	291
Samsonovo water intake	102
Vashutino water intake	4
Obninsk water supply network	2 ÷ 80
The intervention level	7700

Table 1 shows that the maximum value of volume activity for groundwater is 37 000 Bq/l, that is five times as much as the intervention level (7700 Bq/l). The highest tritium activity is observed in the Central water intake (next to the IPPE industrial site) and amounts to about 300 Bq/l that is almost seventy five times as much as the Russian background levels but below the intervention level. In other wells of Obninsk water supply the specific activity of tritium ranges within 1–25 values of the background level (4 Bq/l). In springs near the industrial site there is an excess of the tritium intervention level for drinking water. The volume tritium activity in snow varies from the background values in Obninsk to about 168 Bq/l. It is seen that tritium ingress with snow water reduces tritium concentration in the groundwater bearing horizons in wells and increases the background radioactive pollution with tritium in the IPPE territory.

To supply a town with water, a series of water intakes is built 5–10 km distant from the IPPE industrial site which takes water from Protva and Oka-Tarusa water bearing horizons. Recently, technogenic tritium has been found in some water intakes (Table 2).

The tritium concentration data compared showed that during last 7 years no significant changes had been observed in natural water pollution with tritium in Obninsk and its neighbourhoods. The results indicate that in some cases the situation is stabilized (municipal tap water) and sometimes the volume activity of tritium in the wells under control (Vashutino and Dobroe) has reduced. It should be noted that the above values are lower than the accepted intervention levels.

TABLE 2. Tritium concentrations in municipal water wells and tap water (summary from various sources (Starkov et al., 2003, Vakulovsky, 2003))

Water supply source	Specific activity of ^{3}H, Bq/l						
	1999	2000	2001	2002	2003	2004	2005
Central water intake	620	1330	2160	638	–	452	310
Samsonovo water intake	200	73	–	35	–	43	102
Vashutino water intake	13	5	–	4	–	–	4
Dobroe water intake	490	4	–		3	4	–
Obninsk water supply network	–	–	–	74	70	65	67

«–» – null data

Consider also the data on tritium distribution within the anomaly (Figure 2) in ground water intakes near the IPPE industrial site. Based on data of water well testing, it could be said with the approximation probability $R^2 = 0.80$ that as the distance from a research centre increases the power dependence of tritium distribution has the form presented in Figure 3. Generally, tritium migration in groundwater is thought as being a polluted flow which is directed along a chain of water intakes from the IPPE industrial site to Vashutino intake.

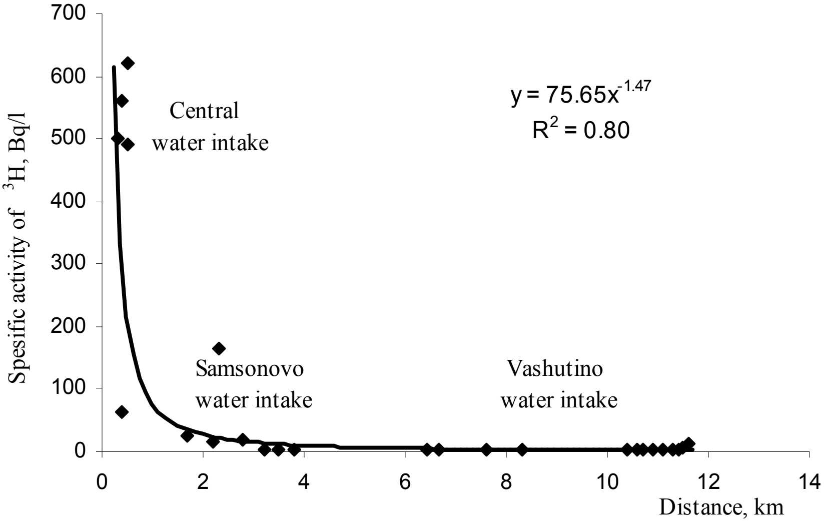

Figure 3. Variations in the specific activity of tritium when moving from the IPPE industrial site

The dilution degree of a tritium flow arriving from the IPPE industrial site is considered in profiles transverse to the river valley. In the Central water intake the degree of tritium dilution as the distance from the river increases is characterized by a linear function (Figure 4):

$$C_T = 1.2L - 141, \tag{1}$$

where C_T is the tritium concentration in water, Bq/l;
L is the distance to the river, m.

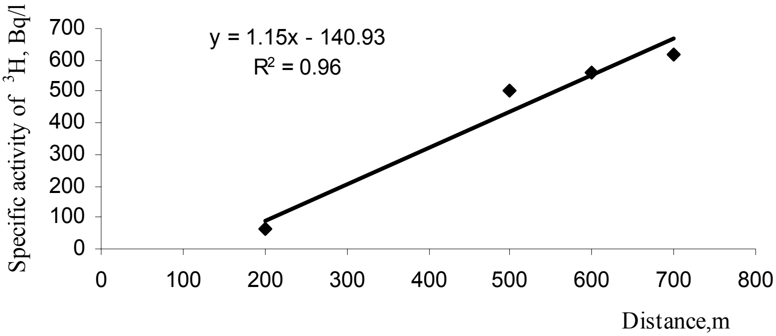

Figure 4. Tritium content dependence in groundwater on distance to the Protva river bed

The analyzed tritium dispersal in a water bearing horizon allows the qualitative assessment to be made of some essential parameters of a filtration flow: the direction of a flow, the rate of mass transport, the mixed volumes of ground and river water and etc. Comparing dispersal parameters of tritium and other chemical elements in water it is possible to isolate technogenic and natural sources and to specify geochemical peculiarities of their migration and to assess health risk for people who use this water for drinking.

6. Health Risk Assessment in Drinking Water Containing Tritium

Now practically all countries and international organizations consider the concept of risk assessment as the primary mechanism in decision making at the international, state or regional level as well as the level of an isolated industry or any other contamination source potentially dangerous for the environment. In our case considered is the health or life risk from technogenic tritium available in the environment.

Radiation risk has been assessed to determine the degree of human impact of the above tritium activity in drinking water. In calculating the life risk coefficients given in RSS-99 and the technique described by Synzynys et al.

(2005) were used. When drinking water with the activity of 67 Bq/l the annual effective per capita dose for Obninsk inhabitants is 1.48 μSv that corresponds to the individual life risk of stochastic effects 1.10^{-7} year^{-1}. The obtained risk value is by an order of magnitude lower than the acceptable risk ($1\cdot10^{-6}$) recommended by the World Health Organization. Thus, under stable conditions at the municipal water intakes there is no need for local authority interference to limit the impact of a considered risk factor.

7. Conclusion

The integrated pattern of natural water pollution with tritium in Obninsk and its neighbourhoods was obtained as a part of the study. Data presented on the specific tritium content in water intakes, springs and tap water indicate that the intensity of tritium ingress into natural water from the IPPE industrial site did not reduce. Groundwater arriving from the IPPE industrial site near a new RAW repository contains tritium with the specific activity exceeding the intervention level 5 fold. In groundwater transit to water intakes the tritium content is much diluted and the specific activity there is by an order of magnitude lower than the intervention level. In mixing with water from distant water intakes there proceeds an additional reduction (another order of magnitude) of the tritium content in drinking water supplied to population (up to 67 Bq/l). It should be noted, however, that Obninsk population is partly forced to drink water with the tritium content exceeding the background level (by 17 times). Beyond the established technogenic anomaly the tritium content in water intakes is at the background value. Radiation risk assessments in drinking tritium water did not reveal the cases of stochastic exposure effects.

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