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**Book of Abstracts**
Enhancing subsurface purification during Managed Aquifer Recharge

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INTRODUCTION

Water quality deterioration due to interaction of infiltrated water with the aquifer is a common occurrence that increases the purification challenge during Managed Aquifer Recharge applications for drinking water production. During Aquifer Storage Recovery (ASR) for example, water quality deterioration may limit the extractable fraction of the stored drinking water (Pyne, 2005). Quality deterioration may be due to natural processes associated with the injection of oxygenated water into anoxic aquifer systems. Natural pollutants frequently associated with declining water quality are heavy metals, such as iron, manganese and arsenic. Concentrations above the aesthetic guidelines have been associated with unusual look, taste or smell of the water. Chronic exposure to manganese in drinking water above the WHO guideline of 0.4 mg/L may have neurological effects while long-term exposure to arsenic at concentrations above 50 $\mu$g/L can cause cancer and skin lesions.

This study explores the effects of reducing the reactivity of sediments around ASR wells by injection of strong electron acceptors to drastically reduce the availability of sedimentary electron donors during an aquifer pre-treatment step. The reactivity of sediments can be consumed in various ways, including the injection of oxygen-enriched water. As oxygen can achieve a maximum saturation of 5 times (100 % oxygen) compared with air, the use of “strong” electron acceptors for aquifer pre-treatment allows a significantly greater oxidation capacity per injected water volume, particularly for highly soluble ionic electron acceptors, such as permanganate ($\text{MnO}_4^-$) (Cavé et al., 2007). An additional advantage of permanganate for aquifer pre-treatment is the increase in the sorption capacity through the generation of manganese-oxide precipitates. Manganese-oxides are a by-product of the permanganate reaction with sedimentary electron donors such as organic matter and iron-sulphides. These precipitates may coat the aquifer minerals and could effectively sequester a range of heavy metals (Buamah et al. 2009) improving the subsurface in-situ purification and minimizing the post-treatment requirements of the extracted groundwater.

METHODOLOGY

The effects of treating the aquifer prior to applying ASR were evaluated using bi-directional columns that simulate the evolution of the water quality in an anoxic aquifer (Antoniou et al 2014). Two air-tight columns were filled with reduced aquifer sediments and were saturated with anoxic groundwater obtained from the same aquifer. The presence of reactive mineral phases was confirmed by geochemical analyses of the sediments. Two diaphragm-metering pumps allowed the injection and extraction of water at a low flow rate. Collection of water samples was made possible via two ports, one at each side of the experimental setup (Figure 1).
RESULTS AND DISCUSSION

Upon infiltration of oxygenated water in the anoxic columns, oxidation reactions with common sedimentary electron donors (iron-sulphides and organic matter) and the associated proton production triggered dissolution of carbonate minerals (ankerite) releasing substantial amounts of manganese in the groundwater. Simultaneously, arsenic was mobilised during the oxidation of iron-sulphides (pyrite) posing additional concerns regarding the quality of the extracted water. To neutralize the manganese production, which persistently compromised the extracted water quality after having extracted 15 % of the injected water, the aquifer sediment was treated with a 0.02 M potassium permanganate solution.

The extended oxidation reactions with sedimentary electron donors caused partial depletion and coating of their reactive surfaces (reactive organic matter and readily oxidisable iron-sulphides) along with an extensive precipitation of manganese-oxides. The high sorption capacity of these precipitates allowed a more efficient ASR application with an extractable ratio of 110 % (as opposed to 15 % prior to treatment) before encountering prohibitive manganese concentrations. Mixed results were observed for arsenic as the extended consumption of iron-sulphides was expected to reduce arsenic mobilisation while the increased pH induced by the reaction of permanganate with the sedimentary electron donors was expected to act against an efficient sorption of anions, including arsenic (Smedley and Kinniburgh, 2002).

CONCLUSIONS

The results suggest that the intense oxidation of sedimentary electron donors around
ASR wells in combination with the resulting extended precipitation of manganese-oxides provide an efficient option for the removal of certain positively charged heavy metals (iron, manganese) from the groundwater before it is extracted. The relatively long travel times towards a well allow longer contact time for heavy metal removal than available during above-ground treatment. A field application of subsurface treatment should consider the potential negative effects on water quality and well performance. The permanganate solution, depending on its purity, might introduce certain trace elements in the aquifer. Such elements, although present in the permanganate solution introduced in the columns, were absent in the extracted groundwater confirming their efficient sorptive removal by the manganese-oxide precipitates.

REFERENCES


Forecasting utilisation of pharmaceutical products to assist in predicting emissions to surface waters

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INTRODUCTION
Research on pharmaceuticals in the environment is growing at a significant rate but, although the body of knowledge on sources, occurrence, environmental fate and effect of these substances is expanding, understanding of the impacts remains limited (Kümmerer 2008). Newly developed drugs constitute a large proportion of pharmaceuticals with the potential for environmental impact (Dong et al. 2013). Daughton (2014) identified 73 pharmaceuticals largely lacking environmental information about occurrence, fate and effects and, although these drugs are among the most frequently prescribed, research continues to focus on drugs of known occurrence in the environment. Petrovic (2014) reasoned that selection of target analytes for new studies is primarily based on published results, causing a continuous neglect of environmental research on newer drugs. Currently, over 1,300 medicinal products are dispensed in the Irish market and therefore selection of analytes for research, or monitoring, can be challenging.

The aim of this study was to identify pharmaceuticals with a rate of utilisation warranting concern. Statistical analyses were developed into a software instrument, named Utilisation Trend and Forecast (UTF) analysis. This instrument was designed to be easily applicable to prescribing/dispensing data in order to provide rapid assessment of utilisation trends. UTF analyses were carried out on a dispensing data sample of 84 most prescribed pharmaceutical products in Ireland and five antineoplastic drugs. Historical trends indicated four substances as potential emerging pharmaceuticals in the environment: pioglitazone, sitagliptin, levetiracetam and pregabalin. These substances were also identified in Daughton (2014) as lacking environmental information. Furthermore, projected forecasts suggested an alarming increase in prescribing of the antineoplastic mercaptopurine. Application of the UTF instrument to national prescribing/dispensing databases can provide an alternative method to predict changes in utilisation and associated emission of pharmaceuticals to the environment that could require inclusion in monitoring programmes.

METHODS
Historical trends of dispensing of pharmaceuticals in Ireland were analysed to generate forecasts of utilisation and identify substances displaying sharp consumption increases. Dispensing data, provided by the Health Atlas Ireland, were used for the analyses. The data, covering the period from 1 February 2008 to 31 August 2013, are observations of pharmacy reimbursement claims representing the utilization pattern of ~73 % of the population. A Utilisation Trends and Forecast (UTF) software instrument was developed in R to rapidly analyse trends and detect changes in utilisation. The UTF instrument computes results by calculating simple percent change between fixed periods of the historical and forecasted trend. Forecasts are generated fitting Holt-Winters (HW) filters to time series of volumes dispensed. HW filters are applied to each dataset in linear method and seasonal additive
method. Accuracy of forecast is evaluated using in-sample predictions. HW methods fitted to whole samples computed 25 month forecasts to September 2015. UTF analyses were carried out on a formulary of 89 of the most frequently prescribed therapeutic drugs in Ireland.

RESULTS

The change in utilisation between year 2008 and year 2015 for five substances identified as potential emerging pharmaceuticals in the environment is summarised in Table 1.

Table 1. Summary of change in utilisation for five substances identified as potential emerging pharmaceuticals in the environment

<table>
<thead>
<tr>
<th>Substance</th>
<th>In-Sample Annual Rate of Change (%)</th>
<th>Forecast Annual Rate of Change (%)</th>
<th>Volume Dispensed in 2008 (kg)</th>
<th>Volume Dispensed in 2012 (kg)</th>
<th>Forecast of Volume Dispensed in 2015 (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pioglitazone</td>
<td>47.9</td>
<td>-4.1</td>
<td>4.2</td>
<td>20.1</td>
<td>18.5</td>
</tr>
<tr>
<td>Sitagliptin</td>
<td>42.6</td>
<td>2.0</td>
<td>65.7</td>
<td>271.4</td>
<td>282.6</td>
</tr>
<tr>
<td>Pregabalin</td>
<td>28.5</td>
<td>12.2</td>
<td>892</td>
<td>2432</td>
<td>3303</td>
</tr>
<tr>
<td>Levetiracetam</td>
<td>23.6</td>
<td>11.8</td>
<td>1793</td>
<td>4189</td>
<td>5735</td>
</tr>
<tr>
<td>Mercaptopurine</td>
<td>13.2</td>
<td>18.8</td>
<td>8.7</td>
<td>14.3</td>
<td>22.3</td>
</tr>
</tbody>
</table>

Utilisation of pioglitazone increased sharply in 2010 and plateaued thereafter whereas utilisation of sitagliptin increased rapidly at the beginning of the sample period but slowed down by 2013. The rate of change for the forecast period was minimal for sitagliptin and negative for pioglitazone. The sharp increase in utilisation of pioglitazone was caused by a switch in prescribing following a health warning issued on another antidiabetic. Historical utilisation trends for pregabalin and levetiracetam were almost linear and continued linearly during the forecast period. UTF analysis for the antineoplastic mercaptopurine reported the highest rate of change for the forecast period (Figure 1.). Trends in utilisation for estradiol and diclofenac were identified as decreasing; however, the decline is attributable to a change in prescribing regime and not market penetration, which remained unchanged during the sample period. All of the four anti-infectives evaluated, amoxicillin, flucloxacillin, cefaclor and clarithromycin displayed a stationary trend and a seasonal patterns of utilisation; the seasonal cycles of two of the substances were different from the other two anti-infectives. Analyses of 89 substances showed that overall trends in utilisation are very rarely stationary and tend to display erratic patterns.
DISCUSSION

The four drugs pioglitazone, sitagliptin, pregabalin and levetiracetam, identified as potential emerging pollutants based on historical trend analyses, were all selected by Daughton (2014) as candidate orphaned chemicals for which environmental knowledge is lacking. Forecast of utilisation of mercaptopurine suggests that the substance is being prescribed at rates that warrant investigation of the occurrence of the substance in the environment. These findings demonstrate the necessity to widen the scope of research on pharmaceuticals in the environment to include emerging substances of limited environmental information. The UTF instrument, developed as part of this research, demonstrated the capability to analyse utilisation trends and identify substance displaying sharp rates of change. The instrument can also detect and forecast seasonal cycles, crucial in the design of monitoring programmes, particularly when targeting mixtures of pharmaceuticals in the environment. The application of the instrument to existing national databases of prescribing/dispensing data can provide continuous monitoring of utilisation and early warning of sharp changes in utilisation. A general conclusion drawn from the results is the irregularity of utilisation trends for most of the substances analysed, demonstrating the benefit of continuous monitoring of utilisation. The UTF instrument, designed to assist in rapid assessment, could be effectively implemented in assisting the prioritisation of research and informing decision making processes.

REFERENCES


ABSTRACT

The African leaders have committed themselves to "ensure sustainable access to safe and adequate clean water supply and sanitation, especially for the poor" and "to plan and manage water resources to become a basis for national and regional cooperation and development". Although the objectives are clear, it takes a great deal of political, economic and technological effort to accomplish them, particularly with the increasing population pressure, combined with economic development, leading to increase the gap between the claim of water and actual availability. The increasing freshwater demand resulting from high population growth rates particularly in urban centres, result in less water available per person, and negatively impacts on the quality of life and livelihoods of the region’s inhabitants. Large numbers of people are affected by water-related diseases like malaria, guinea-worm, cholera, typhoid, bilharzia, etc. This is related to many factors amongst which are low water supply and sanitation coverage.

The serious concerns over a continuous deteriorating water quality and increasing water pollution call for urgent attention to the sustainability of water resources in Africa, which is home to nearly one fifth of the world’s population. Conservation and restoration of environment, biodiversity, and life-supporting ecosystems, where water quality has a critical role, is among the urgent water needs to be addressed as highlighted in the Africa water vision 2025. In response to these water challenges, the countries need to pursue and adapt more sustainable approaches to the use and management of water resources through a true IWRM where water quantity and quality are fully integrated. Specific focus on the prevention, reduction and control of water pollution and on ensuring safe drinking water for all its inhabitants, is needed to address Africa’s water quality challenges.

The workshop was organized by the UNESCO International Hydrological Programme Secretariat and the UNESCO Regional Bureau for Science in Africa as part of the implementation of Focal Area 4.1 "Protecting water quality to ensure sustainable livelihoods and poverty alleviation "of the 7th Phase of IHP (IHP-VII, 2008-2013). The main objective was to help African countries address the challenges of the quality of water resources for their sustainable management. Specific objectives included the identification of the key issues affecting the quality and pollution of water, the evaluation of the main causes and trends, and to make recommendations for solutions and strategies to overcome the challenges of water quality in African countries.

The workshop was attended by about thirty experts from fifteen countries of Africa south of the Sahara and representatives of regional bodies and pools as well as UNEP and UNESCO.

The workshop gathered high-quality contributions, covering a wide range of topics and issues related to water quality in the African context and their linkages with other broader
environmental, socioeconomic, health and development issues. The workshop received outstanding positive feedback from the participants. The process applied for the nomination and selection of workshop participants/experts was highly praised by the participants, who emphasized that this was one of the ways to help strengthen IHP National Committees in Africa and to ensure their active involvement in IHP activities. The workshop discussions recognized water quality as the most crucial water problem facing Africa and recommended that IHP activities in the area of water quality should be strengthened.

Following the general discussion on outcomes of the group sessions, the participants wrapped up the main findings of the workshop sessions and discussions.

Affirming the importance of protecting the quality of Africa’s water resources for healthy people, sustainable ecosystems and thriving socioeconomic development, the participants concluded with the unanimous agreement on a number of key recommendations on next steps and priorities for moving forward to addressing water quality challenges in Africa.

- Realizing the pressing need to build the capacities of African countries to better address the critical water quality issues, it is highly recommended to build a strong knowledge network on water quality, under the International Hydrological Programme of UNESCO, that can act as a pioneer in research promotion, capacity building and experience and knowledge exchange in the Africa region. This network should aim to facilitate knowledge and information exchange among decision-makers, professionals and researchers of African countries on crucial water quality issues, promote a long-term vision for science-based strategies and policies for addressing water quality challenges, and provide a regional platform for exchanging experience and lessons learned among the network members.

- UNESCO-IHP activities on water quality, in particular in the Africa region, should be strengthened through projects, experts’ workshops and capacity building activities with specific focus on water quality and its links with human and environmental health, poverty reduction and other related water resources management and socioeconomic issues.

- As a follow-up to this workshop, a regional workshop on addressing water quality challenges in Africa should be organized biennially, with specific thematic focus on different aspects of water quality management and its links with other environmental, health and socioeconomic issues. Such biennial workshops with the participation of different stakeholders (including decision-makers, researchers, professionals and regional, sub-regional and basin organizations) are of crucial importance in strengthening the capacities of African States to better address the critical water quality through innovative science and policy.
Ecohydrological biotechnology - denitrification barriers as a tool for nitrogen reduction in agricultural catchments

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INTRODUCTION

The production of food and energy for the growing human population of the early twenty-first century has contributed to an increase of more than 10 times in the anthropogenic emissions of nitrogen compounds compared to the end of the 19th century. Agriculture has changed the natural flow of nitrogen (N) and led i.a. to an increase in the amount of ozone in the troposphere, a more acute greenhouse effect due to N\textsubscript{2}O emission, greater acidification of soils and surface waters, reduction of biodiversity, increased eutrophication of aquatic ecosystems and more widespread adverse health effects resulting from the accumulation of nitrates in groundwater used as drinking water. Therefore, on the basis of an ecohydrological system approach, the protection and restoration of water ecosystems should employ methods that use ecosystem properties, which can contribute to the enhancement of environmental potential in four dimensions: water, biodiversity, ecosystem services for society and resilience (WBSR) (Zalewski 2000; 2014). Development of effective methods using the natural potential of ecosystems for the reduction of nitrogen compounds has created an opportunity to increase the efficiency of groundwater protection at the catchment scale, as required by the European Nitrogen Directive and Water Framework Directive and to achieve a good ecological status of the water ecosystem.

One of the biotechnological solutions, which can be applied in the reduction of nitrogen supply to groundwater from point (Phot. 1) and diffuse agricultural pollution (Phot. 2), are the denitrification barriers. The broad scope of research demonstrates that the availability of organic carbon is one of the most important factors which affects denitrification processes in the soil.

External carbon sources, necessary to accelerate nitrogen transformation through ecosystem biotechnologies, can be waste materials like: pine sawdust/straw, brown coal/charcoal lime and straw/lignite (Schipper \textit{et al.} 2010a; Bednarek \textit{et al.} 2010; Bednarek \textit{et al.} 2014).

Agriculture is responsible for the release of about 60\% of river nitrogen pollution in Europe. Nitrates emitted from point and diffuse sources ranged from 200 mg l\textsuperscript{-1} to 2000 mg l\textsuperscript{-1}, and from 50 mg l\textsuperscript{-1} to 200 mg l\textsuperscript{-1} respectively. Construction of barriers around the point-sources such as manure deposition areas reduced nitrates concentration from 52\% to 72\% and increases proportionally with incoming nitrogen load.

MATERIALS AND METHODS (adopted from Bednarek \textit{et al.} 2014)

The source of pollution in this study was an manure heap from a fattening farm which had lain unprotected for 12 years (Phot.1a). The manure was produced by ca. 20 cows. Manure
is removed from the heap twice a year. Since it is unprotected, nitrogen compounds are leached by water run-off. Prior to deciding on the placement of denitrification ditches, groundwater levels and contamination levels were monitored for three months. The average concentration of NO₃ was estimated to be above 300 mg/l, with the highest values being above 2000 mg/l. The dump was constructed using a CAT excavator: the ditch was 1-1.5 m deep and 1 m wide, dug perpendicular to the slope/direction of groundwater flow. A mixture of brown coal and calcium coal was used as the source of organic carbon, constituting about 30% of the wall volume (Phot.1b, c). Brown coal and calcium coal were carefully mixed by the excavator with soil dug out from the trench during construction. Ground waters were at the level 1 – 1.3 m deep. Piezometers were used to take samples of groundwater were taken once a month to analyze nitrate nitrogen (NO₃) and ammonium ion (NH₄⁺) content using ionic chromatography with DIONEX (mg l⁻¹).

RESULT AND DISCUSSION

After the first two years of the operation of the denitrification barrier due the restoration of a point source of nitrogen in Jerwonice village (Demo site), it was observe 65% average reduction of nitrate ions in the groundwater around the ditches (Fig 1; Phot. 1) (Bednarek et al. 2014a).

Ecohydrological biotechnology - denitrification barriers as a tool for nitrogen reduction in agriculture catchments

Figure 1. Average (and +/- DS and Min/Max value) nitrate concentration in ground water before, in and behind ditches in Jervonice demonstration site (from: Bednarek et al. 2014a)

The removal of nitrate from diffused sources (Phot. 2) where much lower concentrations appear amounted to 15-56% and also increases with concentration.

The composition of agricultural sewage (pig/cattle manure) required development of a system which allowed removal both nitrate and ammonium. In such areas of an extreme impact a mixture of lignite and straw appears to be very efficient for the removal of both toxic forms of nitrogen, where a complete reduction of the nitrate load (initial concentration 448 mg l⁻¹) and also ammonia (initial concentration 260 mg l⁻¹) was observed.

The results of the projects presented above and its implementation demonstrate that the development of low cost advanced ecohydrological biotechnologies, for the enhancement of natural processes in groundwater, significantly enhance of the nitrogen reduction in agricultural landscape and should be used for achieving good ecological status of inland waters.

Study supported by:

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PBS1/A8/2012 MIKRAZO - Microbial activators in denitrifying deposits used for the treatment of nitrate pollution for the implementation of the Water Framework Directive and the Nitrates Directive
LIFE08 ENV/PL/000519EKOROB: Ecotones for the reduction of diffuse pollution

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Environmetric & Index Methods in Water Quality Assessment

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INTRODUCTION

One of the difficult tasks facing environmental managers is to convert complex data to information for better defining the sources and typology of the pollution, etc. Environmental data is characterized by high variability because of a variety of natural and anthropogenic influences. The best approach to avoid misinterpretation of environmental monitoring data is the application of multivariate statistical methods (e.g. environmetrics), for environmental data classification and modelling. (Boyacioglu and Boyacioglu 2008). On the other hand, the water quality index method is a useful tool in interpreting the water quality status by producing an index number that can be understood by technical and non-technical individuals. In the study, both methods have been performed to assess spatial and temporal changes in water quality in the Gediz River Basin, Turkey.

STUDY AREA

The Gediz River Basin is one of the most important agricultural areas in the western part of Turkey. With a length of about 401 km and a 17,200 sq km drainage area, the river flows from east to west into the Aegean Sea just north of Izmir. The basin approaches a total population of 2 million. The region has hot dry summers, cool winters and average annual rainfall amount is 500–530 mm. The primary problems in the basin are water shortage, competing use, and high levels of pollution. (Boyacioglu and Gündogdu 2013)

STUDY METHOD

Water samples were collected from 5 monitoring stations over two years on a monthly basis along the Gediz River and its tributaries, assessed and analyzed for biochemical oxygen demand-BOD, chemical oxygen demand-COD, kjehldahl nitrogen-KN, oil& grease-O&G, chloride- Cl, sodium-Na, boron-B, sulfate-SO₄, pH, dissolved oxygen-DO, total phosphorus-TP, suspended solids-SS, nitrate nitrogen-NO₃-N, nitrite nitrogen-NO₂-N, iron-Fe, aluminum-Al, nickel-Ni, lead-Pb, zinc-Zn, chromium-Cr, mercury-Hg and cadmium-Cd.

Variables were divided into three categories as follows:
• organic variables (BOD, COD, KN, O&G)
• physical - inorganic chemical variables (Cl, Na, B, SO₄, pH, DO, TP, SS, NO₃-N, NO₂-N)
• inorganic pollution variables (Fe, Al, Ni, Pb, Zn, Cr, Hg and Cd).

In the first part of the study cluster analysis, the water quality index method was applied to each group of variables and results were evaluated. For index calculations, Turkish Water Pollution Control Regulation (Official Gazette, 2004)-WPCR was used as the reference. According to the legislation, water quality of inland waters is classified into four groups as: high quality waters (Class I), moderate quality waters (Class II), polluted waters (Class III) and highly polluted waters (Class IV). This classification is based on the assessment of about 45 water quality parameters. Considering the existing water quality status of the Gediz River, “Class III” threshold values were chosen as reference guidance. For three groups of variables, the “Canadian Council of Ministers of the Environment Water Quality Index-CCME WQI method” was performed to investigate the water quality status. Instead of including 13 variables, some of them were eliminated from calculations based on similarities between data sets. A cluster analysis was used to investigate similarities. In the second part, the applicability of the Universal Water Quality Index (UWQI) developed by Boyacioglu (2007) has been demonstrated to assess water quality. Subsequently, the results of two applications were compared.

Cluster Analysis (CA):

The similarity between water quality variables was investigated using a cluster analysis (between groups of linkage method and squared Euclidean distance as similarity measure). The cluster analysis organizes sampling entities (e.g. species, sites, observations) into discrete classes or groups, in such a way that within-group similarity is maximized and among-group similarity is minimized according to some objective criteria. (McGarial et al. 2000). In the study, as a result of CA, some variables were excluded from index calculations.

Water Quality Index Method:

CCME WQI: CCME WQI relates water quality data to a selected beneficial water use using relevant water quality guidelines as benchmarks. In this method, the percentage of parameters and tests that fail to meet the guidelines, the deviation from the guideline for tests that do not meet guidelines, are captured in three factors (scope-F1, frequency-F2, and amplitude-F3). The index yields a number between 0 and 100. A higher number indicates better water quality. (Lumb et al. 2006; CCME 2001; Khan et al. 2005)

UWQI: Universal WQI was developed by Boyacioglu (2007) and designed to reflect appropriateness of the quality of surface water source used for drinking water supply. Twelve water quality parameters including Cd, CN, Hg, Se, As, F, NO₃-N, DO, BOD, TP, pH and total coliform were considered as the significant indicator parameters of UWQI to assess surface water sources. Weight factors were assigned to each of these variables based on the expert opinions. Sub-index values were determined using mathematical expressions to assign each parameter a value between 0 and 100. Sub-index functions were formulated based on “the quality required of surface water intended for the abstraction of drinking water in the Member States-75/440/EEC” set by the Council of the European Communities and “Turkish WPCR”

RESULTS

In the dendogram produced by CA for the group “organic variables”, BOD and COD tend to cluster together, which is an indicator of a high degree of similarity. Therefore, COD was eliminated and BOD, KN and O&G were chosen as index components. On the other hand, results of the CA performed for “physical-inorganic chemical” parameters showed that Cl-Na,
B-SO$_4$, pH-DO, TP-SS and NO$_2$-NO$_3$ had good similarity. Thus, Cl, SO$_4$, pH, TP and NO$_3$-N were determined as index components. Among “inorganic pollution” variables, Fe-Al, Ni-Pb, Cr-Hg had good similarity and classified under the same cluster. Based on this result, Pb, Hg, Cd, Zn, Fe was chosen as index components (Boyacioglu et al. 2013).

CCME WQI scores were calculated based on the threshold values set by Turkish WPCR. Results showed that all sample concentrations for “physical-inorganic chemical” variables (Cl, SO$_4$, pH, TP, NO$_3$-N) were lower than the limit values. Therefore, index score was assigned to “100” for this group. On the other hand, not only organic variables (BOD, KN, O&G) but also inorganic pollution parameters (Pb, Hg, Cd, Zn, Fe) were a serious threat to the overall water quality in the region (index scores were ≈20 and 40 for both groups) (Boyacioglu et al. 2013). In addition, to investigate seasonal variations in quality, data sets were divided into two flow periods as “high flow” and “low flow”. Index values were calculated based on the variables (DO, pH, Hg, Cd, TP, BOD and NO$_3$-N) for five stations separately. Results indicated that under high flow conditions, the water quality was slightly better than in low-flow periods due to a dilution effect. Monitoring stations along the river got index scores: 32, 44, 49, 55 and 46 in low and 37, 45, 50, 54 and 55 in high flow period. Due to low index scores, it was concluded that prevention measures should be taken not only in a specific area but also in the whole study region to control pollution sources.

Furthermore, UWQI scores calculated based on DO, pH, Hg, Cd, TP, BOD, NO$_3$-N produced the similar results and revealed that, in the Gediz River Basin water quality was marginal as described by the UWQI categorization scheme. This means that the water quality could not support the use of the source for drinking water supply. Moreover, Hg, Cd, TP and BOD were the parameters bearing risks when present in high concentrations in the region (Boyacioglu and Gündogdu 2013).

CONCLUSION

In the study, water quality data obtained from 5 monitoring stations over two years on a monthly basis in the Gediz Basin, were subjected to CA and water quality index calculations. In the first part, CA grouped water quality variables into several groups based on similarities. CCME WQI was applied to provide a convenient means of summarizing complex quality data. Spatial and temporal changes were investigated by processing data sets categorised based on the flow (as high and low flow period). In the second part, applicability of UWQI has been demonstrated to assess water quality. The overall results showed that environmetric methods can successfully be used to identify natural groupings in the set of data. Furthermore, water quality assessment by means of an index is easier than comparing experimentally determined parameter values with existing guidelines. While some index methods (e.g UWQI) define index determinants, some has flexibility to choose reference standards and index components (e.g. CCME WQI). On the other hand, UWQI has advantages over pre-existing indices by reflecting appropriateness of water for specific use - drinking water supply rather than general supply and has been developed by studying the supranational standard (75/440/EEC). It can be concluded from the results that, index and environmetric methods can be applied as complementary tools in water quality assessment. They can assist decision makers in reporting the state of the water quality and investigating spatial and temporal changes.

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The role of the Kiev reservoir in the chemical element transformation

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The largest river basin in Ukraine is the Dnieper basin with an area of about 504,000 km². The cascade construction of six reservoirs was finished on the Dnieper river in the late 1980ies. The cascade solves the problem of the intra-annual and long-term variability of the river runoff.

Simultaneously, the cascade construction is the source of numerous environmental impacts. A large area of fertile land has been diverted from its use as arable land. The large-scale transformation of the river runoff caused a water regime modification and slowed the water exchange and velocity of the river. As a consequence, hydrobiological conditions and chemical properties of the water were changed. Hence, the river (or part of the river) is converted into a water body with a water exchange that is similar to lacustrine ecosystems. The biological productivity became more intensive and the transition from the monodominant to the polydominant hydrobionts community was registered. The transit process type was transformed into an accumulative one.

It has been proven that the upper Kiev reservoir is the main reservoir in the Dnieper cascade. About 60% of cascade water runoff is formed within the Kiev reservoir. Such a reservoir placement in the cascade system transforms it to a powerful barrier which accumulates a lot of sediments and chemical elements. The most significant barrier function of the Kiev reservoir was fixed during the Chernobyl NPP disaster in 1986 (Kanyvets, 1996).

The Kiev reservoir is a source of drinking water supply of the capital of Ukraine, Kiev, and the chemical composition of the reservoir water has an important economic and social importance. The major ions, nutrients and trace elements among water chemistry parameters were considered here.

The main sources feeding the reservoir are the Pripyat and Dnieper rivers, the overall runoff of which is about ~ 97% of water masses of the reservoir. The high waterlogging degree, which is a peculiarity of these river basins, conveys a significant amount of organic matter and nitrogen compounds in the Kiev reservoir. The contribution of other tributaries (the Teteriv, Irpin and Uzh rivers) is insignificant.

RESULTS AND DISCUSSION

The content of chemical elements in the Kiev reservoir is determined by a tributary, atmospheric precipitation and also transforming processes within the reservoir aquatorium. The conducted research was carried out by calculating mass balances of different mineral nitrogen forms and phosphate ions, major ions (HCO₃⁻, SO₄²⁻, Cl⁻, Ca²⁺, Mg²⁺, Na⁺, K⁺) and the most common trace elements (Fe, Mn, Cu, Zn). The budget input of the balance was formed by the runoff of the Dnieper, Pripyat, Teteriv, Irpin, Uzh rivers. The atmospheric precipitation mass fraction did not exceed 0.6% and was excluded from the calculations. The output part of the balance was assessed by the discharges from the Kiev HPP. The Kiev reservoir provides a daily regulation. Its coefficient of water exchange is about 6–15 ·year⁻¹. The chemical element balances were calculated for the year 2006, which is characterized as a mean water flow year in the Pripyat river and the upper Dnieper.
The results shown in the Figure demonstrate the prevalence of the input part of the balance over the output part for most of the studied compounds.

The largest number of accumulated chemical components in the reservoir is major salts. The regulation of the water runoff caused the narrowing of the water mineralization fluctuations and a significant increase of its maximum value. So, over than 2 million tons of major components of a salt composition are deposited there every year. The predominant part of the salt sedimentation is caused by hydrocarbonate ions (64% of the total amount of precipitated salts or about 1956 thousand tons per year). Concerning the cations, it was defined that the Ca\textsuperscript{2+} is accumulated most actively (255.6 thousand tons per year). It is primarily caused by a bicarbonate-calcium type of the water in the Kiev reservoir and in its tributaries. As can be seen from the results, the decrease in the river flow essentially impacts on the stability of the calcium-carbonate equilibrium. The water transit is predominantly carried out within the riverbed after filling the reservoir, but about 40% of the Kiev reservoir consists of shallows. Shallow water is significantly warmed in summer. This effect has intensified particularly since the beginning of the 1990ies. The amplitude of fluctuations of the water temperature has increased since this period (its absolute values are over 30°C). The calculations showed that the water temperature increase from 5°C to 30°C reduces the CaCO\textsubscript{3} solubility by 2.5 times. The water warming causes the algae growth resulting in an increase of the pH value. Modelling the dependence of the water saturation index by calcium carbonate (SI\textsubscript{CaCO\textsubscript{3}}) vs pH, has shown its linear increase within 6 < pH < 8.5. With a further pH increase, SI\textsubscript{CaCO\textsubscript{3}} slightly decreases due to the forming of the calcium hydrocomplexes starting from pH= 7.25.

The predominance of a nutrient input over the output has been found. Approximately 27.2 thousand tons of mineral nutrients (59% are N-NH\textsubscript{4}\textsuperscript{+}; 39% are N-NO\textsubscript{3}\textsuperscript{-}) and 5.3 thousand tons of mineral phosphorus are fixed. The nitrogen predominance over the phosphorus one is
connected with a significantly higher Clarke number of the nitrogen in the soil (N-0.1–5%; P – 8–10·10^2 %), with a substantial waterlogging of the Pripyat and the upper Dnieper basins and with different directions of their geochemical behaviour. Contrary to major ions, the nutrient accumulation is mainly connected with their assimilation by hydrobionts and with the ratio of formed production-destruction processes.

The direction of the trace element runoff transformation within the Kiev reservoir tends towards accumulation. More than 10.2 tons trace elements (49% of their input part) are accumulated within the reservoir in the mean water flow year. The dominant part (84%) of the trace element budget input belongs to iron. It is contributed by wide wetlands, especially peat bogs that are located in the Pripyat basin. The high concentration of organic compounds (humic and fulvic acids) in the marshes increases iron migration. The conducted research (Osadchyy et al. (2013) showed that about 88-98% of Fe in the freshwater rivers migrate in the form of hydroxofulvate complexes. After entering the reservoir, most high-molecular compounds of iron come to a suspended matter and eventually to sediments. Generally, the flux of the sedimented iron amounts to more than 9000 tons per year. Other trace elements are accumulated together with iron: Cu - 400 tons per year and Zn - 781 tons per year. This phenomenon contributes to the self-purification of water masses. Regarding the manganese, there was a negative annual balance but a significant increase of a manganese concentration in winter was found which is connected with the occurrence of anaerobic conditions during the freezing of the reservoir. The oxygen absence is a cause of a manganese oxide reduction in the sediment, and due to a concentration gradient increase, the reverse Mn flow to the water occurs.

The reservoir water quality depends on the water quality of its main tributaries, the volume of water runoff and internal water body processes. In wet years (1993, 1998), 2.5 times more NH₄⁺, 1.5–6 times more different trace elements were fixed compared to mean water flow years. This is due to a significant waterlogging of the main tributaries and a large number of organic compounds of humus origin that contain nitrogen. Humus acids form strong complexes with trace metals thereby emphasizing an increase of their migration ability.

CONCLUSIONS

The construction of the Kiev reservoir has several environmental effects. The deceleration of the water runoff is the reason of a stagnant zone development and the accumulation of a large number of suspended forms of mineral and organic origin. The results have shown that the Kiev reservoir belongs to a water body with active accumulation processes. About 2-3 million tons of major ions, 30-40 thousand nutrients and 15 thousand trace elements are accumulated per year within the Kiev reservoir. The conclusion regarding a barrier function of the Kiev reservoir is done. The mass transfer of chemical elements in the direction from the water to the sediments with a minimum possibility of re-entering the water environment is observed.

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EU DEMEAU project: Practical application of in-vitro bioassays in water quality assessment

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CONTEXT & OBJECTIVES

One of the objectives of the “DEMEAU” project funded by the European Union, was to promote effect-based methods (in-vitro bioassays) in water quality monitoring. Through various case studies, the usability of bioassays to measure combined effects of emerging and unknown water pollutants and synergistic application with other water treatment technologies were demonstrated.

As for results, the presentation will i) introduce a selection criteria system that helps to compile a relevant bioassay panel for the effect-based screening of drinking, surface and waste waters, ii) briefly provides the basis of drinking and environmental water trigger values elaboration, and iii) summarizes the main results and conclusions of the demonstration case studies. The following methodological and demonstration case studies outputs explain how (in vitro) bioassays can provide cost-effective means for safety evaluations of water samples.

1. SELECTION CRITERIA TO ASSESS THE SUITABILITY OF BIOASSAYS

A recent comprehensive inter-laboratory study described the application of a broad panel of in vitro bioassays to wastewater, recycled water, stormwater, surface and drinking water (Escher et al., 2014). Each type of water showed a characteristic bioanalytical profile with particular groups of toxicity pathways. The most toxicity endpoints were (i) xenobiotic metabolism, (ii) hormone mediated modes of action, (iii) reactive modes of action, (iv) adaptive stress response pathways and (v) developmental and reproductive effects. Since there are numerous bioassays that can be applied to these toxic pathways, various criteria to assess the suitability of the respective bioassays are described in a recent report prepared by the DEMEAU partners. The criteria can be broken down into sub-criteria such as applied/validated to field samples, costs and service available. From an end-users perspective, a number of practical sub-criteria were added, such as possibilities for automation, availability of the bioassay in kit format and cost estimates. In total more than a hundred bioassays with a focus on human health aspects were evaluated with the abovementioned criteria. Table 1 presents the overview of the most promising in vitro bioassays for water quality determination based on the selected (sub) criteria.
Hebert et al.

Table 1: Overview of promising in vitro bioassays for water quality determination

<table>
<thead>
<tr>
<th>Toxicity endpoints relevant for drinking water monitoring</th>
<th>Specific pathway</th>
<th>Most promising bioassay(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xenobiotic metabolism</td>
<td>PXR receptor agonists, AhR receptor agonists</td>
<td>HGS LN, PXR assay, PXR HepG2 assay, DR CALUX, AhR geneblazer</td>
</tr>
<tr>
<td>Hormone-mediated mode of action</td>
<td>(anti)estrogenic activity, (anti)androgenic activity, (anti)glucocorticoid activity</td>
<td>ERα CALUX, YES assay, AR CALUX, AR-MDA-kb2, GR CALUX, GR-MDA-kb2</td>
</tr>
<tr>
<td>Reactive mode of action</td>
<td>Gene mutations, Chromosomal mutations, DNA damage response</td>
<td>Ames fluctuation assay, ToxTracker, Micronucleus assay, ToxTracker, UMUC assay, Vitotox, p53 CALUX, BlueScreen</td>
</tr>
<tr>
<td>Adaptive stress response</td>
<td>Oxidative stress pathway</td>
<td>Nrf2 CALUX, AReC32 assay</td>
</tr>
<tr>
<td>Developmental toxicity</td>
<td>Focus point endocrine disruption</td>
<td>Various nuclear receptor activation assays, H295R assay</td>
</tr>
</tbody>
</table>

2. ESTABLISHMENT OF BIOASSAY TRIGGER VALUES

The need for bioassay trigger values is internationally acknowledged. An attempt to derive trigger values for the ERα, GR, AR and PR CALUX has been carried out in the framework of the DEMEAU and published by Brand et al. (2013). The generation of in vitro bioassay derived data required the establishment of limits of maximum tolerable (drinking) water concentrations by which responses from water samples can be judged. These trigger values were developed taking a suitable point of entree, realistic worst-case pharmacokinetic factors, standard body weight and average daily water intake and were defined by a level above which human health risk cannot be waived a priori and additional examination of specific endocrine activity may be warranted. As limit values for drinking water are aimed to the protection of human health, such limits should be sufficiently conservative to serve as a warning signal. On the other hand, such limits should not be too conservative, to avoid unnecessary and costly additional mitigation measures. In table 2, drinking and environmental water trigger values derived for a selection of CALUX bioassays are given.

Table 2: Derived drinking and environmental water trigger values for a selection of CALUX bioassays

<table>
<thead>
<tr>
<th>CALUX bioassay</th>
<th>Trigger value drinking water*</th>
<th>Trigger value environmental water**</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>ERα</td>
<td>3.8</td>
<td>1</td>
<td>ng 17β-estradiol eq./l water</td>
</tr>
<tr>
<td>AR</td>
<td>11</td>
<td></td>
<td>ng DHT eq./l water</td>
</tr>
<tr>
<td>Anti-AR</td>
<td>21</td>
<td>40</td>
<td>µg Flutamide eq./l water</td>
</tr>
<tr>
<td>GR</td>
<td>21</td>
<td>30</td>
<td>ng Dexamethasone eq./l water</td>
</tr>
<tr>
<td>PR</td>
<td>333</td>
<td></td>
<td>ng Org2058 eq./l water</td>
</tr>
<tr>
<td>DR</td>
<td>50</td>
<td>50</td>
<td>pg 2,3,7,8-TCDD eq./l water</td>
</tr>
</tbody>
</table>

3. DEMONSTRATION CASE STUDIES

Bioscreening of Managed Aquifer Recharge (MAR) samples

Various types of MAR sources (groundwater, surface water and WWTP effluent) from two sampling campaigns - conducted in 2014 and 2015 - were subjected to sample preparation (i.e. extraction) and screening with selected bioassays to characterize their toxicity profile and investigate the impact of micropollutants present in these water samples. The study revealed the importance of endocrine - (particularly the activation of the ERα-, anti-AR, anti-PR receptors), oxidative stress (nrf2-CALUX) and photosynthesis inhibition (combined algae test) pathways, and showed differences between the samples collected within two different time points (two sampling campaigns).

MAR Case study of CASTELLÓN – Spain

Figure 1. Summary activity profile of the tested MAR water samples from the CASTELLÓN sampling site collected at two time points: 06/2014 (Campaign I) and 04/2015 (Campaign II) in the in vitro bioassay panel (on the left)

Results of Figure 1:

Following classification, the activity profile of the MAR samples is modified employing the environmental trigger values as given in table 2. The screening pointed out relevant toxic endpoints and also distinguished between clean and polluted sites. The application of trigger values (thresholds) demonstrates the possibility for estimation of potential environmental risks with in vitro bioassay responses.

Application of in vitro bioassays for Ecotoxicological evaluation of wastewater treatment

In this study, the efficiency of ozonation and various post treatments to reduce ecotoxicological effects still occurring in the conventionally (biologically) treated wastewater was assessed. For an assessment of ecotoxicological effects various bioassays (e.g. Ames fluctuation assay, various CALUX assays, Yeast estrogen screen, bacteria luminescence and photosynthesis inhibition assays) were applied in the laboratory. The investigations revealed that the wastewater treatment with ozone resulted in significantly improved effects in the majority of bioassays as compared to effects measured in the conventionally (biologically) treated waste water. In a few assays (e.g. the Ames fluctuation assay), partially higher effects after ozonation occurred, which could be removed by suitable post-treatments...
with biological activity.

**Table 3**: Changes in effects over various wastewater treatment steps for in vitro bioassays with sample enrichment

### Neugut WWTP - Case study (1st WWTP with full-scale ozonation in Switzerland)

<table>
<thead>
<tr>
<th>Bioassay</th>
<th>Substance group (effect parameter)</th>
<th>biological treatment</th>
<th>ozonation</th>
<th>ozonation + sand filtration</th>
<th>ozonation + GAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>YES</td>
<td>Estrogens (estradiol eq.; ng/l)</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>ERα CALUX</td>
<td>Estrogens (estradiol eq.; ng/l)</td>
<td>↓</td>
<td>↓ (&lt;LOD)</td>
<td>↓ (&lt;LOD)</td>
<td>↓ (&lt;LOD)</td>
</tr>
<tr>
<td>anti-AR CALUX</td>
<td>Anti-androgens (flutamide eq.; ng/l)</td>
<td>↓</td>
<td>Var.</td>
<td>~</td>
<td>~</td>
</tr>
<tr>
<td>PR CALUX</td>
<td>Progestinones (Org-2055 eq.; ng/l)</td>
<td>↓</td>
<td>↓ (&lt;LOD)</td>
<td>↓ (&lt;LOD)</td>
<td>↓ (&lt;LOD)</td>
</tr>
<tr>
<td>anti-PR CALUX</td>
<td>Anti-progestinones (Ru486 eq.; ng/l)</td>
<td>~</td>
<td>Var.</td>
<td>~</td>
<td>~</td>
</tr>
<tr>
<td>PPARy CALUX</td>
<td>Peroxisome proliferator like acting substances (Rosiglitazone eq.; ng/l)</td>
<td>↓</td>
<td>↓ &lt;LOD</td>
<td>↓ &lt;LOD</td>
<td>↓ &lt;LOD</td>
</tr>
<tr>
<td>Ni2 CALUX</td>
<td>Substances inducing adaptive stress (Curcumin eq.; μg/l)</td>
<td>↓</td>
<td>↓ &lt;LOD</td>
<td>↓ &lt;LOD</td>
<td>↓ &lt;LOD</td>
</tr>
<tr>
<td>PXR CALUX</td>
<td>Substances inducing xenobiotic metabolism (Nortriptyline eq.; μg/l)</td>
<td>↓</td>
<td>~</td>
<td>~</td>
<td>~ &lt;LOD</td>
</tr>
<tr>
<td>Amoeba fluctuation assay</td>
<td>Mutagenic substances (increase in number of mutated bacteria colonies (20-fold conc. sample)</td>
<td>↓</td>
<td>Var.</td>
<td>Var.</td>
<td>↓</td>
</tr>
<tr>
<td>Bacteria luminescence inhibition</td>
<td>General toxicity (baseline toxic equivalent conc.; mg/l)</td>
<td>↓</td>
<td>Var.</td>
<td>Var.</td>
<td>↓</td>
</tr>
<tr>
<td>Green algae</td>
<td>Herbicides (Duron eq.; μg/l; photosynthesis inhibition)</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
</tr>
</tbody>
</table>

Note: An arrow pointing down (↓) means decreasing effects in all measurement campaigns, var. marks varying results between different measurement campaigns, and a tick (−) denotes no changes in the results. Crossed out fields mean that no influent samples have been measured and therefore no effect of the biological treatment could be assessed. LOD = Limit of Detection

**Results of Table 3:**

The in vitro bioassays revealed significantly reduced hormonal and ecotoxicological effects after ozonation followed by suitable biological post-treatments. Table 3 gives an overview on the changes of hormonal and ecotoxicological effects in the in vitro bioassays over the assessed treatment steps. In most cases, a decrease in effects could be measured with ozonation followed by sand filtration or granulated activated carbon filtration. In four of twelve effect parameters partly no change or variable results occurred. Progesterone-like acting substances as well as peroxisome proliferator-like acting substances were below the LOD after ozonation and the post treatments.

**CONCLUSION AND OUTLOOK**

The activities of our Bioassay Work Area shed light on the importance of the use of effect-based bioanalytical tools and their broad implementation potential in water quality assessment. The compilation of the selection criteria system enhanced the composition of an in vitro bioassay panel for the earlier reported water quality relevant toxic endpoints. Following the establishment of trigger values, the development of a testing framework using a DEMEAU panel of bioassays has been carried out.

The demonstration studies presented that not only compounds, but complex
environmental water samples can be successfully screened by in vitro bioassays for their toxicity profile and with the aid of trigger values predictable low or high risks can be identified and further actions warranted. Furthermore, using effect-based methods as screening-technique could therefore complement conventional chemical analysis in water quality monitoring by identifying toxic “hotspots” for further investigation, assessing the effect of the entire mixture of compounds present in waters and reduce uncertainty in safety evaluation.

After the completion of the project, attention will be further devoted to the establishment of additional trigger values, the validation of in vitro bioassays (OECD / ISO; ongoing evaluation-assessment), high throughput screening capacity as well as harmonized data analysis. These issues will be addressed in order to aim at a better acceptance of in vitro bioassays in regulatory context and for their straightforward practical applications by water utilities and other end-users:

- **Trigger values** Threshold values for the water quality assessment relevant toxic pathways are a perquisite, not only for drinking water and human consumption (trigger values exist for this, Brand et al. 2013), but for ecosystem health as well. Project partners are currently participating in expert groups and work actively on the establishment of trigger values for many different water quality monitoring relevant toxic pathways (e.g. Kunz et al. 2014; Van der Oost et al. in preparation).

- **Validation** Formal validation is performed by institutes concerning the Validation of Alternatives Methods (VAM). Harmonization of a test method (such as achieving ISO-standards and OECD guidelines) is another dominant prerequisite for regulatory acceptance and facilitates a widespread use.

- **High-throughput screening capacity and quick analysis time** In order to apply effect-based analysis approach as monitoring tool and early warning system for water contamination, rapid turnaround time and cost-effectiveness of the analysis is a required. Using robotics, automated sample workup, miniaturized assay formats, liquid handling devices, sensitive detectors, high-speed plate readers, data processing and control software facilitates, the generation of large number of individual assay data points allows for more efficient screening, while also reducing the costs associated with chemical analysis. A research consortium led by Vitens (Dutch Drinking Water Company) and including several partners of WA4 (BDS, KWR) is currently working on the development of an automated sample preparation platform suitable for assessment of estrogenic activity in drinking water.

- **Harmonized data analysis** Without harmonized data analysis the interpretation and inter-lab comparison of the bioassay results are challenging. Project partners favour, promote and work on simplified and straightforward data analysis strategies (e.g. equivalent concentration derivation at 10% effect level of the positive control compound, PC10 method, Kunz et al., in progress).

- **Smart Integrated Monitoring** For routine water quality assessment, a shift from target chemical analysis of substances towards effect-based bioanalyses of the combined effects of all substances present is suggested (van der Oost et al. 2015)). An effect-based Smart Integrated Monitoring (SIMONI) strategy is proposed to determine the potential ecological risks of micropollutants in surface waters. The first phase of the SIMONI strategy focusses on the hazard identification phase, including DEMEAU panel of bioassays to evaluate eight freshwater samples from eight sites in the Netherlands with different levels of pollution.

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Monitoring status and trends of water quality in inland waters using earth observation technologies

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**SUMMARY**

Characterizing the status of rivers and lakes, identifying trends and understanding emerging problems in the large number of inland water bodies across Europe, using only traditional in-situ methodologies, is extremely challenging. However, Earth Observation (EO) tools can contribute significantly on a trans-national as well as a global scale to new indicators for the Sustainable Development Goals (SDG), where a requirement for the use of these EO methodologies is that they provide independent, standardised and consistent information over a wide range of different water bodies and spatial scales.

Here, current approaches and concepts are described, and processor-independent, inter-comparable, harmonized water quality measures, derived from earth orbiting sensors, are proposed. The capability and validity of a standardized approach is analysed for a wide range of water bodies and scales, using multiple sensors. The capability to monitor changing water quality conditions in different lake types and rivers over a time span of more than ten years is analysed, and the validity as well as the limitations of the approach are discussed. The benefit of satellite-based monitoring services for agencies and water industries is addressed within the scope of actual case studies, and solutions for easy information access and integration through online services is presented (Figure 1).

Figure 1. Web application with online access to global water quality information (eoApp 2015)
STATE OF THE ART AND CAPABILITIES

Multispectral satellite sensors are capable of measuring water column constituents using sunlight in the visible region of the spectrum, which penetrates the atmosphere and waterbody. This light is absorbed and scattered as a function of the particles and dissolved materials in the water body. The reflected light spectrum detected by the satellite sensors can be used to analyse both the in-water and atmospheric properties (Dekker et al. 2001).

A number of suitable multispectral satellite sensors are available, such as: MODIS and the upcoming Sentinel-3 for daily coverage of large water bodies in 300 - 500m spatial resolution; Landsat 5, 7, 8 and Sentinel-2 in 20 - 30m resolution for much smaller lakes and rivers; or commercial high-resolution sensors such as Worldview 2 and 3 (Berger et al. 2012, Dekker & Hestir 2012, Palmer et al. 2015). By combining several sensors it is for example possible to achieve weekly monitoring, globally, of lakes less than 100m in size, or for example to perform historical reviews of water quality parameters going back 30 years.

There are two main groups of algorithms for analysing aquatic satellite data: empirical and semi-analytical approaches typically rely on using band ratios or principal component analysis of band intensities or surface reflectance in order to derive water-quality information (e.g. Brezonik et al. 2005). Although easy to apply, these approaches are limited to localized scales, usually requiring a priori knowledge, and are not necessarily inter-comparable. In contrast, physics-based spectral inversion algorithms have been shown to be capable of delivering quantitative, standardized water-quality information across all relevant spatial and temporal scales (Malthus et al. 2012). Using adaptive, specific optical properties of water constituents significantly increases the validity for retrieving sensitive water-quality parameters such as algae concentrations or suspended matter. Only physics-based approaches provide the potential capability of being valid on continental scales as well as being sensor-independent.

CONCEPT FOR CONSISTENT WATER QUALITY INFORMATION

To assure consistency for standardized products and avoid dependency on a single algorithm, products shall be attributed to independent physical in-water properties. This is relatively straightforward for water quality parameters that are directly related to in-water absorption and scattering spectra. Turbidity, if related to total backward-scattering of particles in the water body, is a globally consistent product, as is Chlorophyll if it is related to the pigment related absorption at a defined reference wavelength. Coloured Dissolved Organic Material (CDOM) is by definition an absorption unit. Specific Optical Properties of water constituents can further relate the consistent and independent products to specific water quality parameters such as suspended matter (related to turbidity), regional chlorophyll products or dissolved organic carbon, which is estimated in relation to CDOM.

The capability of algorithms and processors to deliver such harmonized products for historic, actual and future satellite sensors is a relevant requirement to ensure long-term monitoring and full-scale continuity.

METHODOLOGY

The methodology applied in this study is based on an established multi-sensor processing system, the Modular Inversion and Processing System (MIP) (Heege et al. 2003, Heege et al. 2014). It incorporates the state-of-the-art fully physics-based retrieval algorithms, based on a radiative transfer solver (Kiselev et al. 1995; Bulgarelli et al. 1999) encompassing the full bi-directional properties of the atmosphere, the air–water interface, and the water body itself. Processing modules include land-water-cloud-detection, adjacency and sun glint correction, iterative retrieval of atmospheric properties and the estimation of the scattering and absorption properties of water column constituents (Heege et al. 2014; Kiselev et al. 1999).
Monitoring status and trends of water quality in inland waters using earth observation technologies

The processor provides various internal quality measures used for automated flagging and the adaptation to specific optical properties. The new 2015 processor version has replaced all remaining semi-analytical functions by pure physics-based radiative transfer model calculations to ensure that the full range of properties in natural waters is accounted for correctly, including optical conditions of e.g. extremely turbid water bodies. Different water types covering a range of varying specific inherent optical properties can be defined for use within the retrieval process. In this study, we tested the capability of using a standard set of spectra to cover the variety of oligo- to hypertrophic lakes.

As output, MIP provides a number of water quality related parameters such as water turbidity (linearly linked to suspended matter concentration), organic and inorganic absorbers, chlorophyll concentration, CDOM, Secchi depth, light penetration depth and harmful algae bloom (HAB) indicators for blue-algae. Aside from the HAB indicator, all properties are standardised physical properties as defined above.

The data processing is orchestrated within the EOMAP Workflow System (EWS) to ensure automated, continuous, cost-effective and daily production. The production system EWS-MIP is currently installed in several satellite receiving stations and ground segments worldwide to ensure rapid and efficient access to satellite data, thereby supporting large scale continental consistency tests with MODIS Aqua/Terra and Landsat-8. Decades of data from Landsat 5, 7 and 8 (downloaded from USGS) and MERIS were processed for a number of regions in order to analyse the long-term consistency and validity of water quality outputs. Commercial high-resolution satellites such as Rapideye 1-5, Worldview 2-3, SPOT 5 - and the first Sentinel-2 data - were analysed through dedicated validation campaigns. Data products from the continuous continental production, both demo data as well as commercial services, are now routinely disseminated as a WMS service as well as being provided online for easy access within GIS online solutions or alternatively through web applications (e.g. eoApp 2015, http://eoapp.eomap.com).

RESULTS AND DISCUSSION

The validity of the this approach was analysed for a number of different water bodies in Italy, Estonia, Finland, Germany, Italy, the United States and Vietnam (Heege et al. 2014). Figure 2 shows examples for a number of different sources and countries. In addition, further validation exercises over inland waters for the MIP system were undertaken within

![Figure 2](image-url)
international projects (e.g. EU FRESHMON and GLASS) and commercial contracts (Hausknecht 2010). From Broszeit 2015 and the transnational validation report (Heege et al. 2015) we conclude that the uncertainty of the EO based method is typically 10 - 50%, and equivalent to the methodological differences to and between in-situ approaches. For waters with high CDOM dominated lakes it raised further (factor 2-3 overestimation e.g. Lake Lohjanjärvi in Fig 2). Here the methodology to derive chlorophyll independently from other absorbers seems to be restricted at least when using standard satellite sensors such as Landsat. For turbidity, related suspended matter and CDOM the accuracies are better, without the restriction at CDOM dominated waters. Important to note that the specific spectral properties need to be accounted for within the retrieval procedures. The validity of EO-derived organic and inorganic absorption products as well as chlorophyll in turbid rivers is not yet fully investigated. The status of these validations is regularly updated and accessible online (Heege et al. 2015).

Considering the wide range of concentrations in surface waters - typically over 3 magnitudes - and the challenges involved in retrieving consistent in-situ measures on international scales, the presented EO based approach can be considered as independent, consistent and mature contribution for many UNEP related tasks. Already, multi-satellite water quality monitoring services are used increasingly. Examples include environment impact assessments for the National Italian Institute for Environmental Protection ISPRA, lake monitoring by the Environmental State Agency Baden-Württemberg LuBW, dredging impact monitoring (Hausknecht 2010), sediment monitoring in river Elbe for the Federal Waterways Engineering and Research Inst. BAW (BAW 2013), or lake restoration control (EPA 2014).

Acknowledgements

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The Development of a Decision Support System to Reduce the Risk of Environmental Pollution of the Bosna River

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1. INTRODUCTION

Within the scope of the NATO Science for Peace Programme, a Decision Support System (DSS) has been developed allowing the identification of major risks related to environmental pollution in the Bosna River Basin, including a proposal of the technical solutions for the reduction and removal of the pollution. The Project was developed and performed by the Water Research Institute Bratislava from Slovakia, and the Hydro-Engineering Institute Sarajevo (HEIS) from B&H. The outcomes of the project are both scientific and practical. Both of them constitute a major contribution to the Partner country (B&H). The scientific importance of the project is based on use of the Decision Support System (DSS), addressing the environmental pollution within the EU Water Framework Directive (WFD) Priority Substances and developed by the European Union 6th Framework Programme (FP6) project SOCOPSE.

Novel aspects of the project consisted in using passive sampling for Bosna River screening and applying a unique approach to prioritising the Bosna River Basin’s specific substances. Additionally, knowledge transfer has been one of the major outputs of the project.

2. SCOPE AND OBJECTIVES

The main objective of the project was to develop a Decision Support System (DSS), allowing the identification of major risks related to the environmental pollution in the basin and propose technical solutions for the reduction/removal of the pollution. In the line of the project proposal, the following specific objectives have been achieved:

- Establishment of a “pollution baseline” in the Bosna River Basin based on newly obtained chemical, biological, hydro-morphological and microbiological data;
- Identification of major polluters via systematic screening of urban and industrial waste water streams;
- Prioritisation (risk assessment) of the most relevant “Bosna River Basin specific substances” and establishment of the Emission Limit Values for major polluters;
- Proposal of technical installations to be used for reduction of pollution together with economic analysis;
- Development of investment scenarios for the decision makers (Makovinska et al. 2014)

3. SCIENTIFIC RESULTS

3.1 General information about the Bosna River basin
The Bosna River flows over a distance of 271 km through the central part of Bosnia, with highly developed hydrographical features, several significant tributaries, and a number of small tributaries, insignificantly impacted by the karst terrain, distinguishing it from the other sub river basins in B&H. It is the third-longest river in B&H, divided into seven water bodies and flowing into the Sava River. Generally, the flow regime of the Bosna River is stochastic, except for significant deterministic effects on several tributaries that disrupt the natural flow regime. This primarily refers to the Sarajevo Field area, since water is being abstracted from the water spring of Bosna River "Vrelo Bosne" for the purposes of water supply of the City of Sarajevo.

Based on information and knowledge on local conditions, the following main polluters in the Bosna River basin were identified:

- **Municipalities**: Sarajevo, Zenica and Doboj;
- **Industries**: Prevent Leather (Visoko), Thermal Power Plant Kakanj, ArcelorMittal Zenica, Natron Hayat (Maglaj), Oil Refinery Modriča;
- **Landfills**: Sarajevo and Zenica;

All above-mentioned polluters had permissions for the discharge of wastewater. Industrial polluters and landfills, which were the subject of monitoring, were equipped with wastewater treatment plants, while urban sewage was discharged without treatment (Makovinska et al. 2014).

### 3.2 Establishment of a pollution baseline in the Bosna River Basin

The pollution baseline established within this project could be defined as the current state of pollution in the river, based on the measurement of indicators of present pollution and direct emission loads, with special attention to identification and detection of priority substances required by WFD. Establishment of a pollution baseline, in the Bosna River Basin was based on newly obtained chemical, biological and hydro-morphological data during Bosna River Survey. The results of target and non-target screening were prioritized with the aim to establish “a pollution baseline” in the Bosna River, to prioritize the most relevant Bosna River Basin Specific Substances, and to establish emission limits of the most problematic compounds for major polluters.

From August to November 2012, the Bosna River survey was realised on seven river water bodies. Complex data set about water and sediment quality was obtained. Evaluation (indication) of Bosna River water bodies’ status was done according the WFD requirements based on data measured from samples collected during the Bosna River survey.

Based on the results of the Bosna River Survey, it is possible to classify the ecological status of the Bosna River spring as good, the second water body under direct influence of the Sarajevo agglomeration, was in bad ecological status, while the other water bodies were in moderate ecological status. The indicative assessment of the Bosna River chemical status did not directly express exceedance from the established EQS. On the other hand, evaluation of the chemical status was based on the regular monitoring results. Therefore, results of other matrices measurements and passive sampling were also used for data set extension. This approach allowed indicating existing and potential problems in the Bosna River basin.

The classification of the Bosna River sediment monitoring’s results shows that heavy metals and PAHs are the most problematic compounds in the Bosna River sediments. The major contributors of pollution virtually by all analysed heavy metals are the agglomerations of
Zenica with its industrial surroundings and the agglomeration of Sarajevo - especially in Hg and Cr. Furthermore, analysed organic pollutants - PAHs (phenanthrene, anthracene, pyrene and florantene) pose a risk to the ecosystem virtually along the whole Bosna River. The highest concentrations of PAHs were measured at the last monitored profile (Bosna River - above Modriča) before confluence of the Sava River (Makovinska et al. 2014).

### 3.3 Role of passive sampling in chemical monitoring of priority substances

The recently updated European Union’s Directive on Environmental Quality Standards (EU, 2013) recommends further development of passive sampling techniques as a promising tool for future application in compliance checking and trend monitoring of priority substances. Passive sampling is usually considered as an extraction/equilibration technique that allows determining dissolved concentrations of priority substances in water. Alternatively, the samplers can be considered as a reference environmental matrix with well-defined properties, which are little affected by different environmental conditions.

Passive samplers (PS) identify spatial concentration gradients and patterns of ultra-trace pollutants in Bosna River. With a few exceptions, there is generally no deterioration of the status of the free dissolved PAHs and PCB concentrations in the river since 2008. Concentrations of priority metals at some profiles are close (but do not exceed) to the new AA-EQSs according to the Directive 2013/39/EU. Concentrations of monitored polar pesticides were low and thus measured in ng/L range. For priority polar pesticides (isoproturon, diuron, atrazine, simazine and their metabolites) concentrations were lower than the corresponding EQS (according to Directives 2008/105/EC as well as 2013/39/EU).

### 4. DECISION SUPPORT SYSTEM FOR REDUCING RISK FROM ENVIRONMENTAL POLLUTION IN THE BOSNA RIVER

The Bosna River is the first river in Europe where the general principles of the “Source Control of Priority Substances” (SOCOPSE) approach was applied. Based on the results of the analysis with the applicable selection method, the best solutions (measure option or sets of measures options) were selected upon the advice from the main stakeholder groups. Achieved results helped to prepare scenarios for decreasing of hazardous substances risk in the Bosna River basin and to select the best solution in cooperation with main stakeholders. Biological treatment of urban wastewaters from agglomerations Sarajevo, Zenica and Doboj will significantly reduce surface waters organic, nutrient but also specific pollution in the Bosna River basin. Screening results have showed that the full capacity of some sophisticated industrial wastewater treatment plants can be achieved only by optimization of their operational processes and implementation of the Best Available Technologies (BATs) (Makovinska et al. 2014).

### 5. CONCLUSION

Implementation of the project results will contribute to environmental quality of Bosna River Basin, improvement of quality of surface and groundwater as drinking water source and source of water for industrial and agricultural uses, and enhance public health in the region and its touristic and recreational value. Indirectly, it will also contribute to the quality of water and environment in broader geographical terms, such as Sava and Danube River basins.

The DSS developed within this project could be applied and replicated in other river basins in B&H and, eventually, in the entire Western Balkan area.

### 6. REFERENCES
OECD Proposed contribution to UNESCO Workshop
“Water Quality in Europe: Challenges and Best Practices”
Koblenz, Germany, 1 - 4 December 2015

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ABSTRACT
This abstract has been formed from a number of relevant extracts taken from recent and ongoing OECD work on *The Economics of Water Quality in OECD Countries and BRICS*. This work has not been declassified by OECD Delegates and is intended for discussion at the UNESCO workshop only.

THE CHALLENGE OF EUTROPHICATION IN THE EU AND THE COST OF INACTION
Europe faces significant challenges regarding the control of diffuse pollution, and in particular eutrophication, for a number of reasons:

- Diffuse pollution is challenging to monitor and regulate due to: its high variability, spatially and temporally; high transaction costs associated with large numbers of polluters (farmers, homeowners, car owners), which can also be difficult to identify; and because pollution control may require cooperation and agreement within catchments, and across sub-national jurisdictions and countries (OECD, 2012).
- There are ecosystem delays (the time difference between implementation of abatement measures and actual measurable effects) due to the long-time scales of eutrophication (Gustafsson et al., 2012). Ecosystem responses to measures that reduce eutrophication illustrate that feedbacks and climate change impacts can keep ecosystems in a certain state and cause delays of decadal scale in ecosystem response (Varjopuro et al., 2014).
- The effects of climate change will exacerbate existing water quality problems, due to altered precipitation and flow regimes, altered thermal regimes and, in the case of coastal regions, sea level rise (IPCC 2014). An OECD survey as part of a report on *Water and Climate Change Adaptation* (OECD, 2013) identified that the EU are particularly concerned about groundwater salinization associated with sea level rise, reduced groundwater recharge and increased demand for irrigation during the dry season.
- EU cities will face specific challenges as the impacts of water pollution, whether rural or urban in source, largely fall on cities, as does the value of assets at risk. Future population growth, urbanisation, climate change, ageing infrastructure and more stringent standards (such as those imposed under the WFD and Nitrates Directive), will place extra demands on existing systems and mean that significant investment in drinking water and wastewater treatment infrastructure, upgrades and retrofits are required in order to prevent water-related disease outbreaks and not place additional nutrient, pathogenic and organic loads in river systems.

The cost of water pollution in EU countries is substantial and attempts at estimating national costs are summarised in Table 1. Note that a variety of methodological approaches have been used in the various studies, including in relation to whether they are reporting marginal, average or total costs. As such, results are difficult to interpret out-of-context, and cross-
country or cross-study comparisons can be misleading. Furthermore, the true costs of pollution are also likely to be greater than the estimates suggest given the difficulty of calculating non-market values. Nevertheless, Table 1 serves to illustrate the existence of externalities and a need to adjust water management practices in order to reduce negative impacts on water quality.

Table 1. Estimated annual costs of water pollution in Europe

<table>
<thead>
<tr>
<th>Country</th>
<th>Type of water quality impact</th>
<th>Annual cost (millions)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belgium</td>
<td>Drinking water treatment costs</td>
<td>120 - 190</td>
<td>Dogot et al. 2010</td>
</tr>
<tr>
<td>France</td>
<td>Eutrophication of surface and coastal waters</td>
<td>70 - 1000</td>
<td>Bommelaer 2010</td>
</tr>
<tr>
<td>Netherlands</td>
<td>Nitrate and phosphate pollution</td>
<td>403 - 754</td>
<td>Howarth et al. 2001</td>
</tr>
<tr>
<td>Spain</td>
<td>Nitrate and phosphate pollution</td>
<td>150</td>
<td>Hernandez-Sancho et al. 2010</td>
</tr>
<tr>
<td>Sweden</td>
<td>Coastal eutrophication and Baltic Sea eutrophication</td>
<td>860 - 492 - 1466</td>
<td>Huhtala et al. 2009</td>
</tr>
<tr>
<td>Switzerland</td>
<td>Agricultural pollution</td>
<td>CHF 1000</td>
<td>Pillet et al. 2000</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>Drinking water treatment costs, agricultural pollution of surface water, estuaries</td>
<td>GBP 229</td>
<td>Jacobs et al. 2008</td>
</tr>
<tr>
<td>Europe</td>
<td>Human health and ecosystem impacts from nitrogen pollution of rivers and seas</td>
<td>40-155</td>
<td>Van Grinsven et al. 2013</td>
</tr>
<tr>
<td></td>
<td>Health costs of nitrate in drinking water – colon cancer</td>
<td>1000</td>
<td>van Grinsven et al. 2010</td>
</tr>
</tbody>
</table>


POLICY RESPONSES TO MANAGE WATER QUALITY

Government intervention to reduce pollution typically takes any one, or a combination of, three control methods: Regulation, economic instruments, or voluntary means.

It is now considered in many OECD countries that improvement in point source pollution control has reached a point where further improvements are not necessarily cost-effective (Shortle et al., 2012). As such, there is a strong case for a shift in focus to diffuse pollution prevention and integration with point source management, and the utilisation of cost-effective prevention and abatement practices that could yield more beneficial results in terms of water quality improvements and control-cost savings (Shortle et al., 2012; Shortle and Horan, 2013). However, policies to control diffuse pollution have often had limited success.

The use of voluntary subsidies (payments) and regulatory instruments are the most prominent methods to address diffuse water pollution in OECD countries. However, voluntary subsidies have generally had limited success (Shortle and Horan, 2013), and regulatory measures to control diffuse water pollution are typically poorly enforced (Parris, 2012). Voluntary codes of good practice have not proved able to remedy a problem that does not stem from a lack of information, but from the absence of internalisation of pollution costs (OECD, 2004). There is also evidence that subsidy-based programmes (whether they make existing direct support payments conditional on environmental factors, or are additional, specific financial assistance) in OECD countries have not delivered large cuts in pollution loads because they have failed to target the most polluting farms (ibid).
Whilst regulatory policy instruments to reduce diffuse pollution from agriculture typically restrict the use of polluting inputs (e.g. fertilisers, manure and pesticides) and farm management practices, economic instruments, such as markets, can provide an alternative, potentially allowing for innovation whilst achieving water quality objectives at the lowest cost to society. Another supporting argument for the use of economic instruments is that they raise revenue, which is particularly relevant given that fiscal consolidation and budgetary constraints at state and federal levels has reduced financial assistance (subsidies) to reduce pollution (Shortle et al. 2012).

An example of a water quality market is the Lake Taupo Nitrogen Market in New Zealand, the world’s first diffuse-diffuse water quality cap and trade scheme (OECD, 2015). Nitrogen run-off from farming and other land uses was threatening to undermine the pristine waters of Lake Taupo – New Zealand’s largest and most iconic lake – and to damage a range of economic and cultural activities. In response, the regional government introduced a water quality policy package in 2011 with three components: (1) a cap on nitrogen emission levels within the Lake Taupo catchment; (2) the establishment of the Taupo nitrogen market; and (3) the formation of the Lake Taupo Protection Trust to fund the initiative. A ‘grandparenting’ approach was taken to establish caps for individual farmers based on modelled nitrogen emissions using OVERSEER® (a nutrient budget model at the farm level). The Lake Taupo Protection Trust, a government-funded Trust, purchased and permanently retired land to eliminate some nitrogen. Through trading activity, the target of reducing nitrogen discharges by 170 tonnes – 20% of manageable nitrogen emissions – has been met, three years ahead of time and on budget. A number of conditions can be identified as necessary for a successful water quality market:

- Clearly established property rights and binding regulatory limits on pollution levels are essential for trading activity to occur;
- Trading activity requires sufficiently large differences in pollution control costs between polluters;
- Trading rules must be clearly established, assure that water quality goals will be satisfied and ‘leakage’ avoided, and also be designed to facilitate trading; and
- Successful trading requires the development of institutions for organising trade that are trusted by, and effective for, intended program participants. Stakeholder consultation and willingness to compromise by all parties is required for successful implementation.

REFERENCES


Electrochemical degradation of organic trace contaminants in reverse osmosis concentrates

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INTRODUCTION
Persistent organic contaminants represent a major challenge in wastewater as well as in drinking water treatment. Especially when discharges of wastewater treatment plants are used as an additional source for groundwater recharge and even direct reuse for fresh water supply, care has to be taken not only regarding biological contamination but also in respect of anthropogenic compounds. In the past years, reverse osmosis (RO) has been successfully applied to fulfil this task (Siegrist et al. 2012). The major drawback of this technique is the disposal of the residual concentrates (RO-brines), which contain elevated concentrations of salts as well as of organic contaminants that have been repelled by the membranes (Pérez-González et al. 2012). Up to date efficient treatment methods to deal with those brines are lacking. A solution to overcome this problem might be the degradation of the accumulated chemicals via advanced oxidation processes (AOP), i.e. in the presence of hydroxyl radicals, which represent a strong oxidizing agent. Among several different AOP techniques which have evolved during the past years, electrochemical oxidation using boron-doped diamond electrodes provides the possibility to efficiently produce this kind of reactive species (Panizza et al. 2009).

The overall goal of the presented study was the elucidation of the degradation behaviour of organic trace contaminants during electrochemical treatment of reverse osmosis concentrates using boron-doped diamond electrodes. A special focus was put on the evolution of transformation products. Electrochemical treatment parameters such as current density, pH, and ionic strength have been optimized in order to minimize the generation of potentially toxic oxidation products.

EXPERIMENTAL METHODS
Electrochemical degradation experiments have been performed in batch mode in an undivided cell containing a boron-doped diamond working electrode (25 cm²), a platinum counter electrode and an Ag/AgCl reference electrode. The galvanostatic electrolysis was carried out in real RO brines from a two-stage RO pilot plant or aqueous solutions containing NaCl, NaBr, Na₂SO₄, Na₂CO₃, or a phosphate buffer. Analysis of the reaction kinetics and identification of the obtained TPs was performed with high resolution mass spectrometry and fragmentation experiments using a LTQ-Orbitrap MS (Thermo Fisher Sci.).

RESULTS
Experiments in real RO brines (50.8 mg/L TOC) showed that application of boron-doped diamond electrodes for galvanostatic electrolysis of reverse osmosis concentrates is suitable to degrade organic substances including micropollutants even at low current densities (i.e. 4 – 20 A/m²). Degradation kinetics of the total organic carbon (TOC), i.e. treatment times, are primarily depending on the applied current, while the amount of removed TOC is mainly determined by the applied charge. Figure 1 (black bars, lower scale) illustrates the remaining
TOC after three hours at 10, 25 and 50 mA (30, 75 and 150 mAh). It can be noticed that doubling the applied current from 25 to 50 mA only provides TOC removal enhancement from 46 % to 61 %. The same effect is observed upon extension of the treatment time from three to six hours during electrolysis at 25 mA (Figure 1, red curve, upper scale), resulting in almost equal TOC degradation at the same charge input (150 mAh). The logarithmic plot reveals first order kinetics, indicating mass transfer limited electrochemical reactions. Secondary oxidants (e.g. active chlorine), which are formed during the treatment do not seem to have a significant contribution, since their rising concentration would lead to a steady acceleration of the apparent reaction rate. Nevertheless, they lead to the generation of by-products like chlorate, perchlorate, bromate and halogenated organics.

Degradation experiments with individual trace contaminants (diatrizoate, iopromide, metoprolol, triclosan, tramadol, carbamazepine) showed an even more pronounced mass transfer controlled behaviour. Rate constants for direct electrochemical reactions were almost independent from the applied current and were found to be \( k_{\text{direct}} \approx 2 \times 10^{-4} \text{ s}^{-1} \) at all currents for all substances tested. Nevertheless, reactions with various \textit{in-situ} formed secondary oxidants represented additional degradation pathways for all compounds except iopromide. While for the latter first order kinetics were observed during the whole treatment at all applied currents tested, \textit{in-situ} generation of secondary oxidants gave rise to a steady increase of the kinetic order (acceleration) for the other substances (Figure 2). Since higher applied currents enable a faster production of these reactive species, differences to the initial first order kinetics (no secondary oxidants at \( t = 0 \)) were largest at 50 mA. The degradation of triclosan and tramadol were even accelerated to such an extent, that a kinetic evaluation was not possible in these cases.

**Figure 1.** Left: Remaining TOC after 3 h at 10, 25, 50 mA (black) and temporal degradation behavior at 25 mA (red). Right: TOC degradation kinetics (logarithmic scale) at 25 mA.
Transformation products generated by both direct electrochemical processes as well as by reactions with secondary oxidants have been found. Nevertheless, those products could be further degraded within the same process in most cases.

**CONCLUSIONS**

Based on the presented results, electrochemical treatment can be regarded as a suitable tool to degrade and even mineralize organic contaminants in reverse osmosis concentrates prior to their final disposal. Nevertheless, process parameters need to be optimized for the given conditions in order to avoid formation of potentially toxic by-products. Further research is needed to investigate whether the obtained results are transferable to the large scale for a future technical application.

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Importance of a NEXUS Watershed Monitoring in improving land and water quality and human health; relevance with SDGs

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A STUDY OF FAO LAND AND WATER DIVISION

With increasing competition for water between industrial, domestic and agricultural and environmental purposes, and also climate change impact on availability of land and water resources, many challenges arise.

On the one hand industries and cities are expanding and contributing to higher loads of pollution entering air, water and land resources including agricultural fields—making agriculture a victim of pollution. Additionally, farmers are increasingly looking into non-conventional water resources, like wastewater—whether due its high nutrient content or lack of conventional water resources. When wastewater is used directly, without adequate treatment, this can adversely impact people’s health, by microbiological and chemical contamination of crops, and livestock products, and can also expose farm workers and their families to contaminants, which may lead to skin rashes, parasitic infections, cancers, deadly poisoning, diarrheal disease and in some cases even to death.

On the other hand, usage of chemical fertilizers and pesticides have increased in years both in industrial and also small farming, also contributing to loads of pollution entering the environment, making agriculture the source of pollution. This also adversely impact human and environmental health. For instance, in some countries, irrigation water is also used for human consumption, although it does not meet the potable water standard. This is directly related to the likelihood of the development of diarrheal and other disease. The WHO estimated that two million deaths occur every year from contaminated food or drinking water.

It is evident that there is a link between the pollution and adverse health impact, and that water, sanitation and hygiene play a vital role in human health. This has been always the center of many risk reduction strategies and health management planning. Therefore, existing monitoring for Water, Sanitation and Hygiene (WASH) such as Joint Monitoring Program of UNICEF-WHO (JMP) are well established. By comparison, wastewater and water quality and land management and water resource management (WRM) global and national monitoring capacity is weak, the sectors are more complex and existing data availability is sparse [source: UN Water document]. There is often lack of coherent NEXUS\(^1\) mechanism analyzing the interlinkage between source of pollution, loads and flow of pollution from source to water resources and land, and then to agricultural products and accordingly human body and environment. For reducing and eliminating pollution release in the environment, which is one of the major areas of interest of Sustainable Development Goal, and for developing better management practices and reducing the adverse health and environment impacts, it is important to have an entry point and a problem based approach

\(^1\) Nexus approach in this study refers to multi-disciplinary analyzing of different factors impacting land and water quality

“Water Quality in Europe: Challenges and Best Practice”
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by analyzing the state and identifying the chain of stressors together causing the pressure and state – a DPSIR methodology (EEA 2007).

In this respect and because of the global importance of water and land quality monitoring development, FAO is aiming to develop a NEXUS “water and land quality monitoring mechanism at the watershed level to improve food safety and human health”. The monitoring mechanism will be able to identify the hotspots within a watershed, where the loads of pollutants start and where they will flow and their dilution mechanism. This tool will also link the pollutants loads and flow with level of adverse health incidents occurred in the sub-watershed (at this stage only gastrointestinal diseases). The monitoring mechanism is based on modeling and state of the art, affordable live data measurement sampling tools. It will calibrate a SWAT model (SWAT 2015) for identifying the potential hotspots and will also calibrate live data measurement sensors for monitoring trace amounts of pollutants and pathogens (i.e. nitrate, phosphate, potassium and E.coli). This monitoring mechanism will help collecting quality primary data where necessary, and help policy makers develop sustainable and suitable scenarios for the watershed and later, at national level, to better improve the people’s livelihood and illuminate the loads of pollution.

At this moment this study is done at watershed level in different countries. However, this will set the ground for implementation of a long term national and then regional approach for development and implementation of a tailored risk reduction strategy to ultimately tackle land and water quality and health related issues. It is also aligned with the goal number 3, 6, and 15 and in particular proposed target 6.3 of the Post – 2015 Sustainable Development Goals: “by 2030, improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and increasing recycling and safe reuse by [x] per cent globally”, and its proposed indicators:

“Proposed Indicator 1: Percentage of waste water safely treated”, and

“Proposed Indicator 2: Percentage of receiving water bodies with ambient water quality not presenting risk to the environment or human health”.

And will help countries report based on the indicators measurement.

REFERENCE


Fitness of Antibiotic Resistant Bacteria (ARB) exposed to sub-lethal concentrations of tetracycline near combined sewer overflows in Arno river water (Florence, Italy).

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INTRODUCTION

The large-scale use of antibiotics in human and animal treatment is often cited as contributing to the rise in antibiotic-resistant microbes, particularly in regard to human pathogens (Rizzo et al. 2013). In an urban context, wastewater may contribute as a source of antibiotics released into the environment affecting antibiotic resistant bacteria (ARB) ecology (Allen et al. 2013; Knapp et al. 2010). In both municipal wastewater flows and in agricultural environments receiving water, antibiotics may occur at sub-therapeutic and sub-lethal concentrations (Subbiah et al. 2011). From an ecological perspective, it is not known if such low concentrations are able to exert selective pressure on the microbiome. To date, only a limited number of ecological studies have been undertaken in this field (Subbiah et al. 2011).

To address these knowledge gaps, our main research goal is to model the ecology of ARB in water contaminated by wastewater. The information obtained from this model can be substantial for future water quality assessment work: For example, understanding to what extent urban river waters can be reservoirs of ARB (including treated waters) or support the fitness of such resistant bacteria, is important in developing water quality regulations. We have identified an interesting scenario present at a particular sampling site at the downstream combined sewer overflows (CSOs) of the Arno river in Florence, Italy. In fact, CSOs release wastewater to the Arno when the water flow is intense, thus contaminating the river with wastewaters. We found this sampling site highly interesting and tested the exertion of selective pressure of tetracycline-resistant *Escherichia coli* by simulating the effect of urban river water contaminated with a sub-lethal concentration of tetracycline.
MATERIALS AND METHODS

In-vitro model (mesocosms)

Strains used in this study: Escherichia coli BLX1 tetr and Escherichia coli DH5α tets. River water was sampled in the Arno river (Florence, Italy), filtered twice with Whatman paper then with 0.22μm filters. Populations of resistant (Escherichia coli BLX1 tetr) and sensitive (Escherichia coli DH5α tets) were washed in PBS and equally co-inoculated (10^5 cells/mL by normalizing with a spectrophotometer) in the following mesocosms: i) Arno water with no antibiotics. ii) Arno water with sub-lethal concentration of tetracycline or chloramphenicol (2.5 ng/mL). iii) Arno water with lethal concentration of tetracycline or chloramphenicol (5 μg/mL). iv) Physiological solution without any antibiotic (8.5 gr/L NaCl) (control). Mesocosms where incubated at 22°C, in Eppendorf tubes and the tubes were daily opened under the BL2 cabinet for 10 minutes to allow gas exchange. At 0, 2, 5, 10 and 15 days colonies (CFU) from each mesocosm were picked and patched on selective media (LB + antibiotic) in order to discriminate the resistant and sensitive cells. The ratio of the sensitive and resistant cells was calculated according to the formula (Marvasi et al. 2013):

$$\log(\text{Competitive Index}) = \frac{R_{out}/WT_{out}}{R_{in}/WT_{in}}$$

Each mesocosm was replicated six times and 50 CFU were picked and patched on selective media.

RESULTS AND DISCUSSION

In a first approach we measured that in absence of selective pressure Escherichia coli BLX1 tetr maintains the resistance gene within the 15 days of the experiment. We then measured the fitness of resistant vs sensitive E. coli in Arno river water without selective pressure (no addition of tetracycline) (Figure 2 panel A). On day 0 no variation of fitness was observed. Starting from day 2, the sensitive cells were outcompeting the resistant cells. This is an interesting aspect, in absence of selective pressure the resistance gene seems to be a burden, and the resistant cells, progressively decrease in number (Figure 2, A). To confirm this data, we repeated the experiments in physiological solution (PS) (0.8% NaCl) (Figure 2, B). In physiological solution, the fitness of resistant and sensitive does not significantly
change except on day 15, where the wild type outcompeted the resistant one (Figure 2, B).

Interesting results were obtained for the lethal and sub-lethal concentration of tetracycline (Figure 2, C). At lethal concentration (5µg/mL), two days after the inoculum we observed an increase of the resistant cells, as expected. Interestingly, from day 5 to 15 the resistant cells were not more fit, and we observed a re-establishment of the sensitive *E. coli* (Figure 2, C). This data could be explained if the tetracycline, at some point, is depleted by the mesocosms. This result is indeed not surprising, we observed a similar behaviour in soil in our previous experiments: we speculate that the river water (as well soil) seems to adsorb the tetracycline, *de facto* depleting the bioavailable tetracycline. Organic matter, such as cation- and anion-sorbing sites can be important adsorbents. As result of this putative depletion, the sensitive bacteria were outcompeting the resistant ones. The experiments were repeated at sub-lethal concentration of tetracycline (Figure 2, D). At sub-lethal concentration of tetracycline, the number of resistant and sensitive cells does not significantly change on day 2, however after day 5, the sensitive cells are outcompeting.

We need to remind that these strains are generated in the laboratory, and in the case of naturally isolated resistant strains, the fitness may change due to a reduced energetic burden of the natural resistance gene(s). The genetic regulatory aspect of resistance genes (where regulatory elements are present) may also contribute to the fitness of the resistant cells.

![Figure 2. Competition index (CI) of resistant vs sensitive *E. coli* in absence of tetracycline. A) Arno river water, B) Physiological solution. C) Lethal tetracycline 5µg/mL. D) Sub-Lethal tetracycligne 2.5 ng/mL. By using the competition index (CI) formula, when the CI is negative, the wild type is outcompeting the resistant one, in contrast, when the value is positive, the resistant is outcompeting the wild type. When the index is 0 the ration of the population does not change. (*) shows significant](image-url)
deviation from the mean. Dotted line shows the value 0.

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The new water quality standards for the rivers of Armenia

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ABSTRACT
A new system of surface water quality assessment is introduced in Armenia by the Government of RA for the determination of the ecological status of surface water (See RA Government decree, No 75-N “On Definition of Water Quality Norms for Each Water Basin Management Area Taking Into Consideration the Peculiarities of the Territory”, 27.01.2011). According to the above-mentioned decree, the list of water quality assessment indicators includes 103 hydro-chemical indicators (+1 hydro-biological), 42 of which are EU WFD prior and special pollutants. The water quality assessment system inherited by the Soviet Union, including more than 1300 parameters and maximum allowable concentration (MAC), is no longer used for water quality assessment. According to the Decree, 23 river basins and sub-basins were formed in the territory of RA. A typical list of water quality standards for each of them was developed (used only for that basin). The 5-scale water quality assessment system is based on the natural background concentration (BC) values of hydro-chemical parameters which are calculated for the reference sites of each river basin.

This study has performed a comparison analysis between the MAC and BC values and the norms based on them for definite basins. The comparison analysis was also conducted between the BC values of different rivers and sub-basins of the same river basin.

The conducted analysis showed that: (a) water quality norms should be developed and implemented based on the BCs for more than 23 sub-basins; and (b) water quality standards for river basins should be different for each hydrological season.

INTRODUCTION
Up to 2011, in RA surface water quality assessment system was based on MAC for fishery inherited from Soviet Union. MPC is that concentration of hydro-chemical substances, below which the content of the substance in the water is considered safe for the fish. The MAC values were defined in the USSR for completely different, non-Armenian river basins. However, the same MAC values were mechanically used for the assessment of the rivers’ water quality in different geographical areas and countries of the former Soviet Union, including Armenia. It did not take into consideration the difference of hydro-geographical, hydro-morphological, hydro-chemical and hydro-biological features between different regions and features in particular water basins. In that assessment system, the ecosystem approach was missing, which leads to disability to use it for the assessment of the water ecosystem condition and solve the problem of controlling, maintenance and effective management. The acceptance of listed drawbacks of the MACs system forced to develop essentially new system of parameters for river water quality assessment.

According to the Decree of the Armenian Government in 2011 the normative and legal framework of water quality assessment is completely changed. The new system is quite harmonious to the EU WFD principles. According to the Decree the territory of RA was divided into 14 river basins and 9 sub-basins and the list of 103 hydro-chemical parameters
was defined for each of them separately. The water quality assessment 5 scale system is based on the BCs of water quality parameters. The BC is the amount of naturally occurring chemical substances derived/originating from natural processes in the environment as close as possible to natural conditions, exclusive of specific anthropogenic activities or sources (EPA 2008). The classification is carried out based on the principle of comparison: as high is the value of the concentration of parameters compared to their BC as low is the quality of water. The general algorithm of evaluation of surface water quality for each quality parameter differentiates five classes (RA Government decree, No 75-N, 2011): I or “excellent” class (≤BC), II or “good” class (≤2xBC), III or “moderate” class (≤4xBC), IV or “poor” class (≤8xBC) and V or “bad” class (>8xBC). The overall status of water quality is formed by a quality parameter which shows the worst quality class. Classification is carried out according to the principle if it is bad for one parameter, it is bad in general (“One out-all out” principle).

According to the Decree of the Government the revision of the norms is intended to be conducted in 2017 for the next 6-year.

The main objective of the proposed work is: (a) comparison between the BC values of water quality parameters of definite basins and MAC values, (b) comparison of the BC values of the parameters of the definite basin rivers.

METHODS

The values of the natural BCs of the water quality parameters are calculated based on statistical methods using theoretical log-normal distribution probability function (Pekarova et al. 2008). The calculations of BCs were conducted for the South basins of Armenia: rivers Meghri, Vorotan, Voghji, and Lake Sevan basin rivers: Argichi, Dzknaget, Gavaraget. The monitoring data carried out from 2005 up to 2012 are used for the BCs calculations.

RESULT AND DISCUSSION

Comparison of maximum allowable and background concentrations

The values of MACs for fishery and BCs have been compared. The comparison showed (see table 1) that the water quality parameters can be divided into three groups according to the MAC/BC ratio. The first group includes Al, B, V, Cu, Si. The BCs values in river waters of these parameters are many times higher than the MACs values. The second group includes Chemical Oxygen Demand (COD), NH4+, NO3-, PO43-, Cl-, SO42-, total (P, Zn, As, Cd, Pb, Mn, Fe). The BCs values of these parameters is significantly smaller than the MACs values. The third group includes all the other parameters (5-day Biochemical Oxygen demand, Dissolved Oxygen, pH, ect.): the BCs values of these parameters are close to the MACs values.

Table 1. The MAC (for fishery) and BCs of water quality parameters for many rivers in Armenia

<table>
<thead>
<tr>
<th>Water quality Parameters</th>
<th>MACs for fishery</th>
<th>Southern river basin (BCs)</th>
<th>Sevan Lake basin rivers (BCs)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Meghri</td>
<td>Vorotan</td>
</tr>
<tr>
<td>CODCr, mgO/L</td>
<td>30</td>
<td>13.54</td>
<td>11.14</td>
</tr>
<tr>
<td>NH4-N, mg/L</td>
<td>0.39</td>
<td>0.023</td>
<td>0.017</td>
</tr>
<tr>
<td>NO3-N, mg/L</td>
<td>9</td>
<td>0.631</td>
<td>0.194</td>
</tr>
<tr>
<td>P (total), mg/L</td>
<td>0.6</td>
<td>0.032</td>
<td>0.016</td>
</tr>
<tr>
<td>As (total), mg/L</td>
<td>0.05</td>
<td>0.00088</td>
<td>0.00073</td>
</tr>
<tr>
<td>Cd (total), mg/L</td>
<td>0.005</td>
<td>0.00004</td>
<td>0.000074</td>
</tr>
<tr>
<td>Pb (total), mg/L</td>
<td>0.1</td>
<td>0.00018</td>
<td>0.0001</td>
</tr>
<tr>
<td>Cu (total), mg/L</td>
<td>0.001</td>
<td>0.004</td>
<td>0.004</td>
</tr>
</tbody>
</table>

Source: Vardumyan (2011); Surmalyan and Minasyan (2012)
The second group includes parameters that are indicators of communal domestic sewage and agricultural wastewater, as well as mining wastewater pressure. The observation of long-term monitoring data showed that along the river concentration values of mentioned parameters increase and exceed the BCs, especially after the settlements, but remains low from the value of respective MACs. As the values of MAC for these parameters are incomparably higher than the values of BC, so they are not able to demonstrate the real pollution of river water. The implementation of new standards solved the problem of revealing the real pollution of river water and also the presence of anthropogenic pressure on rivers.

The comparison of background concentration values of the water quality parameters for different rivers of the same basin

As shown in Table 1, the BCs of the rivers of Lake Sevan basin are quite different. These differences are connected with the differences of the hydrological regimes. The rivers Dzknaget and Argichi have mixed nourishment, Gavaraget and many other rivers in basin of Sevan Lake have ground water nourishment (80-95%) (Chilingarian et al. 2002). The base for water quality assessment in this basin are the norms calculated for river Dzknaget or Argichi, which are applied for all rivers of the basin. The differences of the BCs (see Table 1) is an illustration that the assessment of water quality of all basin rivers based on Dzknaget or Argichi river's norms is not scientifically grounded. The fact that the concentrations of quality parameters of ground water and melted water do not coincide during the whole year also illustrates the need of separately developed and implemented norms. For example, the minimum values of $V_{\text{total}}$, $A_{\text{total}}$ concentration in river Dzknaget is observed during the summer (they are 2-5 times smaller than in spring). In contrast, in river Gavaraget the concentration values of heavy metals are the same during spring and summer. The multiple changes of the concentration values in the same river water in different hydrological seasons show the necessity to develop and implement seasonal system of water quality assessment.

CONCLUSIONS

The conducted analysis showed that:

a) The high anthropogenic impacts (pressure of communal domestic sewage water or mining wastewater) on the water quality can not be revealed by using the MAC assessment system. The implementation of the system based on BCs is an effective tool for the assessment of surface water quality and evaluation of real pollution on water quality.

b) Some of water quality new norms developed for relatively large basin, is not the appropriate for using to assess of water quality of all rivers, streams and sub-basin of that river basin, because the values of BC of many parameters vary significantly in streams and sub-basins depending on nourishment of water flow.

The conclusion was carried out: water quality norms should be developed and implemented based on the BCs for much more than 23 sub-basins; and water quality standards for river basin should be different for each hydrological season.

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Institutional and regulatory frameworks of water quality management in Albania

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FRESHWATER: WHY SHOULD WE CARE ABOUT THIS THEME?

Albania has plentiful water resources but often their quality is a problem due to pollution, especially in low-lying areas where most of the population lives and most industrial and agricultural activities take place. General renewable water resources in Albania are about 13 300 m³ per capita per year. These are used for urban, industrial and agricultural purposes as well as for hydroelectricity. Surface waters are a major asset for the economy of the country. They are very important for many uses such as electricity supply, agriculture, fisheries, tourism, industry as well as drinking water supply. Albania is also rich in groundwater resources. The renewable resource in seven main geological strata is 1 250 million m³ / year. Towns and cities as well as industrial, agricultural and farming areas are sources of pollution of surface waters and groundwater. Managing and protecting the aquatic environment is an important activity for the country. To achieve sustainable development, it is particularly important to develop and implement efficient methods and technologies for the rational use of natural resources, taking both their quality and quantity into account, and to control the impacts of resource use on the environment.

LEGAL BASIS

According to the new Law No. 10431 dated 9.06.2011 “On the environment Protection” and the Decision of Council of Ministers No.47, dated 19.01.2014 “On Setting the rules and functions of the organization of National Environment Agency (NEA) and Regional Environment Agencies and in the framework of restructuring the Agency of Environment and Forestry, the National Environment Agency (NEA) has been established. The Albanian NEA is a legal, public and budgetary institution under the Minister of Environment (MoE). NEA, through its central office and REAs, exercises the following functions:

a) Performing the regulatory environment permits in accordance with the relevant legal provisions
b) Monitoring and assessing the state of the environment and prepare a National Programme for Environmental Monitoring
c) Preparing and publishing a report on the state of the environment and other publications relating to the environment
d) Performing scientific research related to the environment or other research to technology development and innovation
e) Determining the TDM-in and EMP
f) Establishing and maintaining an information system for reference documents for TDM-in, approved by the Minister
g) Cooperating with the European Environment Agency and other international environmental organizations and meeting the relevant reporting obligations
h) Developing and managing an environmental information system
i) Creating and managing the Register of Pollutant Release and Transfer
j) Ensuring environmental information of the public on environmental issues
k) Ensuring the implementation of the environmental responsibility principle
l) Managing the forestry database system
m) Preparing and overseeing the National Forest Inventory
n) Developing forest management plans
o) Monitoring forests in the implementation of national and international obligations;
p) Ensuring the development and transfer of technologies related to forests
q) Presenting Minister drafts for technical support funded by the state budget and international donors
r) Reviewing the requirements of environmental impact assessment
s) Advising and cooperating with State Inspectorate of Environment, Forestry and Water Management and other inspectorates in the implementation of environmental legislation, including situations of incidents, accidents and environmental emergencies
t) Preparing the standard format of the request, the information contained in the application and environmental permit format types "A" and "B" and proposing to the Minister for approval;
u) Determining the conditions of the permit type "A" and "B"
v) Preparing the annual administrative report on the activities performed
w) Other functions entrusted to specific legislation

NEA has started procedures for the national accreditation of laboratory for water analysis according to ISO 17025 standards. The LAB of NEA is accredited for 7 parameters of water analyses from the General Directorate of Standardization which approves Albanian standards and adjusts and adopts the European, ISO and other international standards.

Mission of NEA
To regenerate, improve and preserve the environment, while providing a sustainable development.

Vision of NEA
Albania that enjoys a clean, healthy and sustainable environment, enabling improvement of life quality for present and future generations, while maintaining the diversity of natural resources.

ENVIRONMENTAL MONITORING SYSTEM IN ALBANIA
The environmental monitoring system in Albania is based on the DCM No 1189, dated 18.11.2009 “On Rules and Procedures for drafting and implementation of National Monitoring Program. The DCM determines the monitoring institutions under relevant ministries to perform monitoring of some environmental indicators.

The environmental indicators which are not monitored by the designated monitoring institutions will be monitored by specialized institutions contracted by the National Environment Agency, MoE based on a competitive procedure as procurement. Evaluation of the state of surface waters in rivers and lakes and control of their pollution is carried out by monitoring in compliance with the National Programme on Environmental Monitoring prepared every year from NEA and it approved by Order of Minister of Environment. National Environment Agency, Ministry of Environment coordinates and monitors the quality of surface water, bathing water, groundwater and wastewater discharges. The stakeholders of the all process are:
• National Environment Agency
• Institute of Public Health
• Institute of Water, Energy & Environment
• Albanian Geology Service
• Faculty of Natural Sciences
• Agricultural University
• Line ministries

Monitoring of groundwater in the main watershed basins (NEA and Albanian Geological Service)

Monitoring indicators:
• Chemical analysis: Na + K, Mg, Ca, Fe, NO4, HCO3, CO3, Cl, SO4, NO3, NO2, general mineralize, general strength, pH, O2 content and temperature.
• Microminerals: Cu, Zn, Li, Co, Cr, Ni, Mn.
• Monitoring on trophic state of Kune-Vain lagoons and Shkodra lake carried out by Faculty of Natural Sciences
• Monitoring indicators: Chlorophyll –a, b and c, Carotenoid, Phosphor total, BOD, dissolved oxygen

Monitoring on urban discharges in surface water for 8 city NEA

Monitoring indicators:
• Chemical pollution indicators
  - Chemical Oxygen Demand (COD)
  - Biological Oxygen Demand (BOD)
  - Nutrients – nitrogen forms NH4, NO2, NO3
  - Temperature, pH, salinity, dissolved oxygen, suspended solids
• Microbiological pollution indicators
  - Coliform (E.Coli)
  - Streptococcal (St. Fecal)
• Hazardous substances indicators
  - Pb, Hg, Cd, Ni

STATES AND IMPACTS ON THE NATURAL ENVIRONMENT AND HUMAN HEALTH/WELL-BEING, AT THE NATIONAL LEVEL

Wastewater discharges in the main cities are monitored to measure their impacts on rivers, lakes and coastal waters. Monitoring in urban and rural areas is carried out for some cities. Studies on surface water quality are based on information provided by sampling at the 30 stations of the national river water quality monitoring network and monitoring at six lake stations.
Figure 1. Rivers lakes stations monitoring networks

Rivers
During the period 2007-2014, Biological Oxygen Demand (BOD$_5$), a measure of organic pollution) remained at a more or less constant level, indicating continuing organic pollution, caused by regular urban water discharges into rivers. The highest level of BOD$_5$ is found in the Ishem River, Tirana region.
Concentrations of ammonium in rivers show clear changes from year to year and there is a rising trend, notably for 2009-2012, with concentrations apparently decreasing in period 2013-2014.

The annual mean concentrations of nitrate in all rivers have decreased, but levels have stabilised in 2014-2015.
The concentrations of total phosphorus (P-tot) have been relatively stable in all monitored rivers excepting the Ishem.

Lakes
Ohrid Lake
The phosphorus content of 0.006-0.01mg/l, the high content of dissolved oxygen, and relatively high values of transparency, indicate that the water in this lake is oligotrophically stable.
The other indicators of pollution such as nitrate content, although at low levels, should not be ignored because the trends are rising compared with previous years.

Prespa Lake
The oxygen and phosphorus contents show that the lake is already at a mezotrophic tending towards a eutrophic level. The ecological system of the lake requires a detailed study but that will necessitate collaboration between Albania, Macedonia and Greece.
Figure 7. Prespa Lake (a) annual mean average for P-tot(b) annual mean average for DO (State of Environment Report 2008-2014)

Shkodra Lake
The water in the lake is relatively saturated with oxygen; the phosphorus content values are low and decreasing at the bottom of lake; the electrical conductivity of water is rising due to different discharges into the lake.

Figure 8. Shkodra Lake (a) annual mean value for P-tot(b) annual average for transparency (c) annual mean average for DO (d) annual mean value for NO₃ (State of Environment Report 2007-2008)

Figure 9. Shkodra lake, monthly mean value for chlorophyll-a (State of Environment Report 2007)
Groundwaters

Groundwater is a vital source of drinking water for Albania’s people. In low-lying western and south-eastern parts of the country, where about two thirds of its population is concentrated, drinking water comes mainly from groundwater. Intensive exploitation of groundwater often creates hydrodynamic and hydro chemical disequilibrium that result in a permanent pollution risk to nature and human activities.

Groundwater monitoring is carried out in the Drini, Mati, Ishëm-Erzen, Shkumbini, Seman, Vjosa and Zona Jonike basins. Groundwaters generally have good physical and chemical properties, meeting local pollution standards, with no massive pollution of ponds. Some nitrogen dioxide and ammonium is found in some special drilling sites but these are isolated occurrences resulting mainly from poor implementation of rigorous exclusion areas and sanitary protection around the drilling.

![Figure 10. Annual mean value for NO3 mg/l](image)
![Figure 11. Annual mean value for NO2](image)

Groundwater is found to be neutral or alkaline. No acid water has been found in the monitored ponds and drillings.

Monitoring results during the period 2010-2014 indicate that in all basins general mineralisation, nitrate and nitrite content are within the permitted levels and the pH of groundwaters is within the permitted levels for drinking water.

What are the related key drivers and pressures at the national level?

Rivers run near many towns and cities, industrial areas and areas with agriculture including livestock and discharges from all of these are the main sources of surface water pollution in Albania.

Urban wastewater and other industrial discharges directly deposited in watersheds and channels end up in rivers, lakes and coastal areas.

Most cities have common sewage systems for wastewater, rainwater and industrial activities.

Because of poor maintenance of wastewater sewers and small pipe dimensions, leaks from these sewers often carry the risk of polluting the drinking water network.
Suburban areas and rural cities lack sewage systems, and wastewater is collected in septic tanks. All industrial activities located near rivers discharge wastewater directly to them without pre-treatment. The uncontrolled dumping of urban waste in the banks of rivers further increases the problems of surface water pollution. Wastewater treatment plants are being built in Kavaja, Vlora and Pogradec and are under construction or design in other cities.

**CHALLENGES INSTITUTIONS ON WATER QUALITY MANAGEMENT**

The main institutions responsible for water management in the Republic of Albania are the Ministry of Environment and its subordinate institutions, the Ministry of Energy and Industry, Ministry of Transport and Infrastructure, Ministry of Health, Ministry of Agriculture, Rural Development and Water Administration, as well as units of Local Government, Ministry of Finance and Ministry of Interior.

The National Water Council (NWC) is the central decision-making body responsible for the management of water resources. NWC is an inter-ministerial body chaired by the Prime Minister, dealing with issues of management and integrated management of water resources.

The Ministry of the Environment is responsible for the design and implementation of policies, strategies, national plans and legislation for the protection of water resources from pollution, use as rational water resources, improve water environment, protection of surface waters in domestic waters temporary, coastal waters and groundwater, as well as their status. The Department of water resources policy was transferred to the Ministry of Agriculture, Rural Development and Water Administration by the decision of Council of Ministers No 91 of 4.02.2015 The National Water Council in Albania and its technical Secretariat have created structures for the management and protection of water quality.

Strategies have been adopted for the water supply sector and the sanitation sector for rural and urban areas. Some investments have been made, but more needs to be done first to stop the decline in the quality of surface water and then improve it.

The existing legislation needs to be improved and expanded in order to serve as a basis for management and protection actions. The institutional structures also need to be reinforced in order to properly implement the legislation. In the framework of the Stabilisation and Association Agreement, Albania is in the process of bringing legislation for water in line with EU legislation.

The main sources of water pollution in Albania are urban and industrial wastewater discharges. In order to reduce water pollution from urban wastewater discharges new wastewater treatment plants are under construction in cities including Durres, TiraneLezhe-Shengjin, Sarande and Korce, with more in the planning stages.

The construction of new treatment plants should improve wastewater management and also the state of water quality. As such, it should have a significant impact on the environment and human health.

**ALBANIAN LEGAL MEASURES ON WATER QUALITY**

Moreover, the creation of regional agencies for River Basin Management and the National Water Council has resulted in the establishment of an administrative structure for planning the utilisation and management of river basins. Legislation in the area of water consists of laws, international agreements and by laws, such as the Decisions of the Council of Ministers (DCM) and the National Water Council.

**Primary legislation for the water quality problems in Albania**

- Law no. 111/2012 dated 15.11.2012 on 'Integrated Management of Water Resources'
- Law no. 9103, dated 10.7.2003 "On protection of transboundary lakes"
- Law no. 30/2013 dated 13.02.2013, which amends Law no. 8905, dated 06.06.2002 "For the protection of the marine environment from pollution and damage"
- Law no. 34/2013, which amends Law No. 9115, dated 24.7.2003 "On the environmental treatment of polluted waters"
- Law no. 8102, dated 28.3.1996 "On the regulatory framework of the sector of water supply and wastewater removal"
- Decision no. 797, dated 29.09.2010 "On approval of the regulation sanitation management of the quality of bathing water"

**Other Activities related the legislation performance**

To improve implementation of the Law No. 111/2012 of 15.11.2012 “On Integrated Water Resources Management”, a list of measures and actions were undertaken and are on-going by the MoE in the field of Integrated Water Resources Management (IWRM):

1. Draft DCM "On adopting the specific conditions, supplementary documents, deadlines, application forms for authorization and permits for use of water resources" was sent to the National Water Council for prior approval. After this phase, the draft DCM will be sent for comments to the Line Ministries
2. The Order of Minister of Environment No. 1729 of 12.03.2014 “On the set up of the National Registry for the Water Resources Users”, the National Registry of Water Users
3. The database on financial data related to the six River Basin Agencies was published on-line at the website of the MoE
4. Particular attention is given to the bilateral and multilateral relations in the field of management of transboundary waters. Important bilateral activities are undertaken through joint committees with Montenegro. The main focus of the discussions was identification of the topographic differences between Durres (Albania) – Tivar (Montenegro)
5. Under the process of consultancy selection in drafting and designing of the National Water Cadastre with the financial assistance of the World Bank, This GIS based Cadastre will have an all-inclusive inventory of water resources in Albania, water balances, simulation models and water quality parameters, all in accordance with EU requirements
6. MoE is in the final stages of selection of the consultancy to assist in drafting the National Strategy for Integrated Water Resources Management, with the financial assistance of the World Bank

Considerable work has been done in the management of the river basins on the central
and regional level:

1. The identification of the sanitary zones for water utilities in all the six river basins was finalized
2. MoE maybe needs consultants to implement the two River Basin Management Plans for Drin –Buna River and the Semani River
3. In order to start implementing the agreement with a French company for drafting of the River Basin Management Plan for Vjosa River, several meetings took place to discuss the preliminary phases of the project. A field trip in the whole river basin was organized in order to identify the characteristics of the basin, with the participation of the representatives of the French Company, respective River Basin Agency, River Basin Council and Water Department at the MoE

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Water Quality Challenges in Latin America: A Perspective from Colombia

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Water quality in Latin America is highly dependent on increasing population, mining, agricultural run-off, urban and industrial development, and poor watershed management, among other factors. Although many efforts are being made in order to provide safe drinking water and adequate sanitation services to the community, there are still many challenges to overcome, especially viral and bacterial contamination, how to control pollutants released from mining-related processes, eutrophication, pesticide bioaccumulation, emerging pollutants in surface and groundwater, and appropriate legislation to prevent and control contamination. Moreover, still one of the biggest problems is the lack of assessment of the water quality status and its impact on public health. These problems are being addressed through different initiatives, involving both the government, the academy, as well as national and international NGOs, but the work is painstaking. In Brazil, for instance, the largest pesticide consumer in the world, the National Drinking Water Quality Surveillance Program allows monitoring pesticides in water, although less than 20% municipalities registered their data (Barbosa et al. 2015).

Clearly, the established legislative regulations are not enough, and great effort is required to build up management capacity, enforcement, expertise and training, as well as seeking for new funding opportunities.

In the case of Colombia, the country possesses multitude of water sources and some regions are recognized among the wettest places in the world. However, this opportunity is being washed away due to multiple human-made actions that reduce overall water quality. Moreover, unreliable environmental regulations, poverty and corruption put a lot of pressure on these resources, in particular the Magdalena and Cauca watersheds, water bodies with increased pollution load from domestic sewage, industrial and agricultural discharges, and sediments from mining, deforestation and colonization.

Current guidelines for drinking water are more flexible than they have been in the past, and the pressure for mining in fragile ecosystems such as Paramos is threatening water supply for several cities. Water and sediment quality is also at high risk in heavy traffic ports, where several metals and polycyclic aromatic hydrocarbons (PAHs) present in sediments have correlated with cellular toxicity (Caballero-Gallardo et al. 2015). Gold mining areas are especially important sources of mercury, metal that reaches several environmental compartments and is biomagnified through the trophic chain (Olivero-Verbel et al. 2015).
2015), appearing at high levels in several fish-eating communities, in particular the Amazon regions, where high mercury levels in hair is of special concern. Water is also the main transfer platform for PAHs, perfluorinated compounds and endocrine disrupting chemicals that have been found in samples from industrialized areas, where imposex has been documented.

These water quality related threats are linked to human health. In Colombia this parameter has shown high correlation with infant mortality (Guzman et al. 2015). Therefore, policies must be developed and implemented in order to promote better water quality, in particular preventing pollution at its source. It is also clear that extensive research is needed, as many potential toxicans might be present in drinking water, making emphasis on emerging pollutants and biological contamination.

Environmental education is also fundamental to seek political changes that could lead to better water quality standards. The general public lacks access to scientific information, and this requires developing strategies to transfer knowledge that could be easily incorporated to decision-making opportunities. For instance, we have develop EDCs DataBank [http://edcs.unicartagena.edu.co/] (Montes-Grajales and Olivero-Verbel 2015), a database of endocrine disrupting chemicals (EDCs), as a platform for increasing environmental awareness about these pollutants, allowing people to appropriately limit their use. Finally, all successful endeavors from all over the world must be socialized and incorporated in our communities in order to guarantee a better environment for this and next generations.

Acknowledgements
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REFERENCES
Hazardous substances management in surface waters of Turkey

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INTRODUCTION
Hazardous substances in surface waters are the chemicals having a property of toxicity, persistency and bio-accumulation. Industrial chemicals, personal care products, pesticides, pharmaceuticals, detergents and metals are some of the hazardous substance groups commonly used in daily life.

Due to intensive urban, industrial and agricultural activities, surface waters are at risk of pollution with those hazardous chemicals. These chemicals have many adverse effects on the aquatic organisms and humans exposed them through different pathways. That is why protecting surface waters and their chemical qualities against the hazardous pollutants and ensuring sustainable use and integrated management of them have recently gained popularity around the world when the consideration is to leave water heritage to the future generations.

Hazardous substance management in surface waters is also a requirement of the European Union (EU) legislation, Water Framework Directive (2000/60/EC), in order to reach “good water quality” in all waters and ensure healthy water environment for different use alternatives. According to the directive, hazardous substances can be either priority substances or specific pollutants. Priority substances are defined as the substances posing a significant risk for water environment which also including priority hazardous substances among them (Directive 2000/60/EC; Directive 2013/39/EU) and recently reviewed by the Directive 2013/39/EU on EU level. Specific pollutants, on the other hand, are the substances posing a risk on national or river basin level due to being discharged in serious amount and they are designated by Member States on a country basis. Control of priority substances and specific pollutants in surface waters are ensured by the implementation of their environmental quality standards (EQS), concentrations in water, sediment or biota which should not be exceeded in order to protect human health and the environment.

Methodology:
As a candidate for EU membership, Turkey has conducted the scientific projects on the surface water management of hazardous pollutants between the years of 2011-2014 by considering the abovementioned issues. Within the scope of these studies, efforts were being made on the determination of hazardous substances encountered or likely to be encountered in surface water resources due to domestic and industrial discharges (point sources) and agricultural activities (non-point sources), monitoring of these substances in receiving water bodies (i.e. inland, coastal and transitional waters) and wastewaters of treatment plants for point sources, and setting EQSs for water column, sediment and biota matrices.
In these projects, firstly, candidate chemical list was prepared. For the determination of hazardous pollutants originating from point sources, production and wastewater treatment processes of the industrial activities were investigated for the pilot plants, detailed literature survey was conducted and national and international legislations/conventions were searched, as well. For the diffuse pollutants, on the other hand, inventory of pesticides was established by considering the agricultural production pattern and the potential substances that might end up in receiving waters were determined.

After obtaining the candidate list, different prioritization methods like COMMPS (Combined Monitoring and Modelling Based Priority Setting) were applied to the substances in the list. Hazard characteristics, physicochemical properties (BCF, logKow, half-life in water, Henry’s law constant etc.), exposure profiles and production and use patterns of the substances were taken into consideration during the prioritization studies.

Results:
As a result of these studies, specific pollutants of Turkey were designated in line with Water Framework Directive. Specific pollutant list includes 117 substances like heavy metals, halogenated organics, endocrine disrupters and aromatic hydrocarbons from point sources and 133 pesticides from non-point sources. The steps of the selection procedure are summarized in Figure 1. For these substances, maximum allowable and annual average EQSs were also developed by using the acute (LC50, EC50 etc.) and chronic toxicity (NOEC EC10) data of different taxonomic groups (fish, algae and daphnia magna) respectively existing in the literature and applying the methodology mentioned in the Technical Guidance Document for Deriving Environmental Quality Standards (Guidance Document No. 27) which was prepared under the Common Implementation Strategy for the Water Framework Directive (2000/60/EC). Deterministic and probabilistic methods are the two methods provided for the EQS derivation (EC 2011) and the decision to apply one over the other were made based on the number and type of toxicity data available. For the probabilistic method, Species Sensitivity Distribution was applied and ETX 2.0 software was used for this purpose.
Hazardous substances management in surface waters of Turkey

As a future roadmap, it is planned to adapt the specific pollutants and their EQSs in water column, sediment and biota to the national legislation, By-Law on Surface Water Quality, by 2016. In this way, it could become possible to monitor and control these pollutants in surface water environment and to take necessary precautions in time in order to protect and improve water quality when there is an identified risk of not attaining water quality objectives.

REFERENCES


Water quality standards and objectives: Caspian Sea regional perspective

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INTRODUCTION

The Caspian Sea is the world's largest inland water body. So far, its legal status is undetermined; moreover, experts have still been discussing whether it is a lake or a sea. Anthropogenic pressure on the sea including pollution from on- and offshore sources is significant, and because of its land-locked nature, pollutants discharged into the sea remain trapped in it (SoE 2011). This makes the need for mitigation measures to protect the Caspian environment even more urgent.

By 2006, all Caspian littoral states (Azerbaijan, Iran, Kazakhstan, Russia and Turkmenistan) ratified the Framework Convention for the Protection of the Marine Environment of the Caspian Sea (the Tehran Convention), which was the most significant outcome of the Caspian Environment Programme (CEP) that was started in 1995 under auspices of UNEP. Being the first regional and legally binding instrument signed by all five Caspian littoral states, the Tehran Convention serves as an overarching framework laying down the general requirements and the institutional mechanism for the protection of the marine environment of the Caspian Sea (Tehran Convention 2006).

Article 19-3 of the Tehran Convention prescribes that “The Contracting Parties shall, at regular intervals, carry out individual or joint assessments of the environmental conditions of the Caspian Sea and the effectiveness of measures taken for the prevention, control and reduction of pollution of the marine environment of the Caspian Sea.” To accomplish this task, the Caspian Environment Monitoring Programme (CEMP) has been designed, and the countries have agreed that there is a need to set up Caspian regional Water Quality Standards (WQS). They are to be targeted at assessing the quality of the Caspian environment with identification of hotspots and setting long-term water quality objectives (WQOs) for elimination or mitigation of contamination in the Caspian environment.

To provide compatibility of the Caspian State-of-Environment assessments with those of other internationally shared waters, it is essential that the Caspian WQSs are in coherence with the best practices existing in Europe and other regions.

The objective of this paper is to determine the state-of-the art national environmental standards in the Caspian states, and perspectives for setting up regional water quality standards and objectives. Mechanisms for Caspian WQSs development related to the discussed legal instrument are also proposed.
WATER QUALITY STANDARDS

The water quality standards include a set of water quality indicators and their numerical threshold values. Indicators of water quality are derived from physical, chemical and biological parameters of the sea water and thus referred to as physical, chemical and biological indicators.

While physical and chemical indicators for the sea waters have been traditionally applied and legally enforced in the majority of the Caspian states (except Iran), biological indicators are comparatively new to this region but have an advantage of showing impacts of the sea waters on the typical (for the given sea or its part) living organisms (biological species).

Presently, the four post-soviet states (Azerbaijan, Kazakhstan, Russia and Turkmenistan) generally apply numerical threshold values (standards) for marine water quality which have been inherited by them from the former USSR. These standards are referred to as “maximum allowable concentrations (MAC) of pollutants in the sea water” and are an integral part of environmental legislation of those states. MACs were determined for two kinds of water use (the sanitary and fisheries) based on mortality of 50% tested biological organisms.

However, absolute values for MACs and analytical methods for pollutant determination sometimes differ from those adopted in Europe. For example, MACs in the Caspian states are applied to the total concentration of a substance (soluties plus suspended matter) while in Europe they refer to solutes only.

No numerical threshold values (standards) for bottom sediment, biota contamination or biological indicators have been adopted so far in the Caspian states. Introduction of such standards would involve modification of national legislation and increased cost of monitoring programs.

As for Iran, it has no legally binding environmental standards. Although there are no legal standards for bottom sediments or biota contamination in the Caspian states, a large experience in their assessment has been gathered during CEP implementation based on thresholds developed earlier in the North America and Europe for scientific purposes. Some results were published internationally by de Mora et al. (2004a, 2004b), Tolosa et al. (2004).

WATER QUALITY OBJECTIVES

The Water Quality Objectives (WQOs) constitute targets used for planning measures to improve the state of a water body and bring it closer to the WQS or maintain the state at the WQS level if it has been already achieved. The WQOs are usually established on a phase-by-phase basis and manifest a compromise between the needs of economic development and requirements for environment protection. The WQSs serve as a guideline for establishing the WQOs for the water body or its part.

The legislation of both Russia and Kazakhstan provide that water quality objectives are established for each river basin and territorial sea waters. However, no procedure for their approval has been adopted by the Russian government. In Kazakhstan, environment quality objectives subject to being established in case the background concentrations of pollutants exceed the relevant environment quality standards (MACs in the case of water bodies). However, no environment quality objectives have been established under this part of legislation so far.
APPROACHES TO SETTING UP THE CASPIAN REGIONAL WATER QUALITY STANDARDS

Any attempt to set up Caspian regional water/environment quality standards need to preserve a balance between the European trend for multi-parameter coverage (based on biological as well as chemical and physical descriptors) on the one hand and the existing environmental legislation and monitoring capabilities of the Caspian States, on the other hand. An immediate necessity is to negotiate regional standards for chemical indicators for water column, sediments and biota based on national standards of the Caspian states and some European (or others, e.g. CCME (2001), in the case of bottom sediments) chemical standards, while introduction of biological indicators may be addressed in a more distant future.

A legal instrument on information sharing and usage (which is under discussion now) may, among other issues, address the Caspian water quality standards/water quality objectives by stipulating procedures for their development and approval by the Tehran Convention parties. Another option is that the Caspian water quality standards are to be an integral part of the instrument being attached to it as an annex. Besides, the legal instrument could cover procedures for producing reports on the Caspian State of Environment.

In any case, the Caspian WQSs need to be negotiated among the Caspian states and WQSs elaboration may be a part of Terms of Reference of the Tehran Convention Working Group on monitoring and information sharing.

Since the WQSs are closely related to environmental parameters measured in the regional and national monitoring programmes, and given a considerable cost of conducting extended monitoring programmes for the Caspian states, the WQSs may be introduced on a phase-by-phase basis, starting from physical, chemical and only a small portion of biological indicators as prescribed earlier in the Caspian Environment Monitoring Programme. Besides, it is essential that the Caspian Regional Water Quality Standards introduced by the legal instrument shall have no implication for the national legislation of the Caspian states. Otherwise one can hardly expect that the legal instrument is approved.

REFERENCES

Sustainable Water Management System in the Republic of Serbia: an objective goal or a theoretical idea?

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INTRODUCTION

At times when safe and clean water is a prerequisite for successful socio-economic growth, sustainable management of this resource is identified as a priority of national interest, especially in countries that are vulnerable as a result of uneven spatial and temporal distribution of water resources (Bagatin et al. 2014; Blackman and Harrington 2000; Bogardi et al. 2012; Dedijer et al. 2007; Deng et al. 2013; Đukić 2014). The latest reports of the intergovernmental panel on climate change suggest that water resources in the Mediterranean and neighboring regions are particularly vulnerable to changes in global climate (Đukić 2011; EEA 2004). According to some scenarios, the negative trend of increasing number of droughts and floods is expected in many countries of Southern Europe (Ferrer et al. 2012; Hristovski et al. 2010). Consequently, these trends necessitate development and implementation of an integrated national water management system (WMS) in these countries to (1) mitigate the upcoming effects of climate change; and (2) successfully manage the water resources for the next generations.

The Republic of Serbia (RS), located in Southern Europe, is a prime example of a country with a water management system that has not adequately transitioned to address the need of the new socio-economic paradigm. Analysis of the existing situation and identification of barriers often represent the initial steps in overcoming the challenges that hinder the development of a sustainable water management system. Analyses conducted through the prism of regulations, management, engineering and education, which represent principal pillars of every socio-economic system of national importance, could lead towards a development and implementation of an effective integrated water management system because the principal concepts and prudent practices stemming these pillars represent an effective apparatus for determining the sustainability and efficiency of such system. However, in absence of funding and political will, comprehensive analysis is frequently prohibited in countries like Serbia, and examination of existing data related to water management may be the only viable path to catalyze the process of developing and implementing an integrated national water management system. In this context, the presented analysis examines the existing water management system in Serbia.

WATER RESOURCES

Figure 1 summarizes the national water balance for the Republic of Serbia as follows: outside water inflow is 162.5 billion m³/yr; from the annual precipitation of 65 billion m³/yr around 49 billion m³/yr evaporate back into the atmosphere and do not directly contribute to the overall water hydrology of the country; only 16 billion m³/yr or 25% participate to the overall water balance as inland water inflow; total water outflow is 178.5 billion m³/yr (Rossi
The goal of this paper is to explicate the existing barriers hindering the development and implementation of an integrated national water resources management system of Serbia. To achieve this goal: (1) each element of the existing water resources management system in Serbia is examined through the prism of the four principal pillars; (2) the barriers, challenges and issues are identified; (3) directions for their successful overcoming are provided.

The key findings and the outcomes of this study can be extrapolated to many small developing countries with fragile socio-economic and ecological systems.

QUALITY OF SERBIAN WATERS

Environmental indicators, which are used for definition of water quality in Serbia, is based on the Water Quality Index (WQI) method where ten physico-chemical and microbiological quality parameters (oxygen saturation, BOD₅, ammonium ion, pH value, total nitrogen, orthophosphate, suspended solids, temperature, conductivity and coliform bacteria) are aggregated (considered). Previously used classification of waters quality into four classes: I-IV (Official Gazette SFRJ #6/78) is currently in indirect use as an input parameter of quantitative boundary for definition of WQI indicators throughout the numerical range of quality. WQI trends are calculated by Mann-Kendall method and the minimum 5 annual samples for a period of each year were used. Obtained results are illustrated by charts (Figure 2).
According to analysis, clean water (water that meets the requirements of very good and excellent water quality by medium as well as minimum WQI) is rare in the RS. It can be found only in mountain regions, for example, along the Drina in Bajina Basta. On the other hand, the most polluted rivers characterized by very poor quality are located in Vojvodina and include the Danube Tisa Danube canal, Begej and Zlatica River. Analysis of WQI mean values shows that 92% of water corresponds to good, very good and excellent quality (Figure 2, a) and can be classified in I, IIa and IIb class (Official Gazette SFRJ # 6/78). However, according to minimum values of the WQI for the period 2004-2013, 76% of waters in the Serbia belong to category of poor and very poor water quality. Trend analysis of watercourses quality expressed by WQI shows that 35% of the measuring points are determined by increasing, 11% by declining and 54% by insignificant trend change. Considering the high percentage of insignificant trend change in the quality of watercourse, it can be concluded that protective measures against pollution are missing. The qualitative state of Serbia waters can be called status quo.

However, such analysis is results of periodic sampling at certain points of surface waters and cannot be considered as a part of comprehensive program that monitors and tracks the pollution of waters. The obtained results do not link observed trends with the causes of such a state and therefore cannot be used in an integrated water management system.

**CONCLUSION**

The case study of the Republic of Serbia indicates that due to their low adaptive capacity, developing countries are especially vulnerable to the climate changes and increasing depletion of water resources. The extreme floods that took place in May of 2014 illustrate critical situation and call for immediate action toward building of sustainable water management system in Serbia. In accordance with current overviewed position, Serbia is faced with couple main challenges: (1) infrastructure reconstruction/construction of water supply system, sewage systems and WWTP; (2) innovation of legal regulations in accordance with national specificities and harmonization with international one; (3) decentralized institutional reorganization and (4) development of homegrown water professionals capable of initiate and implement reforms. With the aim to catalyst sustainable social progress and economic growth, encouragement of a dynamic, interactive and multiple interactions between specified challenges is essential. Development of an adequate national water management strategy needs to be based on modern scientific knowledge and up-to-date information.

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Water quality of basic rivers in the Republic of Uzbekistan

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For Uzbekistan, water is the prime and vital resource that has always been the main source of livelihood and economic development of the society. The large-scale development of urban areas, industry, agriculture and the impact of climate change has led to the increased pollution of natural water resources in Uzbekistan. Changes in water chemistry due to pollution cause alterations in consumer behaviour and adverse changes in the habitat of aquatic biota. An essential principle of the monitoring of natural waters is the complexity of observing the dynamics of the hydrological parameters and chemical composition of natural waters.

The main aim of the Government’s water sector policy is to promote the rational use of water and to protect water resources. It also aims at improving the efficiency and reliability of the country’s water sector management, ensuring guaranteed water delivery and providing essential services both to society and natural ecosystems for the reconstruction, operation and maintenance of the existing infrastructure. The National Environmental Action Programme of the Republic of Uzbekistan predetermines the policy of the state aimed at improving the quality of surface and groundwater. The latter is based on the legal basis of the 1993 Law on Water and Water Use, with its December 2007 amendments, and the 1999 Law on the Safety of Waterworks. Since 2001, eight Cabinet of Ministers Resolutions have been adopted concerning rivers, and three concerning groundwater.

Water quality monitoring at the national level is carried out by several institutions. The Ministry of Agriculture and Water Management is the state body responsible for water resources management and monitors the discharge and water quality of drainage waters. The State Committee for Nature Protection (SCNP) is responsible for the control and improvement of surface water use and compliance with legislation on nature protection. The State Committee on Geology and Mineral Resources (SCGMR) is responsible for monitoring and managing groundwater. The Ministry of Health is responsible for monitoring drinking, municipal and irrigation water quality in order to prevent contamination by harmful substances. It monitors the microbiological and chemical parameters in drinking water and bathing water. The Centre of Hydrometeorological Service (Uzhydromet) monitors the hydrological regime of rivers, lakes and reservoirs, and is responsible for monitoring the water quality of rivers, lakes and reservoirs.

The SCNP, through its State Specialized Inspectorate for Analytical Control (SSIAC), operates a database covering data from its pollution monitoring. The database is well structured and may provide data classified according to polluting parameters and to individual enterprises. Once every two years, the SSIAC publishes the Information Bulletin on the State of Pollution Sources and their Environmental impact in the Republic of Uzbekistan. Uzhydromet has been operating its electronic database on the quality of surface water since 1996. It publishes the following: daily environmental bulletins, monthly bulletins on water quality in main watercourses according to hydrochemical indicators, nine bulletins a year on the ecological conditions of the Tashkent region’s main watercourses and their water quality according to hydrobiological indicators as well as the yearbooks on surface water quality. These publications are circulated among some 50 public institutions in the country.
They are not easily accessible by the public. The monitoring information of Uzhydromet uploads on its website. The SCGMR operates a groundwater database on the levels and quality of groundwater. It publishes an annual information bulletin on the state of groundwater and its use. These bulletins are circulated among the public authorities in a limited number of copies.

The Centre of Hydrometeorological Service Uzhydromet under the Cabinet of Ministers, together with its thirteen territorial departments, is the main public authority that carries out surface water quality monitoring in the country. It currently monitors surface water quality at 109 gauges on 61 water bodies. The observation points are located only on large water bodies. The current network provides data on some 50 parameters and assesses chemical composition and the presence of suspended and organic matters, main pollutants and heavy metals. Samples are taken manually either monthly or yearly or according to hydrological phases, depending on the size of the water body. The data collected and analysed by Uzhydromet demonstrate stable pollution levels at the monitoring points which are frequently close to the requirements of water quality standards (MACs). Diffuse pollution of surface waters is insufficiently monitored in Uzbekistan.

At present, Uzbekistan uses the water pollution index (WPI) for a comprehensive assessment of the water quality of water bodies. Its calculation is based on six parameters: dissolved oxygen, biochemical oxygen demand (BOD), and four substances with higher values relative to their MACs. The WPI has been used in practice for more than 30 years. The surface runoff of the Amu Darya, Syr Darya, Zarafshan Rivers and their tributaries constitutes the basic water resources of Uzbekistan. A comprehensive assessment of these rivers for the period 2010-2014 was implemented by using the water quality monitoring data of the Republic of Uzbekistan. The WPI, as an indicator of the water quality of these rivers, has been calculated on this basis.

During the period 2010-2014, the water pollution index (WPI) of the Amu Darya River in all monitoring points corresponds to II and III classes of pure and moderately polluted waters. In the monitoring points at Termez water quality has improved (changed from III class to II class), but has deteriorated in Kipchak (changed from II class to III class) (table 1).

Table 1. Comprehensive assessment of water quality in the Amu Darya River for 2010-2014

<table>
<thead>
<tr>
<th>№</th>
<th>Monitoring points</th>
<th>2010 class</th>
<th>2011 class</th>
<th>2012 class</th>
<th>2013 class</th>
<th>2014 class</th>
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</thead>
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<td></td>
<td></td>
<td>2010 class</td>
<td>2011 class</td>
<td>2012 class</td>
<td>2013 class</td>
<td>2014 class</td>
</tr>
<tr>
<td>1</td>
<td>Amu Darya, Termez</td>
<td>1.16 III</td>
<td>1.02 III</td>
<td>1.00 II</td>
<td>0.89 II</td>
<td>0.87 II</td>
</tr>
<tr>
<td>2</td>
<td>Amu Darya, Tuyamuyun</td>
<td>0.97 II</td>
<td>1.06 III</td>
<td>0.75 II</td>
<td>1.08 II</td>
<td>0.90 II</td>
</tr>
<tr>
<td>3</td>
<td>Amu Darya, Kipchak</td>
<td>1.06 III</td>
<td>0.78 II</td>
<td>0.90 II</td>
<td>1.18 III</td>
<td>1.03 II</td>
</tr>
<tr>
<td>4</td>
<td>Amu Darya, Nukus</td>
<td>1.42 III</td>
<td>0.86 II</td>
<td>0.92 II</td>
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<td>0.97 II</td>
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<tr>
<td>5</td>
<td>Amu Darya, Kzildjar</td>
<td>1.07 III</td>
<td>0.80 II</td>
<td>0.92 II</td>
<td>0.89 II</td>
<td>1.12 II</td>
</tr>
</tbody>
</table>

The average mineralization in the Amu Darya River ranged from 618.1 to 1297.7 mg/dm³. The oxygen regime during the period was satisfactory, while the concentration of dissolved oxygen ranged between 8.77 and 10.78 mg/dm³. The average value of the chemical oxygen demand (COD) was 10.73 mg/dm³. The average value of biological oxygen demand (BOD) was 1.48 mg/dm³. The water contamination rate with phenols was averaged at 0.001 mg/dm³. Oil products were detected with levels of 0.01-0.07 mg/dm³. The content of ammonium, nitrate and nitrite was not high, their average concentration was 0.04 mg/dm³,
Water quality of basic rivers in Republic Uzbekistan

0.49 mg/dm³, 0.005 mg/dm³. Respectively the average content of heavy metals was for chromium (Cr VI) 0.47 mg/dm³, copper (Cu) - 1.2 mg/dm³, zinc (Zn) - 2.0 mg/dm³. Water pollution with HCH, DDT and its metabolites could not be proven.

The WPI in all monitoring points of the Syr-Darya River corresponds to III class of moderately polluted waters (Table 2). Only in the station at Namangan, the water quality has deteriorated (changed from II class to III class) in 2014.

Table 2. Comprehensive assessment of water quality in the Syr Darya River for 2010-2014

<table>
<thead>
<tr>
<th>№</th>
<th>Monitoring points</th>
<th>Water pollution index (WPI)</th>
<th>2010 class</th>
<th>2011 class</th>
<th>2012 class</th>
<th>2013 class</th>
<th>2014 class</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>Syr Darya, Namangan</td>
<td></td>
<td>0.97</td>
<td>0.78</td>
<td>0.91</td>
<td>0.84</td>
<td>1.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>II class</td>
<td>II class</td>
<td>II class</td>
<td>II class</td>
<td>III class</td>
</tr>
<tr>
<td>2</td>
<td>Syr Darya, Bekabad (upstream waste water discharge)</td>
<td></td>
<td>1.53</td>
<td>1.64</td>
<td>1.26</td>
<td>1.60</td>
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<td>III class</td>
<td>III class</td>
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<td>III class</td>
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<tr>
<td>3</td>
<td>Syr Darya, Bekabad (downstream waste water discharge)</td>
<td></td>
<td>1.79</td>
<td>1.74</td>
<td>1.17</td>
<td>1.55</td>
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<td>4</td>
<td>Syr Darya, Nadezhdensky</td>
<td></td>
<td>1.75</td>
<td>1.35</td>
<td>1.34</td>
<td>1.40</td>
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<tr>
<td>5</td>
<td>Syr Darya, GPK-S collector</td>
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<td>1.11</td>
<td>1.39</td>
<td>1.21</td>
<td>1.22</td>
<td>1.37</td>
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The average mineralization was 959.8 mg/dm³ with its fluctuations along the river. The oxygen regime during the observed period was satisfactory and the average concentration of dissolved oxygen was 12.2 mg/dm³. The average value of COD and BOD was 12.8 mg/dm³ and 4.19 mg/dm³, respectively the contamination level of phenols was 0.001 mg/dm³. The level of oil products detected was 0.01-0.05 mg/dm³. The content of ammonium, nitrate and nitrite was low, the average value of their concentrations was 0.04 mg/dm³, 0.49 mg/dm³, 0.005 mg/dm³, respectively the content of heavy metals was as follows: Cr (VI) - 0.47 mg/dm³, Cu - 1.2 mg/dm³, Zn - 2.0 mg/dm³. Water pollution with organochlorine pesticides could not be detected.

The WPI of the Zarafshan river in all the monitoring points corresponds to II and III classes of pure and moderately polluted waters (table 3). In the monitoring point at Kattakurgan and Khatirchi, the water quality has improved (changed from III class to II class) during the observed time.

Table 3. Comprehensive assessment of water quality in the Zarafshan River for 2010-2014

<table>
<thead>
<tr>
<th>№</th>
<th>Monitoring points</th>
<th>Water pollution index (WPI)</th>
<th>2010 class</th>
<th>2011 class</th>
<th>2012 class</th>
<th>2013 class</th>
<th>2014 class</th>
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<tbody>
<tr>
<td>1</td>
<td>Zarafshan, Ravathaga</td>
<td></td>
<td>0.98</td>
<td>0.77</td>
<td>0.48</td>
<td>0.82</td>
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<td>2</td>
<td>Zarafshan, Samarkand</td>
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<td>0.91</td>
<td>0.67</td>
<td>0.52</td>
<td>0.87</td>
<td>0.68</td>
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<tr>
<td>3</td>
<td>Zarafshan, Siab collector</td>
<td></td>
<td>1.98</td>
<td>1.33</td>
<td>1.36</td>
<td>1.42</td>
<td>1.87</td>
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<tr>
<td>4</td>
<td>Zarafshan, Kattakurgan</td>
<td></td>
<td>0.93</td>
<td>1.19</td>
<td>0.88</td>
<td>1.12</td>
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<tr>
<td>5</td>
<td>Zarafshan, Khatyrchi</td>
<td></td>
<td>1.20</td>
<td>1.21</td>
<td>0.88</td>
<td>1.25</td>
<td>0.69</td>
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<tr>
<td>6</td>
<td>Zarafshan, Navoi (upstream)</td>
<td></td>
<td>1.56</td>
<td>1.21</td>
<td>1.41</td>
<td>1.08</td>
<td>1.28</td>
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</table>
The average mineralization of the Zarafshan river water increases from its source - 281.9 mg/dm$^3$ to the mouth - 1578.9 mg/dm$^3$, while the average mineralization during the observed period was 734.3 mg/dm$^3$. The oxygen regime was satisfactory and the average concentration of dissolved oxygen was 12.2 9.18 mg/dm$^3$. The average value COD and BOD were 9.47 mg/dm$^3$ and 1.17 mg/dm$^3$. The pollution of the river with mineral nitrogen was not high: ammonia - 0.16 mg/dm$^3$, nitrite - 0.04 mg/dm$^3$, nitrate – 2.02 mg/dm$^3$. The average concentration of toxic metals was: Cr (VI) 0.67 mg/dm$^3$, Cu - 1.6 mg/dm$^3$, Zn - 2.1 mg/dm$^3$. Water pollution with organochlorine pesticides was not detected.

The results of a comprehensive assessment of the water quality in rivers show that the results in all the monitoring points correspond to II and III classes of pure and moderately polluted water for the period 2010-2014. The main pollutants of water are salinity, organic matters (BOD, COD), oil products, nitrogen compounds, heavy metals and phenols.

Water quality is an extremely important factor for all sectors of the economy and it plays a very important role in supporting ecological viability of water ecosystems in Uzbekistan. Water quality monitoring in Uzbekistan suffers from deficiencies, which are mainly due to quality monitoring equipment and the insufficient funding of recent years. Most quality standards are still basically the same quality standards that were used during the Soviet period. Many water quality data are not available to the public. The possibilities for the general public to access water quality monitoring information through communication means are very limited, especially in rural areas. The country does not have an integrated or interconnected electronic database. Therefore, these data are not easily accessible by the public.

REFERENCES


Natural Systems for Water and Wastewater Treatment and Reuse: An Overview

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INTRODUCTION
Increasing water scarcity, escalating population growth, urbanization, pollution of water sources and high treatment costs require innovative and sustainable technologies for water and wastewater treatment and reuse. Natural treatment systems (NTSs) are getting increasing attention in water management in this context. NTSs include a wide range of soil/aquifer-based and vegetation-based systems applied for the treatment of drinking water, wastewater, and urban storm water. Such systems are low-cost, sustainable, robust, and multi-objective targeting simultaneous removal of different contaminants including suspended solids, biodegradable organic matter, nutrients and organic micropollutants (Sharma and Amy 2010). NTSs are cost effective and environment-friendly technologies that can reduce stress on water resources. There is an enormous potential for their application in treatment of water and wastewater in both developed and developing countries and, as such, they should be considered as alternatives or supplements to conventional water and wastewater treatment technologies. Furthermore, NTSs provide innovative ways to promote safe wastewater reclamation/reuse including indirect potable reuse through use of appropriate environmental buffers and psychological barrier.

NATURAL TREATMENT SYSTEMS
NTSs like bank filtration (BF) and artificial recharge and recovery (ARR) have been employed for water treatment worldwide. These methods have been used in Europe for water treatment for more than 100 years. BF could replace or support other treatment processes, thus providing a robust barrier within a multi-barrier system and also decreases the cost of water treatment. ARR can be applied in an area when local geological conditions or water quality is not suitable for BF system (Sharma and Amy 2010). Soil aquifer treatment (SAT) is an attractive NTS for multiple contaminant removal which, in combination with other available wastewater treatment technologies, can produce effluent of acceptable quality for indirect potable reuse. SAT technology can be applied to augment water supply in arid and semi arid regions of the world where groundwater resources have been over exploited. It is equally attractive for developed as well as developing countries as it is robust, removes multiple contaminants, is environment-friendly, and minimizes the use of chemicals and energy. Implementation of SAT ensures sustainability of both surface water and groundwater sources within the context of integrated water resources management.

Constructed wetlands (CW) and waste stabilization ponds (WSP) systems could be employed for wastewater treatment and reuse and at the same time provide important ancillary benefits such as habitat provision and urban greening. Additionally, reuse is not only limited to the water phase (effluent), but also includes nutrient recycling via the appropriate use of biomass (algae, plants) grown in these systems (Rousseau and Lesage 2006; Kumar...
PRE-/POST-TREATMENT AND HYBRID SYSTEMS

The performance of NTSs in removing different contaminants depend on source water quality, local hydrogeological and climatic conditions, and process conditions applied. Depending upon the influent water quality and intended use of the "treated water" from these NTSs, some pre-treatment or post-treatment may be required to reduce clogging and to ensure sufficient removal of all critical pollutants (that were either originally present in the source water or introduced during the soil passage) to meet the guideline values and prevailing (local) water quality standards. Pre-treatment and post-treatment thus form an integral part of the NTSs.

Previous studies have shown that sedimentation, roughing filtration and coagulation pre-treatment enhance the performance of NTSs like ARR and SAT significantly (Schultz 2008; Sharma et al. 2011; Abel 2014). Furthermore combining different NTSs leading to a synergetic "hybrid system" is another attractive option to achieve the water quality objectives and treatment goals. For example, CW could serve as pre-treatment for SAT system by reducing the nutrient load and partially removing some of the organic micropollutants. Figure 2 presents an example of the removal of selected pharmaceutically active compounds in CW, SAT and CW+SAT hybrid system (Tsehaye 2012).
CONCLUSION

NTSs have high potential in water treatment, wastewater treatment and water reuse applications in developed as well as developing countries. They are robust, cost effective and environment-friendly; however these systems need to be adapted to local conditions and water quality requirements for different uses and appropriate pre- and post-treatment system should be provided, if necessary.

REFERENCES


An insight into the nitrate flushing dynamics from a forested catchment

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INTRODUCTION
The understanding of how hydrological conditions trigger flushing of labile nutrients on a catchment scale is still rather poor, especially when we move from the timescale of seasonal variability towards the timescale of a single hydrological event. The main differences in the explanation of the hydrologically driven export of nitrate found in the literature are not necessarily contradictory as they can be ascribed to discrepancies in basic hydrological and climatological conditions, topography, forest soil characteristics and biogeochemical behaviour of forest ecosystems (Cirmo and McDonnell 1997; Aber et al. 2002; Rusjan et al. 2008). The inability to obtain an insight into the interactions between the hydrological and biogeochemical states, which control the nitrate flushing mechanisms, lies in the complexity of event-scale hydro-biogeochemical observations.

Our study presents an investigation of interacting seasonal and hydrological conditions which strongly influence the export of nitrate from a forested catchment in the SW part of Slovenia. The continuous high-frequency measurements of streamwater nitrate concentration in the periods of hydrological events in different seasons provided the ability to study the nitrate export behaviour predefined by seasonal meteorological settings and conditioned by the hydrological events observed.

STUDY AREA AND METHODS
The Padež stream catchment is situated in the southwestern part of Slovenia and comprises 42.1 km² (Fig. 1). The hydrological response of the catchment is fast, which is reflected in the flushing, almost torrential regime of the Padež stream. For most of the year, stream water is present only in the Padež stream and its major tributary, the Suhorka stream, other smaller streams in the catchment being intermittent.

The monitoring system at the Padež catchment is shown in Fig. 1. Precipitation data were obtained from tipping bucket rain gauges located within the Padež catchment; the meteorological data were gathered from the automatic meteorological station positioned in the middle of the catchment (Fig. 1). The water level was recorded continuously with a 5-minute time step in four locations using a 1-D Doppler instrument with an integrated logger. Flow was gauged on stream sections equipped with limnigraphs using two instruments. During low flow conditions, a salt-dilution flowmeter was used, whereas during middle to high flows, a 2D/3D handheld Doppler velocimeter was used. Stream chemistry was measured continuously on a 30-minute time step using a water quality multi-parameter data sonde. The multi-parameter sonde is designed for on-site and flow-through applications and measures water chemistry parameters simultaneously (Brilly et al. 2006). The multiple parameters include: nitrate, temperature, electrical conductivity, depth, dissolved oxygen, Total Dissolved Solids (TDS), Oxidation Reduction Potential (ORP) and pH. Additionally, grab water samples were taken occasionally from January to November 2006 at the site where the multi-
A multi-parameter sonde was installed for laboratory analysis in order to control the multi-parameter sonde readings.

![Figure 1. The Padež stream catchment and the monitoring system.](image)

Observed nitrate flushing dynamics was modelled by implementing the well-known regression tree induction algorithm M5 within the software package WEKA (Wang and Witten 1997; Witten and Frank 2005). The attribute selection considered in the data mining applications should be based on the domain knowledge of the modelled processes. There were 16 attributes that were included into the regression tree construction describing the antecedent meteorological and hydrological state of the catchment (Rusjan and Mikoš 2008).

**RESULTS AND DISCUSSION**

The size of the generated regression trees depends on the predefined number of instances that reach a tree leaf as a pruning factor. The performances of the regression trees in predicting the streamwater nitrate concentration expressed through RMSE and correlation coefficient $r$ were obtained through a 10-fold cross validation.

The measured streamwater nitrate concentrations vs. streamwater nitrate concentrations predicted by the regression tree model are shown in Fig. 2. The regression tree model successfully predicts low to medium nitrate concentration (1 mg/l-N to 4 mg/l-N). The accuracy of the model prediction decreases with an increase in the streamwater nitrate concentration. The regression tree model RT125 with 10 leaves is not adaptable enough to be able to more accurately predict high streamwater nitrate concentrations (above 5 mg/l-N concentrations) which occur only during short periods of hydrograph peaks. Furthermore, the model does not predict nitrate concentrations above 9 mg/l-N, while the measured concentrations during the November hydrograph peak discharges rose to 14 mg/l-N. The performance measures for the two selected regression trees are: in the case of a regression tree with 100 instances in leaves RMSE = 0.97 mg/l-N and $r = 0.92$; in the case of 125 instance regression tree RMSE = 1.02 mg/l-N and $r = 0.91$. 

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CONCLUSION

The results of the measurements show that seasonal hydrological and biogeochemical conditions play an important role in controlling the size of the forest soil nitrate pool which is available for further mobilization by hydrological mechanisms. Regression trees proved to be a powerful and useful data mining tool in extracting additional knowledge from a given database, which helps to review and improve the existent domain knowledge about the mutual seasonal and hydrological controls of the streamwater nitrate pulses. The regression tree model recognized the hydrological and seasonal patterns which lead the forested catchment from the states of being nitrate source limited (early spring hydrographs in March and April), in excess of hydrological mobilizing mechanisms, to the states when the availability of the hydrological mechanisms was exceeded by the size of the accumulated nitrate in the forested catchment (late spring, summer hydrographs and especially the autumn hydrograph).

ACKNOWLEDGEMENTS

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REFERENCES


Analysis of observed and modelled nutrient concentrations in Europe

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INTRODUCTION

Eutrophication of inland and coastal waters caused by excess leaching of nutrients from land or from other sources such as waste water treatment plants, rural households and industries is a major issue in many parts of Europe. Many of Europe’s rivers flow through several countries adding a transboundary dimension to the problem.

Numerical models are frequently for hydrological and water quality assessments but are mainly set up on the local catchment, or at most, national scale. Recent increased availability of open data which can be used for model input has facilitated the emergence of continental scale, multi-basin models with a relatively fine spatial resolution. E-HYPE, a hydrological model application which includes nutrient calculations, is such an example.

Observed data of nitrogen (N) and phosphorus (P) concentrations in water bodies are routinely collected in monitoring programmes across Europe. These data provide a good basis for model calibration and evaluation, and can also be used to detect water quality trends which may be a result of for example shifts in agricultural practices or measures carried out in a river basin.

We investigate the ability of the E-HYPE model to replicate the spatial and temporal variations found in observed time-series of N and P concentrations. Moreover, the monitoring data from several national data bases are examined to detect temporal trends across Europe.

METHODS

Set-up and calibration of the E-HYPE model

E-HYPE is the application of the hydrological HYPE model (Lindström et al. 2010) for Europe. Both hydrology and water quality (nitrogen and phosphorus) are simulated in the model application which have a mean sub-basin area of approximately 250 km². HYPE is a dynamic process-based model using gridded temperature and precipitation as forcing data. All other input data is static, for example land use data and point source information. All model input are derived from open data sources.

The model base calibration was carried out in a step-wise manner following the methodology described in Strömqvist et al. (2012) for a national model of Sweden. In this method, a relatively small number of representative gauged basins are used for calibration, saving the vast majority of observational sites for evaluation. To make more use of the information contained in the observed data, an additional calibration step was added in which retention parameters for large lakes were individually tuned. This step also included the use of regionally adjustment parameters after the initial calibration.
Analysis of observed riverine nutrient data

A database of over 500 water quality observation (Figure 1) points across Europe was collected from national and regional authorities and the GEMSwater database. As well as in calibration and validation, the data set was used together with simulated discharges to examine the spatial and temporal trends in nutrient concentrations across Europe.

![Figure 1](image.png)

**Figure 1.** Sites with measured time-series of nitrogen or phosphorus concentration data used in the analysis.

RESULTS AND DISCUSSION

There is a large uncertainty in many of the data sets and the assumptions used in the model set-up, for example the estimates of point sources. However, an evaluation of model performance at some measurement sites in Europe (Figure 2) show that mean concentration levels are generally well simulated, especially nitrogen. Phosphorus levels are less well predicted which is expected as the variability of P concentrations in both time and space are higher. Figure 3 shows an example model output, in this case the spatial variability in N concentration in rivers across Europe. Such results can be used to further our understanding of nutrient issues across the European continent. Here, observed concentrations of inorganic nitrogen (IN) are compared with simulated total N to verify spatial patterns from the model and the relative importance of IN in different regions. The results indicate the need for more observations in those regions with estimated highest IN concentrations, and the contribution of organic nitrogen to Scandinavian surface waters where the observed IN values are consistently lower than the simulated TN.

The results from such a large scale application may be used for decision support at international, nation or regional scales. A special tool, eEUTCON, for visualization, source apportionment and scenario analysis which is based on E-HYPE simulation results has been developed for this purpose (http://eutrophication.eu/). Previous HYPE model applications have also been used to assess the effects that various nutrient mitigation strategies have on nutrient transport to the sea (Arheimer et al. 2012) and on coastal waters (Arheimer et al. 2015).

Trends in nutrient concentrations are found in many of the observational data sets in Europe. These trends may be a result of improved waste water treatment or shifts in agricultural practices, but may also, partly or fully, be explained by weather-driven variability. The simulated nutrient concentrations from E-HYPE may be used to estimate and filter out the weather-driven variability in the observations, for example by using the method proposed by
Grimvall et al. (2014). This will aid the assessments of the effectiveness of mitigation measures in Europe.

![Figure 2. Scatter plots of modelled versus observed mean total nitrogen and total phosphorus concentrations](image)

![Figure 3. Modelled mean concentration of total nitrogen compared to observed mean inorganic nitrogen concentrations (circles)](image)

**REFERENCES**


Evaluation of advanced wastewater treatment: a multidisciplinary approach

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INTRODUCTION

Water quality is significantly affected by the presence of chemical pollutants and pathogens. Micropollutants such as pharmaceuticals and biocides are occurring in the µg/L- and sub-µg/L-level. They have been detected in effluents of wastewater treatment plants (WWTPs), rivers, streams and in some cases even in drinking water (Richardson and Ternes, 2014). It can be assumed that thousands of chemicals are entering the sewer systems. This number is further increased by the conversion of micropollutants to transformation products (TPs) (Helbing et al., 2010). A multitude of TPs is formed during biological wastewater treatment as well as during processes such as UV-irradiation, ozonation and disinfection via chlorine. Furthermore, an elevated number of microorganisms and viruses are discharged by WWTPs into rivers and streams. Thus, surface water receives a very complex mixture of pathogens as well as organic and inorganic chemicals featuring an extremely high variety of physicochemical properties such as polarity, sorption affinity, biodegradability, reactivity or UV-stability.

The presentation will summarize the final overall results of the German BMBF-project TransRisk regarding i) multidisciplinary evaluation of the treated wastewater (hazard assessment), ii) technical solutions to reduce the impacts on humans and biota and iii) prevention of pollution by communication strategies to involve stakeholders, decision makers as well as the general public.
RESULTS AND CONCLUSIONS

Water quality (hazard assessment)

Within TransRisk, an innovative strategy was developed linking (eco)toxicological, microbiological and chemical approaches for the characterization of hazards associated with the presence and effects of organic micropollutants and pathogenic bacteria in water. This approach comprises the a) elimination of process related chemical and microbial indicator substances (treatment efficiency of processes) as well as the identification of effect based ecotoxicological end points, b) elimination of toxic indicator substances and pathogens c) avoidance of TP formation and improvement of TP dissipation, d) reduction of effects identified via in vitro assays for endocrine interferences, genotoxicity and mutagenicity, e) reduction of ecotoxicological effects in selected organisms via in vivo studies (e.g. Daphnia magna, Gammarus fossarum, Lemna minor, Lumbriculus variegatus, Potamopyrgus antipodarum), f) avoidance of micropollutant-induced selection processes leading to the formation of pathogenic factors (virulence, resistance) and g) implementation of computational approaches such as molecule dynamic (MD) simulations for a preliminary assessment of potential toxicological effects of the TPs formed within the water cycle.

Technology approaches (risk mitigation)

For improving the water quality of WWTP effluents conventional biological treatment is combined with ozonation/biofiltration or ozonation/granular activated carbon (GAC) filtration. All these processes were operated in parallel and were fed with the same wastewater to enable a direct comparison. In addition, the application of iron-manganese alloys were tested as biofilm carrier material applied for potential WWTP post treatment step to achieve an enhanced removal of micropollutants.

The results of the TransRisk project clearly showed that conventional biological wastewater treatment is not capable of completely/significantly removing most of the micropollutants (e.g. virostatics, antibiotics, psycho active drugs, biocides) as well as pathogens investigated. Furthermore, in vitro assays as well as applied in vivo test systems revealed adverse effects of conventional treated wastewater. Post-treatment of the WWTP effluent by O3/GAC or O3/biofilter most of the effects observed disappeared or were significantly reduced. However, some TPs formed either during biological treatment or ozonation (0.7-1.0 gO3/gDOC) were still present in the effluents of the biofilters and in some cases even after passing the GAC filters. For instance, tramadol-N-oxide was removed by the GAC filter but was passing the biofilter, while COFA (ozonation TP of carboxy-acyclovir) was not removed at all. Ozonation was able to remove opportunistic bacteria (e.g. enterococci by 2 orders of magnitude), while the number of clinical relevant antibiotic-resistant genes (ARGs) was not significantly reduced (e.g. ampicillin resistance gene). Within the surviving population after ozonation some ARGs were found to be present with a higher relative abundancy (e.g. vancomycin and imipenem resistance gene), indicate a selective process due to an increased robustness against ozone. However, the post-treatment via GAC filter or biofilter led to a significant reduction of the number of microorganisms with antibiotic-resistant genes. The pilot-scale biofilters filled with manganese oxides and manganese-iron alloys exhibited a partly elimination (>30%) of 9 from 16 detected micropollutants

Communication strategies

The developed approaches for the communication of risks were applied on a regional scale in the Danube Reed area in the south of Germany as well as on national scale. The general public was divided into different groups according to the life style concept. The evaluation of the questionnaire clearly showed an information and communication deficit about the
relevance of pharmaceutical in the aquatic environment. About 50% of the German population (2,000 persons) contacted had never heard from the occurrence of pharmaceuticals in surface or drinking water and roughly 47% still dispose of their expired liquid medicines more or less often via the toilet leading to elevated loads in the sewer. The multidisciplinary evaluation of the treated wastewater and the development of technical solutions to reduce the impacts on humans and biota were found to be an excellent example to develop strategies to solve these problems by including students and the public as it has a direct and authentic link to the todays living and working experiences. In addition, it is crucial for future generations and relevant on local and global scale.

REFERENCES
Priority and Emerging Organic Micropollutants in the Aquatic Environment of Northern Greece

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Pollution of surface waters with organic micropollutants poses a challenge to water protection. The European Water Framework Directive 2000/60/EC (WFD) set up environmental objectives to achieve “good water status” for all European waters by 2015 and established a clear framework to enable these objectives to be achieved (EC 2000). WFD initially introduced a list of 33 priority substances, which had to be monitored by member states. This list was accompanied with defined environmental quality standards (EQS) for these compounds in the Directive 2008/105/EC (EC 2008). Recently, the Directive 2013/39/EC amending previous directives, introduces additional priority substances and their respective EQS values (EC 2013). Moreover, there is also concern for other hazardous chemical compounds that could occur in the aquatic environment (EC 2006). For this reason, specific pollutants have to be identified in surface waters that may be released from certain pollution sources and activities taking place in the examined area. In this context, member states are required to identify chemical pollutants of significance in the water bodies, to establish emission control measures and to achieve quality standards.

In this article, the occurrence and fate of various organic micropollutants in the aquatic environment of northern Greece are presented. Results obtained from various studies on the occurrence and fate of endocrine disrupting compounds during wastewater treatment (Pothitou and Voutsa 2008), their presence and distribution in main rivers and tributaries (Arditsoglou and Voutsa 2008a, 2010; Terzopoulou et al. 2015a) as well as in coastal waters and aquatic organisms (Arditsoglou and Voutsa 2012; Nödler et al. 2013; Nödler et al. 2014). Moreover, the use of passive sampling as a tool for selection and monitoring of the most relevant micropollutants in aquatic environment was studied (Arditsoglou and Voutsa 2008b; Terzopoulou and Voutsa 2014, 2015b).

A complementary approach by active (collection of grab water samples) and passive sampling (exposure of POCIS and SPMDs) was used to assess hydrophilic and hydrophobic organic micropollutants (various classes of pesticides, PCBs, PAHs, pharmaceuticals) in the basin of transboundary Strymonas river, northern Greece. Pesticides were the most frequently detected compounds (Table 1). Moreover, compounds that have been banned in Europe such as atrazine, dichlorprop and methiocarb were also detected. Temporal and spatial variation was observed, with higher concentrations at the periods of high rainfall intensity and/or low flow-rate at sites that are mainly affected by agricultural and urban activities.

A study that was conducted in the coastal area of the Thermaikos Gulf, in the northern Aegean Sea, revealed the presence of phenolic EDCs, mainly nonylphenol and its ethoxylates, octylphenol and bisphenol in all water types (rivers, streams,
canals) and wastewaters (urban and industrial) discharged into the sea. These compounds were also determined in all marine compartments (seawater, suspended particles, sediments). Moreover, other polar compounds such as pharmaceuticals, biocides, stimulants and corrosion inhibitors were also detected in the coastal environment (Table 2).

**Table 1.** Concentration (μg/L) and detection frequency of organic micropollutants in inland water—case study: basin of Strymonas river, northern Greece (Terzopoulou et al. 2015a, b).

<table>
<thead>
<tr>
<th></th>
<th>June-July 2013</th>
<th>August-September 2013</th>
<th>October-November 2013</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Median</td>
<td>FR*</td>
<td>Median</td>
</tr>
<tr>
<td>Alachlor</td>
<td>&lt;LOQ</td>
<td>36.4</td>
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</tr>
<tr>
<td>Aminocarb</td>
<td>&lt;LOQ</td>
<td>27.3</td>
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<td>&lt;LOQ</td>
</tr>
<tr>
<td>1,2-Benzanthracene</td>
<td>0.10</td>
<td>100</td>
<td>0.04</td>
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<tr>
<td>Bisphenol A</td>
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<td>&lt;LOQ</td>
</tr>
<tr>
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<td>&lt;LOQ</td>
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<td>&lt;LOQ</td>
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<tr>
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<td>&lt;LOQ</td>
</tr>
<tr>
<td>Isoproturon</td>
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<td>0.75</td>
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<td>Metolachlor</td>
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<td>&lt;LOQ</td>
</tr>
<tr>
<td>Salicylic acid</td>
<td>&lt;LOQ</td>
<td>18.2</td>
<td>1.41</td>
</tr>
</tbody>
</table>

*FR: percentage (%) of samples with concentrations ≥LOQ*

**Table 2.** Concentration (μg/L) and detection frequency of organic micropollutants in coastal water—case study: northern Aegean Sea (Nödler et al. 2013, 2014)
Priority and emerging micropollutants have been detected in inland and coastal waters in northern Greece possible due to sewage effluents, industrial wastewaters and agricultural practices. These results are comparable with data from similar water bodies in Europe. Phenylurea, diuron, and isoproturon were among the most frequently detected compounds in rivers of 27 European countries (Loos et al. 2009). Similar compounds were also detected in Spain, Portugal and France (Gorga et al. 2014; Palma et al. 2010; Barrek et al. 2009). Although at relatively low concentrations the possible ecotoxicological risk from micropollutants should not be neglected. Thus, actions have to be taken for prevention and reduction of possible pollution sources in the area within the framework of Water Directives.

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Emerging pollutants in surface and waste water of East Ukraine: occurrence, fate and regulation

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INTRODUCTION

Increasing standards of living, economic changes and human population growth lead to the rising use of chemicals in households, industries, agricultures, hospitals, veterinary and aquaculture. During the past 20 years, emerging pollutants such as endocrine disruptors and pharmaceuticals have been detected in surface waters of developed and developing countries and became an issue of international concern. Some of these pollutants were even found in drinking and tap waters, in ground water, marine and ocean waters and aquatic organisms.

Emerging pollutants can be classified in various ways: by chemical properties, mode or route of administration, biological system affected, or therapeutic effects, application, environmental behaviour, etc. Their occurrence in the environment is closely linked to the regional socio-economic profile and policy regulations. The fate of such pollutants is mainly controlled by environmental factors. These assumptions made a base for the research development.

MATERIALS AND METHODS

The research is focusing on the monitoring of endocrine disruptors (alkylphenol ethoxilates and bisphenol A) and pharmaceuticals in water and wastewater of the Kharkiv region, East Ukraine (c.a. 3,000,000 inhabitants). The occurrence and fate of emerging pollutants were studied in natural water and wastewaters, along with socio-economic and regulation issues.

The case study aims at understanding the processes and impacts of environmental and socio-economic determinants on the occurrence, accumulation and distribution of endocrine disruptors (alkylphenol ethoxilates and bisphenol A) (Vystavna 2014) and pharmaceuticals (21 types of widely used drugs) (Vystavna et al. 2012, 2013) in urban watercourses of the Kharkiv region, East Ukraine. The research has been based on the previously performed analyses of origin, physical-chemical properties and behaviour of these emerging pollutants (Vystavna 2013). The study has been implemented since 2008 (Vystavna and Diadin 2015) and included three general stages: (i) monitoring of endocrine disruptors and pharmaceuticals in natural waters; (ii) description and analysis of environmental and socio-economic determinants that influence the water chemistry and (iii) evaluation of trace pollutants as environmental and socio-economic indicators (Vystavna et al. 2013). The monitoring of emerging pollutants in natural water implied the combination of passive sampling techniques in order to evaluate various forms of elements, sources, seasonal and spatial variations, accumulation and environmental risks (Vystavna et al. 2012). The drug consumption patterns were modelled in order to find the relation between the water/wastewater quality parameters and medicaments consumption (Vystavna et al. 2012, 2013). Results revealed the temporal and spatial distribution of endocrine disruptors and
pharmaceuticals in rivers of East Ukraine and help to find the relation between the chemicals consumption patterns and their occurrence in the environment.

RESULTS AND DISCUSSION

Among pharmaceuticals, caffeine (CAF), diclofenac (DICLO) and carbamazepine (CBZ) were detected in all sampling sites in rivers of the study region. The concentration of these and other target compounds showed the tendency: CAF > paracetamol (PARA) ≥ DICLO > CBZ. There were several additional target compounds of psychiatric (diazepam (DZP), amitriptyline (AMI) and fluoxetine (FLUOX)) and anti-inflammatory (ketoprofen (KETO), nordiazepam (NAP)) drugs found in the sampling sites within the urban area. The range of concentrations downstream the municipal wastewater discharge represented the following order: CBZ > DICLO > CAF > ketoprofen KETO > NAP ≥ AMI ≥ DZP > PARA > FLUOX. The labile compounds (CAF and PARA) were dominant in upstream sites, and persistent compound CBZ - downstream the treated wastewater discharge. The prescribed psychiatric drugs (NAP, FLUOX and DZP) were detected in the river only downstream the treated wastewater discharge point. The consumption of these medicaments is strongly regulated by the government, and their occurrence in natural waters is caused with discharges of effluents from hospitals and medical institutions treated together with domestic wastewaters.

Phenolic compounds (AKPs) from so-called endocrine disruptors groups, i.e. 4-tert-octylphenol (4OP), 4-nonylphenol (4NP), nonylphenol-ethoxy acetic acid (NP1EC), nonylphenol monoethoxylate (NP1EO) and diethoxylate (NP2EO), bisphenol A (BPA) were sampled and detected in the studied rivers. AKPs are entering the environment with industrial and domestic wastewaters, run-off from the residential, industrial areas, and landfills. The highest concentration values were found for NP1EC and the lowest - for 4OP. Comparison of the AKP accumulation levels detected in our study and published data has shown that presence of nonylphenols in Ukrainian rivers are more than 10 times higher than in Europe but close to values detected in the natural water of the USA. Such difference can be explained by both environmental (natural dilution and water hydro- and biochemistry) and socio-economic determinants (population density, economic activity, water and wastewater management). The spatial variation of estimated time-weighted average concentrations of phenolic compounds revealed different patterns in upstream and downstream sections of watercourses. Phenolic metabolites ratio BPA/4NP calculated for tracing municipal and industrial wastewaters was significantly higher in upstream parts than in downstream parts of the Udy and Lopan rivers.

Further research will focus on the monitoring and control of emerging pollutants in wastewaters and their removal at the constructed wetlands (Vergeles et al. 2015) in order to assess the efficiency of such ecological technology for improving surface water quality, wastewater management and thus enhancement of water and food security.

The case study is financed within the scope of the UNESCO International Hydrological Programme “Emerging pollutants in wastewater reuse in developing countries” (2014 – 2017).

REFERENCES


Water and Sanitation Safety Planning in Rural Areas of the European Region

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BACKGROUND

Public health, safe water supply and safe sanitation are very much interrelated and are neglected or underestimated in their relevance, particularly in rural communities. Better protection and management of drinking water sources and sanitation facilities are possible, if weaknesses and strengths are identified. To identify possible sources of hazards and risks, it is essential to have knowledge of an adequate quality of water and sanitation, pathways of contamination and the associated risks, as well as the prevention of risks. A water and sanitation safety plan (WSSP) can be one way to obtain and maintain safe drinking water and sanitation systems and to minimise related diseases. The adequate management of a safe drinking water supply system as well as small sanitation systems, whether it is on a small or large scale, concerns many stakeholders who have to be involved in the planning.

METHODOLOGY

The WSSP methodology is based on the Water Safety Plan (WSP) developed by the World Health Organization (WHO). It was first adapted by WECF to local rural conditions in small communities of Eastern Europe and the Caucasus. WSP programmes have been carried out in eight countries of the region in the last years. Some stakeholders requested to provide them with more background information. In addition, the issue of sanitation turned out to be often neglected, although it is of special importance for public health in rural communities as well. The present compendium is thus a consistent further development based on practical experiences.

The WSSP Compendium aims at enabling communities to develop a WSSP for small-scale water supplies, e.g. dug wells, boreholes, springs and piped centralised water supply systems, and at assessing the quality of sanitation facilities such as school toilets. It has been funded by the German Environment Foundation DBU.

The Water & Sanitation Safety Plan (WSSP) compendium consists of three parts:

Part A (How to accomplish a water and sanitation safety plan?) consists of 8 modules, explaining the approach of developing water and sanitation safety plans (WSSP) for small-scale water supplies, and provides basic and practical guidance for developing a WSSP. Two modules focus mainly on WSSP for non-piped water supplies and on small-scale piped distribution systems. Furthermore this part introduces the practical activities in 10 steps to be carried out by a WSSP team and leading to a local WSSP. Examples on the various types of practical activities performed are given, such as risk assessments of water supply or toilets and interviews of different stakeholders. The information collected is subsequently processed and results are provided.

Part B (Background information for developing WSSP) consists of 8 modules, providing

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*“Water Quality in Europe: Challenges and Best Practice”
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technical and regulatory information, e.g. on possible drinking water sources, water treatment and distribution, sanitation and wastewater treatment, water protection and water quality, management of storm water and water-related regulations.

Part C (How to involve schools?) consists of 6 modules, and is an additional part, especially intended for youth and schools. It includes theoretical lessons on general water issues such as the water cycle, and also specific information on school sanitation, water and hygiene. The development of a WSSP is explained especially in terms of involving pupils and citizens. Exercises and suggestions for practical and interactive actions in combination with the tool box are detailed.

The main target groups of part A and B are local authorities and water operators, but also teachers and NGOs while Part C mainly targets teachers, but also youth group leaders and NGOs.

RESULTS
The compendium was firstly applied in rural areas of the Republic of Macedonia and Romania in 2014 and 2015. The activities were as follows:

- Training on how to implement the project and about the development of WSSP
- Measuring the nitrate concentration in groundwater by simple tests and recording seasonal fluctuations and evaluating local public drinking water for contamination by total coliforms and Escherichia coli, with the help of certified laboratories
- Detecting and identifying possible sources of contamination of drinking water, groundwater and health hazards
- Identifying drinking water problems while involving schools, experts and authorities
- Presenting the results at local, national and international levels (through seminars, the media and local fairs), publicity work, awareness-raising and planning actions to increase water quality and minimise risks.

The activities lead to very concrete results on a local level and partly on a national level:

- Concrete action plans to incrementally improve the water and sanitation situation in the village
- Raised awareness of local population and students that they can take their own initiative
- Concrete public health risks identified and dealt with
- Raised awareness among local authorities and decision-makers
- Funding for the renovation of sanitation system in schools
- Support of environmental education in schools, including parts of the compendium in the curriculum

REFERENCES

Water quality: new stressors and new ways of understanding some old ones

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INTRODUCTION

The water quality of the rivers and streams in the United Kingdom has improved markedly over the recent decades as a wide range of pressures on river ecology have been reduced. Figure 1 below illustrates some general pressures on fish in UK Rivers and how these have changed over time (Johnson and Sumpter 2014). What this illustrates is how the system is not static and that we must be ready to respond to new threats or threats uncovered by the successful management of a known one. For example we know that pharmaceuticals have been in the environment since at least the 1950s, but any effect on fish populations would be unlikely to be detected while gross organic pollution is overwhelming all other stressors.

![Figure 1. Evidence taken from the historic scientific literature illustrating the harm to fish by different stressors over time. The width of the line is a qualitative assessment of the degree of harm caused (Johnson and Sumpter 2014)](image)

The aim of the presentation is to look at three current issues in water quality and the management implications for the UK and more widely across the whole of Europe: 1) Emerging contaminants (many now well known), 2) Distinguish which are the most important chemical stressors from the mix of those in our rivers 3) How we can use new monitoring systems to help understand better the potential problems of high nutrient concentrations.
EMERGING CONTAMINANTS

This covers a range of compounds that have become apparent in recent years due to our ability to detect them in surface waters. This has also made us more aware of how many products we use in our everyday lives contain compounds that will find their way into surface water through sewage treatment works (primarily). This list includes pharmaceuticals, flame retardants, personal care products, nanoparticles and drugs of abuse amongst others. The loads of many of these compounds are associated with the size of population served by sewage treatment works that discharge into the rivers, which allows for some assessment of the risk of the chemicals reaching rivers. For example Johnson and Williams (2004) provided a model of human excretion for estradiol (E2), estrone (E1) and ethinylestradiol (EE2) which allowed the calculation of concentrations arriving at a sewage treatment works. Combining this with a river flow model and the predicted no effect concentrations (PNEC) estimated from laboratory studies allowed the assessment of risk across England and Wales (Williams et al, 2009). This work was instigated because of observed effects in fish, but the same methods can be used for predicting likely effects for chemical stressors for which there are no measurements or where effects cannot be so readily identified (e.g Dumont et al. 2014 for nano-Ag and nano-Zn). Similarly Johnson et al., (2015) provided estimates of the lengths of river across the European Union that would fail proposed environmental quality standards for EE2 (12%), E2 (1%) and diclofenac (2%). One of the problems with using these methods is estimating emission factors for the compounds and obtaining parameters for environmental degradation along river systems. Recently, Banjac et al. (2015) published a study where they back-calculated emission factors from over 150 compounds measured in the River Llobregat. Spain. They used Monte-Carlo analysis to assess the uncertainty in the emission factors calculated and the main factors that influenced this uncertainty.

WHICH CHEMICALS SHOULD WE PRIORITISE?

With so many chemicals potentially released into river systems we need to try to prioritise actions and assessments for those that are likely to cause harm (Brooks et al., 2013). There have been several attempts to prioritise emerging contaminants. For example Rotsidou and Scrimshaw (2015) recently prioritised household and personal care products based on product use volumes and potential toxicity or where data were scarce. Donnachie et al. (2015) took an alternative approach based on mining data from the literature on actual exposures and ecotoxicological end points for fish. The ranking was based on the degree of separation between the median reported river concentrations and the median effect concentration. This was done initially for metals (Donnachie et al. 2014) and then applied in a wider context to rank pharmaceutical relative to a range of other chemical stressors Donnachie et al. 2015). Whatever the method used, the aim is to make sure that the chemicals likely to cause some kind of significant harm (e.g. population related endpoint) are identified so that scarce resources can be used in the best way.

IDENTIFYING NUTRIENT SOURCES USING HIGH FREQUENCY MEASUREMENTS

Control of plant nutrient inputs, nitrogen (N) and phosphorus (P) is required by the European Union’s Water Framework Directive. These nutrients might come from point or nonpoint sources and understanding individual source contributions through space and time is important for implementing appropriate programmes of measures. Recently high-frequency (hourly) monitoring of a range of chemical constituents, including N and P is allowing a better understanding of the complex loading patterns that occur through storm events. Bowes et al. (2015) used such data to show how the river P concentration was generally dominated by effluent inputs from sewage works and N from groundwater. Superimposed on this was large diffuse sources of P following spring manure applications and re-mobilisation of sewage-
derived P from bed sediments during rainfall events. This research is moving on to investigate high-frequency biological data, such as chlorophyll concentration, photosynthetic stress (both using in-situ sondes) and flow cytometry and pigment analysis (using water samplers) to go alongside the hourly physical and chemical data, to characterise the phytoplankton community and identify thresholds / multiple-stressor controls on each algal group.

Figure 2. Hourly measurements of temperature, conductivity, turbidity, dissolved oxygen and chlorophyll-a (upper panel) and total phosphorus, total dissolved phosphorus and nitrate (lower panel) from a rural tributary of the River Thames, UK

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General Overview of Asian Water Quality and its Strategic Framework for improved Monitoring Systems

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WATER QUALITY ISSUES IN ASIA

Water quality degradation in Asian Regions is a major issue which should be improved through effective water quality monitoring. This issue can be subdivided into three categories (a) Water quality degradation in environmental surface water, which is mainly used as a source for drinking water (b) Water quality degradation of groundwater caused by anthropogenic /natural contaminants and (c) Water pollution of surrounding coastal zones caused by land contaminants.

(a) Degradation in environmental surface water

Environmental water degradation, such as contaminated lakes and rivers, are caused mainly by wastewater from surrounding cities. Rapid increase of a city’s population in catchment causes a significant amount of nutrients and hazardous materials if there is not an adequate wastewater system. Harmful cyanobacterial blooms (CyanoHAB’s) (Paerl et al. 2011) are found in Chinese Lakes (such as Lake Taihu, Xu et al. 2010), which is under appropriate research development. Lake Biwa in Japan, which used to be under a severe threat of CyanoHAB’s, seemed to overcome this problem through significant reduction of wastewater from catchment areas by building a basin-scale sewage system and tertiary wastewater treatment plant in the catchment zone. On the other hand, Lake Biwa is now suffering a different problem caused by macrophytes (such as Egeria Densa, Haga and Ishikawa 2011). Effective skills in water quality monitoring for the lakes and reservoirs, including large scale rivers are developed mainly through numerical modelling, on-site (field) and off-site (satellite remote sensing) observation. Fundamental mechanisms of eutrophication is now studied at CER-Kyoto University; Lake Biwa Environmental Research Institute (LBERI); Lake Biwa Museum (LBM) of Japan; and Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences (NIGL-CAS); with the collaboration of the University of North Carolina and other universities. These surveys focus on identification of critical nutrients, evaluating long-term ecological and economic sustainability of impacted systems for/throughout CyanoHAB’s. At the same time, serious environmental degradation is reported by persistent organic pollutants (POP’s) such as pesticides and chemical fertilizers in the freshwaters of Middle Eastern countries, being a prominent threat to their use and sustainability.

(b) Degradation of groundwater

Water quality degradation of groundwater is mainly caused by anthropogenic /natural contaminants in most cities. Serious contamination induced by arsenic are found in South-Eastern and Southern Asian countries including India. Salinization is also a major issue for Western Asian countries including Bahrain, Kuwait, and Saudi Arabia; where intrusion of seawater, and increase of Na+ Cl- concentration due to high evaporation (evapo-
transpiration) rate. Since de-salinization of seawater is one of the principal means for supplying drinking water for these countries, saline control is a major issue for all water-related activity. At the same time, contamination by POP’s, nutrients, organic carbons, and by disease-causing germs are another major threat for groundwater; especially in largely populated zones. A specific survey of GW contamination through volatile organic compounds has taken place in Japan (Osaka Pref. University). International collaboration of groundwater chemical-physical interaction is being held in Tunisia through the University of Tsukuba. High expertise in groundwater surveys can be assisted by both direct monitoring and numerical modelling. Establishing and visualizing groundwater pathways and identifying major contaminants on land requires a complete survey of underground structures, which is being developed in Japan.

(c) Pollution of surrounding coastal zone

Water pollution of surrounding coastal zones caused by land contaminants. Recently, due to a heavy load of nutrients and hazard chemicals from the land, surrounding coastal zones are under serious threat for water quality degradation. The East China Sea, and Yellow Sea are the main eutrophic estuaries under those loads from land. Identification of nitrogen’s and phosphorus from land are being studied by CAS and Kyoto University. The high-resolution ocean mode, with nutrients near Japan (JCOPE2), is being developed by JAMSTEC, in the collaboration with the University of Tokyo. This model can adopt the requirements of identifying impacts in coastal zones. Seto-inland sea of Japan, once suffered severe eutrophication, but is now being recovered throughout establishing strict nutrient regulation, and promoting water circulation. At the same time, Osaka Bay and Tokyo Bay are still in eutrophic states, and they are under severe degradation of dissolved oxygen concentration. This water quality degradation is mainly caused by wastewater from large cities with secondary treatment (without nutrient removal). Intrusion of hazardous chemicals and radioisotopes are also a serious issue. In 2005 an accident in a chemical factory caused severe pollution by POP’s in the entire Amur River basin, which needs further survey. Near the Fukushima region, serious contamination can still be found by radionuclides, mainly caused by FNDPP accidents (Yamashiki et al. 2014). Estimation and continuous monitoring and modelling (AdhiragaPratama et al. 2015) is being held in Japan.

STRATEGIC SOLUTIONS

For these overall problems, we are now developing (1) Integrated global/regional scale hydrological models to estimate loads and impact on the ocean; (2) A database for freshwater, focusing on lakes & reservoirs (Global Lakes & Reservoir Repository -GLR; and (3) Integration of water quality monitoring through combining field scientific surveys & state-of-the-art technology, including satellite remote sensing.

Acknowledgements

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Addressing water quality challenges towards water security and sustainable development: The work of UNESCO-IHP International Initiative on Water Quality (IIWQ)

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BACKGROUND

Meeting the global water quality challenge is a prerequisite for sustainable development of the present and future generations. Water quality is intrinsically linked with human health, poverty reduction, gender equality, food security, livelihoods and preservation of ecosystems, as well as economic growth and social development of our societies. Each year millions of people die from water-borne diseases such as diarrhea, from which children under five years old are the most affected, due to poor hygiene, unsafe drinking water and lack of sanitation. A very low level, or inexistent, wastewater collection and treatment coverage is a common challenge in most developing countries, in addition to the lack of access to safe drinking water and sanitation for large portions of their populations. Water pollution, resulting from human activities, disturbs aquatic ecosystems not only in structure but also in function, affecting and modifying the integrity of these systems. The major sources of water pollution are lack or inadequate treatment of domestic sewage and inappropriate management and disposal of industrial and agricultural wastewater. In addition, emerging pollutants represent a new and complex aspect of the global water quality challenge faced by developing countries, but also developed countries, because of the potentially high risks they present for human health and the environment. Water quality degradation thus translates directly into environmental, social and economic problems.

More efforts need to be dedicated to promoting scientific research, knowledge dissemination, and the sharing of effective solutions, technologies, policy approaches and best practices to respond to water quality challenges faced globally. Ultimately, these efforts will help ensure water security for sustainable development in the 2030 Agenda and the attainment of the Sustainable Development Goals (SDGs).

Aligned with the 2030 Agenda and SDGs, IHP activities on water quality aim to mitigate effects of human activities on the quality of water resources, prevent and reduce pollution, and protect water quality for sustainable development of the present and future generations.

UNESCO-IHP RESPONSE TO THE GLOBAL WATER QUALITY CHALLENGE

Water Quality in the Seventh Phase of IHP (IHP-VII, 2008-2013)

Water quality was addressed in the Seventh Phase of IHP, with a renewed focus through the dedication for the first time of a specific thematic area - Focal Area 4.1 “Protecting water quality for sustainable livelihoods and poverty reduction”, under Theme 4 “Water and Life-Support Systems”. The Focal Area 4.1 aimed to strengthen and develop the scientific knowledge base on the quality of surface and ground waters to attenuate contamination of
water sources and to protect the quality of current and future water supplies for all their uses. It also contributed to the attainment of the Millennium Development Goals by facilitating the sharing and exchange of effective solutions and best practices on access to safe drinking water and sanitation. UNESCO implemented numerous activities and extra budgetary projects to accomplish IHP-VII’s objectives on Protecting Water Quality for Sustainable Livelihoods and Poverty Alleviation.

Water Quality in the Eighth Phase of IHP (IHP-VIII, 2014-2021)

The significant achievements and effective implementation of a wide range of activities on water quality during IHP-VII have led to a high prioritization on water quality issues in the IHP-VIII phase, bringing water quality to the forefront of IHP priorities. Under the overarching theme “Water Security: Responses to local, regional, and global challenges”, IHP-VIII Strategic Plan emphasizes water quality issues as one of the main themes for UNESCO’s work on water during this 8-year period, designating IHP-VIII Theme 3 particularly on “Addressing water scarcity and quality”.

**Theme 3: Addressing Water Scarcity and Quality**

This Theme focuses on the protection of the world’s freshwater resources to reduce impacts on human well-being and the natural environment to protect the water resources, prevent and reduce pollution, and enhance and restore water quality. The objectives of the Theme include: Strengthening the knowledge base on the quality of the world’s water resources; improving the understanding and management of water quality; integrating quality-quantity management and science-based decision-making, enhancing legal, policy and institutional frameworks for improved water quality management, and promoting new innovative tools for water quality management and pollution control.

**Focal Area 3.4: Addressing Water Quality and Pollution Issues Within an IWRM Framework – Improving Legal, Policy, Institutional, And Human Capacity**

This Focal Area aims at improving the understanding, knowledge, and institutional and regulatory framework on water quality for the sustainable use of water resources. Effective water quality management, in the context of an Integrated Water Resources Management (IWRM), requires an enabling environment in the form of policy, legal and institutional frameworks such as instituting water pollution licensing and enforcement systems for sustainability in order to address water quality and pollution issues. The focal area also focuses on strengthening human and institutional capacities to improve water quality management and pollution control.

**Focal Area 3.5: Promoting Innovative Tools for Safety of Water Supplies and Controlling Pollution**

This Focal Area aims to develop and promote new innovative tools for water quality management and pollution control for sustainable livelihoods as well as promoting joint research on particular water quality issues and challenges through an integrated water pollution management framework. It also aims to foster the sharing and exchange scientific information on water quality challenges. Meeting water quality challenges in a holistic way requires an integrated water pollution control framework to respond to a complexity of issues including sources of contaminants, lack of authority to enforce and difficulty of monitoring.

**UNESCO-IHP INTERNATIONAL INITIATIVE ON WATER QUALITY**

The **International Initiative on Water Quality (IIWQ)** was established in response to the urgent need for global action to improve the quality of the world’s freshwater resources and
to mitigate the continuing degradation of water quality, which is causing serious threats to human health and ecosystems. The IIWQ was officially endorsed by the IHP Intergovernmental Council of UNESCO at its 20th session in 2012 (Resolution XX-4), reflecting the recommendation of the UNESCO workshop “Addressing Water Quality Challenges in Africa”, held in Nairobi, Kenya, in March 2011, and the UNESCO consultation meetings on water quality in other regions in Asia and the Pacific, Middle East, the Americas and Europe.

Key Thematic Areas
The Initiative is implemented in an interdisciplinary, participatory and cooperative manner, characterized by activities and projects of interdisciplinary and trans-sectoral scopes, which focus on specific water quality issues under three key thematic areas:

- Safe drinking water and sanitation
- Water quality management
- Wastewater management and reuse

Each thematic area shares four common objectives to contribute to global efforts on:

- Ensuring access to safe drinking water and sanitation as a human right
- Protecting water quality for human well-being and ecosystem integrity
- Integrating quality-quantity management of water resources towards water security
- Responding to future water quality challenges

Objectives
For the achievement of its main goal, IIWQ activities are entrenched within several specific objectives. These objectives focus on promoting scientific research, knowledge and effective policies, building capacities and enhancing the knowledge base, bringing together science and policy relevant expertise, creating awareness and facilitating the sharing of best practices. Specifically, IIWQ aims at:

- Promoting scientific research, innovation and technologies
- Building the knowledge base and capacity
- Bridging the science-policy interface for science-based policies and strategies
- Creating awareness
- Fostering scientific cooperation and exchange

IIWQ Experts Advisory Group
The IIWQ Experts Advisory Group was established with the aim to provide technical and experts' advice on the state-of-the-art on water quality challenges and priorities, as well as on future directions of IIWQ, and to facilitate scientific exchange and promote collaboration in this area to support IIWQ activities. In addition, it also aims to support countries in the implementation of the 2030 Agenda SDG targets on water quality and wastewater.

The Expert Advisory Group brings together water quality specialists from variety of governmental and non-governmental organizations, research institutions and the academy in different regions, globally. The First Meeting of IIWQ Experts Advisory Group was held in Kyoto in July 2015, which brought together over 20 water quality experts and specialists from all regions of the world.
PROMOTING SCIENTIFIC RESEARCH AND EFFECTIVE POLICIES TO RESPOND TO WATER QUALITY CHALLENGES

UNESCO, through its International Initiative on Water Quality (IIWQ) under IHP, supports Member States in responding to water quality challenges by promoting scientific research, mobilizing and disseminating knowledge, facilitating the sharing and exchange of technological and policy approaches, fostering capacity building, and raising awareness on water quality issues. IHP implements a wide spectrum of activities to protect the world’s freshwater resources and enhance water quality in an interdisciplinary and integrated manner.

REFERENCES
