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DEPARTMENT OF AQUATIC ENVIRONMENTAL ENGINEERING

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THE QUANTITATIVE USE OF PASSIVE SAMPLERS TO UNRAVEL MASS FLOWS OF PESTICIDES IN RIVER CATCHMENTS

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1 MOTIVATION & OBJECTIVES

Pesticides are among the most neglected pressures in the WFD monitoring and pressure analysis in many countries. The reasons are obvious: their monitoring is cumbersome due to the very dynamic occurrence that these substances display in surface waters. Traditional regular time-step sampling is simply not fit to quantify the emission of pesticides from agriculture and other sources. Their occurrence is strongly related to their seasonal use and precipitation events that are able to mobilize the substances via surface run-off mainly. Modelling of pesticide emissions is also rarely used to predict this pressure on surface waters. There is no model that could establish itself as a standard for different scales and successful case-studies are few. In addition to the lack of sufficient monitoring data a major deficit is the availability of reliable data on pesticide use in catchments which is needed as input for the model. Landscape hydrological models also require good skills in hydrological calibration, which can also shy away inexperienced users. The objective of the Wark catchment case-study consisted of setting up a monitoring scheme that would allow for a dynamic characterisation of the immission situation and could serve as a calibration/validation set for a modelling project of the catchment. The monitoring should provide information on the type of sources and the geographical location of the main (diffuse) pesticide emissions. In that respect a combination of monitoring techniques and strategies have been adopted with a strong emphasis on the feasibility of passive sampler use in dynamic emission situations.

2 MONITORING DESIGN

The Wark catchment has a surface of 82 km^2 in a mixed hydrogeological context of Devonian schists (lower eastern catchment) and early Trias red sandstone (western catchment). Soils are mainly stony-loamy cambisols and luvisols. Land use is dominated by agriculture. The Wark has 3 tributaries, the Fel, the Mechelbach and Turelbach. At baseflow in summer the Wark displays a discharge at the mouth of 50 L/s while the tributaries are below 10 L/s.There are four biological treatment plants and a few minor mechanical plants in the catchment with a sum of 7200 population equivalents and a total discharge of 12 L/s. There are several discharge gauges in the catchment but only the one at the outlet is reasonably calibrated and reliable in terms of data availability.

The monitoring strategy relied on a discharge-triggered autosampler at the catchment outlet, close to the gauge, whose purpose was the high resolution sampling of flood wave events during the pesticide application season (see monitoring techniques autosamplers for further details). Data from autosamplers provide the basis for load calculation and can also be used to decipher the flow components in flood waves (through inspection of the chemographs).

Campaign	Aim	Validation strategy	Location(s)	Parameters
Event-triggered autosampler	Capture pesticide runoff in flood waves	Verify pesticide use and runoff behaviour in the catchment on 12 events	Catchment outlet	Pesticides, Anions, o-PO$_4$, NH$_4$, POC, DOC, part. P
Passive Samplers (POCIS) River	Continuous monitoring of pesticide immission concentration	Two-week exposure of POCIS provide mean concentrations to verify mass balances	6 sampling locations in the Wark and tributaries	Pesticides

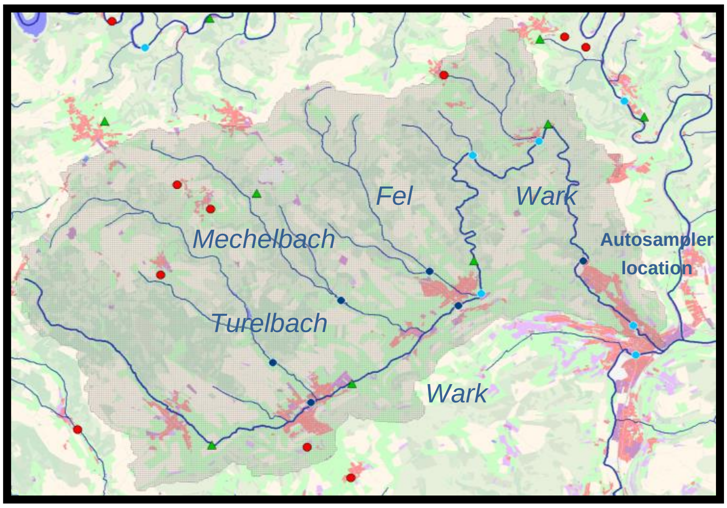


Figure 1: Location of the passive sampler measurement stations (blue dots). The autosampler is at the outlet of the catchment. Agricultural surfaces are coloured in beige.

3 RESULTS OF THE SAMPLING CAMPAIGNS

3.1 Autosampler Warken

The autosampler in Warken has been installed in the second half of March 2011 and operated with a depth probe as trigger to launch a sampling cycle. A total of 17 events have been sampled during 2011 and about half of them were exploitable for pesticide load calculations.. Figure 2 shows the events that were sampled in green as opposed to those where the trigger threshold was too high or did not react for technical reasons. The event on June 1st is depicted in Fig. 3. The graph shows the discharge of the event, conductivity for flow component identification as well as chemographs of the mother substance and a prominent metabolite. Single spot samples are depicted with their concentrations, the number of samples per event ranged between 12 and 24. The chemographs have been fitted with a pulse function in order to allow for a discrete calculation of the event loads ($\sum(Q_iC_i)$, with i being the 15 min discharge measurement step). The event mean concentration (EMC) was accordingly calculated as the average of all fitted C_i. EMCs will serve in the following to calculate non-monitored events with passive sampler data.

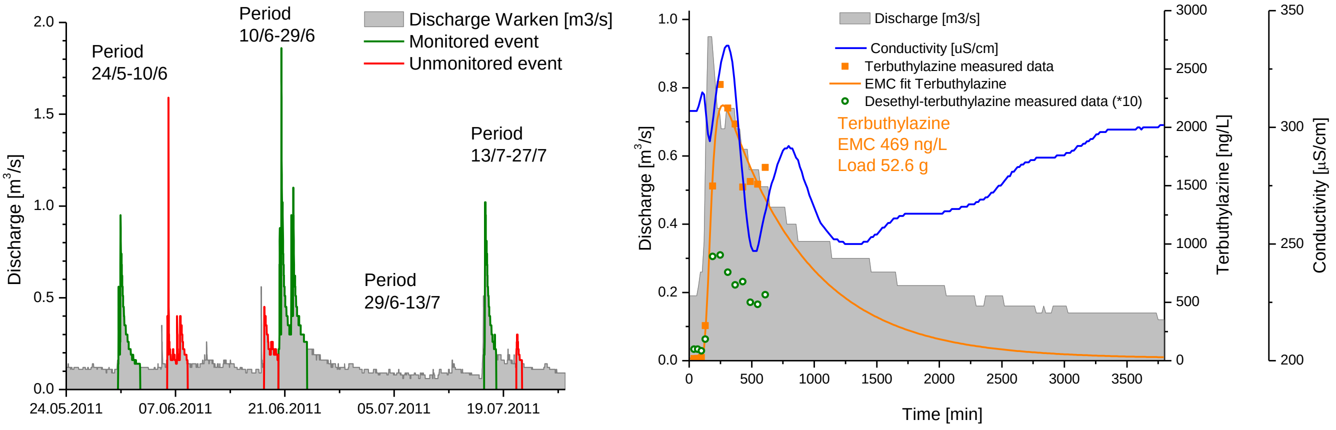


Figure 2 & 3: Suite of events during summer of 2011. Autosampler events in green. Chemograph of the event of June 1st featuring EMC and load.

3.2 POCIS time series

Passive samplers yield average concentrations of a compound during the period of exposure in the monitored water column. Here the focus rests on the quantitative use of passive sampler data in order to calculate loads of pesticide immissions at spatially distributed river monitoring stations. The raw signal of a passive sampler that has been exposed for 2 weeks (as in this study) contains low-flow exposure conditions which are expected to be dominated by groundwater inputs and emissions from WWTPs and whose ambient concentration should be rather constant and at low level. On the other hand the two week period might also feature flood events which at least during the application season should yield high concentrations due to surface runoff of pesticides. Hence the 2 week average gained from a passive sampler extract should indeed reflect the average exposure to a pesticide but does not inform on the peak concentrations during flood events. The information provided by the raw passive sampler data are shown in the series of 2 week averages from May to November 2011 on the Warken sampling site (Fig.4). The representation is logarithmic because of the strong differences in pesticide concentrations. The periods of use and subsequent emission of pesticides is clearly visible for terbuthylazine a soil effective herbicides in maize that are applied in June and obviously also after harvest and whose emissions are decaying hereafter. For comparison carbamazepine a recalcitrant drug has been depicted to show the steadiness of WWTP contribution. Passive samplers are ideal to continuously cover the immission situation in surface waters although their performance is limited to substances that are retained by the resin. Sulcotrione for instance, a prominent herbicide in maize in Luxembourg, which has been detected by the autosamplers is not detectable in passive samplers.

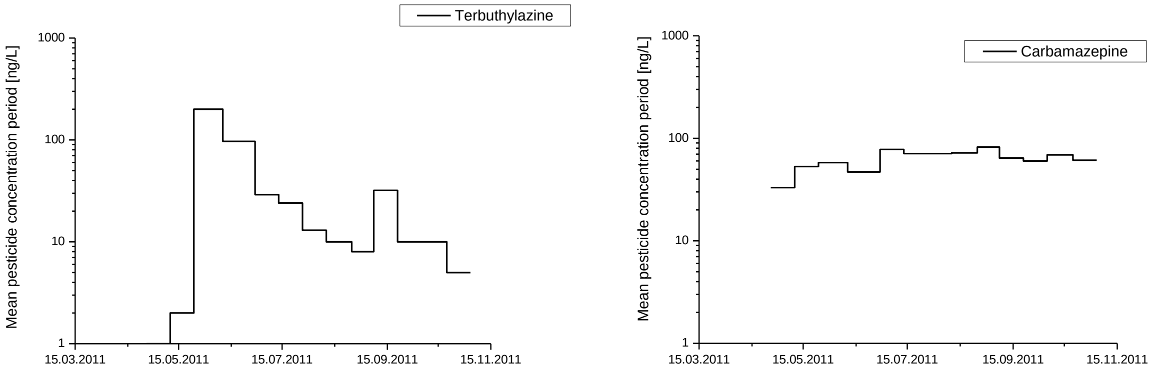
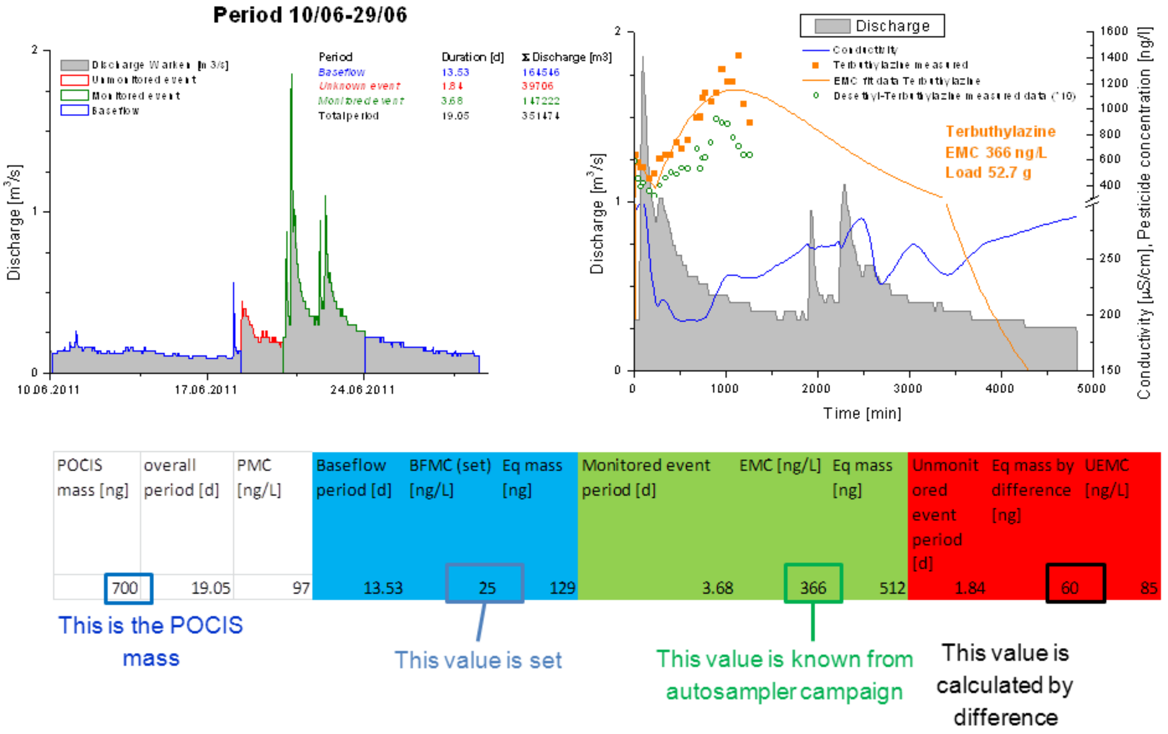


Figure 4: Fourteen day time weighted averages for terbuthylazine and carbamazepine (pharmaceutical) in 2011 in Warken.

4 EMC calculations

Passive samplers can be quantitatively exploited if a few assumptions hold. The most important is that passive samplers conserve the compounds the have accumulated during a high concentration exposure period like a flood waves during following low-concentration phases. The second is that the sampling rate of a passive sampler is identical in a flood-wave than in a low-flow situation. For details on this discussion please refer to the monitoring techniques chapter on passive samplers in the reference at the end of this paper. Based on these assumptions passive sampling is time proportional and the accumulated mass of a compound can be distributed as a function of the duration of the different periods within a sampling exposure time. In Warken, the data from the autosampler allow for a verification of this principle as event mean concentrations are available and the length of the event is known. Figure 5 shows the principle of the calculation: first the length of the base flow and the events are determined. One big event on June 21st has been covered by the autosampler but the smaller event before did not trigger a sampling. The mass of compound recovered from the POCIS is known, the base flow concentration needs to be set according to grab samples that have been taking during low-flow in that period and the EMC of the second flood event is known from the autosampler campaign. Base flow and monitored event concentrations are transformed to accumulated masses with the respective lengths of period and the sampling rate R_S for the substance. The mass for the uncovered event is then calculated by difference and transformed to an EMC with the length of the event and the R_S.

This exercise can be repeated for every period leading to a complete series of EMCs for every relevant flood event. The calculation of loads is then made by multiplying the EMC by the event's discharge sum. This is not as straightforward as it sounds since very steep concentration peaks coinciding with flashy discharge can lead to underestimation of the real load with an event-based method. Comparing discrete load sums vs. event load calculations for the year 2011, the event load was underestimated by 35 % on June 1st while June 21st and July 18th showed no difference between both calculation methods. This applied for all substances which lead to the conclusion that the causes are purely hydrological.



POCIS mass [ng]	overall period [d]	PMC [ng/L]	Baseflow period [d]	BFMC (set) [ng/L]	Eq mass [ng]	Monitored event period [d]	EMC [ng/L]	Eq mass [ng]	Unmonitored event period [d]	Eq mass by difference [ng]	UEMC [ng/L]
700	19.05	97	13.53	25	129	3.68	366	512	1.84	60	85

This is the POCIS mass

This value is set

This value is known from autosampler campaign

This value is calculated by difference

Figure 5: Schematic display on how the mass collected by the passive sampler is distributed among periods.

The same procedure is possible for those passive samplers where no autosampler data can assist in unravelling the distribution of the accumulated mass between flood events. Here, another assumption helps extrapolating the observations from the catchment outlet station of Warken to all other measurement stations. It states that the relationship between the pesticide masses mobilized in the events is purely hydrologically driven and that this ratio can be extrapolated to all stations. Hence the overall absolute pesticide mass contained in a passive sampler is variable from one station to another taking into account the emissions in each sub-catchment but the ratio of the emitted masses between events of one period is determined in Warken with the autosampler data and fixed throughout the whole catchment. Fig 6. identifies the sources of terbuthylazine in the Wark river basin: the largest load originates from the Mertzig region.

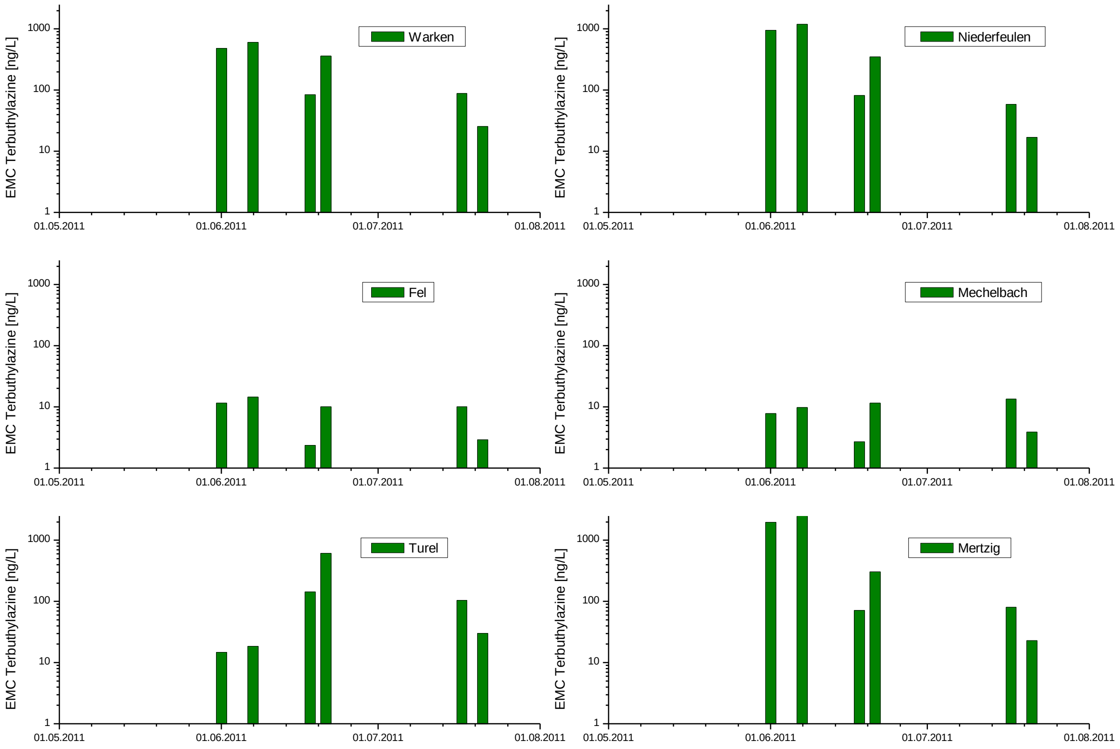


Figure 6: Event mean concentration for the passive sampler stations throughout the river basin.

5 CONCLUSIONS

The case-study on the Wark aimed at providing quantitative load data with advanced spatial resolution for modelling purposes based on the combined use of auto- and passive samplers. The concept worked out very well and could be validated for several substances including terbuthylazine, flufenacet and s-metolachlor. Compounds that are not retained by passive samplers and hence relying only on autosampler data had much more restricted data on their behaviour (insufficient temporal coverage) and source identification.

6 REFERENCES

This Contribution is a shortened text of the book published at the end of the LIFE+ M3 project (contract LIFE07 ENV/L/000540); http://www.life-m3.eu/fileadmin/M3-life/downloads/Book.pdf

EMISSIONS OF BIOCIDES TO THE AQUATIC ENVIRONMENT

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1 BACKGROUND

Sustainable urban storm water management and proactive water protection both require clarification to what kind and which extent micropollutants end up in storm water runoff from urban sources and what ecotoxicological effects are to be expected. The transfer pathways of pollutants from urban areas into wastewater treatment plant effluents and natural water bodies demonstrates the challenge for sustainable water management (Fig. 1).

In fact, heavy metals emitted by traffic or pesticides applied for non-agricultural purposes are known for their widespread occurrence in aquatic systems. Hundreds of biocides regulated under the EU Biocidal Products Regulation (BPR, 528/2013) are used as antimicrobial active substances in 23 product types. Biocides may enter the aquatic environment and are frequently detected in surface or ground water. For example, in Switzerland organic biocides such as diuron, carbendazim, mecoprop, and Irgarol are found (Balsiger et al. 2007, Burkhardt et al. 2011, Wittmer et al. 2011). The substance Irgarol was detected in small rivers over several months without any seasonal concentration pattern, however, findings are quite limited or even the number is decreasing due to stopped use (AWEL, 2008). Terbutryne, which was registered as a pesticide in the EU up 2005, has been found in receiving waters of urban catchments (Quednow, 2007). The occurrence and effects of antifouling paint booster biocides in the aquatic environment are well known. A few biocides are covered by the EU Water Framework Directive (WFD), e.g. terbutryne, isoproturon, diuron, and Irgarol. Metalorganic biocides are not specifically highlighted under WFD since copper and zinc are covered.

The observations caused concern about these pollutants since active ingredients from biocide products enter surface waters where aquatic organisms may be affected. A question that is regularly posed in this context is to what extent substances expected from agricultural application might also originate from urban areas and pollute diffuse surface and ground water (Figure 1). Literature presenting data to sources, release and field studies is scarce. Consequently, a large number of biocides are not well studied and application amounts uncertain. Further guidance documents regarding potentially harmful substances, for example in construction materials, can be found in the BPR and the draft indicative list of dangerous substances of the Construction Products Regulation (CPR).

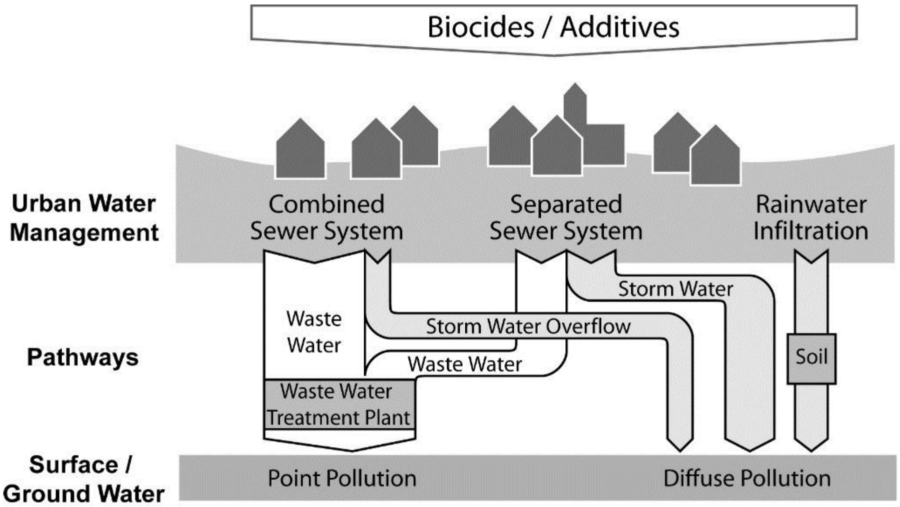

Figure 1: Pathways of biocides and their emission as point and diffuse pollutants to receiving water. Waste water enters surface water mainly as a point-source via waste water treatment plants.

2 MATERIAL AND METHODS

2.1 Amounts

We reviewed for product types 7, 8, 10, and 21 application amounts of the main biocides in Switzerland, the release and pathways to environmental compartments. For the survey targeted questionnaires to biocide manufacturers, formulators, associations and users are sent and carried out interviews with experts. An additional plausibility check made in consideration of reasonable data from Germany.

2.2 Leaching

Additionally, we studied the release to the aquatic systems. Paints and plasters of facades, roof waterproofing membranes for flat roofs (bitumen and plastic sheets), antifouling etc. are considered as potential sources. Since the use of biocides in exterior paints and plasters against algal and fungal growth is regarded as state-of-the-art in heat-insulated facade systems, we investigated plasters as a potential source of organic biocides in the aquatic environment specifically. In the laboratory leaching of biocides from three render formulations was evaluated: one render containing free, another render containing encapsulated biocides (terbutryne, OIT, DCOIT) and a control render without biocides. The renders were applied on extruded polystyrene panels and water samples generated over nine immersion cycles of the panels in accordance with standard EN 16105. Concentrations were measured by LC-MS.

2.3 Occurrence

In a field study, residential and commercial buildings mainly with flat roofs are connected to a separated stormwater system (Fig. 2). In the investigated sub-catchment, four aged buildings, paved parking lots and roofs are connected to the storm water channel. The facade runoff is collected in a drainage system installed around each building which discharges directly to the storm water channel of the separate sewer system. The biocidal ingredients of all coatings and roof materials have been assessed and the initial biocides stock calculated. Their dynamic occurrence is tracked by flow proportional sampling in the storm water sewers at two sites.

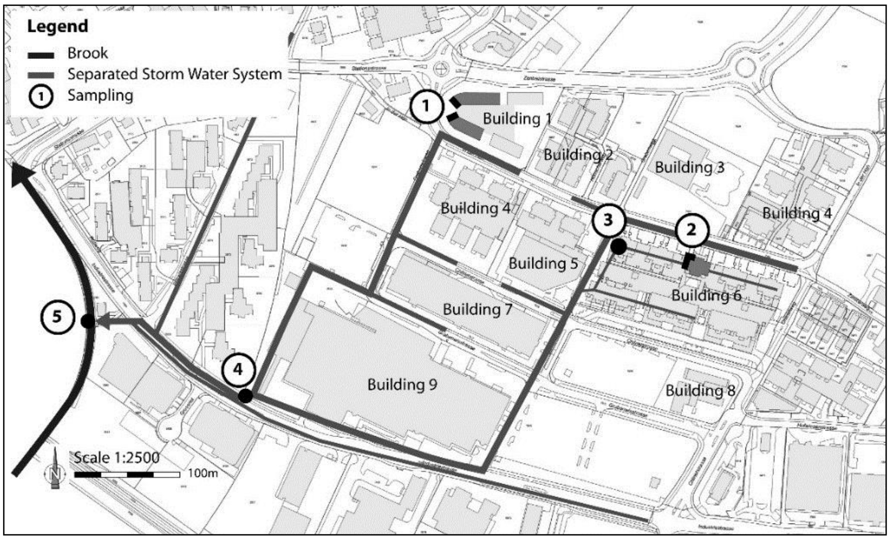

Figure 2: Discharge of storm water to receiving waters in the studied urban catchment regarding runoff from building envelopes and paved surfaces, respectively. 1,2: sampling of facades runoff at new and aged coatings, 3: storm water sampling of five buildings; 4: Sampling of a defined catchment with known building materials; 5: Sampling of discharge to the brook of the entire separated sewer system catchment.

Analysis of e.g. carbendazim, terbutryne, diuron, and mecoprop is performed with LC-MS/MS for. The sub-catchment of sampling site 4 encloses an area of about 14 ha (Figure 2). Residential and commercial buildings as well as paved streets and parking covers roughly one-third of that area, each. 80% of the buildings are not older than five years (Figure 2: building 1-7). It is estimated that nearly 95% of the rainfall discharges directly to the storm water system or via drainage systems of buildings and underground parking.

3 RESULTS AND DISCUSSION

3.1 Amounts

Little is known about biocides used and their transport behaviour although it is state-of-the-art of materials protection. As an example, in paints and plasters for facades different algaecides and fungicides are applied, in particular products applied on thermal insulation systems. For PT 7 products the biocide suppliers always offer two to four biocides in combination, in order to control several organisms at the same time. Architectural paints and renders with polymeric binders have significant market share with a consumption quantity of about 26,000 t in Switzerland in 2011 (Burkhardt et al. 2013). As a result 10 to 30 tons are used annually. Microencapsulated biocides are on the market since 2001 (e.g. AMME™ products) and reach about 80% market share in façade coatings in Switzerland in 2011. The estimate products for masonry (PT 10) yields to <0.1 tons per year. In Germany, the biocide consumption for paints and rendersfor exterior applications was between 200 to 400 t/a and for masonry preservatives (PT 10) between 10 and 50 t/a. The consumption of wood preservatives in Switzerland amounted to 4,800 tons, of which 2700 tons for the treatment of wood during storage and 2,100 tons of applications. The wood preservatives contain 4.8 to 48 tons a.i. biocides with IPBC, propiconazole, permethrin and diclofluanid as the most important agents. Antifoulings PT21 was used with 9 to 15 tons.

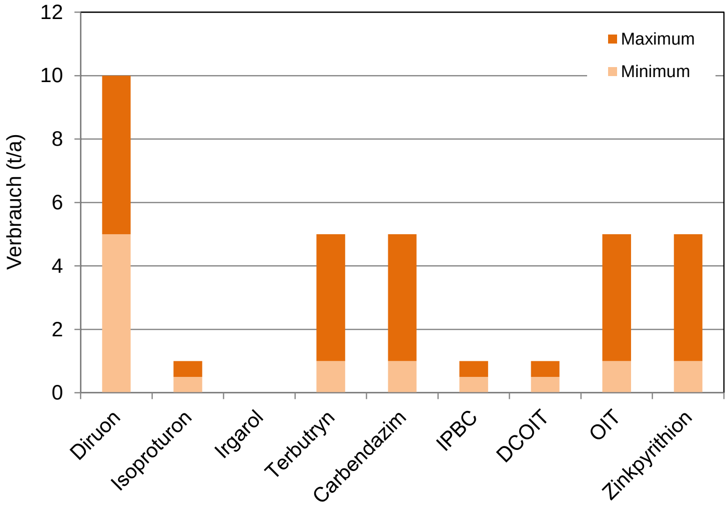

Figure 3: Amounts of the most important biocides used in PT 7 products (paints, renders).

3.2 Leaching

Experimental data demonstrate the biocides release as a function of product properties such as biocide properties (Kow, solubility), material composition, embedding, and environmental factors following an exponential release function. The concentrations of biocides in the facade runoff decreased exponentially. The highest emission of active ingredients is observed in the early stage of exposure and in the early stage of each leaching event (50 to 60% of the total release in first 15 minutes). In comparison with free biocides, microencapsulated biocides reduce leaching of biocides by a factor of 2 to 10 (Burkhardt et al. 2013). The results showed a decrease in leaching especially in the initial phase compared to free biocides. The leaching of the active compounds is dependent on the partitioning between water and plaster matrix. Based on the amount remaining in the products after exposure, degradation plays a role in the overall mass balance.

The results reveal that a number of biocides are negligible or of decreasing importance, however, a few are widespread in use and need to be investigated more specifically due to their persistence and ecotoxicity.

Table 1: Cumulative emission (mg/m^2) and relative emission (%) of three biocides over the period of nine immersion days. The relative emission is based on the absolute emission normalized to the initial amount (Burkhardt et al. 2013).

	Free biocides		Encapsulated biocides	
	(mg/m^2)	(%)	(mg/m^2)	(%)
Terbutryne	69	3.4	18	0.9
OIT	240	12.0	14	0.7
DCOIT	5	0.3	0.2	0.01

3.3 Occurrence

In most buildings, initial amounts range between 0.03 and 0.6 g/m^2 for each biocide. Hence, for a building complex with a surface of about 4500 m^2 area, up to 5 kg of biocides were applied in coatings. However, not all parts of facades are exposed to rain and facades runoff, respectively, and an unknown proportion may evaporate directly from the coatings. The most persistent biocides, such as terbutryn, diuron, carbendazim, and mecoprop, were determined at sampling site 5, representing a catchment of about 30 ha. It has been shown that the entire pathway from the building envelope to receiving surface water is traceable, e.g. for terbutryne which is exclusively applied on facades. Furthermore, the results indicate that water quality standards of 0.1 µg/L are exceeded up to ten-fold after the first flush of storm water runoff. In general, the first flush exhibits even higher concentrations.

At new facades with initial biocide content of 1,700 mg/m2 terbutryne, concentrations of 100 to 800 µg/L terbutryne were measured in runoff. The averaged losses per runoff event reached 170 µg/m2 terbutryne from northwest facade and 30 µg/m2 terbutryne from the southwest. Compared with the WFD limit value of 65 ng/L terbutryne, measured concentrations close to the source are significant higher. Under the same field conditions, concentrations of diuron applied in the facade of an aged building (about 4 years) were in runoff more than 100-times lower than at new buildings.

Measured concentrations of diuron and terbutryne in the stormwater runoff and receiving water were in the range of up to a few hundred ng/L. With the exception of high terbutryne concentrations in the runoff of new facades, the concentrations in the storm water actually tended to increase up to the receiving waters, i.e. maximum concentrations rise from 0.14 µg/L to 1.8 µg/L detected in the discharge outlet. Low concentrations observed in the range of up to a few hundred ng/L at another sampling site clearly highlight the importance of the age of the coatings. Dilution with non-polluted runoff lower the pollution of stormwater and in receiving waters. Terbutryne is applied exclusively in exterior coatings and can be used as a tracer for the impact of facades to storm water quality.

4 CONCLUSIONS AND OUTLOOK

The use of biocides is common practice for control of microbial deterioration or disinfection. Stormwater analysis has shown significant concentrations, although most biocides are potentially degradable and adsorbing at soil and sediments. We demonstrated that “best practice” may reduce the environmental impact at the source. The reduction is dependent on material properties or application strategies, such as the type of root protection agent and material modification. Overall, the results of leaching from materials or applications, on monitoring runoff and the occurrence of biocides in the storm water underline the importance of urban sources for the diffuse water pollution. With regard to sustainable water protection, it is important to account for both rural and urban sources. This may lead to a substantial reduction of contaminants in surface and ground waters. Source-control (encapsulation, restrictions) and end-of-pipe measures (adsorber in stormwater treatment systems) are both promising to limit the environmental impact.

For biocides used in construction materials a model COMLEAM (Construction Materials Leaching Model) has been developed by HSR to assess the leaching and environmental risk previous to the application in catchments. Experts from different European countries experienced in leaching of dangerous substances from construction materials and modelling of substance transport in the environment set-up the expert platform ESTIMATE to coordinate their activities and to develop a joint strategy supporting national and European stakeholders. A flexible software platform will be developed to predict environmental concentrations under different conditions of use and the spatial impact of released substances. Model calculations for ranges of construction and environmental parameters support the definition of standard parameters for environmental risk assessments.

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MICROPOLLUTANTS

A CHALLENGE FOR RIVER BASIN MANAGEMENT USING THE EXAMPLE OF THE SWIST CATCHMENT

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ABSTRACT

As part of its activities, the Erftverband undertakes specification of substance flows in the Erft river basin to establish emission and immission inventories. Herewith, anthropogenic micropollutants play an important role.

In the course of studies pathways as from sewage treatment plants, combined and separate sewer systems as well as landscape runoff components (surface water runoff, interflow and drainage water flow) are investigated. Different monitoring measures are in operation depending on the pathway. A valid monitoring strategy for detecting organic micropollutants in river basins must take into account spatial and temporal variability. Substance inputs enter the river via punctual or diffuse pathways and occur in a continuous, episodic or event-specific manner.

With the example of the Swist river, a tributary of the Erft, the approach to collecting valid information for organic micropollutants (pesticides, pharmaceuticals and industrial chemicals) and to addressing relevant pathways as a basis for appropriate management strategies will be discussed as well as new methods to minimize anthropogenic micropollutants in rivers.

TOWARDS ASSESSING THE RELEVANCE OF MICROPOLLUTANTS IN STORMWATER DISCHARGED TO BERLIN SURFACE WATERS

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1 INTRODUCTION

Untreated stormwater runoff can be an important source of pollutants affecting urban surface waters. For example, in Berlin each year 78% or 54 million m³ of stormwater are discharged mostly untreated into receiving surface waters. Beside “classic” stormwater pollutants (e.g. suspended solids, COD, phosphorous or heavy metals), trace organic substances such as biocides, plasticizers, flame retardants and traffic related micropollutants (e.g. vulcanizing accelerators originating from tire wear or combustion by-products such as PAHs) started to come into focus in recent years (Zgheib et al. 2012, Gasperi et al. 2014). To evaluate for the first time city-wide annual loads of these trace organic substances entering urban surface waters through stormwater discharge, an event-based, one-year monitoring program was set up in the city of Berlin.

2 METHODS

Monitoring points were selected in 5 catchments of different urban structures (old building areas <1930 [OLD], newer building areas >1950 [NEW], one-family houses with gardens [OFH], highly frequented streets >7500 vehicles per day [STR] and commercial areas [COM]) to consider catchment-specific differences. These catchment types represent the majority (>80%) of the connected impervious area of Berlin. At each monitoring point automatic sampling and flow measuring devices were installed in separate storm sewers. Volume proportional samples (one composite sample per event) are analysed for a comprehensive set of 95 micropollutants determined from literature review (see Table 1) as well as standard parameters (TSS, total P, phosphate, ammonium, COD and BOD). In addition, a sixth sampling point was installed at a small urban river receiving stormwater discharge (“Panke”) to determine peak concentrations of the same micropollutants during storm events. Details of the selection process and monitoring strategy can be found in Wicke et al. (2014).

Table 1: Groups of substances analysed with examples and application.

Substance groups (# compounds)	Examples	Application
Phthalates (8)	DEHP	Plasticizer in plastic materials
Organophosphates (6)	TCPP, TBEP	Flame retardants, plasticizer
Biocides / Pesticides (19)	Glyphosate, carbendazim, mecoprop (MCPP), diuron	Gardens, exterior paints, wall conservation
Industrial chemicals (17)		
benzothiazoles (3)	benzothiazole	Vulcanising accelerator (tires)
benzotriazoles (3)	benzotriazole	Corrosion inhibitors
alkyl phenols (4)	nonylphenol	Synthetics, tire abrasion
others (4)	MTBE, bisphenol A, PFOS	
Polycyclic Aromatic Hydrocarbons PAH (16)	Benzo[a]pyrene 16 EPA PAH (PAH 16)	Combustion processes, tire wear
Polybrominated Diphenylether (9)	PBDE	Flame retardant
Organotin compounds (5)	Mono-,di-, tributyltin	Wood preservative, antifouling
Polychlorinated Biphenyls (PCB) (7)	PCB 153	coolant and insulating fluid
Heavy metals (10)	Copper, zinc, titanium	Brake and tyre wear, building materials

A load model is being developed to estimate annual loads for Berlin from results of the different catchment types considering separate sewers (separate sewer), combined sewers via waste water treatment plants (WWTP) and combined sewer overflows (CSO) as pathways for stormwater runoff to lakes and rivers. Average annual stormwater runoff is calculated for each catchment type by coupling GIS data on city structure (SenStadtUm 2014) with the water balance model ABIMO (Glugla et al. 1999). Loads were then calculated for the different pathways based on the main assumptions, that (i) concentrations of one catchment type is representative for all areas of this type and (ii) average concentrations of all sampled events of one catchment type are representative for all rain events. For the sake of comparison calculated loads were compared to selected sewage-based substances, such as carbamazepine (CBZ) and ibuprofen.

3 RESULTS AND DISCUSSION

3.1 Catchment-specific concentrations

First results of the monitoring programme show that 66 of the 95 micropollutants were detected in stormwater runoff. So far, for 15 contaminants average concentrations >1 µg/L were determined, especially in the group of phthalates, flame retardants organophosphates, PAHs and heavy metals, whereas organotin compounds, PBDE and PCB were not detected (Fig 1). Fig 1 also indicates that the sum of all trace organic compounds is in the order of 10 µg/L at median and can be significantly higher for single events.

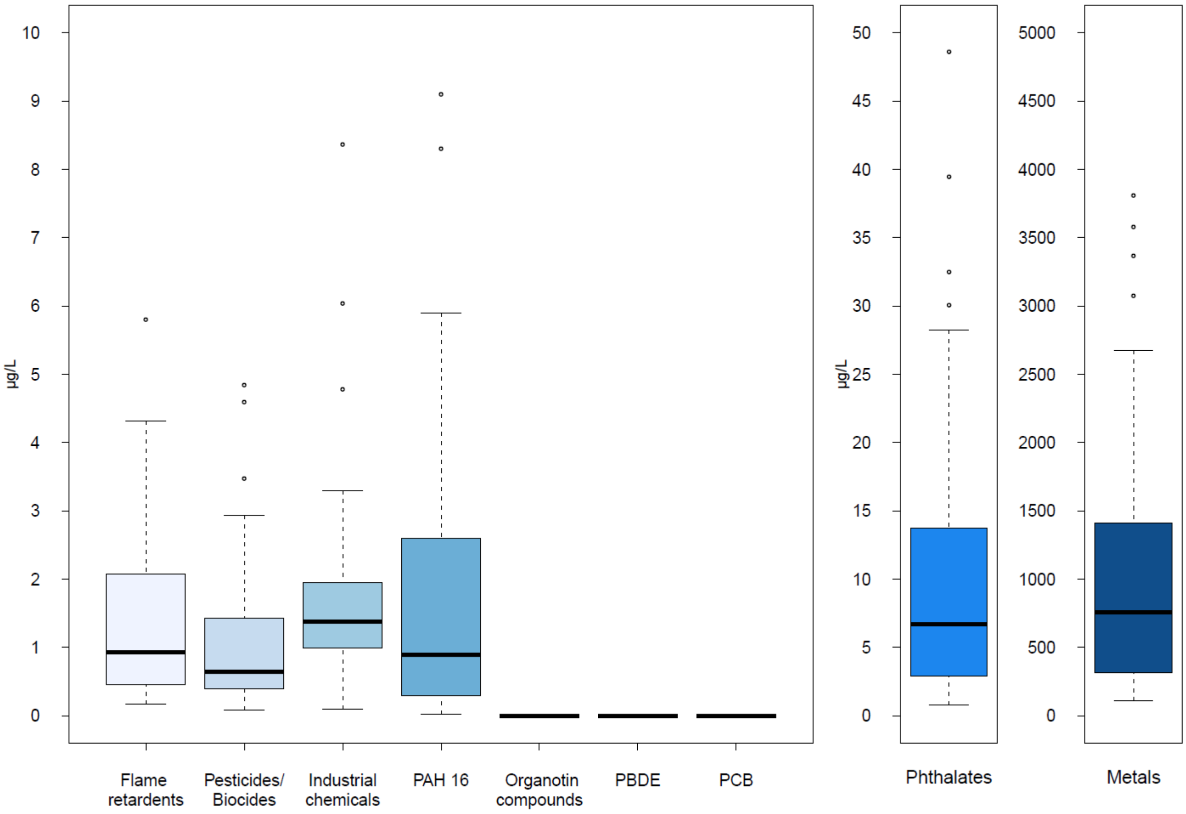

Figure 1: Concentrations of micropollutant groups (sum of all micropollutants per group, see Table 1) in stormwater of 5 different catchment types. Values from May 2014 – March 2015 (n=75-126).

Furthermore, results indicate catchment specific differences for a number of micropollutants (Fig 2). For instance, concentrations for traffic-borne benzothiazoles (vulcanizing accelerators used for production of tires) and PAH (sum of EPA 16 PAHs) are highest in road runoff (STR), although also present at the other catchment types as small roads <7500 vehicles per day are also part of those. Organophosphates (flame retardants) are highest in the old building areas, potentially due to application of insulation materials during extensive renovations in recent years. For biocides, catchment specificity depends on individual compounds. Whereas mecoprop (contained in bituminous sealing membranes for roofs, Bucheli et al. 1998) can be found in all catchments with roof runoff, carbendazim (fungicide, in urban context applied in exterior paints and silicone sealants) is mostly found at monitoring station OLD, probably also due to recent renovation efforts. On the other hand, concentrations of glyphosate (broad spectrum herbicide) are highest in monitoring catchment of one-family houses with gardens (garden application) and old houses (possibly application for weed control on sidewalks) (see Fig 2).

Comparison of dry and wet weather samples in the urban stream shows high peak concentrations during storm events for many substances, such as DIDP + DINP (4-fold increase during storm events), TBEP (14-fold increase), PAH 16 (15-fold increase) or glyphosate (25-fold increase), confirming the relevance of stormwater as source for micropollutants in receiving surface waters.

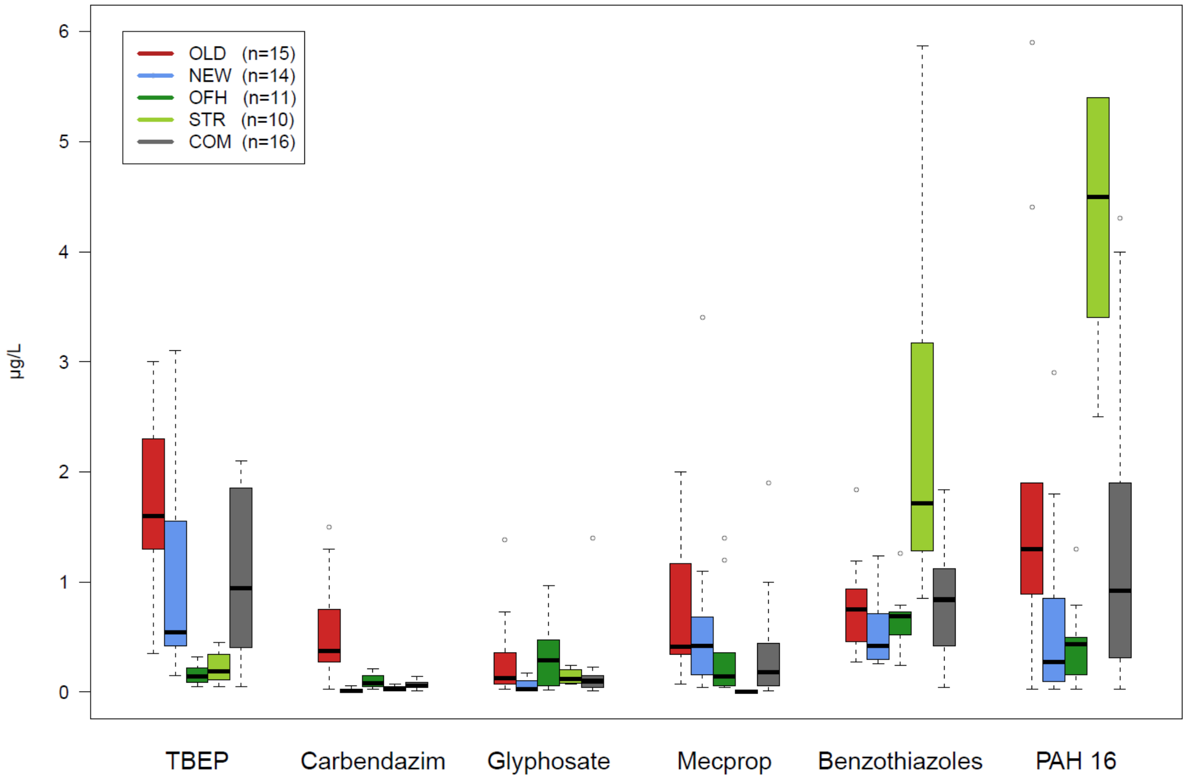

Fig. 2: Concentrations of selected micropollutants in stormwater of 5 different catchment types. Values from May 2014 – March 2015. OLD - old building areas <1930; NEW - newer building areas >1950; OFH – one-family houses with gardens; STR – large street runoff; COM - commercial areas. Benzothiazoles: sum of benzothiazole, hydroxybenzothiazole and methylthiobenzothiazole.

3.2 Estimation of city-wide loads

The simulated stormwater runoff of $69 \cdot 10^6$ m^3 yr^{-1} enters Berlin lakes and rivers by 69% via separate sewer, by 23% via WWTP and by 9% via CSO. In comparison a total of $218 \cdot 10^6$ m^3 yr^{-1} of sewage is collected, of which 99.7% is treated in WWTP and 0.3% are discharged via CSO (Berliner Wasserbetriebe 2014).

Fig. 3 gives an overview of calculated substance loads to surface waters from stormwater and sewage. In addition, overall importance of pathways is shown regarding total substance loads from both sources. The order of magnitude of micropollutant loads ranges from ~10 to ~1000 kg/yr, standard parameters are several orders of magnitude higher. Several stormwater-based micropollutants (e.g., DIDP + DINP, TBEP or PAH 16) show loads similar to those of sewage-based pharmaceuticals CBZ and Ibuprofen. Micropollutants that occur both in sewage and stormwater show loads in the same range (DEHP or thiazoles) or clearly higher loads from sewage (triazoles or BPA). This is reversed for some standard parameters, particularly heavy metals Cu and Zn (10- and 3-fold higher loads from stormwater).

Regarding pathways, either WWTP or direct inputs via separate stormwater sewers dominate depending on substance, while CSO is of minor importance between 0.3% (for CBZ) and 18% (for DEHP). In general, WWTP-share is highest for sewage-based substances with low elimination at WWTP, whereas share via separate stormwater sewer is highest for stormwater-based substances with high retention at WWTP. Accordingly, maximal WWTP share is found for CBZ with 99.7 % and maximal share via separate stormwater sewer is found for DIDP + DINP with 88.0 %. Interestingly, substances with different properties (e.g., both sewage and stormwater based, such as DEHP, or stormwater-based with low elimination at WWTP, such as MCPP) can show important shares via several pathways.

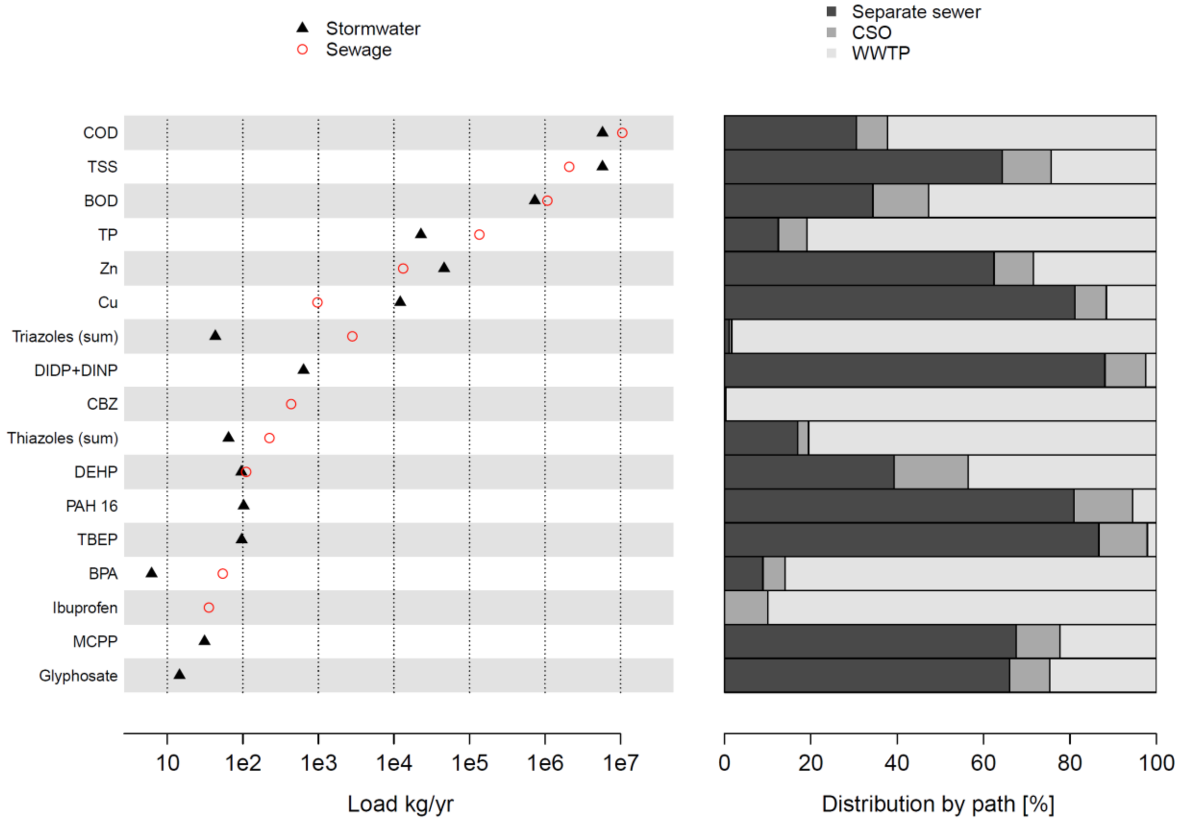

Fig. 3: Load estimates and pathways to Berlin surface waters. Left panel: Absolute load calculations, separately for the two sources “stormwater runoff” and “sewage”. Missing symbols indicate that no loads are expected from respective source. Right panel: Relative importance of pathways to surface water, jointly for both sources. See text for substance and pathway abbreviations.

4 CONCLUSIONS

Results indicate that stormwater discharge may be a relevant source of micropollutants to urban streams, particularly in cities dominated by separate sewer systems. Catchment-specific differences need to be considered to understand micropollutant patterns in urban stormwater and potentially prevent loads at the source. Micropollutant loads via stormwater runoff can reach the same order of magnitude as loads via sewage of well-studied parameters, such as pharmaceutical residues. However, load calculations need to be refined by assessing potential concentration dependencies of external factors such as rain characteristics. Moreover, uncertainty must be assessed for the entire load model. Finally, (expected) toxicity needs to be taken into account when discussing the relevance of the observed substance loads.

5 ACKNOWLEDGEMENTS

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QUO VADIS, DANUBIUS?

PROGRESS AND CHALLENGES OF NUTRIENT POLLUTION CONTROL IN THE DANUBE RIVER BASIN

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1 INTRODUCTION

The Danube River Basin (DRB) is the second largest river basin in Europe with a total catchment area of about 800,000 km². It is the most international river basin of the world as its territory is shared by 19 countries. More than 80 million people with different cultures and languages call DRB their home.. The Danube River itself has more than 2800 km length and a long-term average discharge of 6,500 m^3/s. However, not only the impressive size and flow rate make the basin unique and complex. Besides cultural differences the basin shows high variety of natural factors (e.g. topography, geology, hydromorphology, climate, hydrology) and diverse socio-economic and political conditions (land management, economic power, infrastructural development, EU membership).

The necessity of a harmonised basin-wide watershed management including nutrient pollution control has long been recognised and countries in the watershed have been collaborating for decades and made significant efforts to ensure the sustainable and equitable use of freshwater resources in the basin. In 1998 the International Commission for the Protection of the Danube River (ICPDR) was established to implement the Danube River Protection Convention (DRPC, ICPDR, 1994), the major legal instrument for cooperation and trans-boundary water management in the DRB. The ICPDR has also been nominated by the Danube countries as the platform for the implementation of all transboundary aspects of the EU Water Framework Directive (WFD, EC, 2000) in the DRB. The current management cycle of the WFD will terminate at the end of 2015 when the updated Danube River Basin District Management Plan (DRBM Plan) has to be published.

Status of surface water bodies in the Danube river system is largely influenced by the inputs of pollutants from both, the point and diffuse sources. Analyses of nutrient emissions – one of the significant water management issues identified for the DRB - and their impacts on water quality and elaboration strategies to reduce nutrient pollution have a long story in the DRB. According to the recent risk assessments twenty percent of the surface water bodies are at risk to fail good ecological status/potential by 2021 due to nutrient pollution (ICPDR, 2015). The Black Sea, the ultimate receiving marine water of the Danube, is sensitive to eutrophication and the severe eutrophic conditions of the late 80ies might be developed again if waste water is inappropriately treated and agriculture is intensified but at the same time mismanaged.

This paper highlights the current figures of nutrient emissions entering the Danube and its tributaries, the progress has been achieved in pollution control over the recent years and future challenges and actions needed in order to further decrease nutrient inputs of the river. These results and outcomes have been incorporated into the draft DRBM Plan – Update 2015 (ICPDR, 2015) which is currently being elaborated by the ICPDR.

2 METHODS

The ICPDR has been gathering detailed data on point sources within the DRB. Information on agglomerations, urban waste water treatment plants and direct industrial dischargers have been collected via specific templates for the reference years 2011/2012. These are in line with the reporting requirements of the EU Member States (MS) under the Urban Waste Water Treatment Directive (UWWTD, EC, 1991a) and the Regulation on European Pollution, Release and Transfer Register (E-PRTR, EC, 2006), however they request of a sub-set of these databases only which is likely to be available also in the non-EU MS. On the top of this, some additional information have been also collected which are not obliged by the EU but have particular importance regarding pollution assessments (e.g. nutrient discharges). The data have been analysed, assessed and mapped to provide with a basin-wide overview on the point source emissions and the related infrastructural developments and further needs.

To assess the diffuse nutrient emissions, the MONERIS model (Venohr *et al.*, 2011) has been applied for the entire DRB for the period 2009-2012. MONERIS is a catchment scale, lumped parameter, long-term average and empirical water quality model which was developed to support regional decision making on nutrient emission reduction strategies. The model application has a long story in the DRB (e.g. IWAG, 2005; ICPDR, 2009; ICPDR, 2015) resulted in a comprehensive database set up for the basin and an enhanced model algorithm. Model input dataset has been updated using several ICPDR, international and national data sources for the reference period and the model has been validated against measured river loads. Model results have been evaluated and mapped to identify regional scale emission hot-spots within the basin and to better understand the main pathways and sources of nutrient emissions and their proportions.

3 RESULTS

3.1 Emissions via urban waste water

In total, a waste water load of about 85 million population equivalent (PE) - at around 5,600 agglomerations above 2,000 PE - is generated in the basin. The distribution of the agglomerations according to their size and connection rates to collecting systems and treatment plants (Figure 1) clearly influences that of the generated loads. Collection and treatment of waste water are in a highly enhanced status in the upstream countries, at good conditions in some countries in the middle-basin whilst significant proportions of the generated loads are not collected or collected but not treated in the downstream states. Seventy-three percent of the overall PE of the basin are treated with at least secondary treatment or addressed through individual systems, whilst 27% need basic infrastructural development aiming to achieve biological treatment. The overall load generation at agglomerations above 10,000 PE is 67 million PE, 60% of this load are subject to tertiary treatment. This indicates that waste water treatment for 27 million PE at agglomerations above 10,000 PE should be further improved (according to the requirements of the UWWTD for sensitive areas).

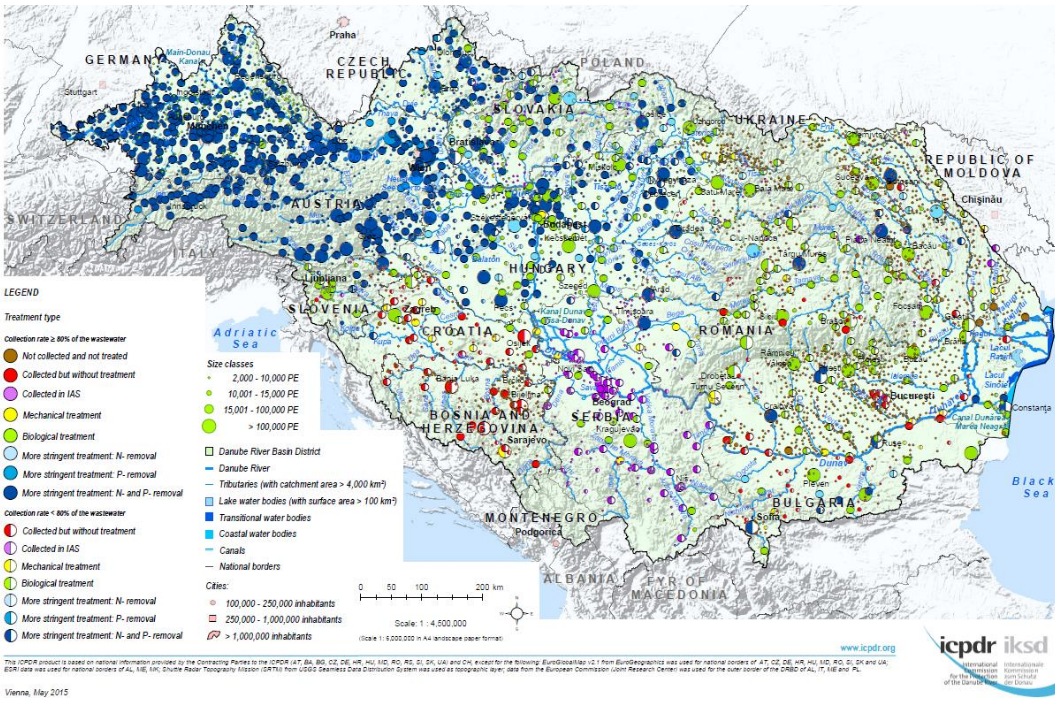

Figure 1: Situation of urban waste water collection and treatment in the DRB (reference year: 2011/2012).

At the basin scale 84,000 tons per year total nitrogen (TN) and 11,000 tons per year total phosphorus (TP) are emitted into the surface waters from the waste water collection and treatment facilities. 25% (TN) and 36% (TP) of the emissions can be linked to untreated waste water discharged directly into the recipients (Figure 2). About 3% and 5% of the nutrient releases stem from plants having mechanical treatment, whilst the proportion of the waste water treatment plants with secondary treatment is 26% (TN) and 29% (TP). Some 45% and 30% of the nutrient emissions are discharged from plants with stringent technologies. Regarding the middle sized and big agglomerations (above 10,000 PE), 43% (nitrogen) and 57% (phosphorus) of the nutrient emissions are related to less stringent technologies indicating that further improvement of the treatment at these settlements can significantly reduce the nutrient discharges at the basin scale.

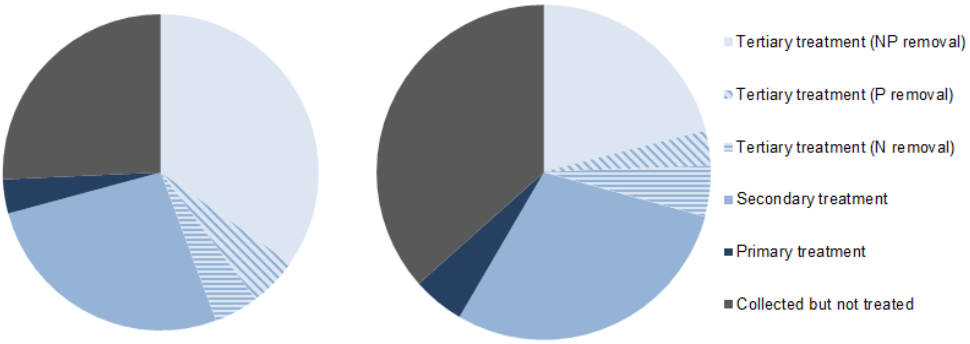

Figure 2: Share of the collection and treatment systems in the total emissions via urban waste water discharges; left: nitrogen, right: phosphorus.

3.2 Emissions via point and diffuse sources

According to the recent MONERIS calculations, the TN emissions in the Danube river basin are 693,000 tons per year (8.7 kg per hectare and year) for the reference period 2009-2012. The regional distribution of the emissions is shown in Figure 3.

This map illustrates nitrogen emissions entering the surface water bodies from catchment areas. The emissions were calculated according to long-term average hydrological conditions over the period of 2009-2012, using the most recent available data within the same period. Calculation was implemented using the MONERIS model (Venohr et al., 2011).

This ICPDR product is based on national information provided by the Contracting Parties to the ICPDR (AT, BA, BG, CZ, DE, HR, HU, MD, RO, RS, SI, SK, UA) and CH. EuroGlobalMap data from EuroGeographics was used for all national borders except for AL, BA, ME where the data from the ESRI World Countries was used; Shuttle Radar Topography Mission (SRTM) from USGS Seamless Data Distribution System was used as elevation data layer; data from the European Commission (Joint Research Center) was used for the outer border of the DRBD of AL, IT, ME and PL.

Vienna, May 2015

Figure 3: Area-specific long-term average total nitrogen emissions in the DRB (reference years: 2009-2012).

Regions with high agricultural surplus and shorter groundwater residence time and/or bedrock layers with lower denitrification capacity produce the highest area-specific emissions. Urban areas with significant point sources and urban runoff generate remarkable local fluxes as well. The groundwater (base flow) pathway is responsible for 52% of all TN emissions in the Danube basin and thus the most important pathway (Figure 4 left). Nitrogen inputs via tile drainages have a proportion of 14 %, whilst urban runoff, surface runoff, direct atmospheric deposition and erosion show a contribution of 10%, 7%, 2% and 2% respectively. Diffuse inputs dominate the basin-wide nitrogen emissions as they have a proportion of 88% in total. Emissions via point sources (urban waste water treatment plants, sewers without treatment plant and industrial dischargers) contribute with 12 % to total nitrogen emissions.

Regarding the main sources (Figure 4 right), agricultural fields dominate the nitrogen emission sources showing a proportion of 54%, although only 36% of the emissions from agricultural areas are related to fertiliser or manure application, whilst the remaining 18% are caused by atmospheric deposition. Urban areas (waste water discharges, runoff from paved surfaces and combined sewer overflows) and natural lands where atmospheric deposition provides nitrogen input are significant source areas as well. This indicates that a part of the nitrogen emissions might stem from outside the basin and transported via atmospheric deposition that can difficultly be controlled. Natural background pollution is less important on basin-wide level.

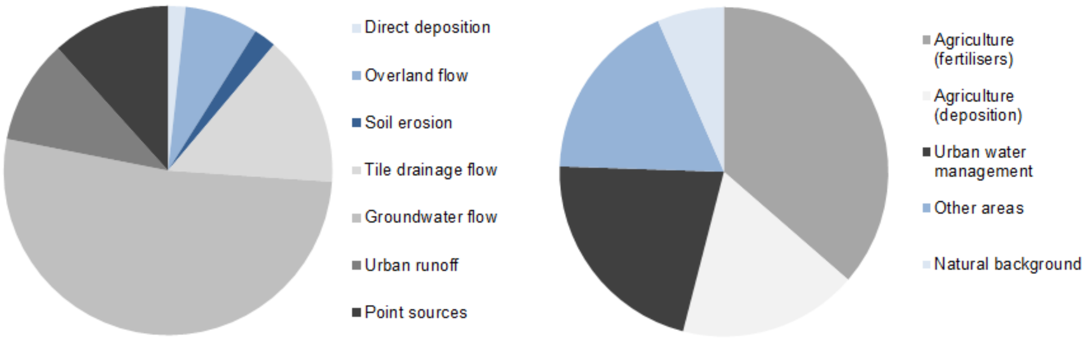

Figure 4: Proportion of the pathways (left) and sources (right) in the total nitrogen emissions.

TP emissions in the Danube river basin are 42,000 tons per year (530 g per hectare per year) for the reference conditions. Hilly regions with intensive agricultural activity or mountainous areas producing high background emission rates generate the largest P inputs of the surface waters (Figure 5). Similarly to nitrogen, point sources and paved urban surfaces significantly contribute to the total emissions as well. TP emissions via the different pathways are presented in Figure 6 (left). The most important diffuse pathway in the Danube river basin is the runoff from the urban systems (surface runoff from paved areas, discharges via combined sewer overflows and emissions from unconnected population) which is responsible for 33% of all TP emissions. Emissions via erosion contribute with 25% to total phosphorus emissions, base flow has a proportion of 14%. Surface runoff, atmospheric deposition and tile drainages contribute with 2% or less to the total phosphorus emissions. All diffuse sources have a total share of 76%, whilst point sources pathway has a contribution of 24%.

Source apportionment (Figure 6 right) shows the clear dominance of the urban areas producing 57% of the phosphorus emissions. Agriculture is responsible for 29% of the total emissions, whilst the rest belongs mainly to background emissions. This suggests a high potential of measures addressing the urban water management to reduce the phosphorus emissions. However, the agricultural pressure could strengthen due to the potential future agricultural development especially in the middle and lower parts of the DRB.

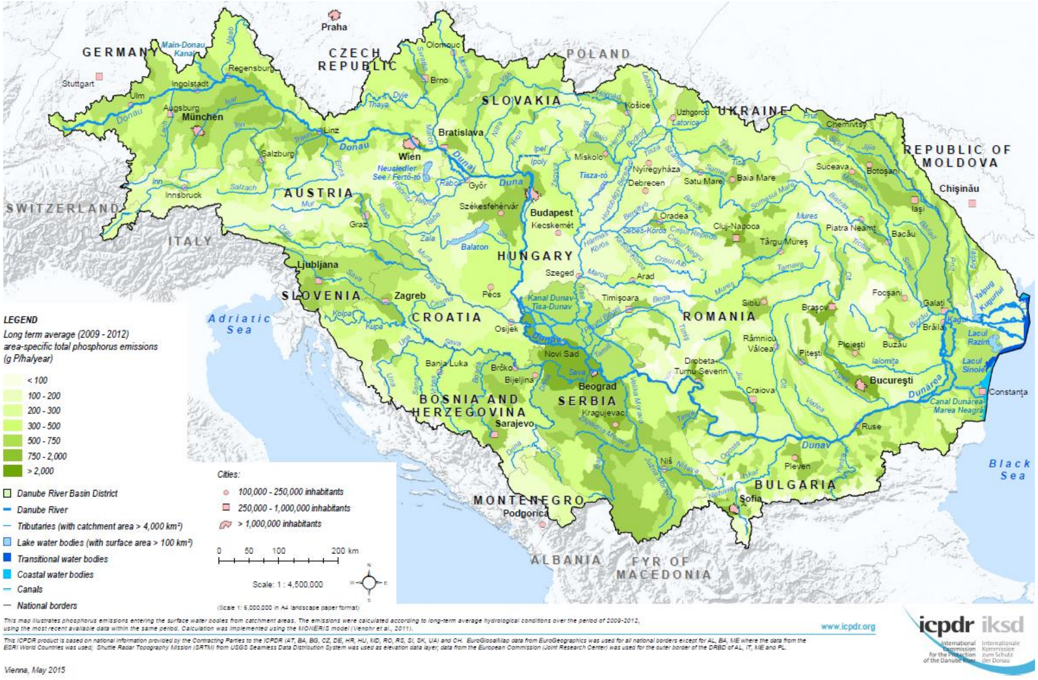

Figure 5: Area-specific long-term average total phosphorus emissions in the DRB (reference years: 2009-2012).

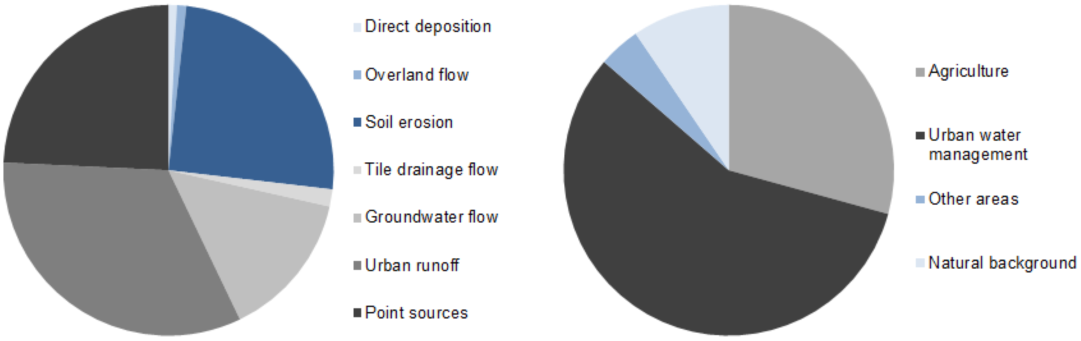

Figure 6: Proportion of the pathways (left) and sources (right) in the total phosphorus emissions.

3.3 Nutrient river loads

The calculated river loads are 440,000 tons per year (TN) and 17,000 tons per year (TP) for the reference period (2009-2012). These numbers indicate remarkable retentions in the river network comparing them to the total emission values. Thirty-six percent of the TN emissions entering the river systems are retained during the in-stream transport mainly by denitrification. Some 59% of the TP emissions do not reach the river mouth particularly due to settling in reservoirs and floodplains. Modelling results reasonably fit the observed river loads at both, the basin-wide and the regional scale, although smaller inconsistencies for single cases can be found.

4 DISCUSSION

The ICPDR’s ultimate objective for nutrient pollution is the balanced management of nutrient emissions via point and diffuse sources in the entire DRB ensuring that neither the waters of the DRB nor the Black Sea are threatened or impacted by eutrophication. The 1st DRBM Plan (ICPDR,

2009) summarizes, on the basin-wide level, the basic measures in the urban waste water, industrial and agricultural sectors and other supplementary measures like best agricultural practice recommendations as the main actions to be taken to address nutrient emissions.

Remarkable decrease is visible regarding the nutrient point source emissions in the Danube basin in comparison to the results of the 1st DRBM Plan. For the reference year of the 1st DRBM Plan (2006) 130,000 tons per year TN and 22,000 tons per year TP pollution was reported via direct urban waste water discharges. The recently reported point source nutrient emissions are significantly lower in comparison to those of the 1st DRBM Plan, the TN and TP discharges declined by 36% and 48%, respectively. TN emissions remained at the same level in comparison to the 1st DRBM Plan although point source emissions via waste water significantly decreased. This is, however, compensated by a higher emission from agriculture via fertilisers and manure which is a consequence of the updated input data set rather than that of intensified agriculture. TP emissions declined by 30% due to the improved waste water treatment. In addition, higher differences can be found for the proportion of the various pathways and for several regions of the basin. Reasons of these differences are model developments and the updated input data in comparison to the 1st DRBM Plan.

The current long-term average (2003-2012) observed river loads estimated from measured river discharge and nutrient concentration data at the river mouth (station Reni) are 490,000 tons per year (TN) and 25,000 tons per year (TP). Analysing the trends in nutrient river loads over the past decades a significant reduction in the transported nutrient fluxes to the Black Sea can be detected. However, the recently transported fluxes are still considerably higher than that of the early 1960ies representing desired load targets (TN: 300,000 tons per year, TP: 20,000 tons per year), which means a TN and TP load reduction need of 40% and 20%, respectively. This requires further decrease of both, the point source and diffuse emissions generated in the Danube basin.

The measures under implementation have been substantially contributing to the reduction of nutrient inputs into surface waters and groundwater in the DRB but further efforts are still needed. Enhancement of the urban waste water collection and treatment and application of BAT should continue. In the EU MS these issues are legally required by the UWWTD and the Industrial Emissions Directive (IED, EC, 2012). Upstream countries have only limited possibilities as they have already introduced nutrient removal at the vast majority of the agglomerations, even for the smaller sized settlements. Middle and downstream countries can, however, remarkably enhance the overall treatment status of the plants, particularly at the agglomerations over 10,000 PE, where the introduction of the tertiary treatment technologies is lagging behind. Efforts to extend the introduction of phosphate-free detergents to all Danube countries are also likely to be needed, whereas EU MS are obliged to use P-free dishwasher detergents from 2017 (EC, 2012).

Countries should intensify their efforts to accelerate the identification and implementation of measures (best management practices) to reduce nutrient pollution particularly via diffuse pathways from agriculture. In particular, EU MS should reinforce action programmes within the designated Nitrate Vulnerable Zones (NVZ) or over the whole national territory in the EU MS as requested by the Nitrates Directive (ND, EC, 1991b). In addition, measures under the Codes of Good Agricultural Practice are recommended to be implemented outside the NVZ. Efforts are needed to ensure necessary financial investments and clarification is required how to finance agricultural measures. Countries should make use of the CAP-reform and other national programs available. Between 2014 and 2020, over 100 billion EUR will be invested (in the EU MS) to support environmentally friendly farming practices and agri-environmental measures from both, the direct payment (cross compliance and greening) and rural development pillars. One of the challenging future tasks of this field is to better understand and realistically predict the possible future economic drivers, the agricultural development and changes and their anticipated impacts.

5 CONCLUSIONS

Nutrient pollution is one of the significant water management issues identified for the DRB. Although nutrient fluxes have significantly dropped in the last decades due to the measures have been implemented in waste water, industrial and agricultural sectors but also due to the declined intensity of agriculture resulted in lower nutrient surpluses, the nutrient pollution of a number of surface waters within the DRB and the fluxes reaching the Black Sea are still higher than the required or desired level. Implementation of measures should continue including introduction of nutrient removal technology at the urban waste water treatment plants (at least for the middle sized and large agglomerations), application of P-free products for consumer laundry and dishwasher detergents and implementation of agri-environmental measures and best management practices in the agriculture.

6 ACKNOWLEDGEMENTS

The results and assessments of this paper are parts of the draft DRBM Plan – Update 2015, which has been elaborated in December 2014 and updated in June 2015 by the ICPDR.

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AN INVENTORY OF EMISSION SOURCES AND PATHWAYS AND A QUANTIFICATION OF EMISSION LOAD IN THE CZECH REPUBLIC

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1 AN INVENTORY OF EMISSION SOURCES AND PATHWAYS AND A QUANTIFICATION OF EMISSION LOAD IN THE CZECH REPUBLIC

1.1 Introduction

Emissions of pollutants are significant anthropogenic pressures with important impact to status or potential of surface water bodies. Pollutants originate from different human activities (households, industry and agriculture) and from different sources. They are transported to surface water by different pathways: waste water discharges, applications into soil or air releases and subsequent atmospheric deposition and transport by groundwater. The final impact to surface water quality is affected by pollutant characteristics and pollutants behaviour in soil, subsoil and water body as well. The Czech project “Emissions and their Impact on the Aquatic Environment” (2012 – 2014) was oriented on apportionment of pollutant emission from different sources and pathways.

The aim of the project was processing tools - methodology and software and the solution was designed so that the results could be applied on a national scale within the framework of river basin management plans. The focus of the project was mainly based on the requirements of Directive 2000/60/EC (Water Framework Directive) and 2013/39/EU (setting environmental quality standards) further specified by guidance document no. 28 (Preparation of an Inventory of Emissions, Discharges and Losses of Priority and Priority Hazardous Substances) of the Common Implementation Strategy (CIS). The methodology and software were validated in a pilot catchment area (the river Vltava). The results were used on a national scale in the production of river sub-basin management plans of the Czech Republic for the second planning cycle when evaluating adverse pressures and impacts on the status of surface waters and proposals for relevant programme of measures. The article provides some brief information about the methodology and results of the project, including the possibility how to use the results in water management, particularly in River Basin Management Plans.

1.2 Methodology

The methodology establishes principles for the assessment of emissions impact; it describes the individual steps, from the identification of relevant pollutants in the catchment area, through the analysis of pollution sources and pathways, to the classification of the significance of groups of sources and pathways for individual substances and water bodies (see Fig. 1).

1.2.1 Pollutant sources and pathways of contamination

In the Czech Republic catchment areas, 79 pollutants were identified (including 30 priority ones pursuant to Directive 2013/39/EU) whose emissions and occurrence in surface waters may threaten the achievement of good status of water bodies (including 25 at the significant territorial scale). Among the priority hazardous substances which are a risk in the Czech Republic are anthracene, DEHP, brominated diphenyl ether, benzo(a)pyrene, benzo(b)fluoranthene, benzo(ghi)perylene, benzo(k)fluoranthene, cadmium and mercury. The characteristic sources and pathways of pollutants were identified for these hazardous substances.

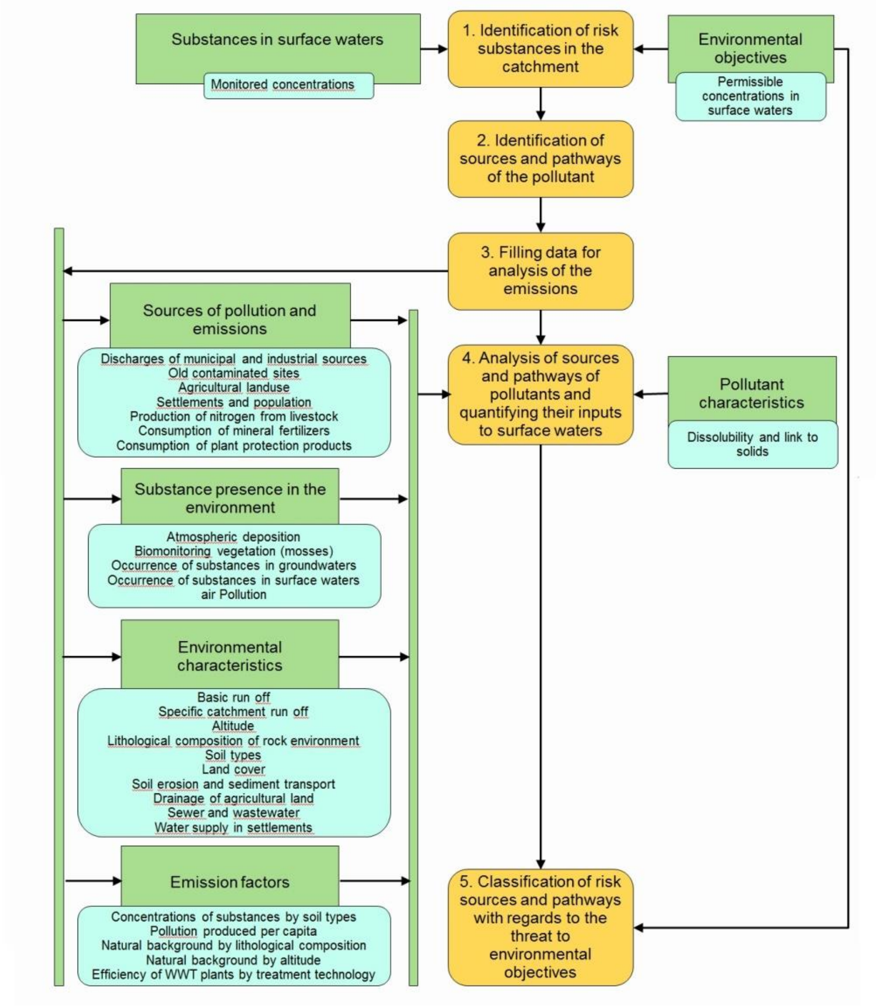

Figure 1: Schematic diagram of the procedure for evaluating the impact of emissions and input data

1.2.2 Analyze of risk sources and pathways, quantifying pollutants inputs, risk classification

Analysis of the sources and pathways of pollutants uses a wide range of data available on a national scale. Data was collected for the project on the occurrence of pollution sources and inputs of substances into surface waters, the occurrence of substances in the environment (groundwater and surface waters, atmospheric deposition, vegetation) and environmental characteristics (rock environments, precipitation conditions, soil types, etc.). At the same time, emission factors were processed (coefficients of substances inputs per unit, designated by expert estimate) where emissions data are not available. The analysis also takes into account the properties of individual substances. Groups of pollution sources and pathways are classified for individual water bodies and pollutants with respect to environmental objectives for achieving good surface water status.

1.3 Results and their use in water management planning

The methodology was applied in four out of 10 Czech sub-catchments, represented about 36% of the entire Czech territory. The results could be divided on quantified gross emission loads and identification of risk areas ("hot spots") on water body level. For each assessed source (or pathway) of emissions was identified their significance.

1.3.1 Quantification of emission discharges from urban and industrial sources

Discharges from urban and industrial sources were quantified based on E-PRTR and UWWTD reporting data plus national registers of authorised waste water releases. The national registers include monitored pollutant concentrations (from 2 to 24 measurements per year) and annual waste water volume. Data from un-connected households were estimated by emission factors of generated emission load per capita.

1.3.2 Quantification of diffuse emissions from natural background

Natural background nutrient emission load was calculated according to the concentrations from reference sites (areas without significant anthropogenic pressures) and categorised in compliance with surface water body typology. Emission load of metals (Al, As, Be, Cd. Cu, Ni, Pb, Cr and Hg) from natural background were estimated from concentrations in non-polluted groundwater.

1.3.3 Diffuse emissions from agriculture

Nutrient emission load from agriculture were calculated for non-erosion phosphorus input and nitrogen from manure only due to lack of detailed information. Value of non- erosion phosphorus was estimated from according to the phosphorus concentrations in agriculture areas referred to soil types. Although information about erosion phosphorus was available, their reliability was low and they were not used.

Nitrogen input from manure to surface water was calculated from number of livestock and their average production of nitrogen and reduction of nitrogen in soil incorporated intensity of agriculture and irrigation. Because information about use of artificial fertilizer is available on large administrative units only, surface water at risk due to artificial fertilizer were assessed based on percentage of agriculture area in sub-basin of water body.

Pesticides from agriculture were assessed for some most risk pesticides (about 7 frequently used active substances) – 2,4 D; acetochlor, alachlor, MCPA, metazachlor, metolachlor and terbuthylazine. Their measured concentrations are very low and it is difficult to set reduction factor for them. Hence surface water bodies at risk due to these pesticides were identified based on amount of pesticides on agriculture areas (including crop information) and hydrological characteristics of soils in water body sub-basin.

1.3.4 Emissions from atmospheric deposition

Emissions from atmospheric deposition were assessed on the entire area (not only directly to water surface). It is not possible to calculate real input from soil to surface water. The most significant pollutants in the Czech Republic are As, Cd, Hg, Ni, Pb and polyaromatic hydrocarbons (particularly benzo(a)pyrene). Risk surface water bodies were identified from other sources of information – areas with higher concentrations of pollutants in air or in moss and rarely from available information about “wet” (concentration in precipitation) or bulk (including deposited matter) atmospheric deposition.

1.3.5 Assessment of emission significant sources on water body level

Sources of emissions, which could inflict (alone or together with other sources) not achieving environmental objectives (particularly good status) of surface water, were identified as “significant”. Groups of emission sources and pathways for specific water bodies and pollutants were classified by proportion of estimated emission load (compared to permitted concentration and long-term specific flow in sub-basin of surface water body). Emission load from source was identified as significant, when was above 20% of water body “capacity” or as very significant (above 100%). The very strict limit (20%) was used because of cumulative effect of more sources and/or possible adverse effect of low flows. Also risk water bodies for non-calculated emission inputs (as pesticides or atmospheric deposition) were identified as risk.

1.3.6 Use of results in river basin management planning

The results of the project are available at http://heis.vuv.cz/projekty/emisevoda. They were used on a national scale in the production of river sub-basin management plans of the Czech Republic for the second planning cycle when evaluating adverse pressures and impacts on the status of surface waters and proposals for relevant programme of measures.

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RIVER LOAD ESTIMATION OF PRIORITY SUBSTANCES IN AUSTRIA

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1 INTRODUCTION

One of the aims of the EU Water Framework Directive (WFD) is to achieve the good water status for European rivers. The WFD defines environmental quality standards (EQS) for priority substances such as heavy metals and organic pollutants. In case of exceedance of EQS the knowledge of the significance of loads emitted via different pathways is a first basis to derive efficient measures to reduce the concentrations of potentially problematic substances in the environment. The aim of this work is the estimation of emissions via different pathways for Hg, Pb, Cd, Ni, PAH, PBDE, PFOS and TBT for Austria and for three selected catchment areas. Additionally, uncertainties, deficits in data base and needs for improvements are identified.

2 METHODOLOGY

2.1 Calculation of emission loads via different pathways

In compliance with MONERIS (Venohr et al., 2009, Fuchs et al., 2010) emission pathways addressed in this study are discharges from wastewater treatment plants and industrial point sources, urban runoff, sealed surface runoff, surface runoff, drainage system, groundwater (base- and interflow), atmospheric deposition and erosion. Beside erosion and atmospheric deposition emission loads are based on multiplication of Austrian specific pathway discharges (Gabriel et al., 2011) and substance concentrations. Regarding topicality, mean annual discharges from wastewater treatment plants, urban areas and sealed surfaces are based on more recent investigations of Clara et al. (2014a). The total discharge amounts to 1.805 m³/s. Thereof 70% originate from groundwater.

Main Austrian sources of information are Clara et al. (2014a), the water monitoring program by the Federal Ministry of Agriculture, Forestry, Environment and Water Management of Austria, Offenthaler et al. (2009) as well as Freudenschuss et al. (2010) for soil contents. Major problems of the concentration data were uncertainties caused by low sample numbers, fluctuations in concentrations due to local conditions and measurements below the limit of detection (LOD) or limit of quantification (LOQ). Especially for PBDE, PFOS and PAH only a very limited number (n<10) of measurements in groundwater are available. Metals are frequently analyzed in ground- and surface waters and a large number of samples has been investigated but especially Hg and Cd were either non detectable or measured below the limit of quantification (LOQ). Hence the calculated results are highly biased and associated to high uncertainty. In some cases no information on soil contents and discharged loads from industrial point sources is available. Taking into account analytical uncertainties caused by concentrations below LOD and LOQ, two different evaluation approaches were implemented. For the minimum approach non detects were set equal to zero and measurements <LOQ=LOD. For the maximum approach non detects were set equal to the LOD and measurements <LOQ=LOQ. Calculated minimum and maximum concentrations were compared to literature and if necessary adapted to literature concentrations. Considering ranges in soil contents minimal or maximal values were used in the correspondent approaches. Beside the Dornbirner Ach (specific data available by Clara et al., 2014b) all calculations of emission loads via different pathways are based on nationwide mean concentrations as no regional specific concentrations were available.

Calculations of emission loads via erosion and atmospheric deposition are based on MONERIS approaches (Venohr et al., 2009). Required data (e.g. soil loss, enrichment ratio) were estimated by Gabriel et al. (2011) catchment level. Except of PFOS, mean ER was considered in emission load calculations.

The report “Emissionsabschätzung für prioritäre Stoffe” (Trautvetter et al., 2015) provides further information about discharges and summarizes pathway and substance specific concentrations used for the emission loads estimation.

2.2 Estimation of modelled and monitored river loads and evaluation

According to Venohr et al. (2009) retention due to sedimentation and export to riverbanks during flood events may play a decisive role for the phosphorus transport in rivers. As no information about quantifications of the retention for heavy metals, PAH, PBDE and TBT exist, the phosphorus retention approach of Venohr et al. (2009) was applied for modelling of river loads for these substances. Due to rare potential for adsorption to sediments and degradation, for PFOS no retention was assumed.

For calculations of river loads from monitoring data 2000-2014, measured concentrations below LOD were processed according to the evaluation approaches mentioned above. Only for Ni and Pb sufficient concentration data is available and immission loads could be estimated. For Hg and Cd a large database exists, but mostly these compounds are either not detected or found only below the LOQ. For PFOS no in stream measurements are available. Immission loads were calculated by mean annual flows (eHyd- data base) and mean concentrations (H2O- data base). For the overall estimation of the net-export of substances out of Austria the loads for Mur, Drau, Danube and Inn were summed up.

2.3 Case study watersheds

Emphasizing differences in emission pathway distribution via regional conditions (e.g. precipitation, land use) emission pathways of three selected catchments with a size of (~200 to 400 km^2) have been calculated and compared to nationwide pathway distribution. Selection criteria were watershed size and differences in land use (urban, rural) as well as precipitation and river discharges. The three chosen catchment areas are i) “Dornbirner Ach”, representing catchment area influenced by high impacts of waste water, ii) “Strem”, representing low flow and high impacts from agricultural land use as well as relevant impact from waste water, and iii) “Gusen”, representing a catchment area influenced mainly by agricultural land use.

3 RESULTS

The high differences between the results of the calculation with minimum and maximum approach reflect the uncertainty of emission estimates. Anyway, it can be concluded that on an Austrian wide level more than 80 % of the heavy metal emission loads originate from diffuse pathways as erosion, groundwater and surface runoff. The distribution of the PAH emission loads shows similar results whereby 80 – 95 % of the PAH emissions are caused by groundwater, surface runoff and runoff from sealed urban areas. Around 80 – 90 % of the PBDE emissions originate from groundwater and surface runoff. By contrast the share of emission of PFOS via discharges of wastewater treatment plants on total emissions lies between 45 – 75 %. Up to 40% of the TBT input is caused by point sources, whereas urban runoff, runoff from sealed surface and atmospheric deposition also represent relevant TBT emission pathways. However, these results are to be interpreted with care as the calculation of the contribution via groundwater and surface runoff are based on a very limited number of samples (n<10). This limited dataset is used for the Austrian wide assessment although representativeness is questionable. Nevertheless the results provide first estimates and should be evaluated by strengthening the database by the generation of suitable monitoring data.

Compared to the Austrian results, main pathways in the catchment area of the Dornbirner Ach are industrial discharges, discharges from WWTP, runoff from urban areas and from sealed areas. By contrast emission loads in the catchment areas Strem and Gusen mainly originate from erosion, whereby emissions from municipal waste water management (point discharges and urban runoff) in the catchment area of the Strem has more influence than in the Gusen catchment area. In Fig. 1 the share of emission pathways on the total load for Ni and TBT is shown exemplary for the overall Austrian estimation in comparison to the estimation for the selected catchment areas.

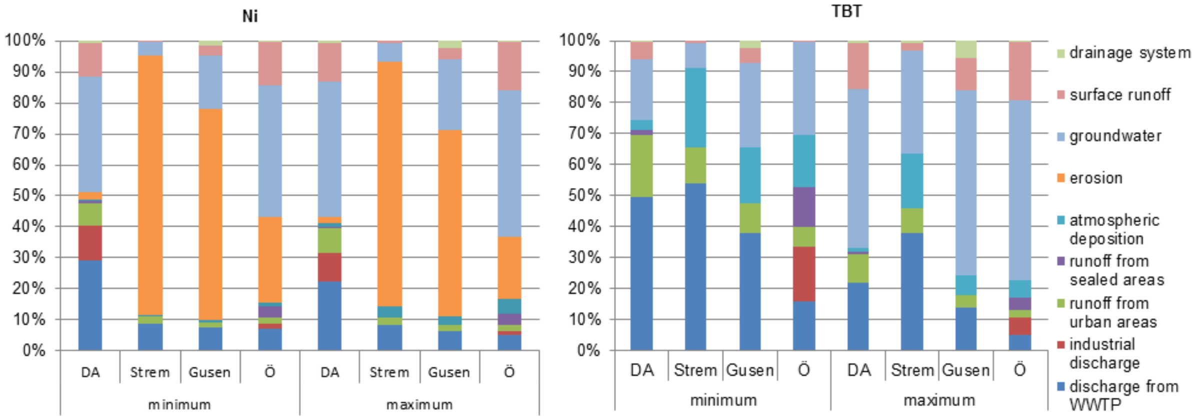

Figure 1: Share of emission pathways [%] in total emission loads in Austria (Ö), Dornbirner Ach (DA), Strem and Gusen for PFOS and Ni

As shown in Fig. 2 (left side) deviations between modelled and monitored in stream loads vary between 10 and 40% for Ni. Similar results are observed for Pb. Due to poor monitoring data availability comparisons of modelled and monitored loads of Hg, Cd, PAH, PBDE, PFOS and TBT were not possible. Rough assessments on expected concentrations in streams were determined and compared to measured concentrations (presented based on minimal and maximal approach, see chapter 2.1) and guideline values of the WFD. In general modelled concentration of Pb, Cd and partially Ni comply with the environmental quality standards defined in directive 2013/39/EU. For PBDE and TBT (figure 2, right side) the probability to exceed the EQS is given whereas for PFOS modelled concentrations are above the EQS. However, for TBT no clear assessment is possible (see figure 2) and reliable monitoring data is required to clarify the existing uncertainties.

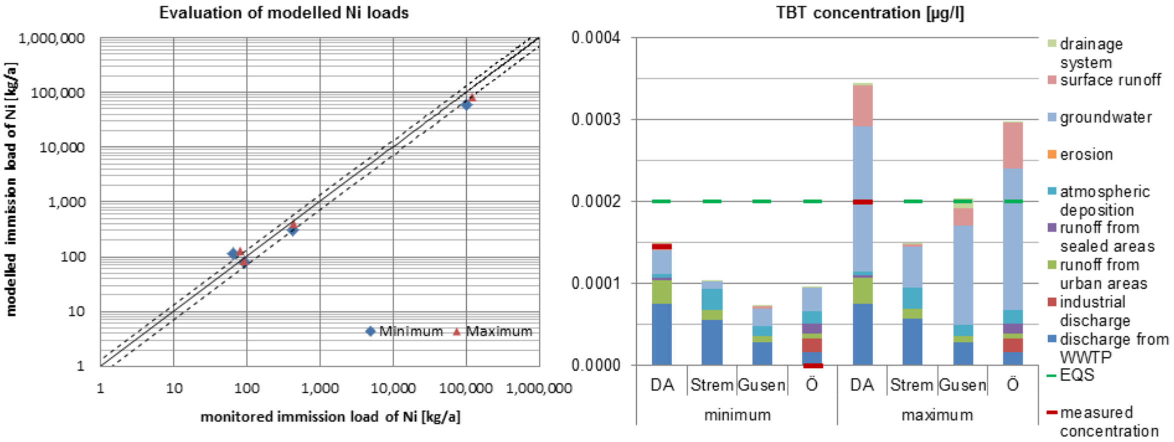

Figure 2: Evaluation of modelled Ni load (left side) and comparison of modelled and measured TBT concentrations and EQS (right side)

4 CONCLUSION

The investigations give a first overview on the contribution of different pathways to the overall emission to surface waters for selected priority substances. The results provide first estimates for expected instream concentrations as monitoring results are either below LOD or missing. Uncertainties of estimates are still very significant. For evaluating and improving the results, nationwide monitoring of concentrations in groundwater, surface runoff and runoff from urban and sealed areas need to be implemented. Thereby, the investigations should take account to local and regional differences by choosing sampling locations of catchments with different characteristic in respect to land use, population density, industrial activity and water availability. Considering the low concentrations, analytical methods of sufficient sensitivity have to be used in order to generate data on the occurrence of specific pollutants in various matrices.

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STORAGE OF POLLUTED SEDIMENTS IN THE ODRA RIVER CHANNEL

AN INFLUENCE OF THE RIVER CHANNELIZATION

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1 INTRODUCTION

The Odra river (western Poland) was channelized repeatedly from the first half of the 18th century by channel straightening and narrowing with the regular array of groynes. Since the beginning of 19th century, intensive channel narrowing by groynes has reduced the width of the upper Odra River on average twofold to 61 m whereas, channel gradient increased to about 0.4‰. This induced channel incision in this reach by about 3 m, most intensive as early as the eighteenth century (Ciszewski, Czajka, 2015). In the middle reach, the river was intensively channelized from 1819 until the end of the nineteenth century, first by straightening and then by narrowing with groynes. The width of the natural channel decreased from about 200–250 m to 120 m by filling of groyne basins with alluvial deposits (Ciszewski, Turner, 2009). In the lower Odra the average river discharge amounts to about 350 m^3/s (at the mouth over 500 m^3/s). The channel gradient falls below 0.15‰ and extreme variability of flow (Qmax/Qmin) is low, being only 12, compared to 200 in the upper course. The river channel was modified here in the second half of the nineteenth century when groynes as long as 150 m were constructed leaving navigation way about 124 m wide.

Construction of groynes on the Odra preceded rapid development of heavy industrialization and induced intensive accumulation of fine-grained deposits rich in organic matter and heavy metals. The upper reach of the Odra have been strongly contaminated by industrial and domestic effluents from the Upper Silesia and Ostrava Coal Districts. In both regions coal mining began at the end of the eighteenth century, rose rapidly from the 1860s, and peaked before World War I. The trend continued in communist industry, promoting the growth of coal extraction after World War II. It was accompanied by intensive extraction and reworking of copper ores and development of heavy industry in the middle reach of the river.

At the beginning of the 20th century groyne fields partially filled with deposits were dissected by a bank line with a new system of groynes, and parts of these fields were keyed into the floodplain. These deposits have been identified in vertical profiles along banks of the Odra river both in groyne-created basins and on the floodplain. Grain size, organic matter, Zn, Pb, Cd and Cu content and ^{137}Cs was used for sediment dating and, stratigraphy and chemistry have been diagnostic features for these deposits.

2 RESULTS

2.1 Sediments of the upper Odra river

Stratified even 4-m-thick, 20th century sediment sequences have been found in groyne fields of the upper, incised river reach. Typically, profiles consist of laminated deposits overlying basal gravels. The sharp borderline between basal gravels and overlying fine-grained, polluted deposits proves a drastic change of the fluvial sedimentary environment in these river reaches. However, there are also 19th century groyne infills, weakly polluted, with invisible stratification (Fig. 1).The sediment stratification is typified by dark layers separated by bright, sandy, and less polluted strata. The content of organic matter in black layers exceed even 50%, Zn content over 2500 mg/kg and average Pb content over 1500 mg/kg. The average rate of sediment accretion in groynes is higher than on the floodplain and reaches 5 cm/year. These deposits occur in the narrow zone dozen or so meters wide. Permeable gravels of former river bed underlaying near-bank deposits favour water percolation and metal redistribution as a result of the water table fluctuation particularly in the lower section of profiles. It is suggested by the highest concentrations of lead, zinc and cadmium at a depth of 4 m in sediments accumulated in the mid-19th century in spite of the peaking of industrialization and the pollution of the Odra River with heavy metals in the 2nd half of 20th century (Ciszewski, Czajka 2008).

Figure 1: Infills of the 19th century groyne basins at Racibórz (Ratibor) in the upper reach of the Odra river rests over remnants of former bank revetments 3 m over the present water table.

2.2 Sediments of the middle Odra river

Groyne deposits observed in the middle reach of the Odra River, with organics contents exceeding 10% and polluted with heavy metals, are on average about 2 m thick. Their stratigraphy is more differentiated than in the upper Odra river course but they display a clear distribution pattern. In the outer part of groyne there are uniform organic silty deposits of a loose structure. The age of these deposits, estimated by the peak of copper distribution in some profiles, identified with maximum metal loadings from the copper mining district in 1980 (Ciszewski, 2003) signify a high accumulation rate of the order of 6 cm/year. It is related to the discharge of polluted fine grained sediments reach in organics with mining and municipal sewages.

In the inner part of groyne, which became a part of the floodplain, upper silty layer polluted with copper, zinc and lead can be 1.5 m thick and rest on gravels of the pre-regulation channel overlaid by coarse-grained sands of the former side channel bar. Preservation of uncohesive sandy deposits at the average water table indicates a general lack of river bed erosion in this reach which is confirmed by the constant minimum annual water stages over the last 150 years. This reach was dominated by processes of channel narrowing induced by lateral accretion in groyne basins whereas accumulation of the top layer over the recent 25 years with the rate of 1cm/year was relatively slower. This value undoubtedly represents the highest present-day deposition rate which could be observed on the floodplain in this reach because the largest flow velocity gradient, which induces high rate of deposition, is observed immediately at river banks (Wyżga, Ciszewski, 2010).

Generally, deposits polluted with heavy metals of this reach can occur within three distinctive geomorphic units. In the first zone furthest from the channel, polluted deposits up to 0.5 m thick can cover unpolluted coarse sands and gravels of 18th century channel bars. In the second zone adjacent to the river banks, deposits accumulated in groyne fields from the second half of the 19th century can be up to 3 m thick and frequently contain coal particles and metal concentrations several orders of magnitude above background levels. In the third zone comprising groyne fields within the present channel, contaminated deposits are usually several decimeters thick in small groyne fields and about 2 m thick in the larger ones (Ciszewski, Turner 2009).

Figure 2: Groyne basins at Ścinawa (Steinau) in the middle Odra river reach are filled partially with deposits up to 2 m thick.

2.3 Sediments of the lower Odra river

In the lower reach, polluted 20th century sediments occur only in the top 30 cm of floodplain and groyne deposits. The age of the Cu and Pb peak in these sediments on the depth of 8–10 cm (from about 1980) indicates that the recent average accretion rate is about 3–4 mm/year. The rate tallies with the rate for the whole dark, organic polluted sediment layer, which rests on sandy deposit at the depth of 30 cm. The presence of slivers of bricks in the bottom deposits may suggest that they occurred below the horizon of the floodplain surface in 1930 when the groynes in this reach were rebuilt, which involved some bank remodeling. The results obtained for profiles from floodplain margins give a generally constant deposition rate after this date, of the order of a few millimetres per year for the organic layer. An estimated low rate of deposition, compared to the upper and middle Odra, fits well with the observed floodplain topography with a lack of levee, only partial filling of groyne basins, and the small amount of suspended sediment transported in the lower Odra River reach. These features are concordant with vertical channel stability proved by constant water stages over the whole of the twentieth century, suggesting a small influence of groyne construction on fluvial sediment conveyance. In this reach the sediment accretion rate is relatively low and the deposits fill only some of the groyne basins, mostly in the middle of the basins (Fig. 3).

Figure 3: Groyne basins at Frankfurt a/O are filled slowly with sediments.

3 CONCLUSIONS

Contemporary fluvial processes in the channelized Odra river differ markedly from that observed usually in natural channels. Instead of lateral accretion of deposits in a meander belt of the unregulated rivers, the floodplain of the Odra river has been formed since half of 19th century solely by vertical accretion. More intensive processes of erosion and accumulation induced by channelization works in 2nd half of 18th and in 19th century followed slow adjustment to artificial channel forming structures. These processes are still relatively intensive in the upper reach, characterized by the largest stream power and continued channel training works. The groyne construction became the most important factor reducing the polluted sediment transfer from the channel on the floodplain to extreme flood episodes. It initiated the expansion of the floodplain margins which, in vertically stable reaches, are equal in height to the rest of the floodplain. Vertical accretion deposits are preserved in wider reaches on former sand bars and in narrow channel or small groyne fields on silt-clay deposits resistant to erosion. These deposits are the characteristic feature for the near-bank accumulation in the channelized river. Preservation of 19th and 20th century polluted sediments was favoured by the long-lasting and repeated channel narrowing and the construction of bank reinforcements.

Channelization of the formerly severely polluted Odra river induced intensive accumulation of fine-grained deposits of silt and sand fraction rich in organic matter and containing heavy metals in concentrations exceeding the geochemical background. These deposits fill groyne basins and form floodplain margins over the channelized river course. Overall, lateral extent of these deposits is controlled by the morphology of the pre-regulation channel. The zone of thick stratified deposits of industrial origin, which could be named “industrial alluvium”, is confined to the width of the pre-regulation channel and contemporary active groyne fields and does not exceed about 30 m width in the investigated sites (Ciszewski, Czajka 2015). The thickness of these deposits within a given river reach is related to the degree of river pollution and the intensity of fluvial processes controlled by channel-training works. This includes the channel straightening as well as the degree of channel narrowing by bank reinforcements and groynes.

Dense stratification with fine organic layers is typical of vertically unstable upper river reach, where 4-m-thick sediment sequences overlie gravels of former channel bars. The high rate of sediment accretion in this reach, of the order of 5 cm/year, and its stratigraphy are related to channel constriction followed by downcutting, simultaneous with severe river pollution.

In a severely polluted middle river reach stabilized by regulation structures, 2-m-thick slack water deposits are composed of uniform strata of polluted silts abundant in organic matter. The rate of sediment accretion is very high and reaches 5 cm/year. It decreases at higher levels of groyne fields and in floodplain locations that are inundated less frequently by larger floods producing coarser grained deposits. Typically, these deposits are stratified with dark layers intercalated with bright, sandy, and less polluted strata.

In the stable and relatively less polluted lower river reaches, floodplain dark deposits are finely laminated or laminas are indistinguishable and the average rate of deposition is of the order of a few millimetres per year.

Sediment stratigraphy plays an important role in cycling of metals in the sediment-water system. The uncohesive sand and slit of industrial alluvium which fill groyne basins and contain heavy metals are potentially the most significant secondary source of pollution on both rivers. They may by remobilized already during lower than bankfull water stages. 19th and 20th century sediments stored in the narrow, dozen or so meters wide zone plays the most important role in pollutants cycling within the river system in period of years or tens of years whereas, heavy metals stored over the rest of floodplain may re-enter the river system in the perspective of several hundreds or more than thousand years. It seems that controlling lateral channel stability by careful maintenance of structures protecting these narrow banks strips is essential for localization of contaminant mainly in incised river reaches whereas more cohesive silt-clay deposits of stable river reaches are more resistant to erosion and play minor role in the cycling of metals along the river.

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ASSESSMENT OF DIFFUSE TRACE METAL INPUTS INTO SURFACE WATERS ON BASIN SCALE –

COMBINING PROCESS BASED SIMULATIONS WITH EMPIRICAL ESTIMATES

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ABSTRACT

As a result of mining activities since the 13th century, surface waters of the German Mulde catchment suffer from deleterious dissolved and sediment attached lead (Pb) and zinc (Zn) inputs.

Lateral, sediment attached trace metal inputs are associated to soil erosion and resulting sediment inputs into surface waters. Since soil erosion by water is related to rare single events, monitoring and empirical estimates reveal certain shortcomings. This gap in knowledge can only be closed by process based model calculations. Concerning these calculations it has to be considered, that Pb and Zn are predominantly attached to the fine-grained soil particles (<0.063 mm). The selective nature of soil erosion causes a preferential transport of these fine particles, while less contaminated larger particles remain on site. Consequently trace metals are enriched in the eroded sediment compared to the origin soil.

Leaching rates of trace metals with drainage water are significant criterions for assessing trace metal concentrations of soils and associated risks for ground water pollution. However, the vertical transport rates of trace metals in soils are difficult to quantify. Monitoring is restricted to small lysimeter plots, which limits the transferability of the results. Additionally the solid-liquid-transfer conditions in soils are highly variable, primarily due to the fluctuating retention time of percolating soil water.

This paper aims to introduce both, a new method that allows the assessment of trace metal leaching rates from contaminated top soils for standardised transfer conditions and a process based modelling approach for sediment attached trace metal inputs into surface waters.

Pb and Zn leaching rates amounts to 20 Mg ha^{-1} yr^{-1} resp. 114 Mg ha^{-1} yr^{-1}. Deviations to observed dissolved trace metal yields at the Bad Düben gauging station are caused by plant uptake and subsoil retention.

Sediment attached Pb and Zn input rates result to 114 Mg ha^{-1} yr^{-1} and 173 Mg ha^{-1} yr^{-1} , which increase measurements by 10 to 25 times. This can only be caused by an inappropriate sampling regime. Routine sampling seems to reflect base load of trace metals rather than total trace metal loads.

INSTRUMENTS OF THE INTEGRATED POLLUTANT / SEDIMENT MANAGEMENT IN THE ELBE CATCHMENT AREA

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1 INSTRUMENTS OF THE INTEGRATED POLLUTANT / SEDIMENT MANAGEMENT IN THE ELBE CATCHMENT AREA

The investigation of the pollutant situation of the Elbe catchment area in the course of the first management plan in accordance with the EC Water Framework Directive (WFD) has shown that contaminated sediment of the Elbe and its tributaries represents a significant secondary source of pollutant emissions, which have an impact as far as the North Sea.

Unpolluted sediments are an essential and integral part of rivers and their flood driven embankment structures (wetlands / marshes). They provide a central function with regard to the dynamics, productivity and diversity of water bodies. On the other hand polluted sediments may be regarded as a long-term memory reflecting the negative environmental footprint of industrial development. Thus, they can be used – like a history book – to gain information about the pollutional background of a particular part of the drainage area.

Several pollutants, being discharged into the river system through various pathways, tend to bind to solids. In marginal river structures with low flow they accumulate und build up a polluted fine-textured sediment layer. In case of a flood flow, these fine sediments may be dispersed, which leads to a remobilization of the contaminants and as a result, to an uncontrolled downstream relocation of the polluted material. This process may repeat itself over hundreds of kilometers, leading to an accumulation of pollutants in the sediments, if further sources are passed. Eventually, a large charge of contaminants enters the Elbe estuary and finally, the marine environment. In addition, Elbe fish still cannot be recommended for human consumption without restrictions, agricultural products in the flood plains are still exposed to contamination and the relocation of the sediment for the maintenance of the depth of water, unavoidable for the Hamburg Port Management, is affected by the pollutant loading of the Elbe sediment.

The relevant pollutant cocktail of the Elbe sediments comprises 29 elements and compounds. The historical and recent pollution sources (primary and secondary point sources, diffuse sources) are found throughout the whole Elbe river basin.

Basically, organic pollutants such as Dichlorodiphenyltrichloroethane (DDT), hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs) and the Haloether are predominantly derived from the Czech Republic. Heavy metals such as cadmium (Cd), zinc (Zn), mercury (Hg), copper (Cu), lead (Pb) and the metalloid arsenic (As), but also the dioxins / furans (PCDD / F) and the hexachlorocyclohexane (HCH), originate mainly from the Mulde and Saale. Hamburg is still primary source region for organotin compounds (TBT and derivates).

Thanks to comprehensive remediation and environmental protection measures in the industrial sector and the massive dismantling of industry in central Germany, the pollutant load could be significantly improved. Particularly between the mid-1980s to the end of the 1990s the contamination levels of many substances have been reduced to less than one-tenth of its former maximum values. However, there has hardly been a further improvement since the 2000s until today. To achieve a good quality of fresh deposited suspended matter, which would allow a permanent safe use, it requires a further reduction in eight of the 29 Elbe relevant pollutants between 16% and 99%.

An improvement of the loading situation is possible only through a holistic sediment management in the whole Elbe catchment area which comprises in particular measures for the reduction of pollutants in the upstream river catchment area.

At the same time, this strategy corresponds with water management requirements of environmental directives such as the EC Water Framework Directive (WFD) and the EC Marine Strategy Framework Directive (MSFD). These are, to reach and keep the good ecological and chemical status, and to fully guarantee all functions and services that are necessary for the intended human uses.

As a consequence, the member states in the International Commission for the Protection of the Elbe River (ICPER) and the German River Basin Community Elbe (RBC Elbe) decided to develop a sediment management concept including recommendations for an economic and ecologically handling of sediments and dredged material. The concept combines the issues of sediment quantity, hydromorphology and sediment quality as well as ecological and use-oriented sediment aspects in one concept.

For the promotion of this topic the project “Remediation of contaminated Elbe Sediments – ELSA” was set up in 2010 and renewed in 2014. This project is a close cooperation of the Hamburg Ministry of Urban Development and the Environment, the Hamburg Port Authority and the Hamburg Ministry of Economy. The most pressing interest from a Hamburg point of view is to initiate the straight improvement of the contamination levels in the Elbe – especially those of the sediments – and further give professional advice and if required financial support.

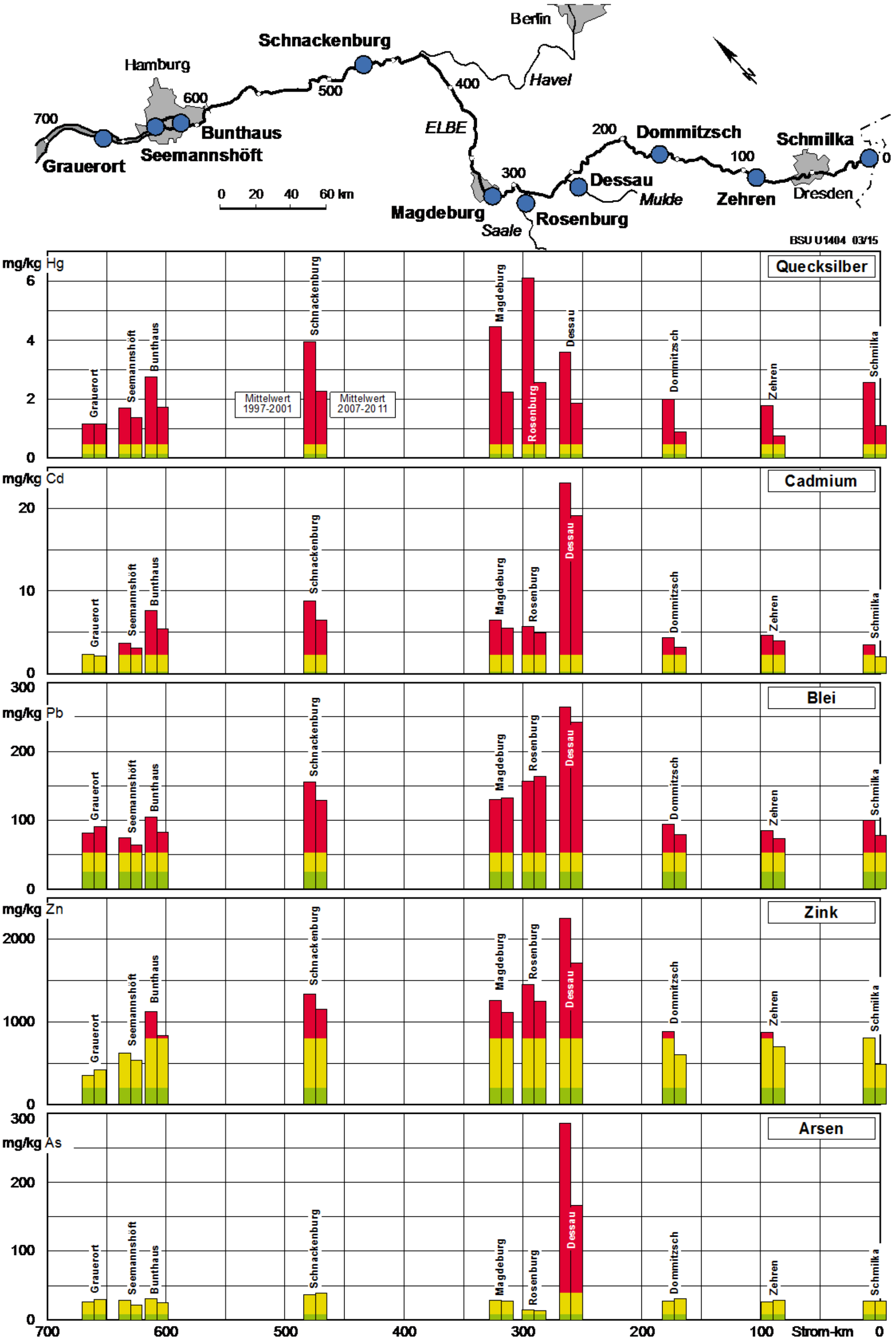

Figure 1: Comparison of selected inorganic contaminants in the longitudinal section of the Elbe – mean values from 1997 until 2001 and from 2007 until 2011 (sedimentation basin, monthly pooled sample, in fraction < 20 µm). Assessment in accordance with RBC Elbe (2013) / ICPER (2014); green: below the lower threshold value, yellow: between the lower and upper threshold value, red: above the upper threshold value

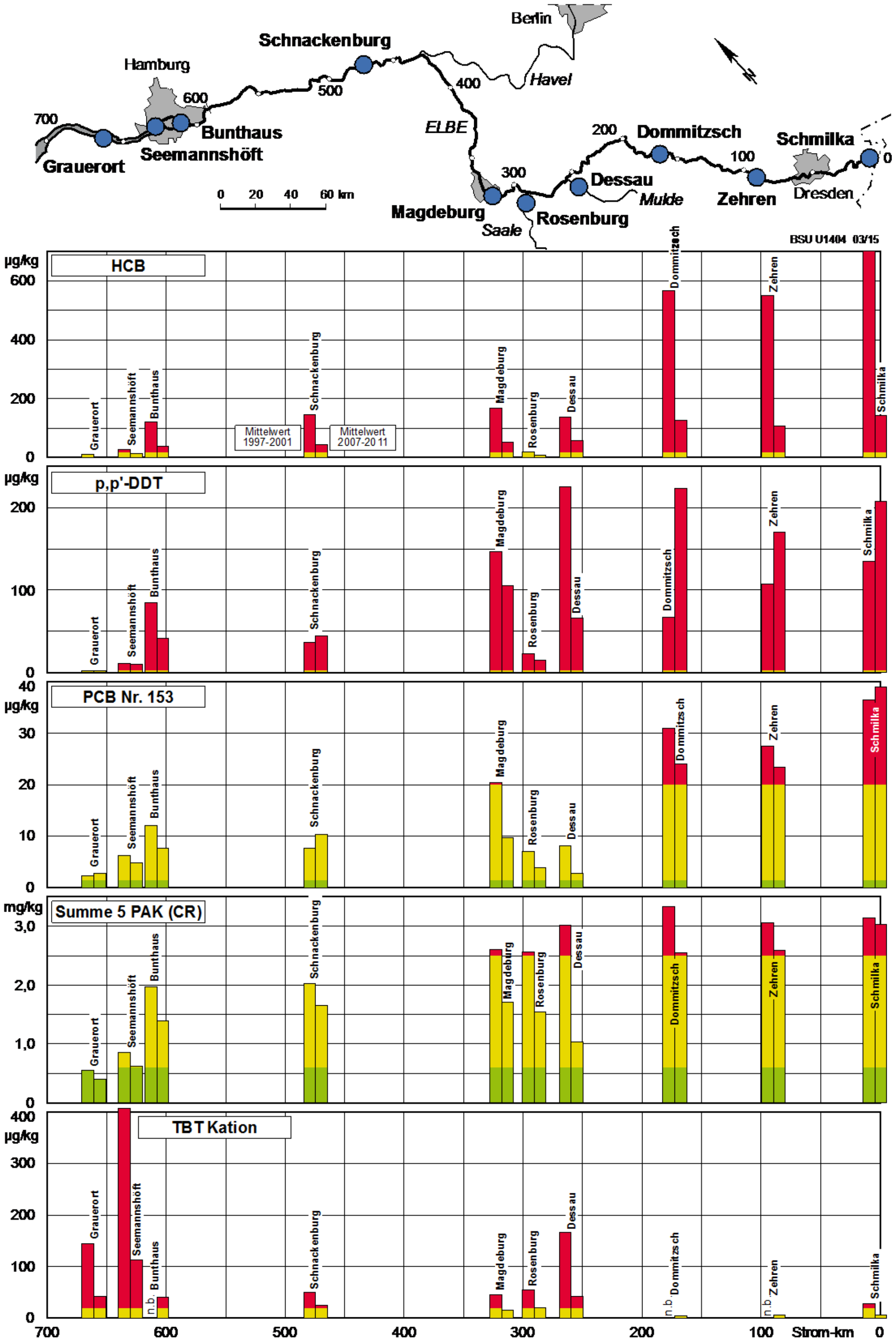

Figure 2: Comparison of selected organic contaminants in the longitudinal section of the Elbe – mean values from 1997 until 2001 and from 2007 until 2011 (sedimentation basin, monthly pooled sample, in fraction < 2 mm). Assessment in accordance with RBC Elbe (2013) / ICPER (2014); green: below the lower threshold value, yellow: between the lower and upper threshold value, red: above the upper threshold value

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ETHINYLESTRADIOL IN SURFACE WATERS – ANALYSIS OF CONSEQUENCES OF THE PROPOSED ENVIRONMENTAL QUALITY STANDARD (EQS)

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1 INTRODUCTION

The active pharmaceutical ingredient 17α-Ethinylestradiol (EE2) is a synthetic estrogen which is above all applied as a contraceptive. Given the endocrine effects of EE2, contamination of surface water with this compound is under specific consideration in order to prevent from adverse effects on humans or aquatic organisms. With the latest amendment of the EU Water Framework Directive (WFD) in August 2013, EE2 has been put on the new watch list of compounds that are considered as possible priority pollutants (EU, 2013). IIn 2011, the Scientific Committee on Health and Environmental Risk proposed an environmental quality standard (EQS) as low as 35 $pg \cdot L^{-1}$ for EE2 in surface waters which is controversially discussed. According to the German surface water regulation (OGewV) compliance of surface water concentrations with this quality standard is evaluated by the annual average of measured concentrations from monthly grab samples (AA-EQS). However, in the aquatic environment EE2 concentrations are expected to be below the actual analytical detection limit rendering a specific challenge for chemical analysis. Therefore, practically no quantitative data of EE2 concentrations in German surface waters are available as basis for exposure assessment and risk management. As an alternative, results of model simulations can be used for this purpose. To evaluate the range of expected EE2 concentrations in surface waters we performed a geo-referenced exposure assessment with the model system GREAT-ER in two exemplary catchments.

2 MODEL SIMULATIONS

2.1 The georeferenced model GREAT-ER

The model system GREAT-ER (“Geography-referenced Regional Exposure Assessment Tool for European Rivers”) has been developed to simulate and assess chemical burden of European river systems from point sources by means of a spatially explicit, geography referenced modelling approach (Fejtel et al., 1997; Matthies et al., 2001). Main objective of GREAT-ER is the calculation of local aquatic exposure concentrations at a river basin scale. The model has been successfully applied in various catchments to simulate concentrations of household chemicals (Bester et al., 2008; Price et al., 2009; Wind et al., 2004), pharmaceuticals (Alder et al., 2010; Aldekoa et al., 2014) and zinc (Hüffmeyer et al., 2009). Recently, an updated version of the model including features for defining and evaluating risk management scenarios has been published (Kehrein et al., 2015). The model assumes steady-state conditions with more or less constant emissions from point sources such as sewage treatment plants. Emission factors on a per-capita base are used to estimate the average mass flow of the chemicals into sewage treatment plants which implicitly includes the assumption of homogeneous consumption of the substance among the general population. For pharmaceutical ingredients the consumption is corrected for the fraction that is excreted unchanged from the human body. Partly elimination of the substance during sewage treatment is considered depending on the actual treatment technology. Within the river system, loss processes such as sedimentation or degradation are modeled as first-order processes. To account for temporal variations of input variables (e.g. flow rates) or uncertainties of model parameters (e.g. emission factors) stochastic simulations using Monte Carlo analysis are performed. Therefore, probability distributions are used as model input instead of deterministic values. As a result, concentration distributions for each river reach in the catchment are delivered. Assuming log-normal distribution of the concentrations statistical analysis allows for calculating the 10th and 90th percentiles giving an indication of the range of expected concentrations.

2.2 17α-Ethinylestradiol (EE2)

The synthetic estrogen 17α-Ethinylestradiol is mainly used in contraceptive pills. In 2009, the consumption of EE2 in Europe was 262 kg of which roughly 50 kg were used in Germany. These sales figures were used to estimate average per-capita consumption of EE2. Approximately 40% of the ingested amount leaves the body unchanged mainly with urine. Emission factors for EE2 were defined as the product of average per-capita consumption and excreted fraction. The respective amounts are transported via the sewer to the next sewage treatment plant (Johnson & Williams, 2004). Due to incomplete elimination up to 25% of total EE2 then enter surface waters with treated effluent (Baronti et al., 2000; Johnson et al., 2000). Loss by sedimentation in the river is expected to be small because of the relatively low octanol/water partitioning coefficient of EE2 (log K_{ow} = 3.67; Williams et al., 2009). Photolysis half-life at the water surface has been reported to be in the range of 5 days (Jürgens et al., 2002) indicating minor losses by this degradation process during travel time along a river. The substance is known to provoke estrogenic responses in fish at low concentrations. For example, Parrot & Blunt (2005) showed decreased egg fertilization and sex ratio (skewed toward females) after exposure to EE2 concentrations as low as 0.32 ng L^{-1}. Therefore, chronic effects after prolonged exposure to low concentrations cannot be excluded.

2.3 Case studies with EE2

Simulations were performed in the catchments of River Main and River Ruhr, both tributaries of the Rhine River. The Ruhr watershed in North-Rhine Westphalia with a total area of approximately 4,500 km² is characterized by high population densities especially in the downstream area where the majority of the 2.3 million people live. The watershed of River Main extends over 27,000 km² in Bavaria and Hessen and is populated by 7 million people. It is largely of rural character with congested urban areas around the cities of Nürnberg and Frankfurt. The model was first run assuming average flow rates (MQ) in all river reaches to evaluate the spatial distribution of average EE2 concentrations in the two catchments. The predicted environmental concentrations (PECs) are divided by the proposed EQS (35 pg L^{-1}) to give the risk characterization ratio. Values larger than 1.0 indicate exceedance of the criterion possibly requiring risk management actions. Subsequently, a more detailed analysis of the temporal variation of expected concentrations was performed at selected sites using monthly discharge scenarios derived from long-term gauging data.

3 RESULTS AND DISCUSSION

Simulations for average flow rates show that in the Ruhr watershed only very few small tributaries are predicted to exceed the AA-EQS, while in the Main watershed many tributaries along the whole river are likely to exhibit RCRs larger than 1.0 (see Figure 1).

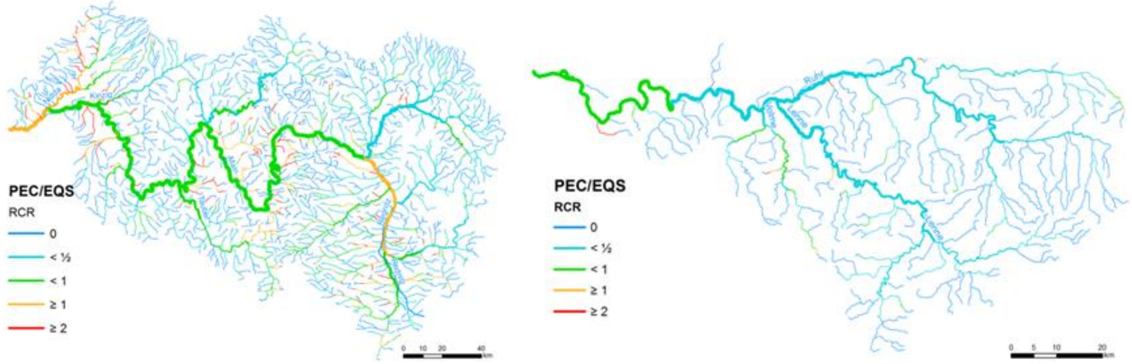

Figure 1: Risk characterization ratios for EE2 at average flow rates in surface waters of the Main watershed (left) and the Ruhr watershed (right)

However, predicted concentrations were mostly below the actual analytical quantitation limit (100 - 300 pg L^{-1}) for EE2 rendering identification of exceedances of the quality criterion by means of monitoring virtually impossible. Due to the variability of river flow rates monitoring data from monthly grab samples represent just one specific situation in time and space and do not form a sufficient base for detailed risk assessment. Average PEC values from model simulations allow for first evaluation of the spatial concentration distribution, but are also not apt for detailed risk assessment under variable flow rate conditions at different sites. Therefore, a more detailed analysis was exemplary performed for one selected site in the Main River close to Frankfurt (gauging station *Frankfurt-Osthafen*) where the average PEC was actually below the annual average EQS. Using the annual flow rate distribution from long-term gauging data (Figure 2, left) the respective EE2 concentration distribution at this site was predicted (Figure 2, right).

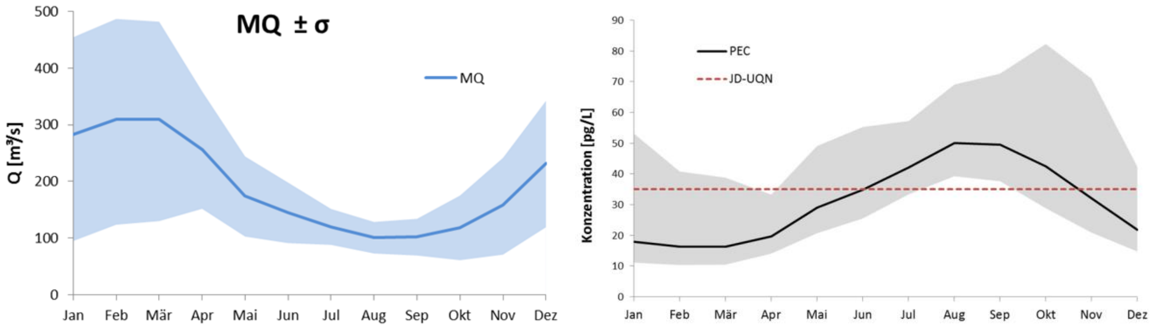

Figure 2: Annual flow rate distribution at gauging station Frankfurt Osthafen (left) and respective predicted EE2 concentrations

It can be seen that exceedance of the EQS is likely during the summer period (June – October) with high probabilities especially in August and September. Although the WFD criterion was fulfilled on average in this case, prolonged periods of higher concentrations are likely to occur. It is therefore highly questionable whether the arithmetic mean of concentrations from monthly grab samples constitutes a solid and reliable basis for evaluation of EE2 contamination in particular and the chemical state of surface waters in general. We suggest using model simulations to evaluate surface water concentrations of EE2 combined with targeted monitoring of treated effluent samples for validation.

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MONITORING POTENTIAL IMPACTS OF DOMESTIC WASTEWATER TREATMENT SYSTEMS ON SURFACE WATER QUALITY IN POORLY PERMEABLE SUBSOILS

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1 INTRODUCTION

In Ireland, the wastewater of approximately 500,000 (CSO, 2012) homes is discharged to domestic wastewater treatments systems (DWWTSs). Since 2009, legislation and policy measures aimed at regulating the construction and operation of DWWTSs have been introduced into Irish legislation and policy (EPA, 2009; S.I. 180 of 2013, EPA, 2013 (a) and (b)), largely in response to Ireland's obligations under the Water Framework Directive (Directive 2000/60/EC).

DWWTSs have been proven as an effective means of domestic wastewater treatment (Gill et al., 2007; 2009) when correctly sited, constructed and maintained, largely as a result of contaminant attenuation in the subsoil underlying the treatment area. However, 39% of the land in Ireland is deemed to have inadequate percolation characteristics with respect to DWWTSs (EPA, 2013 (a)) where hydraulic failure of DWWTSs is likely to occur as a result of poorly permeable subsoil or shallow, impermeable bedrock. In these cases there is potential for direct delivery of DWWTS effluent to nearby surface water receptors via shallow or surface preferential flow paths, or via direct pipeline connections. Recent research has highlighted the potential for DWWTSs to act as a source of pollution to surface waters (Neal et al., 2005; Arnscheidt et al., 2007; Withers et al., 2012), particularly in terms of phosphorus (P) loading. Low baseflow during dry periods and ecologically sensitive seasons means that chronic P inputs to small headwater (low order) streams become more significant due to reduced dilution capacity (Jarvie et al., 2008).

The aim of this research is to quantify the impact of DWWTSs on surface water quality, particularly in terms of P loading, through the monitoring of low order streams in densely populated rural catchments, with poorly permeable subsoils.

2 MATERIALS AND METHODS

To achieve the aim of the research, it was necessary to select small study catchments featuring low permeability subsoil, dense clusters of DWWTSs in close proximity to headwater streams, in areas of High to Very High Likelihood of Inadequate Percolation. In total, four study catchments were selected through ArcGIS mapping of relevant data layers; three featuring poorly permeable subsoil, one featuring a shallow, well-drained subsoil underlain by impermeable bedrock. To date, two study catchments have been instrumented and monitored.

Two primary monitoring points were selected along the stream length – one, the 'control' site (i.e. and un-impacted site) located as far upstream as the flow in these low order streams would allow whilst also remaining upstream of the majority of the DWWTSs in the catchment, the other (i.e. an impacted site) located downstream of the DWWTS clusters. These monitoring points (Figure 1) were instrumented with CTD units for the continuous measurement and recording of in-stream conductivity, temperature and water depth. Autosamplers were also stationed at the upstream and downstream monitoring points for one week, once a month, taking samples every seven hours following the methodology recommended by Jordan and Cassidy (2011). A rating curve for the stream discharge at these points was established from several stream discharge and stream stage measurements throughout the monitoring period. Grab sampling points were also selected along the length of the stream channel during catchment surveys, with grab samples collected at these points twice per month.

Samples were analysed for the following P fractions: dissolved reactive phosphorus (DRP), total dissolved phosphorus (TDP) and total phosphorus (TP), dissolved unreactive phosphorus (DuRP) and particulate phosphorus (PP). Nitrate, nitrite, ammonia and total nitrogen, along with total coliforms, *E-coli*, *Enterococci* and *Clostridium perfringens* and boron were also measured. Testing of the stream water samples for the presence of human-specific bacteroidales (Bac-Hum) and for the presence of human specific faecal sterols was also carried out.

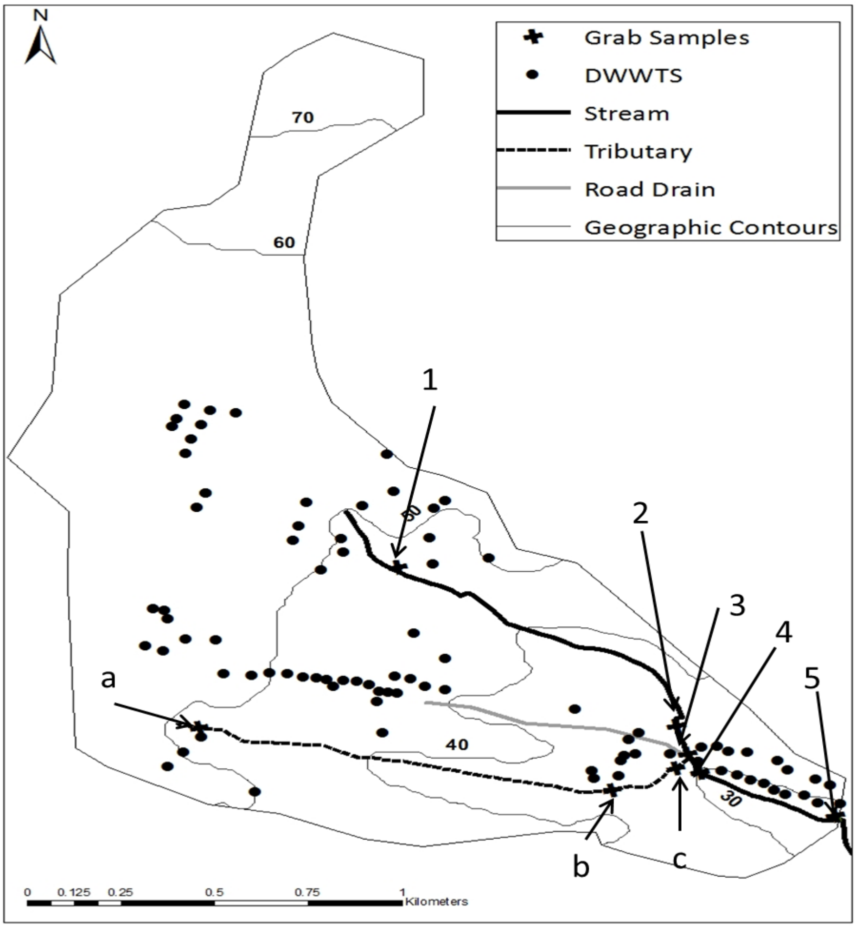

Figure 1: Map of Study Catchment 1, illustrating dense clusters of DWWTS located close to a small stream and its tributaries. Sampling Points 1 and 5 are the primary monitoring sites – the location of the CTD units and the autosamplers, upstream and downstream of the DWWTS cluster, respectively. Points 2,3 and 4 are grab sampling points along the main stream, and points a,b and c are grab sampling points along the small tributary. The total area of the catchment is 2.9 km^2, with pasture as the dominant landuse activity along with small areas devoted to non-commercial forestry, golfing and arable crops.

3 RESULTS

Figure 2 illustrates the average monthly P concentrations for the monitoring points upstream and downstream of the DWWTS cluster in Study Catchment 1. The average monthly DRP and TP levels were higher downstream of the DWWTSs than upstream, though in general P levels appeared to be unusually high in this catchment – often exceeding the threshold of 0.035 mg-P/L for ‘Good’ ecological status. DRP levels were highest from July to September, coinciding with a warm, dry period. For October 2014 the difference between upstream and downstream DRP appeared to be minimal in contrast with the upstream/downstream differences observed in other months. Particulate P appears to be the dominant P fraction from the averaged data; however, a closer look at individual data points in Figure 2 reveals that differences between the fractions vary considerably within the sampling week.

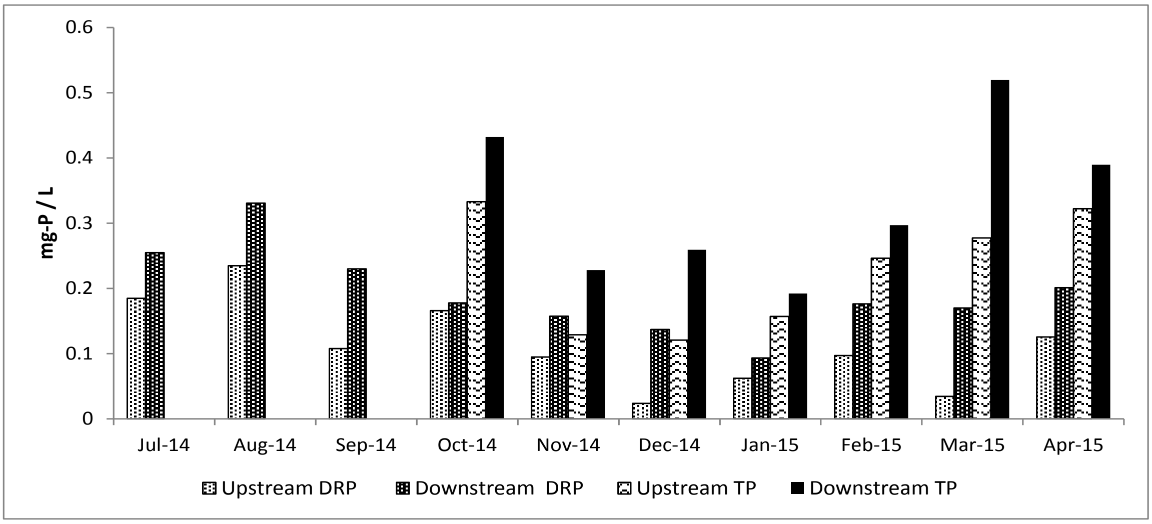

Figure 2: Average values of Phosphorus in Study Catchment 1 from July 2014 to April 2015. (*Note: Upstream refers to Upstream of DWWTS cluster*) (Note: No TP values for July, August and September of 2014)

Figure 3 illustrates the 24/7 P monitoring from the study period to date (mg/l P) at the downstream monitoring site, re-arranged into monthly averages and into an hourly sequence to illustrate potential daily patterns in in-stream P levels. DRP levels were highest at 02:00, 09:00, 12:00 and 16:00. TP levels appeared to be highest at 04:00, 11:00, 14:00, 21:00 and 22:00.

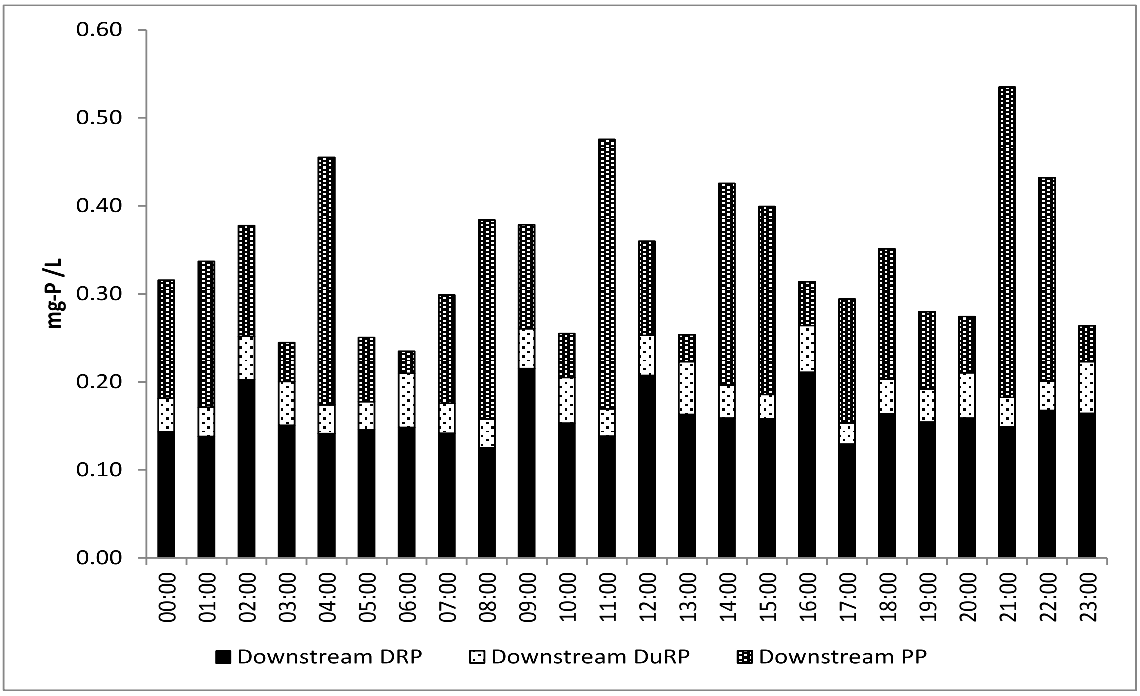

Figure 3: Fractions of Total Phosphorus (mg-P / L) at the downstream monitoring point in Study Catchment 1. The sum of the fractions in each column represents the TP value.

Whilst the average monthly values indicated an increase in P downstream compared to upstream, the individual data points sometimes illustrated higher P values upstream compared to downstream. Bearing in mind that the upstream point in this study was selected as the 'control' site where anthropogenic influences on the water quality were thought to be minimal, these results were surprising. Elevated levels of ammonia and nitrite were also detected at this point – often at higher concentrations than at the downstream monitoring point. In addition, human-specific Bacteriodales and human specific faecal sterols were also detected at this point, as well as boron (a chemical associated with domestic wastewater). The Bac-Hum and human-specific faecal sterol indicators were also detected at the downstream monitoring point. Table 1 illustrates changes in water quality along the length of the stream channel from grab samples collected twice a month.

Table 1: Water quality data from bi-monthly grab samples collected throughout the catchment. The Sample Site designation follows that illustrated in Appendix A. Sample Site one is the upstream monitoring site; Sample Site 5 is the downstream monitoring site (see Figure 1).

Sample Site	**Distance from Catchment Outlet**	**DRP**	**TP**	**Ammonia**	**Boron**
	(m)	**(mg/L PO_4-P)**	**(mg/L P)**	**(mg/L NH_3-N)**	**(mg/l B)**
1	1590	0.09	0.27	0.425	0.085
2	602	0.10	0.24	0.085	0.165
3	441	0.21	0.39	0.508	0.13
4	405	0.19	0.33	0.300	0.175
5	0	0.16	0.33	0.265	0.135
a	1900	0.07	0.29	0.0325	0.03
b	840	0.29	0.34	0.064	0.155
c	495	0.19	0.30	0.120	0.095

Lower P levels were observed in Study Catchment 2, though the 0.035 mg/L P value was exceeded at the downstream moinitoring site in 3 out of the 10 months. At the upstream monitoring point, DRP was rarely observed to rise above the limit of detection (0.01 mg-P /L), aside from July and August of 2014 – an extended dry period. Downstream of the DWWTSs, there was a slight increase in P (up to 0.025 mg-P/L). Particulate phosphorus was the dominant form of P, indicating that the likely source is particulate-bound P transported from the land surface during rainfall events. In addition, conductivity and nitrate levels were consistently higher at the downstream site than the upstream site. Ammonia and nitrite were generally below the limit of detection at both upstream and downstream in this catchment, although on occasion, nitrite and ammonia were present at detectable, albeit low, levels at the downstream site (maximum NO_2 detected at downstream = 0.03 mg NO_2-N /L; maximum ammonia at downstream = 0.01 mg-NH_3-N /L). Boron levels were undetectable at the upstream monitoring point in Catchment 2, and only occasionally detected downstream of the DWWTS cluster. Human specific Bac-Hum and Faecal sterols were detected downstream of the DWWTS cluster but not at the upstream monitoring point.

4 CONCLUSION

To date, results indicate that there is a change in stream water chemistry between the monitoring points upstream and downstream of the DWWTS clusters, although it is too early in the project to determine whether this change is due to the presence of DWWTSs and if so, what the extent of the DWWTS impact is in relation to the concurrent nutrient impact from agricultural practices in the catchment. In both catchments, DRP values appear to be lower in the winter months than in the summer months, possibly reflecting the increase in stream discharge observed for the winter months, and the influence of small, chronic point sources of P such as DWWTSs during the summer low flow period. Another possible explanation for the higher summertime P levels at the downstream site in Catchment 1 is the presence of a small holiday village in the middle of the catchment which is occupied from June to September (*pers. comm.*)

The upstream site in Catchment 2 appears to be the perfect control site, with minimal anthropogenic influences on water quality. This does not appear to be the case with the control site in Catchment 1. The nearby DWWTSs appear to be having a detrimental and detectable influence on stream water quality, as evidenced by occasional high P values and the detection of human specific sterols, Bac-Hum and Boron at this monitoring site.

While the number of DWWTSs upstream of the upstream monitoring point in catchment 1 is much lower than for the downstream monitoring point (19 compared to 93 respectively), given the very low flow exhibited at the upstream point (Point 1), it is possible that the upstream DWWTSs have a disproportionate effect on water quality, compared to the downstream site. In addition, there are a number of direct connections from DWWTS settlement tanks to the stream throughout the catchment. Further research and the extension of this study to another two study catchments will aid in clarifying the matter.

No discernible daily P patterns were distinguishable. In catchment 1, DRP values appear to be highest at 02:00, 0.9:00, 12:00 and 16:00, whilst TP values appear highest at 04:00, 11:00, 14:00 and 21:00. There were clearly changes in P levels throughout the day; however, further data are required to determine if these changes are reflective of internal P cycling, changes in stream discharge or daily patterns of water usage in the catchment.

The findings of this project will allow for calibration of a modelling tool that can be used to assess the potential impact of DWWTSs on surface water quality, and act as a potential aid for environmental policy makers. This modelling phase will also upscale the findings of the project and apply them to larger, more complicated catchments.

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DEVELOPMENT OF A TOOLBOX FOR INTEGRATED WATER QUALITY MODELLING SUPPORTING RIVER MANAGEMENT PLANNING

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ABSTRACT

A flexible water quality modelling framework has been set up to quantify total catchment nitrogen and phosphorus loads and to assess the impacts of potential mitigation measures. As required under the EU Water Framework Directive legislation, River Basin Management has to be based on quantitative information regarding the effect of restoration and mitigation measures at the ecological and chemical quality of surface waters. Comprehensive understanding of catchment nutrient loading will assist the river basin planning process and allows a more efficient implementation of management options to prevent further ecological degradation of the aquatic ecosystems.

An approach will be presented that includes the set-up of an integrated catchment water quality tool being applied in different catchments in New Zealand, Turkey and the Netherlands. The general toolbox combines both hydrological and water quality modelling tools and supports water managers in their river basin management and understanding.

The Waituna Lagoon in Southland (20.000 ha), New Zealand, is subject to increasing nutrient loads and the water manager is fearing a shift to turbid water state. In collaboration with the client DairyNZ, a framework consisting of a distributed hydrological model (WFLOW), a seasonal waste load model (OVERSEER) and a water quality model (Water Framework Directive Explorer WFD-E) has been set up and calibrated against existing monitoring data. In-river nutrient concentrations and total nutrient load contributions to the lagoon were simulated with the modelling framework.

In the Büyük Menderes, Turkey, the so-called River Basin Explorer tool has been developed in close cooperation with the local authorities and stakeholders. The tool is required to evaluate the impact of the measures being identified in the present draft River Basin Management Plan for the Büyük Menderes River Basin. This modelling framework is in this case a combination of a 0-dimensional River Basin Simulation Model (RIBASIM) and a water quality model (WFD-E). The latter is composed of an ecological module determining the ecological status of a water body quantified by EQR (ecological quality ratio) according to Turkish ecological knowledge rules, combined with an emission module estimating nutrient loads from diffuse and point sources.

The last example covers a nutrient analysis in the Meuse catchment (Belgium, France, Germany, Luxembourg and the Netherlands) requested by the International Meuse Commission. Aim of the study is to evaluate the effect of planned nitrogen mitigation measures in the 3rd Draft RBMP at the nitrogen loads to the North Sea. For the Dutch part of the Meuse river basin, the modelling framework consists of 4 sub-models: a North Sea model (Delft3D-GEM), the Dutch emission Database (PRTR), a nutrient model (STONE) and a water quality model (WFD-E).

These three example studies present a flexible water quality modelling approach which can be applied to different catchments worldwide to assess water quality and water allocation issues and to evaluate the impact of different mitigation measures in the process of river basin planning.

POSTER

Numerical modelling of fine-grained sediments remobilization in heavily polluted streams. Case study: Elbe and Bílina River, Czech Republic

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ABSTRACT

The study realized within the framework of international initiative ELSA provided by the Hamburg Department for Urban Development and the Environment (Freie und Hansestadt Hamburg – Behörde für Stadtentwicklung und Umwelt) and agreed by the International Commission for the Protection of the Elbe River (ICPER) aimed to estimate remobilization of channel and riparian fine-grained sediment in localities heavily polluted by industrial emissions. Four characteristic stream stretches in Czech Republic were analyzed: (A) Elbe River at the confluence with Bílina river (from Ústí nad Labem to the German border); (B) Bílina river (Elbe left tributary), draining industrial and mining areas of Northwest Bohemia; (C) Midstream reach of Czech Elbe and it's riparian zones by the confluence with Vltava river, affected by the prevailing chemical industry and (D) fluvial lakes in the riparian zone of Czech Elbe river downstream of Pardubice burdened by old loads from heavy chemical and oil industry. In total numbers 131 km of river stretches were analyzed by numerical modelling in order to obtain representative information of the current state.

Sediments of clay and silt character bedded in the side channels, weir backwaters and riparian water-courses are regarded to be heavily polluted by wide range of toxic matters. In the sediment samples, there were found elevated concentrations of persistent organic matters (PCB, DDT, HCH, PAHs etc.), heavy metals, and others. The pollution in sediment is resulting from the unregulated heavy industrial production in the focused areas in the second half of the 20th century during the soviet era that still contributes significantly to the Elbe river pollution.

The main goal of the study was to evaluate the risk of remobilization of polluted sediments by the assessment of discharge (values and return periods) and flow conditions initiating remobilization of sediments from the river bed. Thus the risk of remobilization of fine-grained sediments was evaluated in order to define a threshold discharge value after that the spreading of pollution further downstream can be expected. The modeling stems on basic assumption, that once the sediment is elevated from the bed, it could be transported for large distances in the form of wash load. The evaluation was made on the basis of numerical hydrodynamic calculation coupled with sediment transport model. The MIKE by DHI modelling software with different levels of schematization was used accordingly to the flow conditions and available data sources. For 50 km long stretch of Bílina river the 1D schematization of hydrodynamic model (MIKE 11) was selected as the discharges driving remobilization were expected within the extent of channel capacity due to the stream

regulation. For the lower and middle courses of Elbe river and the riparian zones evaluation the 2D schematization (MIKE 21 C) was selected. It enabled to distinguish flow characteristics in the zone with complicated hydrodynamic conditions. The sediments characteristics were resulting from the field surveys and laser granulometry analysis. Sediment samples were regarded as cohesive or non-cohesive according to the d50 value resulting from the granulometry curves together with the information about the amount of the silt and clay fraction. The non-cohesive sediment transport was solved as a total load (qt) recalculated into bed load and suspended load part according to Engelund Hansen relation within the numerical simulation model MIKE 21 C RM (River morphology). The cohesive sediment transport was solved on the basis of advection-dispersion formula (Enggrob and Tjerry 1998) where the erosion is represented as a source term and accumulation is represented by the sink term. Moreover the morphological changes were calculated and computational bathymetry was updated accordingly. Resulting bed level change was used for determining the sediment remobilization in focused areas.

The unsteady simulation was based on the synthetic hydrograph representing average flood wave derived from the observed historical floods. The moment of sediment transport initialization was observed and assigned to the statistically evaluated causal discharge value integrated along the cross section.

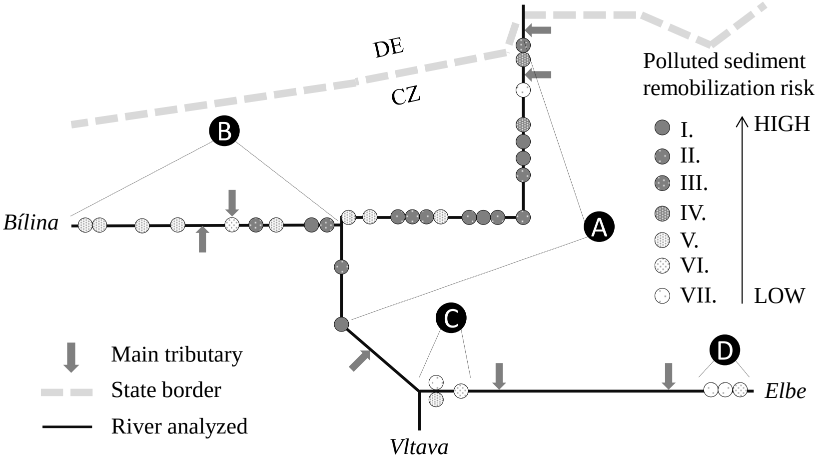

Figure 1: Scheme of fine-grained sediments remobilization competence in the studied sites

The major contribution of the study was the identification of threshold values for potential remobilization of sediment burdened by old loads in different environments connected by the similar problem (Fig 1). These threshold values serve as important information for identification and mitigation of risks related with old loads and hydrological extremes. From methodological point of view the study verified validity of applied distinct approaches for fine-grained sediment remobilization assessment and identified application limits.

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A hydrogeochemical - isotopic approach for assessing factors controlling the regional pollution of an urban alluvial aquifer

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ABSTRACT

The alluvial aquifer of the Meuse River is contaminated at regional scale in the urbanized and industrialized area of Liège in Belgium, in particular by inorganic pollutants such as sulphate, nitrate and ammonium. The sources of those contaminants are numerous: brownfields, urban waste water, subsurface acid mine drainage from former coal mines, atmospheric deposits related to former pollutants emissions in the atmosphere ... Sulphate, nitrate and ammonium are typical pollutants of the aquifer and tracers of the possible pollution sources.

In the Water Framework Directive context, a detailed hydrogeochemical characterization of groundwater was performed. The aim is to determine the origin of the inorganic contaminations, the main processes contributing to poor groundwater quality and the spatial extent of the contaminations. A large hydrochemical sampling campaign was performed, based on 71 selected representative sampling locations, to better characterize the different vectors (end-members) of contamination of the alluvial aquifer and their respective contribution to groundwater contamination in the area. Groundwater samples were collected and analyzed for major and minor ions and metallic trace elements. The analyses also included stable isotopes in water, sulphate, nitrate, ammonium, dissolved inorganic carbon, boron and strontium.

Different hydrogeochemical approaches are combined to obtain a global understanding of the hydrogeochemical processes at regional scale. Hydrochemical interpretations are based on classical diagrams, spatial distribution maps, geochemical equations, multivariate statistics such as self-organizing maps and isotopic analyses. With this combined approach, the location of the contaminant sources and most contaminated sectors of the alluvial aquifer together with a better understanding of geochemical processes involved are obtained.

Redox processes strongly influence the composition of groundwater, specifically for compounds degrading the quality of groundwater in the area (sulphate and ammonium). The highest concentrations of sulphate can be associated with the post-mining stage in the acid mine drainage process. Various reactions involving nitrogen compounds have been identified and allow a better understanding of causes of high concentrations of ammonium. Denitrification and sulphate reduction are also demonstrated based on isotopic ratios. Several areas with particular geochemical phenomenon were delineated.

Transport and Deposition of Heavy Metals and Arsenic during the June 2013 Flood of the River Elbe

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1 INTRODUCTION

The June 2013 flood of the River Elbe was an extreme event (see http://undine.bafg.de) during which a special monitoring programme (SMP) on the quality of water and suspended solids (SS) was coordinated by the BfG. An overview of results is given in Schwandt & Hübner (2014). Hübner & Schwandt (2015) have calculated load balances of heavy metals and arsenic in the Elbe section from Lutherstadt-Wittenberg to Magdeburg. In the present study the adjacent river section from Magdeburg to Dömitz is examinated.

2 STUDY AREA, DATA SOURCES, AND METHODS

From the SMP-data and daily mean river discharges from the Federal Waterways and Shipping Administration, daily and event-related loads (3-20 June 2013) of SS (measured as total suspended solids) and selected contaminants were estimated (Schwandt & Hübner, 2014). Here, we try to calculate a balance of SS-bound heavy metals and arsenic between the sampling points at Magdeburg and Dömitz (Fig. 1). To estimate the contaminant depositions on floodplains, we used the calculation approach by Krüger et al. (2014), who differentiated between a zone within 230 m distance from the riverbed with intensive SS sedimentation (zone A; 5.6 t/ha) and more distant flooded areas where deposition is weaker (zone B; 2.1 t/ha) (Fig. 1). The concentrations of heavy metals and arsenic in the SS on the floodplains were calculated from the event-related loads of these elements divided by the event-related load of SS, both at Magdeburg.

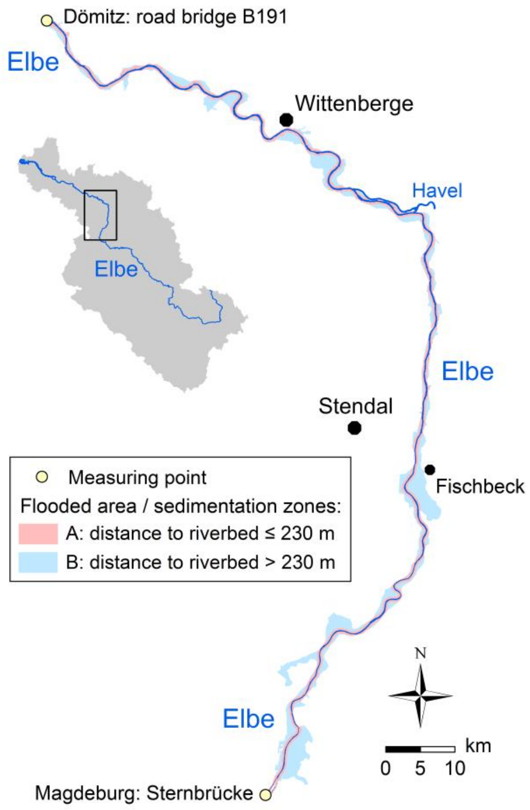

Figure 1: Flooded area of the River Elbe between Magdeburg and Dömitz (Elbe-km 326-506; 9-11 June 2013; data: BfG) with sedimentation zones after Krüger et al. (2014)

3 TRANSPORT AND DEPOSITON OF HEAVY METALS/ARSENIC

The loads of SS and SS-bound heavy metals/arsenic at Magdeburg and Dömitz from 3 to 20 June 2013 estimated from SMP-data are listed in Table 1 (lines 2, 5). The contribution of the River Havel in this balance is negligible, because the Elbe inputs of about 1000 t SS into the Havel polder (on 9 and 10 June) were in the same range like the outputs from the polder and by the Havel itself during the flood (3 to 20 June). The input of Elbe-SS into the flooded area near Fischbeck after the dyke failure there on 10 June (the flooded area beyond the dyke is not shown in Fig. 1) was estimated at less than 4000 t and was also neglected here.

The differences between the loads at Magdeburg and Dömitz (Tab. 1, line 6) can be explained entirely by deposition on the floodplains (Tab. 1, line 4c) using the calculation approach by Krüger et al. (2014). The calculated depositions of SS, lead, and arsenic exceed only very slightly the load differences between Magdeburg and Dömitz (105-107 %). In the case of cadmium, copper, and zinc - in arithmetic terms - about 130-150 % of these differences were deposited on the floodplains.

Table 1: Deposition of SS and SS-bound heavy metals/arsenic on the floodplains of the River Elbe between Magdeburg and Dömitz during the flood from 3 to 20 June 2013 after the calculation approach by Krüger et al. (2014)* (DTR: distance to riverbed; loads rounded)

1 Flooded area (total) [ha] : 19 407 Zone A ≤ 230 m DTR [ha]: 7 012 Zone B > 230 m DTR [ha]: 12 395	**SS**	**Pb**	**Cd**	**Cu**	**Zn**	**As**
2 Load of River Elbe at Magdeburg [t]	123 000	18.400	0.480	10.100	78.800	8.400
3 Contamination on SS [mg/kg]		150	3.92	82.1	641	68.2
4 Deposition on flooded area:						
a Zone A [kg/ha]	5 600*	0.838	0.022	0.460	3.600	0.382
b Zone B [kg/ha]	2 100*	0.314	0.008	0.172	1.346	0.143
c Zone A + zone B [t]	65 300	9.800	0.260	5.400	41.800	4.500
5 Load of River Elbe at Dömitz [t]	62 200	9.100	0.310	5.900	51.600	4.100
6 Difference (line 2 - line 5) [t]	60 800	9.300	0.170	4.200	27.200	4.300
7 Ratio between line 4c and line 6 [%]	107	105	153	129	154	105

4 CONCLUSIONS

The depositions on floodplains calculated after the approach by Krüger et al. (2014) are in rather good agreement with the loads of the River Elbe estimated from SMP-data; the great importance of floodplains as sinks for SS and contaminants is highlighted. Because by far most of the SS and SS-bound contaminants are usually transported in the course of the flood before the peak, dyke failures near the time of the flood-wave crest can be expected to cause only minor depositions.

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Identification of the model of pollutants distribution in the surface waters based on field studies

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1 INTRODUCTION

Identification of the mathematical model of pollutants distribution in rivers and reservoirs is necessary for forecasting the impact of environmentally hazardous facilities on surface water [1]. Use of these models in the decision support systems when calculating of pollutants transport in the surface waters [2] is associated with the determination of hydrological model parameters (flow rate, diffusion coefficients, self-cleaning and so on. [3]). Identification of a pollution source function, which makes boundary conditions of a current task, is particularly topical. There are point and diffuse pollution sources. The main point sources of anthropogenic load on surface water bodies are industrial enterprises discharges. The diffuse pollution sources are tailing dumps and accumulating reservoirs for waste and discharge mine waters, which cause the pollution of adjoining water bodies through their infiltration into ground water and surface wash-off. The task is to determine a filtration rate of pollutants from groundwater according to field observations.

2 IDENTIFICATION METHOD FOR THE POLLUTANTS DISTRIBUTION MODEL

Modeling of pollutants distribution is based on mixing and transferring solutions filtered through groundwater. The model takes into account the interaction of pollutants with suspended particles in the watercourse (sorption and desorption processes) and their settling down to the bottom as sludge deposits. The model is represented as a system of differential equations:

$$\begin{cases} \dfrac{\partial U}{\partial t} = \dfrac{\partial}{\partial x} a(x) \dfrac{\partial U}{\partial x} - V_1(x) \dfrac{\partial U}{\partial x} - \lambda(x, V_1) U + \mu_2(x, V_1) S + f(x,t); \\ \dfrac{\partial S}{\partial t} = \lambda(x, V_1) U - \dfrac{V_2(x) \partial S}{\partial x} - (\mu_1(x, V_2) + \mu_2(x, V_1)) S; \\ \dfrac{\partial R}{\partial t} = \mu_1(x, V_2) S. \end{cases}$$

where *U (x, t)* - concentration of pollutants in the watercourse; *S (x, t)* - concentration of pollutants in the suspended sediments; *V (x)* – flow rate; *a (x)* - coefficient of molecular or turbulent diffusion; *f (x, t)* - function of the source of pollution into the water flow; *R (x)* - function of accumulating pollutants in the sediments; *λ (x)* – sorption coefficient of pollutants at their transferring from the flow into the suspended sediments; *μ1 (x)* – sedimentation coefficient of pollutants at their transferring from the flow into the bottom sediments; *μ2 (x)* - coefficient of sorption-desorption in "water-suspended sediments" system; *t* - time; *x* - coordinate in the direction of pollutants moving in the watercourse.

The system of equations is solved using the method of finite-difference approximation at choosing appropriate boundary conditions. Hydrological parameters of the model are determined by measurements. The identification of a pollution source function is carried out on the base of water sampling for hydrochemical parameters.

The calculation of mixing contaminated groundwater with river water for each elementary cell is made using the formula:

$$U_i^{n+1} = \frac{U^n_{\mathrm{p}_i} Q_{\mathrm{p}_i}\tau + U^n_{\mathrm{гр}_i} Q_{\mathrm{гр}_i}\tau + (W - Q_{\mathrm{p}_i}\tau - Q_{\mathrm{гр}_i}\tau)U^n_{\mathrm{гр}_i}}{W}$$

where: W - water volume in the elementary cell; $\mathrm{U}^{\mathrm{n}}_{\mathrm{p}_i}$ – pollutants concentration in the river flow; $\mathrm{Q}_{\mathrm{p}_i}$ – river discharge; $\mathrm{U}^{\mathrm{n}}_{\mathrm{гр}_i}$ - pollutants concentration in the water filtered from the soil; $\mathrm{Q}_{\mathrm{гр}_i}$- water discharge from the soil; τ - time step.

The highly mineralized water is accumulated in Dombrovsky open pit (Kalush town, Ivano-Frankivsk region, Ukraine). The pit acts as a diffuse source and affects water quality in the Sivka River as a result of filtering saline solutions and surface wash-off (Fig. 1).

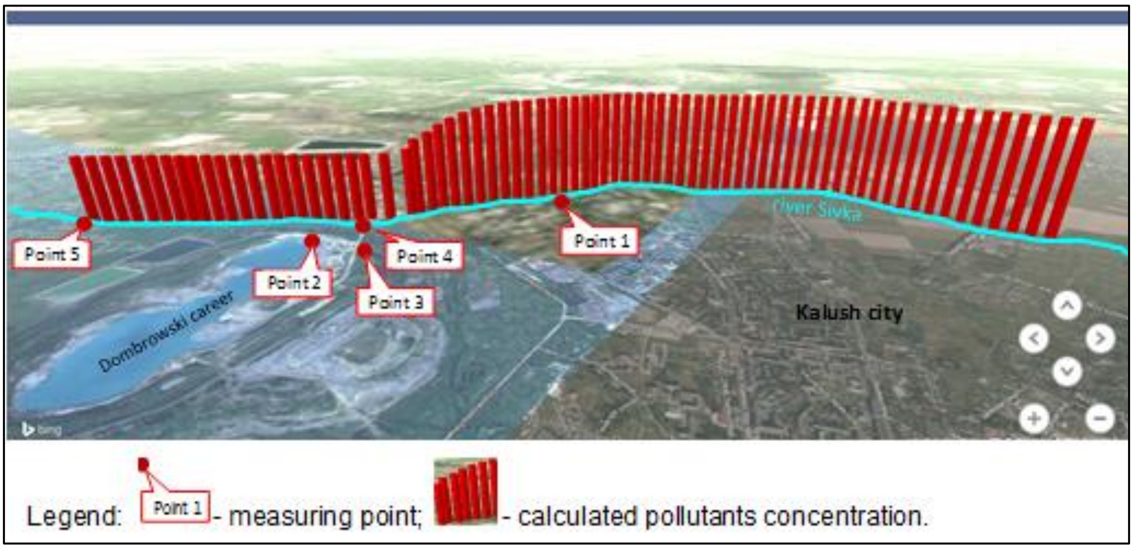

Figure 1: Pilot facility layout

Considering the fact that bottom sediments in the Sivka River are large gravel-pebble formations where sorption processes are not intensive (λ→0 and μ≈0), they can be ignored when building the model. Then for given conditions a difference model will be the following:

$$U_i^{n+1} = U_i^n + \frac{\tau}{\Delta x}\left[\left(a^2(x)\frac{U_{i+1}^n - U_i^n}{\Delta x^{\square}} - V_1 U_i^n\right) - \left(a^2(x)\frac{U_i^n - U_{i-1}^n}{\Delta x} - V_1 U_{i-1}^n\right)\right] - \tau\lambda U_i^n$$
$$+\tau\left(U_i^n + \frac{(U_{\mathrm{гр}i}^{\square} - U_i^n)\tau Q_{\mathrm{гр}i}}{W}\right), i = 1, \dots, m.$$

The identification of pollutants distribution model was made on the base of field observations. In the affected area the flow rate ranges 0.1-0.3 m/s and flow discharge is 0.2-0.4 m3/s. For the modeling the values were taken as following: V (x) = 0,2 m/s, Q (x) = 0,3 m3 /s, elementary cell Δx = 100 m, filtration area – 1000 m.

Boundary condition is left $U_i^0 = U_ф$ - background, that is the background concentration is maintained; at the right border (modeling section is 5km) the concentration is equal to the previously calculated one. To calculate a polluted groundwater discharge (Qhri) using the error method it is set some initial value Q_{rpi}^0 of a saline solution concentration by chlorides, sulfates and dry residue in the upper part of Dombrovsky open pit. The calculations revealed that the volume of polluted water which fell into the Sivka River within the section of 1000m is 0.0004 l/s (34560 l/day).

3 CONCLUSIONS

The developed mathematical model of pollutants distribution and their interaction with the suspended and bottom sediments in rivers allows simulating different scenarios of accidental releases of pollutants into rivers and reservoirs to take preventive actions.

The proposed method allows identifying the function of point and diffusing sources in the model of pollutants distribution in streams and reservoirs. The carried out research at the pilot facility on the Sivka River proves the effectiveness of model parameters identification based on the field observations. The model allows considering different emergency scenarios for Dombrovsky open pit.

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Real-time-monitoring of nutrients and physico-chemical parameters for detection and differentiation of impacts in small and middle scale catchments

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ABSTRACT

The quality standards of surface waters increase steadily and they bear new challenges for water policy. To plan and execute of measures it is of particular importance to very precisly know the origin and pathways of the various impacts in a catchment area. However, since rivers are very dynamic systems, this claim can often not been realised by simple manual sampling. Therefore, online measurements generating values in very high frequencies can be a very useful complement to these measurements, especially in small and middle scale catchments.

METHODOLOGY

To this aim we have developed several measuring stations as mobile trailers which can be installed nearby the river. The water is transported by a submerged pump into a sample basin from where the overflow is drained back into the river by an outlet on the opposite side (see fig. 1). Measuring devices for nutrients (NH_4, NO_3, TOC, PO_4 and total P), oxygen, temperature, pH value, conductivity and turbidity are immerged into this basin to analyse the water quality in a 5 to 10 minutes frequency. The collected data are stored in a data logger from where they are transferred to a central computer via GSM. They are then evaluated and interpreted considering climatic data and discharge as well as geology, land use, wastewater dischargers etc. in the catchment.

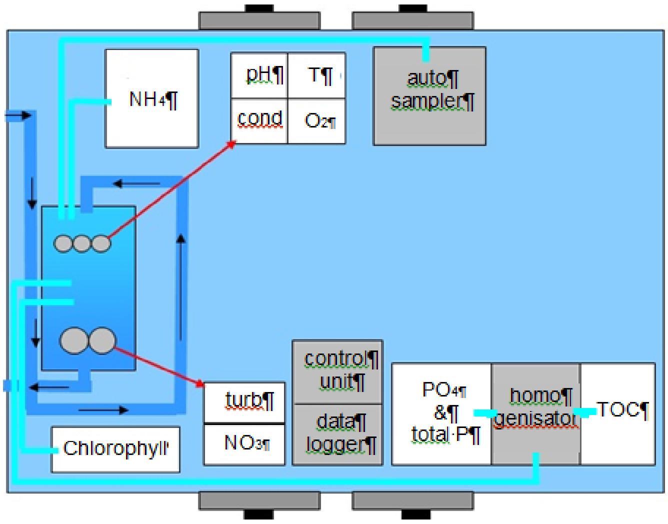

Figure 1: Schema of mobile measuring station

RESULTS

The evaluation and interpretation of different parameter combinations considering the data mentioned above allow to draw different conclusions, universal ones as well as catchment- or site-specific ones and to detect impacts entered by surface flow (see fig. 2) and interflow which is characterised by the time offset between the maxima of discharge and concentration (see fig. 3).

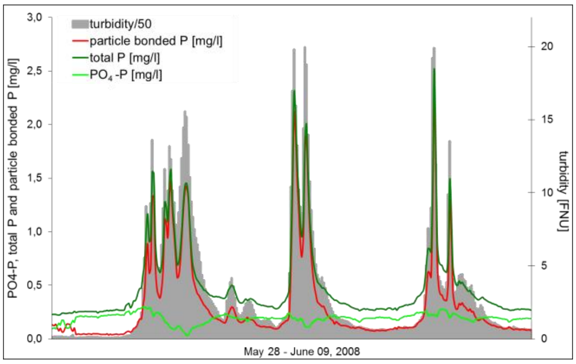

Figure 2: diffuse pollution: phosphorus impacts (P-fertilisers) by surface discharge (June 2008)

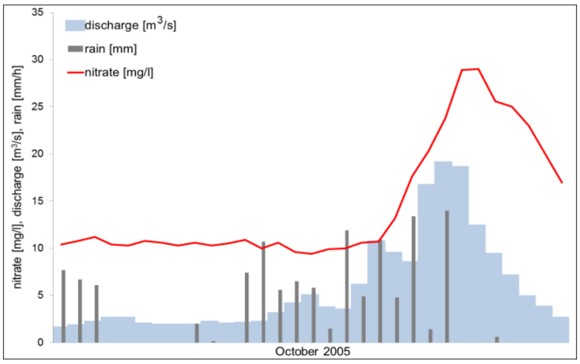

Figure 3: diffuse pollution: nitrate impacts (N-fertilisers) by interflow (October 2005)

It is thereby possible to differentiate between agricultural discharge (see above) and industrial and urban waste water (e.g. by detection of the operation rhythm of a waste water plant, see fig. 4) or discharges of storm overflows causing long term deficiency of oxygen (see fig 5).

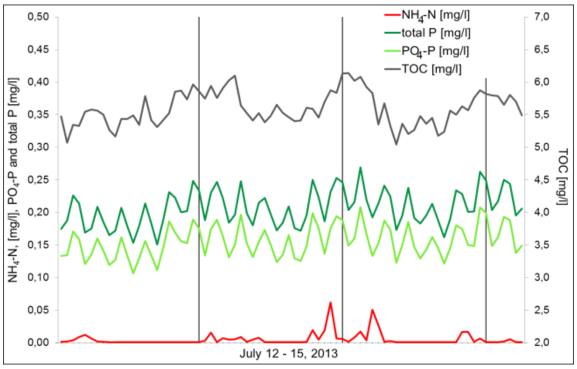

Figure 4: pollution from point sources: phosphorus cycles caused by a wastewater plant (July 2013)

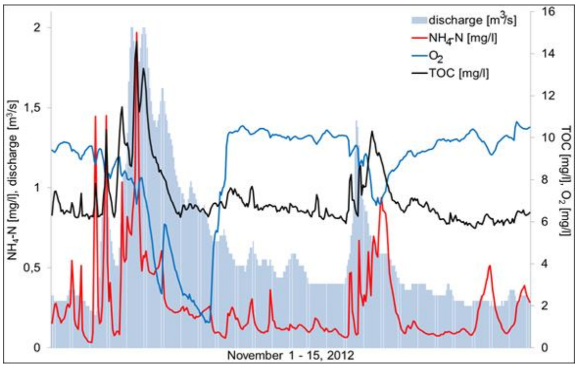

Figure 5: pollution from point sources: impacts from storm water basin (November 2011)

Not only the origin but also the level and duration of impacts can be traced, natural phenomena, geological backgrounds and seasonal variations can be detected and loads be calculated exactly.

CONCLUSIONS

Real-time measurements in high frequencies do not only allow monitoring of concentration changes in surface waters. They also enable the differentiation of impacts from point and diffuse sources as well as the detection of their origin and emission pathways. Furthermore the mobile measuring stations turned out to be very flexible considering spatial as well as methodological aspects and can easily be adapted to different requirements. The results enable authorities to plan and take effective measures to improve the water quality and to support and control the implementation of the European Water Framework Directive and other demands of water management.

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Bacterial wax esters in the Danube river sediments as possible indicators of environmental stress

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ABSTRACT

We investigated the molecular inventory in Danube River surface and core sediments and identified bacterial wax esters with 28 to 34 carbon atoms with C_{30}, C_{31}, and C_{32} homologues being most abundant. The identified wax esters consist of various combinations of *normal*, *iso*, and *anteiso* fatty acid and alcohol moieties, showing different isomeric distributions for compounds with odd and even carbon numbers. Wax esters have seldom been investigated in rivers, but we speculate that they represent a bacterial response to change in environmental conditions and that they can serve as markers for environmental stress.

1 INTRODUCTION

Wax esters are an important class of lipids made of long-chain fatty acids esterified with long-chain fatty alcohols. In some prokaryotes, the main function of wax esters is to serve as storage compounds for energy and carbon as a hedge against starvation as they grow on various substrates. In addition, wax esters can act as depositories for a surplus of fatty acids produced during growth on recalcitrant carbon sources, or as storage of evaporation-resistant lipids - as a strategy to maintain a basic water supply in the case of desiccation (Rontani, 2010).

Only limited data are available on bacterial wax esters from fresh water environments. Cranwell (1983) investigated wax esters in recent sediments of two productive lakes and suggested that C_{27}–C_{36} normal and branched ones may be derived from aquatic and microbial sources.

2 MATERIALS AND METHODS

2.1 Sediment sampling

Sediment sampling has been performed during the Joint Danube Survey 2, organized by the International Commission for the Protection of the Danube River. The samples investigated in this study derive from ten locations along a ~200 km river stretch, from the metropolitan area of Belgrade to the Iron Gate I Reservoir (Serbia/Romania) (Figure 1).

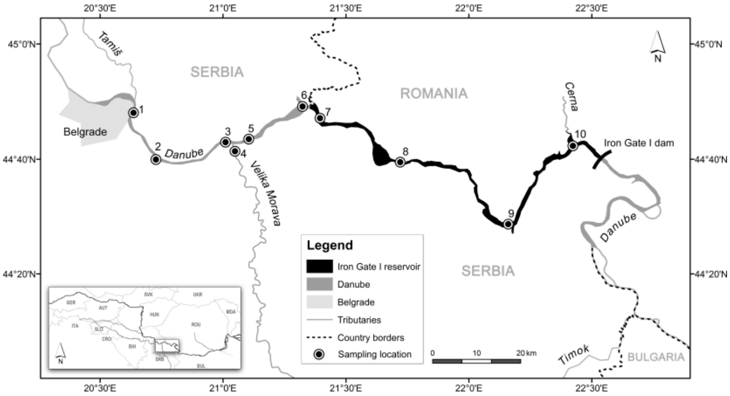

Figure 1: Map of the investigated stretch of the Danube River, showing the locations from which the samples were collected.

2.2 Extraction, clean-up, and quantification

Wax esters from river sediments were isolated by an accelerated solvent extractor (at 120°C and 4 MPa) with dichloromethane as solvent. The extracts were solvent exchanged to *n*-hexane and further fractionated using column chromatography. Wax esters were analyzed on an Agilent 7890A gas chromatograph coupled to an Agilent Technologies 5975C inert XL mass selective detector.

3 RESULTS AND DISCUSSION

The identified wax esters with 28 to 34 carbon atoms with C_{30}, C_{31}, and C_{32} homologues being most abundant. They consist of various combinations of *normal*, *iso* (*2-methyl*), and *anteiso* (*3-methyl*) fatty acid and alcohol moieties, showing different isomeric distributions for compounds with odd and even carbon numbers. Carbon chain lengths and methyl branching are typical for bacterial lipids and provide circumstantial evidence that these wax esters are of bacterial origin.

Wax esters concentrations in surface sediments vary from 0 to 741 µg kg^{-1} with a significant enrichment recorded at locations with high concentrations of organic nitrogen and total phosphorus and a relative high proportion of aquatic vs. terrestrial organic matter, all pointing to high primary productivity. Composition of wax esters differs in the sediments from the stream and from the Iron Gate I Reservoir.

In a 70 cm long core wax esters concentrations decrease significantly with depth following first-order kinetics. ^{137}Cs dating suggested that the core sediments are less than three years old (Micić et al., 2013). This implies a very rapid diagenetic and/or biological degradation of wax esters in young fluvial sediments and an unlikelihood of preservation in the geological record.

Wax esters have seldom been investigated in rivers, but we speculate that they are markers for environmental stress. Which environmental conditions encountered in these sediments cause bacteria to generate wax esters remains, however, unclear.

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CrossWater – Modelling micropollutant loads from different sources in the Rhine basin

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ABSTRACT

The contamination of fresh surface waters with micropollutants originating from various sources is a growing environmental issue. The challenges for an effective political regulation are numerous, particularly for international water basins. One prerequisite for effective management is the knowledge of water quality across different parts of a catchment. In this study, the spatial patterns of micropollutant loads and concentrations from different use classes are investigated with a mass flow analysis and compared to the territorial jurisdictions of actors involved in managing micropollutants and water quality. The whole Rhine river basin without the delta constitutes the study case.

The loads and concentrations in rivers are modelled based on empirical relations between source area, river discharge and micropollutant concentration. The source area of micropollutants depends on the specific use of a compound. The focus of this study is on i) herbicides from agricultural landuse, ii) biocides from material protection on buildings and iii) human pharmaceuticals from households.

1 MODEL APPROACH

As a first approximation of loads in river sections, the estimates of spatially distributed consumption/applied mass of micropollutants was multiplied with empirical loss rates independent from discharge or precipitation. Mean concentrations have been obtained by dividing the load estimates by mean discharges.

To obtain dynamic estimates of loads and concentrations, the release of micropollutants is calculated with empirical loss rates related to river discharge for agricultural herbicides and to precipitation for biocides. For the pharmaceuticals the release is coupled to the metabolism rates and elimination rates in WWTP.

$C_{herbicide}(t) = \varepsilon \times \frac{1}{A^2} \times M_{avail}(t) \times Q\,(t)$ (Leu et al., 2010)

$C_{biocide}(t) = \frac{M_{appl} \times \beta \times P(t)}{Q(t)}$ (Wittmer et al., 2011)

$C_{pharmaceutical}(t) = \frac{M_{cons} \times f_{human} \times (1-e)}{Q(t)}$ (Ort et al., 2009)

M_{avail}, M_{appl}, M_{cons} : available mass of compound per catchment estimated by downscaling statistical input data (for herbicides sorption and decay are considered)

ε, β: calibrated substance-specific loss rates

f_{human}, e: human metabolism and WWTP elimination rate

A: total area of each catchment normalizing available mass and discharge to a unit catchment

2 DATA INPUT

National consumption or application data of micropollutants is scaled to the subcatchments by the ratio of site-specific and national source areas. The source areas are estimated on the basis of GIS data on agricultural landuse, vector data of buildings, wastewater treatment plant (WWTP) locations.

Time series of over 1000 stream gauges determine the discharge at the subcatchments. At ungauged catchments a reference station is selected with the map correlation method (Archfield and Vogel, 2010).

3 FIRST RESULTS

The river loads are calculated with the stationary approach multiplying loss rates from the literature (Wittmer et al., 2010) with the catchment-specific available mass of micropollutants. The accumulated river loads in the Rhine compare reasonably well to 7-day composite samples obtained during a sampling campaign in 2011 (Ruff, 2014).

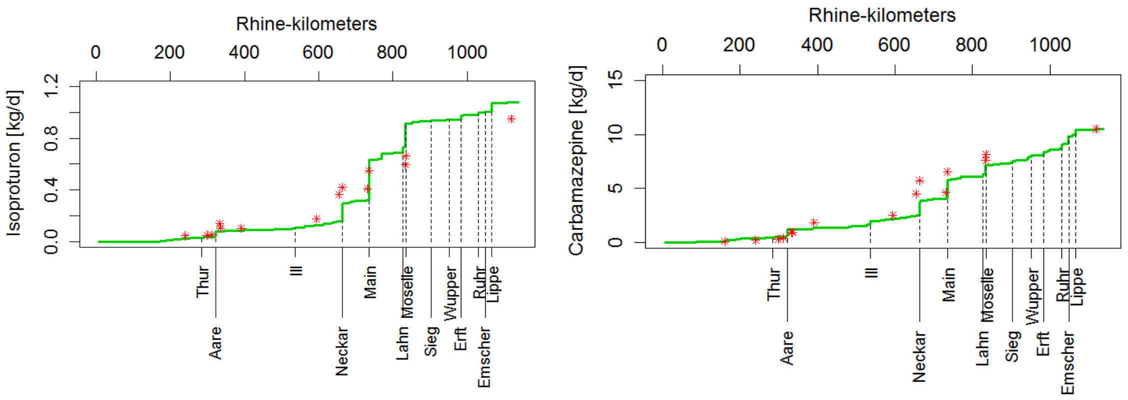

Figure 1: Accumulated river load (green) in the Rhine for isoproturon (herbicide) and carbamazepine (pharmaceutical) compared to point measurements (red)

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The impact of different proportions of a treated effluent on the biotransformation of selected micro-contaminants in river water microcosms

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ABSTRACT

The effect of different proportions (0–10%) of a selected treated effluent (TE) on the biotransformation rates of selected micro-contaminants in river water (RW) microcosms was investigated. Unsystematic results were observed: Caffeine and valsartan were faster degraded in the presence of 10% TE whereas the biodegradation of metoprolol was inhibited in presence of ≥0.1% TE. Presented results clearly demonstrate that changing biodegradation rates in RW-microcosms can be induced even by very low proportions of TE.

1 INTRODUCTION

Biotransformation of micro-contaminants is a very complex field in environmental sciences and it is difficult to understand the subject and all essential factors in its entirety. However, for a proper risk-assessment a sound understanding of the fate of micro-contaminants in the aqueous environment is necessary. Preliminary studies (e. g. Hillebrand et al., 2013) suggest that biodegradation rates of micro-contaminants in the aqueous environment depend on the water matrix. The focus of the study presented here is the systematic comparison of biotransformation rates of caffeine (stimulant), carbamazepine (anticonvulsant), metoprolol (antihypertensive), paracetamol (analgesic) and valsartan (antihypertensive) in aerobic RW-microcosms spiked with different proportions of TE.

2 MATERIAL & METHODS

Samples of RW and TE were collected from the same locations, in which a matrix-dependent stability of micro-contaminants was already observed (Hillebrand et al., 2013). For the preparation of the batch tests several glass bottles (1-L) were spiked with 50 µg of each compound. Experimental degradation matrices (0.5 L) were prepared in 0.5-L volumetric flasks by mixing RW with different fractions of TE: 0%, 0.1%, 1%, and 10% (v/v). The matrices were transferred into the spiked glass bottles (resulting concentration: 100 µg L^{-1} of each analyte) and 50 g of sterilized gravel (grain size 4–6 mm) were added as natural substratum to stimulate biofilm formation. All experiments were performed in duplicate and abiotic control batches (5 µg L^{-1} NaN_3) were prepared. All batches were incubated at 17 °C on an orbital shaker (150 rpm) and a head space of ≥500 mL remained as O_2-reservoir. The batches were sampled after 3, 6, 10, 14, 21, and 32 days and the analytes and selected biotransformation products (BTP) were separated and quantified by HPLC/ESI-MS-MS.

3 RESULTS & DISCUSSION

As expected from the previous study, the biodegradation rate of caffeine increased with increasing concentration of TE in the matrix. Valsartan was also much faster degraded in presence of 10% TE compared with RW and smaller proportions of TE and the evolution of the valsartan BTP valsartan acid followed this trend. However, the degradation rates of paracetamol and metoprolol decreased in the presence of TE. For paracetamol effects were observed at ≥1% TE compared to the pure RW. For metoprolol effects were noticed in the presence of ≥0.1% TE. Furthermore, this trend was confirmed by an altered BTP-evolution. Selected results are presented in Figure 1. No significant degradation of carbamazepine was observed in any of the microcosms. Detailed information can be found in Nödler et al. (2014) (open access).

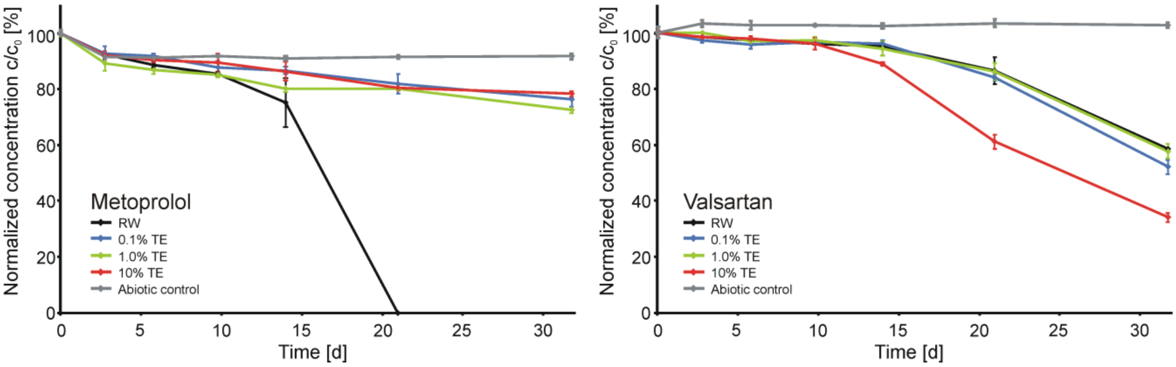

Figure 1: Concentrations of metoprolol and valsartan in the microcosms.

The here presented results clearly demonstrate changing biodegradation rates in RW-microcosms induced even by very low proportions of the selected TE. There are multiple potential reasons for the observations such as the presence of adapted microorganisms, micro-nutrients, compounds which may influence bioavailability of substrates or co-factors, etc. As the TOC concentration of both RW and TE were in the same order of magnitude, an enhanced co-metabolism was unlikely the reason for the here presented observations. Furthermore, no acute toxicity was observed in the TE by the luminescent bacteria test. Substantial amounts of phosphorus (P) were introduced by the TE. However, an experiment with additional P in RW demonstrated that the enhanced P-supply by the TE was not responsible for the observed effects. There is a substantial need for further research to understand the triggering processes for the observations.

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Basin water management: carec cases from small watersheds in central asia

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ABSTRACT

PREREQUISITS TO BASIN WATER MANAGEMENT IN CENTRAL ASIA: CHANGING IN NATIONAL WATER LAWS

Central Asian republics started the movement toward the Integrated Water Resources Management (IWRM) since 2002 when they agreed the Johannesburg Declaration on Sustainable Development. In the first place there are must be legislative framework for a new water policy.

The most successfully the process of transition to IWRM was initiated in Kazakhstan. In 2003, a new Water Code was adopted and replaced that of 1993. Basin Councils were established and operate in all basins supported mostly by international donors.

In 2011 Tajikistan developed the strategy of water sector reforming. In 2012, the whole chapter on the basin management and protection of water resources was added to the Water Code. Five major river basins systemic with the most suitable institutional framework for the reform process will be gradually transferred to the Hydrographic management with the participation of all stakeholders. Code also defines the establishment of the National Water Council, Water Basin Council, Basin Water Organization (management).

The main principles of state water policy in Kyrgyzstan set forth in the provisions of the Water Code, the Law "On the Water", "On Environmental Protection". Though the National water strategy is not developed yet, a regulatory framework allows for work on basin planning - development of the Basin plans, use and protection of water resources.

Thus the Water Cods of Kazakhstan, Kyrgyzstan and Tajikistan foresees establishment of Basin Councils in each large-scale hydrographical basins in the countries.

SMALL BASIN COUNCILS AS A SOLUTION FOR COOPERATION ON SMALL TRANSBOUNDARY WATERSHEDS: CAREC EXPERIENCE IN CENTRAL ASIA

The most interesting basins in Central Asia for international financial support are the basin of Syr-Darya River, Amu-Darya River and Zeravshan River. However, 35% of water flow in Central Asia is forming by small watersheds and about 70% of population lives in the small basins.

Based on the water policy and legislative assessment since 2012 CAREC implements several projects on IWRM, funded by different donor organizations, such as U.S. Agency on International

Development (USAID) and European Commission in cooperation with German International Cooperation (GIZ). CAREC projects aimed at fostering transboundary cooperation on small transboundary watersheds between CA countries.

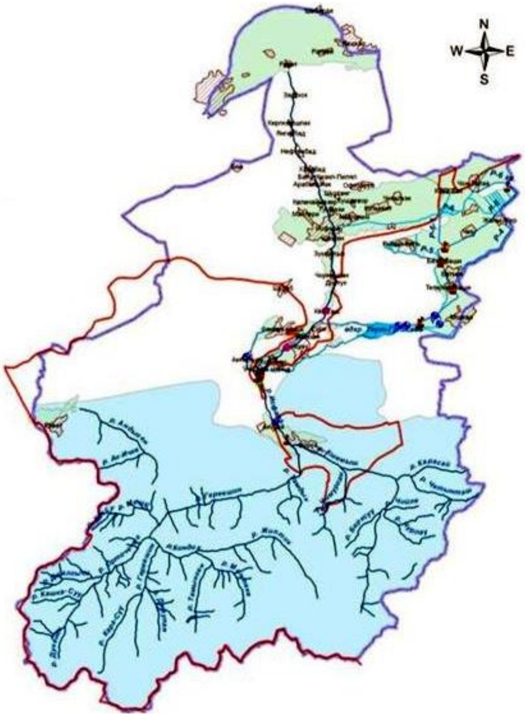

Figure 1: Isfara River Basin

One of the interesting case illustrates the possibilities of basin approach is Isfara river basin which is located in northern Tajikistan and south-western Kyrgyzstan. The Isfara river basin belongs to Sugdh Oblast in Tajikistan and to Batken Oblast in Kyrgyzstan. About 185,000 people live in the basin. Several Tajik and Uzbek enclaves located inside Kyrgyzstan's territory led villages to be bisected by the Tajikistan-Kyrgyzstan border and to Kyrgyz ethnic majorities in Tajik villages. To meet the problems in the basin, the joint multi-stakeholders' committees were created on both Kyrgyzstani and Tajikistani parts of the basin.

Local multi-stakeholders' committees or Small Basin Councils (SBC) were created in 2012 and since that time, regular meetings are conducted twice a year. SBC took active part in the decision making through the basin planning process, development of Basin Plans on both Tajikistani and Kyrgyzstani parts of the basin, implementing pilot projects and monitoring on the implementation.

The texts of Integrated Water Resources Management Plans for Isfara River basin were developed. The main goal the plans for Isfara river is to ensure the effective use and protection of water resources through implementation of integrated water resources management principles. The members of SBCs took active part in development and discussion of the Plan, inter alia in the development of "Problems Tree", which became a base for development of the list of activities to be implemented to solve the existing problems in the basin.

One of the examples of the activities from the list is purchasing the tractors for both Kyrgyzstani and Tajikistani parts of the basin. Isfara river is the mountainous river, and has a high index of sedimentation. Water shortage could be partly solved by the cleaning the canals and increasing the coefficient of capacity efficiency of irrigation network. To ensure the project sustainability after its completion, the tractors will be transferred to the ownership of the WRM department of Isfara city (Tajikistan part of the basin) and to the Batken city administration (Kyrgyzstan part of the basin).

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Climate change, urbanization and river organic pollution: a global assessment

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ABSTRACT

Organic river pollution by domestic wastewater affects people worldwide. We present here for the first time a global analysis of the combined effects of increasing urbanization (increasing pollutant loading) and climate change (decreasing river discharge, thereby decreasing river dilution capacity of organic pollutants) on river organic pollution. As an overall indicator of organic river pollution, historical (2000) and future (2050) Biochemical Oxygen Demand (BOD) concentrations are calculated along global river networks. Our model accounts for human BOD production in urban areas, wastewater treatment, downstream transport, dilution and natural degradation. Our results indicate that the number of people affected by organic pollution is projected to increase from 0.8 billion in 2000 to 2.8 billion in 2050. The significant impact will be in developing countries, including regions of Africa, South America, Caribbean, India and China. Our results also point to an urgent need for affordable urban sewage control solutions.

GLOBAL ASSESSMENT OF IN-STREAM BOD CONCENTRATION

Figure 1 illustrates in-stream BOD concentrations for global rivers in the year 2000 and 2050. Urbanized river systems in developing regions, including India, China and Africa exhibit the most significant deterioration of river water quality. The major increase of BOD concentrations is also in these regions, where affordable wastewater treatment is limited.

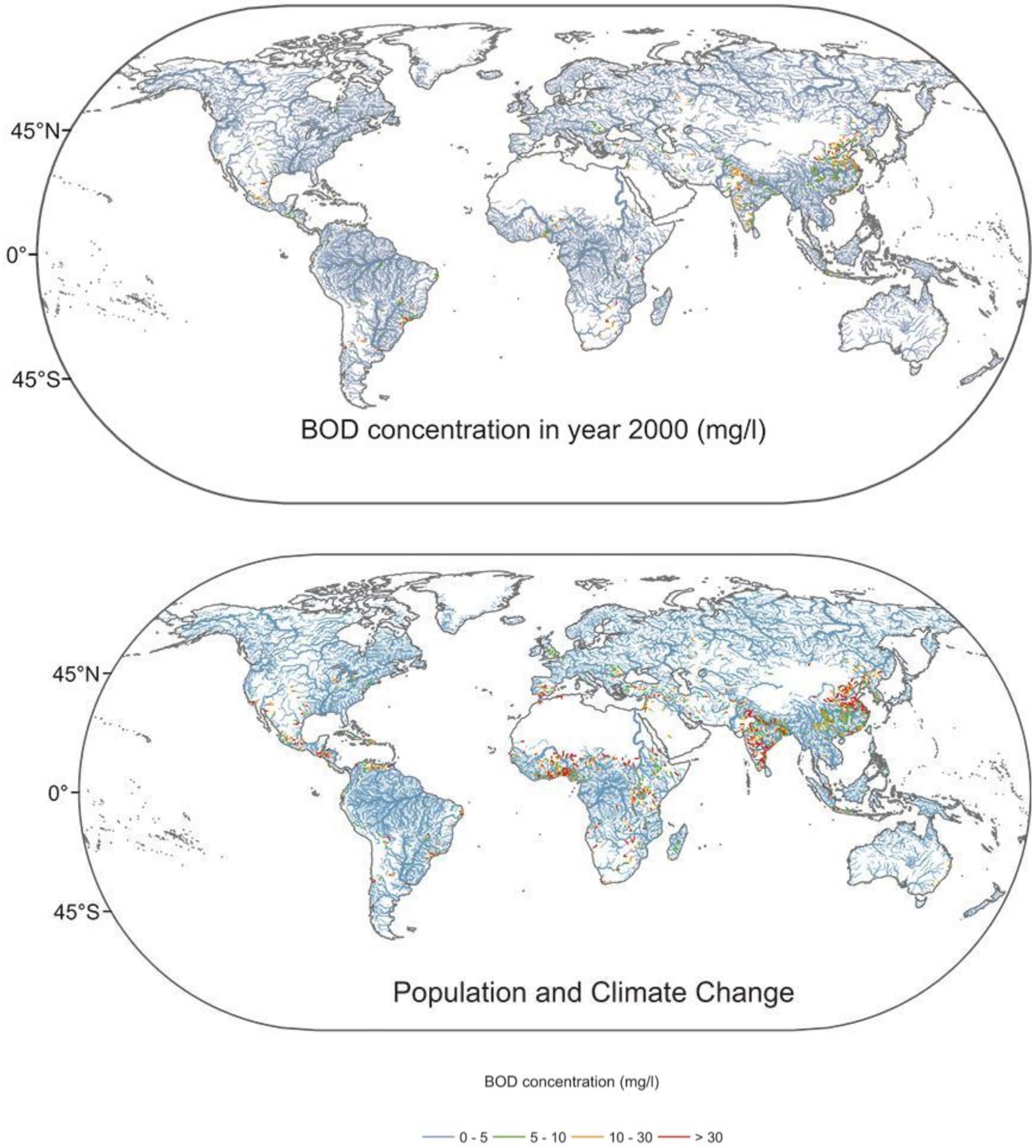

Figure 1: Organic river pollution, expressed as in-stream BOD concentration in mg/l, in the year 2000 (above) and 2050 (below) due to the combined effect of urban population change and climate change.

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