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Micropollutants in urban receiving waters

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Meiner Familie

Abstract

Currently half of the world's population resides in cities. The ongoing urban land consumption has a tremendous impact on the entire water balance of urban areas. Apart from water quantity, the water quality has also strongly deteriorated. In particular, micropollutants from domestic and industrial wastewater are of growing concern. Despite their low concentrations, micropollutants can act as endocrine disruptors and chemosensitizers and, thus, pose a threat to aquatic ecosystems and to human health.

In this study water flow and micropollutant mass flow is characterized and quantified within an urban catchment area. To this end, a one-year-monitoring program was conducted to determine the concentrations of the micropollutants bisphenol A, technical 4-nonylphenol, caffeine, galaxolide®, tonalide® and carbamazepine in untreated and treated wastewater, surface water and groundwater.

Micropollutants were ubiquitously found in all the tested urban water sources. With the help of descriptive and multivariate statistical methods, measured concentrations were evaluated and a conceptual source model was derived. Micropollutants were only partially removed in the municipal wastewater treatment plant, leading to contamination of the receiving surface water. Moreover, combined sewer overflow was contributing to micropollutant input to surface water. The presence of micropollutants in the groundwater was in part a result of wastewater losses by sewer leakages and in part due to infiltration of contaminated surface water.

In the next step, the temporal and spatial variability of micropollutant concentrations and loads was evaluated. The surface water loads of caffeine, tonalide® and galaxolide® were characterized by a pronounced seasonality, pointing to temperature-dependent removal processes. After rainfall, loads of technical 4-nonylphenol and caffeine were increased, indicating an intermittent input from combined sewer overflow and surface runoff. The variability of micropollutant concentrations in the groundwater could only be partially explained. The periodic occurrence of caffeine in groundwater downstream of a small stream was related to the intermittent infiltration of contaminated surface water. Overall, the high variability of micropollutant concentrations was a result of spatially and temporally variable input from sewer leakages and different transport and attenuation processes.

The quantified urban water balance was characterized by a high temporal dynamic. Although a large portion of the study area's surface is sealed, only 11% of the precipitation was contributing to the surface runoff to the combined sewers. Due to the resulting high infiltration rate and the low evapotranspiration, the rainfall-induced groundwater recharge process was fast and the recharge rate high. The sewage system was on the one hand loosing wastewater to the groundwater but, on the other hand, drained the study area’s groundwater. The micropollutant load release from the study area was dominated by the input of treated wastewater into the surface water. Nevertheless, combined sewer overflows and the groundwater discharge contributed a significant part of the released loads. Therefore, these pathways should be included into micropollutant risk assessments. The different temporal dynamics of micropollutant release pathways – constant input from wastewater treatment plants and from groundwater discharge on the one hand and intermittent input from combined sewer overflow on the other hand – can result in potential chronic as well as acute effects on aquatic biota.

Kurzfassung

Derzeit lebt die Hälfte der Weltbevölkerung in Städten. Die fortschreitende Urbanisierung übt einen hohen Druck auf den gesamten Wasserhaushalt städtischer Gebiete aus. Dabei wird neben der Wasserquantität die Wasserqualität deutlich gestört. Insbesondere werden Mikroverunreinigungen aus häuslichen und industriellen Abwässern mit wachsender Sorge gesehen, da sie trotz ihrer geringen Konzentrationen, beispielsweise durch hormonelle Wirkungen, eine Gefährdung für aquatische Ökosysteme und die menschliche Gesundheit darstellen können.

In dieser Arbeit werden Wasserflüsse und Schadstoffflüsse von Mikroverunreinigungen in Abwasser, Oberflächenwasser und Grundwasser eines urbanen Einzugsgebiets charakterisiert und quantifiziert. Dabei wurden die Kontaminanten Bisphenol A, technisches 4-Nonylphenol, Koffein, Galaxolid®, Tonalid® und Carbamazepin im Rahmen eines einjährigen Monitorings in ungeklärten und geklärten Abwasser, Oberflächenwasser und Grundwasser untersucht.

Mikroverunreinigungen traten in allen urbanen Wasserkompartimenten ubiquitär auf. Mit Hilfe deskriptiver und multivariater statistischer Methoden wurden die gemessenen Konzentrationen evaluiert und ein konzeptionelles Modell des Eintrags abgeleitet. Demnach wurden die Mikroverunreinigungen in der städtischen Kläranlage nur teilweise entfernt und folglich über den Kläranlagenauslass in die Oberflächengewässer entlassen. Zusätzlich trugen Kanalisationsüberläufe zum Eintrag in Oberflächengewässer bei. Die Grundwasserverunreinigung konnte auf Leckagen aus dem Abwassernetz und teilweise auf die Infiltration belasteten Oberflächenwassers zurückgeführt werden.

In einem nächsten Schritt wurde die zeitliche und räumliche Variabilität der Schadstoffflüsse bewertet. Dabei zeigte sich eine ausgeprägte Saisonalität der Schadstoffflüsse von Koffein, Galaxolid® und Tonalid® in den Oberflächengewässern, die auf einen temperaturgesteuerten Abbau dieser Substanzen hindeutet. Eine zeitweilige Erhöhung der Massenflüsse von technischen 4-Nonylphenol und von Koffein nach Regenfällen konnte auf den intermittierenden Einfluss von Kanalisationsüberläufen und Oberflächenabflüssen zurückgeführt werden. Im Grundwasser konnte die Variabilität der Schadstoffkonzentrationen nur teilweise erklärt werden. Das periodische Auftreten von erhöhten Koffeinkonzentrationen im Abstrom eines Baches wurde dabei der zeitweiligen Infiltration von belastetem Oberflächenwasser zugeordnet. Die vorgefundene hohe Variabilität der Konzentrationen im Grundwasser wird als Resultat des zeitlich-räumlich sowie stofflich variablen Eintrags aus der Kanalisation und der unterschiedlichen Transport- und Abbauprozessen angesehen.

Die Quantifizierung des Wasserhaushaltes im Arbeitsgebiet wies auf eine hohe zeitliche Dynamik der Wasserflüsse hin. Obwohl das Einzugsgebiet einen hohen Versiegelungsgrad aufweist, trugen lediglich 11% des Niederschlags zum Oberflächenabfluss in die Mischkanalisation bei. Aus der resultierenden hohen Infiltrationsrate und der durch die Oberflächenversiegelung geringen Evapotranspiration folgte eine sehr schnelle und hohe, regen-induzierte Grundwasserneubildungsrate. Das Grundwasser interagierte mit dem Abwassernetz, das sowohl Abwasser durch Leckagen in den Untergrund verlor aber ebenso Grundwasser drainierte. Die mit den Wasserflüssen verbundene Fracht an Mikroverunreinigungen aus dem Arbeitsgebiet wurde von der Einleitung geklärter Abwässer in die Oberflächengewässer dominiert. Allerdings trugen sowohl Kanalisationsüberläufe, als auch der Grundwasserabstrom signifikant zur Gesamtfracht aus dem Arbeitsgebiet bei und sollten daher in der Risikobewertung hinsichtlich Mikroverunreinigungen aus urbanen Arealen mit berücksichtigt werden. Die unterschiedliche zeitliche Dynamik des Schadstoffausstoßes über die konstanten Pfade der Kläranlage und des Grundwassers auf der einen Seite und des intermittierenden Eintrags aus Kanalisationsüberläufen auf der anderen, führt dabei sowohl zu möglichen chronischen als auch zu potentiell akuten Effekten in aquatischen Lebewesen.

Résumé

À ce jour, la moitié de la population mondiale vit à l'intérieur des villes. Cette utilisation du territoire a un énorme impact sur le bilan hydrique urbain. Non seulement la quantité de l'eau est désormais limitée mais sa qualité s'est également détériorée. Les micropolluants provenant des eaux usées domestiques et industrielles représentent une préoccupation grandissante. Malgré leur présence en faible concentration, ces micropolluants peuvent agir comme perturbateurs endocriniens et comme sensibilisants chimiques et ainsi, peuvent constituer une menace envers les écosystèmes aquatiques et la santé humaine.

Dans cette étude, le flux d'eau et des micropolluants est caractérisé et quantifié à l'intérieur d'un bassin versant urbain. Pour arriver à cette fin, un an de surveillance a été effectué afin de déterminer les concentrations des micropolluants de bisphénol A, de 4-nonylphénol technique, de caféine, de galaxolide®, de tonalide® et de carbamazépine dans les eaux usées traitées et non-traitées, dans les eaux de surface et souterraines.

Les micropolluants ont été trouvés dans tous les zones d'eau urbaine. À partir de l'application de méthodes descriptives et statistiques multivariées, des concentrations mesurées ont été évaluées et un modèle conceptuel a été dérivé. Les micropolluants étaient seulement partiellement retirés des eaux usées de l'usine de traitement municipale ce qui a conduit à la contamination des eaux de surface. De plus, le débordement des égouts contribuait également à l'insertion de micropolluants dans ces dernières.

Ensuite, la variabilité temporelle et spatiale des concentrations et des charges et des micropolluants a été évaluée. Les charges en caféine, tonalide® et galaxolide® des eaux de surface étaient caractérisées par une forte saisonnalité ce qui traduit un processus d'élimination dépendant de la température. De plus, les augmentations des charges de 4-nonylphénol technique et de caféine sont causées par les chutes de pluie, indiquant un apport intermittent provenant de la combinaison des surplus d'égouts et des eaux de ruissellement. Quant à la variabilité de la concentration des micropolluants dans les eaux souterraines, elle n'a pu être que partiellement expliquée. L'occurrence périodique de la caféine dans les eaux souterraines en aval d'un petit cours d'eau était reliée à l'infiltration intermittente de l'eau de surface contaminée. Globalement, la grande variabilité de la concentration des micropolluants était un résultat d'apports spatialement et temporellement variables provenant de fuites d'égouts et de différents processus de transport et d'atténuation.

Le bilan hydrique urbain quantifié était également caractérisé par une grande dynamique temporelle. Bien qu'une large portion de la surface de l'aire d'étude soit scellée, seulement 11% des précipitations contribuaient au ruissellement de surface vers l'ensemble des égouts.

Dû au fort taux d’infiltration et à la faible évapotranspiration, la recharge souterraine causée par la chute de pluie était rapide et son taux de recharge élevé. D’un côté le système d’égout perdait des eaux usées vers les eaux souterraines tandis que d’un autre côté, il drainait l’eau souterraine de l’aire d’étude. La charge de micropolluant, libérée de l’aire d’étude dans les eaux de surface, était dominée par l’apport d’eaux usées traitées. Néanmoins, l’ensemble des surplus d’égouts et les décharges d’eau souterraine contribuent de façon significative aux charges relâchées. Par conséquent, ces trajectoires devraient être inclus dans l’évaluation des risques. Les différentes dynamiques temporelles des trajectoires de migration des micropolluants - apport constant provenant de l’usine de traitement d’eaux usées et provenant de la décharge souterraine d’un côté et un apport intermittent découlant de surplus d’égouts d’un autre côté -peuvent résulter en des potentiels chroniques comme en des effets aigus sur le biote aquatique.

Table of contents

List of figures

List of tables

List of abbreviations

AHTN	tonalide®
B	boron
BPA	bisphenol A
BTEX	benzene, toluene, ethylbenzene, xylene
CAF	caffeine
CBZ	carbamazepine
$C_{i,gw}$	micropollutant concentration percentiles in groundwater
$C_{i,tww}$	micropollutant concentration percentiles in untreated wastewater
$C_{i,uww}$	micropollutant concentration percentiles in untreated wastewater
Cl	chloride
CSO	combined sewer overflow
C_{ww}	concentration of micropollutants in wastewater
EmC	emerging contaminants
ET	potential evapotranspiration
GC-MS	gas chromatography-mass spectrometry
GW	groundwater
h_{gw}	elevation of groundwater surface
HHCB	galaxolide®
h_{ww}	elevation of wastewater within the sewer
K	potassium
KS-Test	Kolmogorov-Smirnov-Test for normality
LOD	limit of detection
$M_{i,cso}$	released mass flow of micropollutant i by CSO to the surface water
$M_{i,gw}$	released mass flow of micropollutant i by groundwater discharge out of the sewershed boundary
$M_{i,tww}$	release of micropollutant i by treated wastewater to the surface water
$M_{i,uww}$	load of micropollutant i from the sewershed by untreated wastewater pumped to the WWTP
n	number of samples
Na	sodium
NP	technical 4-nonylphenol
O_2	oxygen
p	p-value of Kolmogorov-Smirnov-Test
P	precipitation
pK_{ow}	logarithm of partitioning coefficient octanol/water

PPCP	pharmaceuticals and personal care products
Q_{cso}	annual amount of combined sewer overflow to the surface water
Q_{ex}	annual amount of groundwater exfiltrating to the sewage system
Q_{gw}	annual amount of groundwater discharge out of the sewershed boundary
Q_{rch}	annual amount of groundwater recharge
$Q_{rch,rain}$	annual amount of groundwater recharge from precipitation
$Q_{rch,ww}$	annual amount of groundwater recharge from wastewater losses
Q_{ro}	annual amount of surface runoff to the sewage system
Q_{tww}	annual amount of treated wastewater from the WWTP
Q_{ww}	annual amount of strict wastewater flow from the sewershed, without runoff and exfiltration flow from groundwater
$Q_{ww,cso}$	annual amount of wastewater in combined sewer overflow
$Q_{ww,cso}$	annual amount of wastewater discharge by CSO
$Q_{ww,ex}$	annual amount of combined wastewater pumped from the sewershed, without surface runoff
$Q_{ww,p}$	annual amount of combined wastewater pumped to the WWTP
σ	standard deviation
SFW	surface water
SO_4	sulfate
T	water temperature
WWPS	wastewater pumping station
WWTP	wastewater treatment plant

Chapter 1

Introduction

1.1 Background

Urbanization is an emerging issue with ecological, economical and social implications. Currently half of the world's and 70% of Europe's population is living in urban areas. According to the United Nations by 2050 these numbers are going tor rise to 70% and 84% respectively (United Nations, 2008). In the year 2000 urbanized areas made up 3.7% of Europe's surface. Between 1990 and 2000 the annual land consumption by housing, services and recreation was 50 000 ha which refers to half of the total land consumption (based on Corine land cover 1990 and 2000 for 23 European countries, http://www.eea.europe.eu/). Of course, there are positive aspects of this development such as more efficient use of land resources and more effective work of public transport and centralized waste treatment, reducing per capita emissions of contaminants (Diamond and Hodge, 2007). Nevertheless, urban land use leads to enormous pressure on the environment. Aside from drastic changes in the water balance, manifold, often diffuse and poorly regulated emissions have a negative impact on the quality of air, soil and urban water resources (Diamond and Hodge, 2007). This environmental stress is likely to increase with further urbanization.

The city's inhabitants need a reliable source of clean potable water. In history, settlements often relied on groundwater from springs and shallow wells. With industrialization and an accelerated urbanization, population's and industry's water demand increased. Due to the heavy abstraction, groundwater tables underneath cities were declining and as a consequence of unregulated waste management groundwater quality became more and more degraded (Howard, 2001). Cities increasingly became importers of water from remote sources. Overexploitation of groundwater underneath urban areas, declining water tables, the resulting land subsidence and, for costal cities salt water intrusions still are a major concern in many cities of the world (Howard, 2001; Jago-on et al., 2009). However, over the recent decades, in the developed world, abstraction volumes have been reduced and groundwater levels are rising again. Consequently, pumping has to be employed increasingly to prevent flooding of underground structures (Vazquez-Sune et al., 2004).

Maintaining the quality and quantity of urban water resources is recognized as a very complex scientific task including different spatial and temporal scales. The key to understand the deterioration of urban water resources is the knowledge of the tremendous impact of urbanization on the entire water balance (Fig. 1). On the one hand, surface sealing in urban areas leads to an increase of surface runoff and thus to a reduction of water infiltrating into the subsoil. On the other hand, water is imported into the urban areas by water mains and transported after usage within the sewage system. Water can leak from these subsurface infrastructures as artificial groundwater recharge, increasing the net recharge underneath urban areas (Lerner, 2002). Surface runoff can also be transported in the sewage system as artificial interflow and mix with wastewater in combined sewers. When the water amount exceeds the capacity of the sewage system, this contaminated storm water can discharge into surface waters. The interaction of the different urban water compartments is complex in time and space and still leaves many questions open (Thomas and Tellam, 2006; Taniguchi et al., 2009).

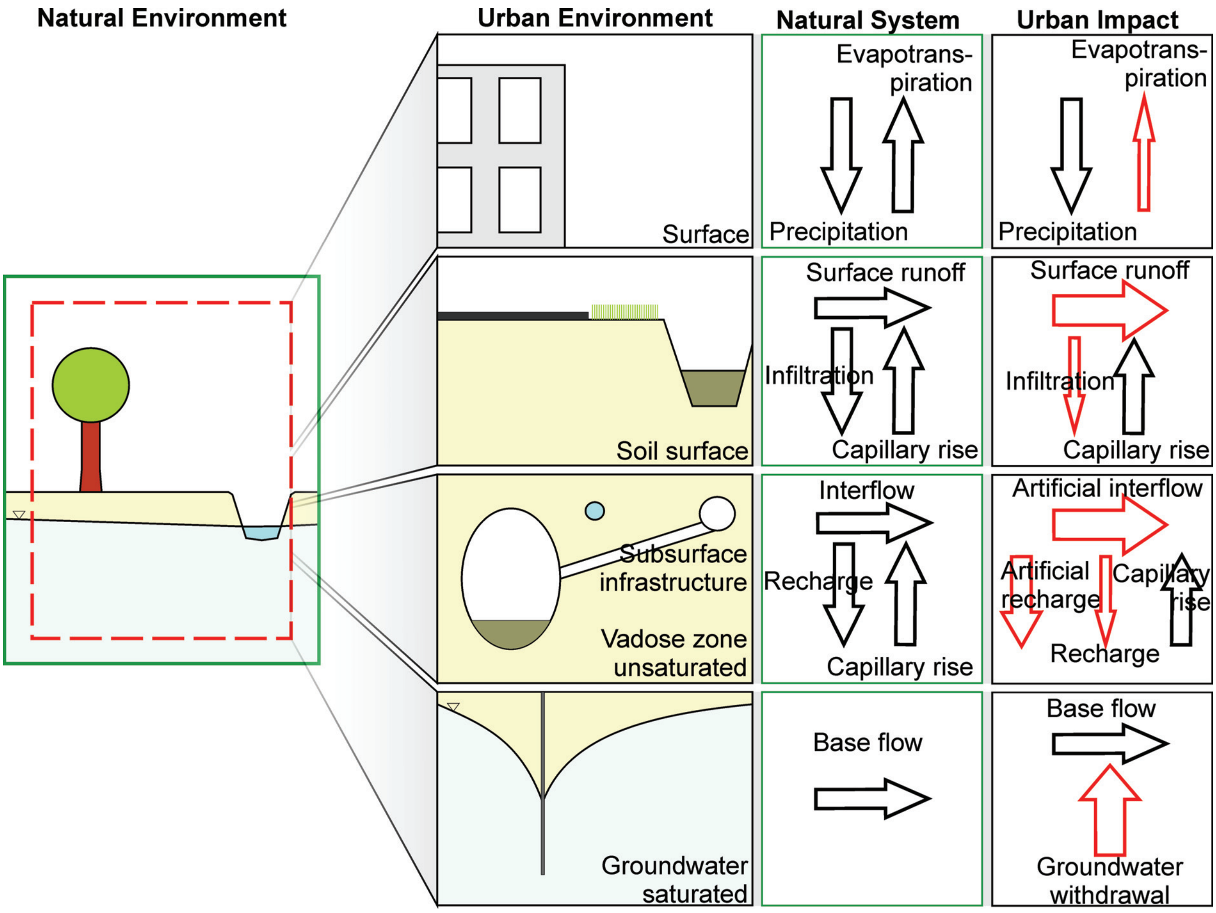

Fig. 1: Urban impact on the water balance. The red arrows represent water flow which is modified or newly introduced by urbanization.

The disturbance of the natural water balance is closely connected with deteriorating quality, since new pathways for contaminants are introduced. Probably most challenging is the variety of chemicals from human and industrial activities released via different wastewater sources.

We live in a "chemical society" with thousands of chemical compounds available in the products of our daily life (Drangert and Cronin, 2004). Due to the concentrated accumulation, the transport and the treatment of wastewater in urban areas, urban water resources are at particular risk. The wastewater-borne contaminants are often present in waters in low concentrations ranging from pg L^{-1} to ng L^{-1} and are therefore termed "micropollutants" (Schwarzenbach et al., 2006). The wide range of properties, the complex mixtures and the toxicological concern especially of a long-term exposure demands new sustainable strategies to prevent water resources from this subtle contamination.

The present and future tasks concerning the management of urban water resources are not new. The urban population needs a reliable supply of clean drinking water on the one hand; on the other hand, wastewater has to be treated and storm water has to be managed. By coping with this challenge, we have to keep the principles of the water framework directive of the EU in mind (European Commission, 2000) which states that water is "a heritage which must be protected, defended and treated as such". This also applies to urban water resources. Urban surface waters and groundwater have to be managed in a way that ensures sustainability.

1.2 Objectives and structure

This work is centered on the quantification of the water balance and the characterization of micropollutant mass flow in urban areas. More specifically, this thesis addresses the quality and quantity of wastewater, surface water and groundwater in an urban catchment area in the city of Leipzig, Germany. The main objectives are (1) to characterize the occurrence of micropollutants in the different water compartments, (2) to describe the different temporal and spatial distribution of the micropollutants (3) to quantify the urban water balance, and finally (4) to quantify the annual mass fluxes of micropollutants and to determine the relevance of different release pathways.

In this thesis, a holistic methodical approach is employed accounting for the complexity of interactions between wastewater, surface water and groundwater in urban areas. In order to achieve this approach, the study area was carefully chosen. Of specific importance for a comprehensive quantification of water flow in and between the different urban water compartments is the position of the catchment of groundwater and the catchment of wastewater - the sewershed. An area within the city of Leipzig was chosen, where the both catchments are in a congruent constellation. This watershed-sewershed approach allows the assessment of micropollutant loads from the sewershed's wastewater as the source to the catchment's groundwater and the surface water as recipients.

The first screening of the study area's groundwater and surface water revealed a ubiquitous presence of micropollutants but also a high temporal and spatial variability of concentrations in time and space (Musolff et al., 2007). Thus, a monitoring program of water quality as well as quantity was conducted over the period of 13 months to provide a reliable database for the investigations. For the evaluation of the derived dataset, univariate descriptive and multivariate statistical methods were applied. The urban water balance was quantified using numerical water flow models as well as conceptual water balance models. The database for the models relied on an existing comprehensive dataset concerning geological settings, land use and the sewage system. Own examinations of the hydraulic properties of the sediments and measurements of groundwater and surface water level fluctuation completed this database.

The thesis is structured in chapters, each of them representing a distinct study.

The third part of the introduction, chapter 1.3 "Micropollutants – challenges in hydrogeology", is a published essay on the major concerns about micropollutants in the water cycle, the role of groundwater and the future tasks of groundwater professionals.

Chapter 2 includes two related published conference papers on the statistical properties of micropollutants concentrations in the water compartments of the study area. Different statistical methods were applied to learn about the micropollutant occurrence and to conclude on pathways and fate. The first of the two papers is a summary of the measurements after half a year of monitoring. The second paper extends these findings using further refined methods after the completion of the monitoring. Both papers use the terms "emerging contaminants" and "xenobiotics" alternatively to the term "micropollutants".

Chapter 3 is a published paper on the temporal and spatial distribution of micropollutant concentrations in the urban receiving water of the study area. For wastewater and surface water, contaminant loads were estimated and discussed in regard to the fate of different micropollutants.

Chapter 4 quantifies the water balance of the sewershed-watershed area and uses the micropollutant concentration measurements from the monitoring to estimate annual pollution loads. Here, conclusions on the relevance of different pathways are drawn and implications for the aquatic environment are discussed.

In the concluding chapter 5 the results of this thesis are recapitulated and implications of the findings are discussed. The perspective directs to future questions to be investigated in regard to micropollutants in urban receiving waters.

1.3 Micropollutants – challenges in hydrogeology

This chapter is published as an essay:

Musolff A (2009) Micropollutants - challenges in hydrogeology. Hydrogeology Journal 17: 763-766

1.3.1 Introduction

In the 1990s, clofibric acid, a metabolite of lipid regulators, was found in the drinking water of Berlin, Germany (Heberer and Stan, 1997). This drug made its way from households via wastewater treatment plants to surface waters and further into the water work’s wells by artificial groundwater enrichment and bank filtration. All over the world, hundreds of pharmaceuticals, hormones, additives of personal care products and detergents (collectively referred to as PPCP) have been found in wastewater, surface water and groundwater. Schwarzenbach et al. (2006) pointed at the contamination of water systems with these industrial and chemical compounds as “one of the key environmental problems facing humanity”. Most of them are present only at low concentrations in a range of pg L^{-1} to ng L^{-1} and therefore are termed micropollutants.

In contrast, concentrations of macropollutants such as inorganic nitrogen, phosphate or BTEX (benzene, toluene, ethylbenzene and xylenes) are orders of magnitude higher (Schirmer and Schirmer, 2008). The latter are relatively well known with respect to source, spatial extent, behaviour and remediation. Micropollutants, on the other hand, are ubiquitously present in complex mixtures and therefore much more difficult to assess (Schwarzenbach et al., 2006).

1.3.2 Toxicological relevance of micropollutants

Although the concentrations of micropollutants in the surface water and groundwater are low, micropollutants are an emerging issue. In recent years, an increasing number of studies revealed severe toxicological effects of micropollutants. There is no doubt that most pollutants are diluted to a concentration level where acute toxicity for aquatic life and human health is not given. Pharmaceuticals are present below therapeutic doses used in human and veterinary medicines. However, pharmaceuticals are designed to be bioactive and have a specific mode of action. Toxicity is not always related to this mode of action. Often, side effects may play a major role for the environmental impact of these substances (Fent et al., 2006b). A considerable number of micropollutants can mimic hormones and act as endocrine disrupters. Widely known is the sexual disruption in fish (Jobling et al., 1998). Moreover, micropollutants can interact and behave as chemosensitizer. Environmentally relevant mixtures of pharmaceuticals can interact in a complex way leading to adverse effects in cells (Pomati et al., 2008). For instance, Luckenbach and Epel (2005) proved that polycyclic musks which are used in personal care products can inhibit the activity of multidrug efflux transporters in mussel’s gills. Consequently, substances with low toxicity can lead to an increased presence of xenobiotics in cells since they hinder the self-protection of cells. Aside from these findings much work needs to be done to understand complex impacts of micropollutants on the aquatic ecosystem. There is a major lack of knowledge of chronic effects due to a long-term exposure to micropollutants (Fent et al., 2006b). Furthermore, metabolites or degradation products of micropollutants may also pose a threat to the aquatic environment (e.g., Schmitt-Jansen et al., 2007).

1.3.3 Micropollutants in the aquatic environment

Micropollutants enter the aquatic environment primarily via treated and untreated wastewater (Daughton and Ternes, 1999). Thus, wastewater treatment plants are a major source for the contamination of surface water. Moreover, untreated wastewater can temporarily affect surface water resources by combined sewer overflow during rainstorms. Sewer leakage and bank infiltration are relevant pathways for micropollutant contaminations of groundwater. The continuous input of micropollutants via these sources results in a serious risk for surface water as well as groundwater resources. On the other hand, similar to the fate of macropollutants, processes such as sorption and degradation lead to an attenuation of micropollutants. Chemical attenuation such as photolysis or sorption and biological attenuation are documented for surface water (Gurr and Reinhard, 2006). For groundwater on the field scale, Swartz et al. (2006) obtained persistence for most micropollutants under anoxic conditions while oxic conditions lead to preferential losses. Osenbrück et al. (2007) reported attenuation of pharmaceuticals (0-60%) and polycyclic musk fragrances (95-100%) on the pathway of infiltrated river water. One major question of micropollutant contamination is whether attenuation can balance the input. Barcelo and Petrovic (2007) termed micropollutants “pseudo-persistent” because removal rates may compensate the continuous introduction into the environment. Another question also remains: Are micropollutant concentrations too low for effective biodegradation as the lower limits for enzyme affinities may not be met (Daughton and Ternes, 1999)? Selected examples of micropollutants and related environmental problems are given in Tab. 1.

1.3.4 Micropollutants as potential wastewater indicators

Environmental research focuses mainly on input, distribution and fate of micropollutants in surface water. To date, only a few studies deal with the contamination of groundwater. Often, surveys on water contamination describe the inventory of micropollutants in the manner of case studies. Furthermore, micropollutants are used to describe the wastewater impact on groundwater. Indeed, their unique origin, their persistence and conservative transport properties make some micropollutants good wastewater indicators. This applies in particular to the complex issue of groundwater in urban areas. Urbanization disturbs the water balance in manifold ways. Due to surface sealing, infiltration of water is reduced and runoff increases. On the other hand, large amounts of water are transported into urban areas. Losses from the water infrastructure such as water mains and the sewage system form artificial groundwater recharge (Lerner, 2002). These losses can make up a considerable fraction of total groundwater recharge in urban areas. Furthermore, wastewater losses can have a significant impact on the groundwater quality. As direct measurements of water and contaminant fluxes are seldom possible, an indicator approach can help to assign deteriorated water quality to urban sources (Barrett et al., 1999). Here, the indicator properties of some micropollutants can be helpful. For instance, Fenz et al. (2005) used the antiepileptic drug carbamazepine to quantify sewer leakages to the groundwater in the city of Linz, Austria. Wolf et al. (2006) used iodated X-ray contrast media for the same task in the city of Rastatt, Germany. With the help of optical brighteners from septic systems, Murray et al. (2007) were able to determine the groundwater flow direction in a karst aquifer in Texas, USA. Thus, micropollutants can help to improve our knowledge of the pathways and on the quantification of wastewater in the groundwater. So do we as hydrogeologists benefit from the presence of micropollutants in groundwater? Do we have a new tool to solve our problems, e.g. in assessing urban groundwater resources? Indeed, first applications are promising. But the indicator approach bears the potential to be misled. We should not forget the major concern of wastewater presence in groundwater. The author believes that this is, first of all, groundwater quality. Quality deterioration from wastewater results from pathogens, macropollutants as sodium, chloride, nitrogen and phosphorus compounds, sulfate, and, of course, micropollutants (Drangert and Cronin, 2004). Micropollutant indicators may provide additional information but there are known and reliable ways to assess pathogens and macropollutants from wastewater contamination (e.g., Barrett et al., 1999; Strauch et al., 2008). In the author's judgement, a major application for the use of micropollutants as indicators is micropollutant contamination itself. Persistent and conservative micropollutants such as carbamazepine can help to evaluate transport and removal of other less persistent micropollutants. Furthermore, representatives for classes of micropollutants with comparable properties can be used and thus may reduce analytical efforts. Much work has still to be done to effectively use micropollutants as indicators. We need to know much more on source concentrations, input timing and locations as well as transport properties and degradation processes in the aquatic environment.

Tab. 1: Selected examples of micropollutants.

Component	Usage	Related problems
Bisphenol A	Industrial chemical; production of polycarbonate	Estrogenic activity (Jin et al., 2008); ubiquitously found in urban surface water and groundwater (Musolff et al., 2007; Osenbrück et al., 2007); persistent in groundwater under anaerobic conditions (Ying et al., 2008)
Technical 4-nonylphenol	Industrial chemical; mixture of isomers; metabolite of alkylphenol polyethoxylates (industrial surfactants)	Estrogenic activity (Vethaak et al., 2005; Jin et al., 2008); high persistence in anaerobic groundwater (Ying et al., 2008)
HHCB (galaxolide®); AHTN (tonalide®)	Additives in personal care product; polycyclic musk fragrances	High potential for bioaccumulation; can act as chemosensitizer (Luckenbach and Epel, 2005)
17α-ethinylestradiol	Synthetic estrogenic hormone; contraceptive	High estrogenic activity in the lower ng L^{-1}-range (Jin et al., 2008)
Phenazone	Pharmaceutical; analgesic drug	Persistence in anoxic groundwater (Massmann et al., 2006); estrogenic activity in interaction with other pharmaceuticals (Fent et al., 2006a)
Diclofenac	Pharmaceutical; non-steroidal anti-inflammatory drug	Toxicity of phototransformation products (Schmitt-Jansen et al., 2007); pro-inflammatory properties in low concentrations (Schirmer and Schirmer, 2008)
Carbamazepine	Pharmaceutical; antiepileptic drug	Persistence in urban water cycle (Fenz et al., 2005); potential enrichment in water cycle

1.3.5 Future tasks for hydrogeologists

Future studies on micropollutants in the aquatic environment should go far beyond case studies, singular snapshot sampling programs and simple indicator-based balances of wastewater in the groundwater. A comprehensive risk assessment is needed. Schwarzenbach et al. (2006) suggest the assessment of micropollutants by understanding the exposure on the one hand and by understanding the effects on organisms on the other hand. Thus, the characterization and comprehension of input, distribution and fate of micropollutants in the aquatic environment is an essential prerequisite for exposure assessment. The known strategies for the comprehension of contamination from research on macropollutants have to be adapted to meet the special characteristics of micropollutant contamination.

In the author's opinion, the major problem in assessing micropollutants in natural waters is the concentration variability. Musolff et al. (2007) found highly variable concentrations of micropollutants in time and space in all urban water compartments. In the surface water, highly variable concentration distributions can be partially traced back to temporal sewer overflow events during heavy rainstorms. Compared to macropollutants typically found in well-defined contaminant plumes with a single or a few source zones, micropollutants in the groundwater originate from point source inputs along leaky sewers or from surface water - groundwater interactions. These multiple point sources on the small scale act as linear diffuse sources on a larger scale. Superimposed on the spatial distribution of the leaks in the sewer network is a temporal variability in concentration and composition of micropollutants in the wastewater. Moreover, sewer leaks may not be a continuous source. Depending on the hydraulic situation and the wastewater's composition, colmation layers may temporarily inhibit wastewater exfiltration (Fig. 2). In receiving waters, concentration seasonality is likely to occur. Variable seasonal flow conditions lead to different degrees of dilution. Seasonally varying water temperature induces different removal rates. Source variability and seasonality result in complex spatial and temporal patterns of micropollutant concentrations in all water compartments. Thus, it is crucial to know where, when and how to take samples for measuring micropollutants.

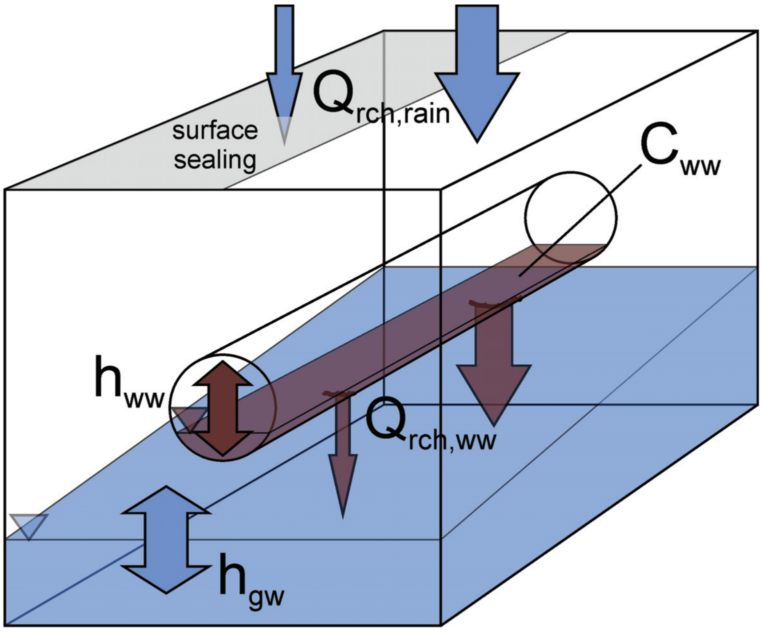

Fig. 2: Scheme of a leaky sewer section and factors controlling the spatial and temporal distribution of micropollutants in the receiving groundwater. The following variables are considered to be spatially and temporally variable: $Q_{rch,\ rain}$ rate of groundwater recharge from precipitation; $Q_{rch,\ ww}$ rate of wastewater exfiltration; C_{ww} concentration of micropollutants in wastewater; h_{gw} elevation of groundwater surface; h_{ww} elevation of wastewater within the sewer.

Promising approaches to characterize micropollutant contamination were introduced in recent years, including techniques to measure concentrations in the field, to evaluate these data as well as modeling approaches to characterize distribution and fate. Schirmer et al. (2007) suggest the application of both spatiotemporally high-resolving as well as integrating concentration measurements. Spatiotemporally high-resolving techniques include direct-push technologies or multilevel sampling in wells. Spatially integrating pumping tests were successfully applied to measure heterogeneous contaminant mass fluxes downstream of urban areas (Leschik et al., 2009). Time-integrating passive sampling can be applied to estimate robust mean micropollutant concentrations in wastewater, surface water and groundwater (Bopp et al., 2005). Data analysis strategies have to address the diversity of micropollutants and sampling concepts. Musolff et al. (2008 [Chapter 2.1]) successfully applied multivariate statistics to estimate wastewater and micropollutant impact on surface water and groundwater. Contaminant mass flux estimations on a larger time scale are capable of assessing adverse accumulative, chronic effects of wastewater input. Barber et al. (2006) estimated mass fluxes of micropollutants in the surface water on the watershed scale. They found several endocrine disrupting chemicals in elevated concentrations with increased population densities along a stream. By incorporating groundwater - surface water interactions, Reinstorf et al. (2008) went one step further. For the city of Halle (Saale), Germany, mass fluxes of micropollutants were estimated in surface water and groundwater. Surface water loads of musk fragrances and endocrine disrupting chemicals increased significantly during the passage through the city. With numerical flow and transport models the distribution and fate of micropollutants can be assessed in a way that goes beyond the black box models of mass flux estimations. Using process-based, transient models, the spatiotemporal variability can be adequately addressed. Transport of micropollutants can be modeled in the same way as of dissolved macropollutants. The crucial point is the definition of the input function of the micropollutants. Field applications of micropollutant transport models in groundwater are rare. Greskowiak et al. (2006) simulated concentrations of the analgesic drug phenazone during artificial groundwater recharge. Phenazone was found to be redox-sensitive and mainly controlled by the temperature of the infiltrating water. To the best of the author's knowledge, so far there is no study that numerically models groundwater transport from temporally variable sewer leakages.

Wastewater inputs into the aquatic environment cannot be totally avoided. There is evidence for ecotoxicological effects of micropollutants. Since groundwater is a valuable ecosystem and a source of our drinking water, the challenge for hydrogeologists is to accurately monitor and estimate the amount of inputs into the groundwater system, the mass flow rates in the aquifers, the mass flow rates from and to other compartments of the aquatic systems. The key issue is to understand and to describe the temporal dynamics and the spatial variability of micropollutant inputs, transport and fate in the groundwater. This insight will also be essential for the promising usage of micropollutants as wastewater indicators.

Finally, holistic approaches are needed, incorporating wastewater as the source and surface water as well as groundwater as a receptor. Including a sufficient treatment of uncertainty, this knowledge will contribute to a comprehensive risk assessment of micropollutants for aquatic ecosystems and human health.

Chapter 2

Assessing micropollutants in urban receiving waters

2.1 Assessing emerging contaminants – case study of the city of Leipzig

This chapter is published as:

Musolff A, Leschik S, Reinstorf F, Strauch G, Schirmer M (2008) Assessing emerging contaminants - case study of the city of Leipzig, Germany. In: Trefry MG (ed) Groundwater Quality: Securing Groundwater Quality in Urban and Industrial Environments. IAHS Publ. 324: 178-185

Abstract Urban water resources and emerging contaminants such as pharmaceuticals and personal care products are a matter of growing concern. To assess urban water pollution, all elements of the urban water balance have to be taken into account. This concept is the central point of the project WASSER Leipzig – Water- and Sewershed Study of Environmental Risk. Emerging contaminants are assessed within an urban watershed incorporating groundwater, surface water, untreated and treated wastewater. First measurements show a ubiquitous presence of emerging contaminants in all urban water compartments. Effluents of wastewater treatment plants as well as combined sewer overflows are sources for the contamination of surface water. By the use of multivariate statistics, groundwater contamination due to emerging contaminants can be related to wastewater input. Pathways are leaky sewers and the infiltration of contaminated surface water.

2.1.1 Introduction

Quality and quantity of urban water resources are matters of growing concern. The supply of drinking water, collection and treatment of wastewater, as well as the control of storm water, bear potential for environmental, social, economic and political conflicts (Barraqué, 2006).

Within this context, the new group of emerging contaminants (EmC), including pharmaceuticals and personal care products (collectively PPCP) as well as endocrine disrupting industrial chemicals, is a matter of growing concern (Schirmer et al., 2007). The main source for EmC is wastewater that is produced, transported and treated in large amounts in urban areas. Thus, urban waters are hotspots for the pollution with EmC. Only little is known on the risk of these substances for human health and the aquatic ecosystem (Schwarzenbach et al., 2006). So far, only a few attempts have been made to quantify the input fluxes of EmC to urban groundwater and surface water, and to characterize their transport and fate in the field.

In the study WASSER Leipzig (Water- and Sewershed Study of Environmental Risk in Leipzig), the Helmholtz Centre for Environmental Research – UFZ places emphasis on input pathways of EmC to urban waters, their fate in an urban watershed as well as on the ecotoxicological risks of those pollutants. The medium-term aim is to contribute to a risk assessment concerning EmC for human health and ecosystems.

For assessing urban water resources, the entire urban water balance has to be taken into account. Compared to a natural system, the water balance in urban areas is disturbed as surface sealing reduces infiltration and increases runoff. Water mains and sewage systems form large networks in the urban subsurface. Losses from these networks form an artificial groundwater recharge (Lerner, 2002). As direct measurements of groundwater recharge or runoff are seldom possible, the quantification of associated EmC fluxes to urban waters is a sophisticated task. In our opinion, this task is best achieved with an integrated approach: In an urban watershed, the wastewater as an element of the urban water balance and its catchment area – the sewershed – has to be taken into account. Therefore, a study area with a matching urban watershed and sewershed provides the best basis for an integrated quantification.

Different studies in past years provide a good overview of possible EmC pathways to urban water resources. By far the best studied contaminant sources for surface water are wastewater treatment plant (WWTP) effluents, as during the treatment EmC often are only partially removed (Daughton and Ternes, 1999). Due to combined sewer overflow during storm events, untreated wastewater is temporally discharged into surface water (Buerge et al., 2006). Studies on EmC in groundwater are much scarcer. Rutsch et al. (2006) report that up to 20%

of the wastewater's dry weather flow is lost due to leakage. Thus, EmC can be expected to be present in urban groundwater.

In this paper we present the first results of EmC concentration measurements in an urban watershed in the city of Leipzig, Germany. By comparing the EmC concentrations in different water compartments and applying multivariate statistics, an initial conceptual model of EmC input can be derived.

2.1.2 Material and methods

Site description

The study site covers an area of 18 km^2 and is located in the western part of the city of Leipzig (Fig. 3). Land use is composed of residential areas, used and disused industrial areas, green spaces and forest. The northern part of the study area is dominated by the flood plains of the rivers Elster, Luppe and Nahle. These rivers are influenced by urban development in the south of the city of Leipzig. Moreover the rivers pass 5 km within of the city of Leipzig, before entering the study site. The geological structure is characterized by Quaternary sediments covering Proterozoic and Carboniferous bedrock and Tertiary sands. The Quaternary sediments consist of gravels and sands forming a highly permeable aquifer with a thickness of approximately 8 m. In the flood plain, alluvial clay covers the aquifer. Within the study area, a watershed can be defined based on groundwater elevation data. The groundwater flows from the south towards the northern flood plain. The sewage system has a length of 64 km, forming a sewershed that is congruent with the watershed boundary. Wastewater is pumped to a wastewater treatment plant (WWTP) in the eastern part of the study area that has a capacity of 463 000 population equivalents (Wiegel et al., 2004).

Emerging contaminants and inorganic water quality parameters

Based on previous studies (Reinstorf et al., 2008), six EmC were chosen as indicators representing wastewater input to urban waters:

- bisphenol A (BPA), endocrine disrupting industrial chemical
- technical 4-nonylphenol (NP), degradation product of nonylphenol polyethoxylates with estrogenic activity, mixture of isomers
- galaxolide® (HHCB) and tonalide® (AHTN), polycyclic musk fragrances
- caffeine (CAF), psychomotor stimulant
- carbamazepine (CBZ), antiepileptic drug

The analysis of the water samples was done using solid phase extraction and gas chromatography. Detection limits were 0.2 ng L^{-1} for galaxolide® and tonalide®, 1 ng L^{-1} for technical 4-nonylphenol, bisphenol A and caffeine, and 2 ng L^{-1} for carbamazepine. Details are described in Braun et al. (2003).

Additionally, all water samples were analyzed with regard to the inorganic water constituents. The following parameters were used to determine the anthropogenic impact on the water quality: temperature, pH, oxygen, sulfate, chloride, bi-carbonate, nitrate, sodium, boron, calcium, potassium, magnesium. With these analyses, the EmC concentrations can be compared to the conventional, inorganic anthropogenic indicators. It further supports our analysis with information about the overall evolution and anthropogenic influence on urban waters.

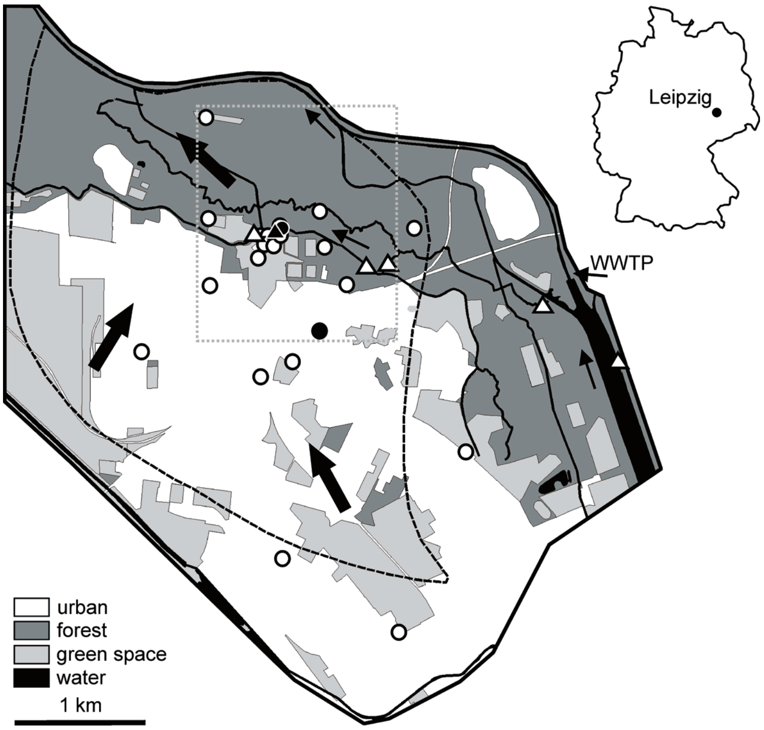

Fig. 3: Land use of the study site and location within Germany. The dashed line marks the watershed. Dots indicate observation wells of the sampling program, triangles surface water sampling locations (filled – 1 month, hollow – 3 month sampling interval). Bold black arrows indicate the general groundwater flow direction, small arrows the river flow direction. The dotted rectangle marks the position of Fig. 6. WWTP – location of the wastewater treatment plant effluent.

Sampling

A first screening of groundwater and surface water for the EmC and inorganic water quality parameter was conducted in 2006. The results are provided in Musolff et al. (2007). Based on these findings, 22 observation wells and six surface water sampling locations were selected for a one-year monitoring program of EmC and inorganic water quality that commenced in April 2007. The selected locations are sampled every three months. Two observation wells, one surface water sampling location and the influent and effluent of the WWTP are sampled monthly.

Data analysis

Data analysis of the EmC concentrations and distributions has to address the diversity of the problem as different indicators with different properties are used. Therefore, multivariate statistics are applied. Correlation analysis and factor analysis reveal similarities in input of different EmC markers as well as the inorganic water quality parameters, and may provide information on differentiating processes such as transport and degradation. The factor analysis is a method of data reduction and allows the formation of a few factors (random variables) from the multiple input variables. These factors are able to describe the variance of the entire data set. The EmC concentrations were used in combination with inorganic indicators. As an extraction method, principle component analysis was used; the matrix was rotated with the varimax method (Brown, 1998). The result is a set of factors with which the variables correlate (amount of correlation is given by the factor loading, range of values: –1 to 1). For each sample and each factor, a score is computed. This score indicates to what extent the factor describes the sample. Scores of 0 represent mean impacts, positive values an impact above average.

2.1.3 Results and discussion

Results of the monitoring program, including half a year of sampling and of the multivariate analysis, are given below.

Emerging contaminant concentrations in urban waters – overview

Emerging contaminants can be found in all samples from urban waters, with concentrations in the range of ng L^{-1} to µg L^{-1} (Fig. 4). Standard deviations of the concentrations are noticeably high (Tab. 2), pointing out the high variability of EmC in surface water as well as in groundwater. Only a limited number of samples are available for the untreated and treated wastewater and so only a preliminary discussion is possible.

Tab. 2: Standard deviation of EmC concentrations in groundwater and surface water in ng L^{-1}.

	Technical 4-nonylphenol	Bisphenol A	Caffeine	Galaxolide®	Tonalide®	Carbamaze-pine
Groundwater	177	5924	7	2.9	1.3	26
Surface water	192	9325	555	30.3	7.4	261

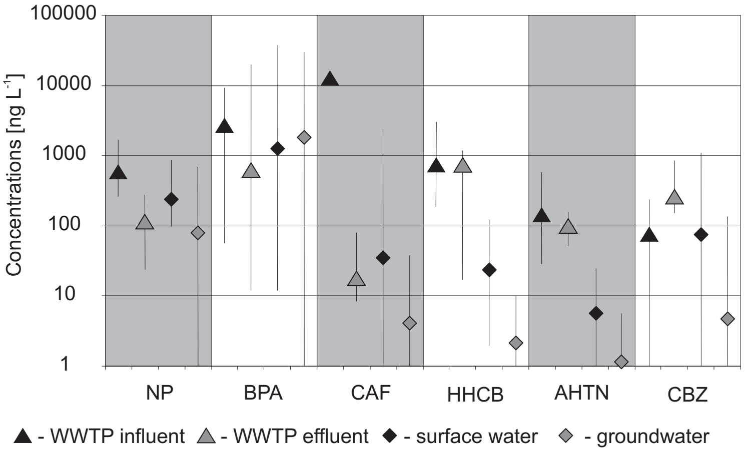

Fig. 4: Median, minimum and maximum of EmC concentrations in untreated and treated wastewater (number of samples, *n* = 5), surface water (*n* = 18) and groundwater (*n* = 38) (NP – technical 4-nonylphenol, BPA – bisphenol A, CAF – caffeine, HHCB – galaxolide®, AHTN – tonalide®, CBZ – carbamazepine).

Emerging contaminants in the WWTP influent and effluent

The concentrations for caffeine and technical 4-nonylphenol are considerably lower in the WWTP effluent than in the influent. For bisphenol A and tonalide®, median concentrations are lower in the treated than in the untreated wastewater. A partial retention in the WWTP can be assumed for these substances. Galaxolide® and carbamazepine concentrations do not change significantly on the passage through the WWTP, indicating a higher persistence during the treatment. Thus, WWTP effluents are a major EmC source for surface water in the study site.

Emerging contaminants in the surface water

Median concentrations of technical 4-nonylphenol, bisphenol A and caffeine in the surface water are higher than in the WWTP effluent. As the surface water has already encountered the influence of treated wastewater from settlements further upstream, we assume an additional source to be the reason for temporarily high concentrations of EmC. Similar to the findings of Buerge et al. (2006) regarding caffeine in Swiss lakes, we trace these high concentrations of caffeine, technical 4-nonylphenol, bisphenol A and carbamazepine in the surface water back to sewer overflow events. Future work will incorporate an analysis of temporal variations and the relationship to rainfall events. Retention, for instance by sorption on aquatic sediments as described by Heberer (2002a), could be the reason why the polycyclic musk fragrances do not follow these trends and show lower concentrations in surface water.

Emerging contaminants in the groundwater

Compared to surface water, median concentrations of caffeine, galaxolide®, tonalide® and carbamazepine are significantly lower in the groundwater. The concentrations of bisphenol A are characterized by a higher median in groundwater; technical 4-nonylphenol has comparable median concentrations in both types of water. Both substances show a high variability (see also Tab. 2). At the moment there is no explanation for these two exceptions.

Multivariate statistics for groundwater samples

For the multivariate analysis, three outliers were removed (two exceptionally high concentrations of bisphenol A and one of caffeine; the reason for these may be a contamination during sampling or analysis). A significant (0.01 level) positive correlation was found for the concentrations of galaxolide®, tonalide® and caffeine, for bisphenol A and caffeine, as well as for bisphenol A and galaxolide®. Thus, these substances show similarities. These findings are also expressed in the factor analysis.

The factor analysis of the EmC and inorganic indicators allows a reduction of the 18 variables to five factors explaining 78% of the overall variance. Factor loadings are given in Fig. 5.

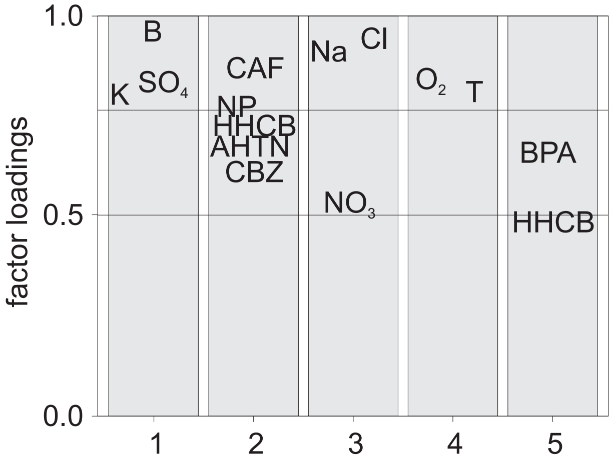

Fig. 5: Positive loadings of the five factors. Only indicators with positive loadings over 0.4 are included. Abbreviations are given in Fig. 2. T – groundwater temperature.

Factor 1 represents highly mineralized groundwater with high concentrations of boron, sulfate and potassium. It is likely that this water represents urban-influenced recharge from landfills, construction waste and abandoned industrial sites, since no natural sources for the high concentrations of boron and sulfate are known. Ford and Tellam (1994) report a comparable impact on the groundwater in the city of Birmingham, UK. Factor 2 combines caffeine, technical 4-nonylphenol, galaxolide®, tonalide® with carbamazepine and explains 18% of the total variance. Standley et al. (2000) consider the combination of caffeine and musk fragrances as a unique indicator for wastewater input into surface water. We transfer this approach to groundwater and extend this combination with 4-nonylphenol and carbamazepine. Thus, groundwater samples characterized by a high score of Factor 2 show a contamination by wastewater. Factor 3 is characterized by high loadings of sodium and chloride. As natural sources for these substances are not known in the study site, anthropogenic sources such as road de-icing salts have to be taken into account. Factor 4 combines oxygen and groundwater temperature. High values are located in the western and southern part of the area, where no alluvial clay is present. The absence of the clay cover results in aerobic conditions and higher groundwater temperatures in summer. Factor 5 combines bisphenol A and galaxolide®, explaining 7% of the total concentration variance. Since galaxolide® is also incorporated into the wastewater Factor 2, we relate Factor 5 to wastewater input to groundwater as well.

Thus, only Factor 4 represents natural conditions while all the other factors combine variables that indicate anthropogenic impacts on the groundwater quality. Emerging contaminants are not combined with inorganic wastewater indicators such as potassium or boron. As factors 2 and 5 both represent a wastewater impact on groundwater, the differentiation between these factors may be due to different transport properties or degradation processes that cannot be distinguished as yet.

The spatial distribution of EmC in the groundwater is highly variable. Fig. 6 shows the distribution of the Factor 2 scores in the groundwater of the study site.

Of the groundwater samples taken from the vicinity of sewer sections, just two are characterized by a high score of Factor 2, indicating a wastewater impact. The samples from the other wells near sewers show only a below average impact. Here, the different conditions of the sewage system (occurrence and distribution of leaky sections) and the surrounding geological settings probably have an influence. In the vicinity of a little stream in the central part of the study site, the impact of Factor 2 is high. Overflows of untreated wastewater to this stream are known to occur and temporarily contaminate the surface water. Here, losses from this contaminated surface water are considered as an input pathway for EmC to the groundwater.

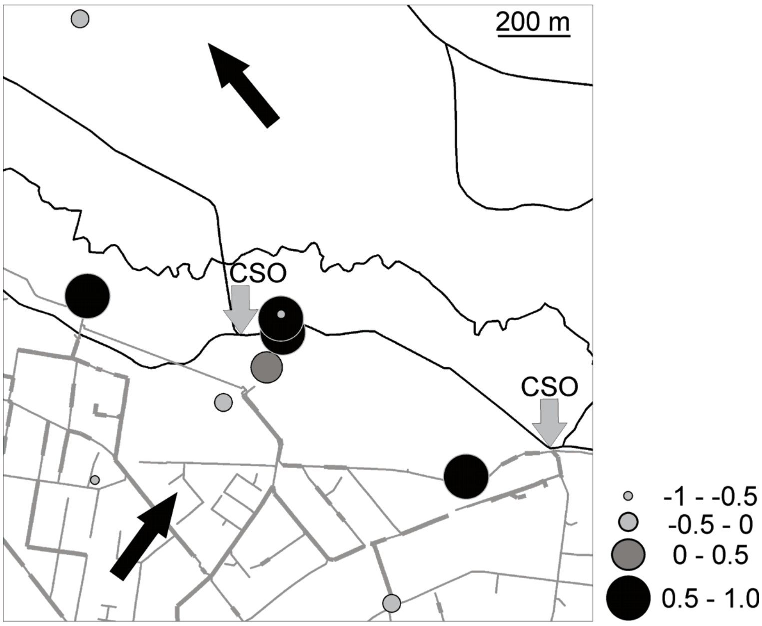

Fig. 6: Wastewater impact on the groundwater of the central part of the study site shown by the spatial distribution of the mean scores of Factor 2. Score values over 0 are characterized by an impact above average. Grey lines indicate the sewer network (bold lines represent sewers with known damage), black lines the urban streams, bold black arrows the groundwater flow direction, the small arrows river flow direction. CSO – locations of sewer overflow to the stream.

2.1.4 Conclusions

First measurements of a monitoring program, taking groundwater, surface water, wastewater and WWTP effluents into account, allowed a primary assessment of EmC input pathways in an urban watershed. Emerging contaminants are ubiquitous in the urban waters in the city of Leipzig. We consider the following sources and pathways for EmC in urban waters as a conceptual source model. A comparison of untreated wastewater with WWTP effluent revealed a partially retention of caffeine, technical 4-nonylphenol and bisphenol A during the treatment process. The polycyclic musk fragrances and carbamazepine were characterized by a higher persistence during the treatment process. Thus, effluents of WWTPs are a source for EmC in the surface water. Moreover, surface water is contaminated by the input of untreated wastewater from combined sewer overflows. The use of multivariate statistics for the groundwater samples reveals the origin of all investigated EmC as wastewater. By comparing the spatial distribution, leaky sewers as well as infiltrated contaminated surface water were assumed to be contaminant sources. Results of the factor analysis indicate a differentiation of EmC through transport or degradation.

Future work will incorporate further analysis of the temporal and spatial variability of EmC concentrations. Results from passive sampling devices will provide robust time-integrating

EmC concentration values. Furthermore, the use of integral pumping tests will provide estimates of EmC mass fluxes in groundwater from leaky sewers and contaminated groundwater.

2.2 Statistical methods to evaluate the impact of xenobiotics on urban receiving waters

This chapter is originally published as:
Musolff A, Leschik S, Reinstorf F, Strauch G, Krieg R, Schafmeister M-T, Schirmer, M (2009) Statistical methods to evaluate the impact of xenobiotics on urban receiving waters. Proceedings of the International Conference XENOWAC – Xenobiotics in the urban water cycle, 11 – 13 March, Paphos, Cyprus.
This manuscript was extended following the invitation to be potentially published in a special issue of “Water Science and Technology”.

Abstract Xenobiotics in urban receiving waters are an emerging problem. A sound knowledge of xenobiotic input, distribution and fate in the aquatic environment is a prerequisite for risk assessments. Methods to assess the impact of xenobiotics on urban receiving waters should address the diverse characteristics of the target compounds and the spatiotemporal variability of concentrations. Here, we present results from a one-year-monitoring program concerning xenobiotic concentrations in an urban catchment area in untreated and treated wastewater, surface water and groundwater. Univariate and multivariate statistical methods were applied to characterize the xenobiotic concentrations. Correlation and factor analysis revealed a pronounced pattern of xenobiotics in the surface water samples. The negative proportionality of several xenobiotics to the water temperature hints to seasonal attenuation as a concentration influencing process. Moreover, dilution of xenobiotics was found to influence the surface water concentrations. Hence, these two processes more control the xenobiotic occurrence in the surface water than the less pronounced concentration pattern in the wastewater sources. For the groundwater samples, we assume that foremost attenuation processes lead to the found differentiation of xenobiotics. Findings of this data-driven approach to xenobiotic concentrations should be incorporated in physically-based models of the xenobiotic impact on urban receiving waters.

2.2.1 Introduction

Xenobiotics are a diverse group of substances including active compounds of pharmaceuticals and personal care products (collectively PPCPs) and various industrial chemicals. Schwarzenbach et al. (2006) pointed at the pollution of water resources by these emerging contaminants as “one of the key environmental problems facing humanity”. The introduction of xenobiotics by wastewater sources into the aquatic environment is seen with increasing concern (Schirmer and Schirmer, 2008). Persistence and pseudo-persistence (continuous input compensates removal/ transformation) of xenobiotics have led to a ubiquitous presence in the entire water cycle. Occurrences are known in precipitation (Fries and Püttmann, 2004; Peters et al., 2008), surface water (Wiegel et al., 2004), soil water (Massmann et al., 2006) as well as in groundwater (Musolff et al., 2007). Xenobiotics pose a possible threat to aquatic ecosystems and to human health, since they can act as endocrine disruptors (Fent et al., 2006b) and chemosensitizers (Luckenbach and Epel, 2005). Of special concern is the effect of xenobiotic mixtures (Pomati et al., 2008), transformation products (Schmitt-Jansen et al., 2007) and the impact of a long term exposure (Fent et al., 2006b).

A risk assessment of xenobiotics in water resources should be based on a comprehensive knowledge on the input pathways and dynamics, the environmental transport characteristics and finally the fate of these substances. While macropollutants such as inorganic nitrogen, phosphate or BTEX (benzene, toluene, ethylbenzene and xylenes) are well known in source, spatial extent, behavior and remediation, the assessment of xenobiotics is still in its infancy (Schirmer et al., 2007).

Xenobiotic contamination of water resources is mostly related to the input of wastewater. Thus, water in urban areas is particularly vulnerable to xenobiotic contaminations, since here, large amounts of wastewater are produced, transported and treated. Effluents of wastewater treatment plants (WWTP) and overflows of combined sewers are typical input pathways for urban surface water. Losses of wastewater from the sewage system can pollute the urban soils and the groundwater (Leschik et al., 2009). The major problem in assessing xenobiotics in urban water resources is a high variability of concentration in time and space (Musolff, 2009 [Chapter 1.3]). This is a result of the spatial distribution of input sources as for instance leaky sewers for groundwater contamination. Moreover, input sources such as sewer overflows and sewer leakages can have intermittent character and, thus, vary significantly over the time. Superimposed, there is a high temporal variability of xenobiotic concentrations in wastewater as the major source. This results in spatiotemporal concentration variations in urban receiving waters in order of magnitude as observed by Musolff et al. (2007). There is a need to develop a sound methodology to sample and analyze xenobiotics and to evaluate the results, accounting for the special characteristics of these pollutants.

To address the variability of xenobiotic impacts on urban receiving waters we conducted a one-year-monitoring program. Six species of xenobiotics were observed in the WWTP influent and effluent, in the surface water and in the groundwater within an urban watershed: bisphenol A (estrogenic precursor in the polycarbonate production; BPA), technical 4-nonylphenol (estrogenic metabolite of surfactants in detergents and pesticides; NP), caffeine (psychomotor stimulant in food and pharmaceuticals; CAF), galaxolide® (chemosensitizing polycyclic musk; HHCB), tonalide® (chemosensitizing polycyclic musk; AHTN) and carbamazepine (antiepileptic drug; CBZ). The first results of six month of measurements were published in Musolff et al. (2008) (Chapter 2.1). By comparing the median concentration of xenobiotics and their spatial distribution in the different water compartments the following conclusions were drawn:

- BPA, NP, CAF, and AHTN were partially retained in the WWTP
- HHCB and CBZ were characterized by a higher persistence in the WWTP
- Thus, WWTP effluents were a relevant source for the xenobiotic contamination of the surface water
- Temporally elevated concentrations of CAF, NP, BPA and CBZ in the surface water are related to intermittent sources, such as sewer overflow events
- Groundwater contamination with xenobiotics were a result of wastewater losses from leaky sewers and in part of the infiltration of contaminated surface water
- In all urban water compartments, xenobiotic concentrations were characterized by a high variability in time and space

Here, we concentrate on the application of univariate and multivariate statistical methods on the monitoring results. Especially multivariate statistical methods proved to be capable to deal with multiple hydrochemical and geochemical data. For instance, concentration patterns based on the same biogeochemical processes, such as biotransformation or changing redox conditions, can be recognized. Thus, it is possible to reduce the number of input variable and learn about the “effective dimensionality” of the dataset. The effective dimensionality is defined as the number of statistically independent processes that is required to reproduce the variance of the dataset (Lischeid and Bittersohl, 2008). Reimann et al. (2002) applied factor analyses to regional geochemical data in order to reveal hidden multivariate structures. Fitzpatrick et al. (2007) used principal component analyses and hierarchical cluster analyses to investigate the effect of different land use types on surface water chemistry. Fröhlich et al. (2008) characterized the hydrochemical fingerprint of water sources in a complex catchment by the use of the same methods.

We hypothesize, that the use of statistical methods are capable to characterize the impact of wastewater-borne xenobiotics on urban receiving waters. The applied methods may help to understand the concentration variability and to learn about concentration influencing processes.

2.2.2 Materials and methods

Study site

The medium scale study site (18 km^2) is located within the city of Leipzig, Germany (Fig. 7). The southern part is dominated by urban land use such as residential areas, industrial areas and green space. The northern part is characterized by the forested floodplain of the river Weisse Elster and its tributaries Nahle and Luppe. This river system receives water from the municipal wastewater treatment plant (WWTP; 463 000 population equivalents) in the eastern part of the study site and moreover from several WWTPs south of Leipzig. Two small streams within the study site receive water from the Weisse Elster River system and from sewer overflow events but are not influenced by the municipal WWTP (Musolff et al., 2007, Musolff et al., 2008 [Chapter 2.1]). The shallow aquifer system consists of highly permeable Quaternary sands and gravels and discontinuously distributed Tertiary sands covered by a floodplain-loam in the northern part of the study site. Groundwater flows from the south to the rivers in the eastern and northern part, forming a catchment area with a size of 9.5 km^2. The sewer network forms a catchment area (sewershed) congruent to the groundwater's catchment. Therefore, a water and contaminant mass balance is possible including wastewater as the xenobiotic source and groundwater as the recipient in a "watershed-sewershed"-approach (Schirmer et al., 2007). In this approach, groundwater contamination with xenobiotics within the watershed is assumed to have its origin in the sewershed's wastewater. As the surface water has its origin in the Weisse Elster River, its chemical composition may be influenced by the watershed-sewershed-area as well as by the Weisse Elster catchment.

Field work

To account for xenobiotic concentration variability on different temporal and spatial scales, we conducted a one-year-monitoring program of water quality in different water compartments. Untreated and treated wastewater samples were monthly taken in the municipal WWTP after primary sedimentation and in the effluent. The surface water was sampled every month at one location and every three months at four locations. Groundwater samples were monthly taken at two observation wells and taken every three months at seven observation wells (see also Musolff et al., 2008 [Chapter 2.1]). Samples from the wastewater and the surface water were taken as grab samples. Groundwater was sampled by the use of submerged pumps. Field work included in-situ measurements of pH, Eh, water temperature, electrical conductivity and dissolved oxygen. Xenobiotic samples were collected in 1 L glass bottles and stored at cool and dark places for analysis.

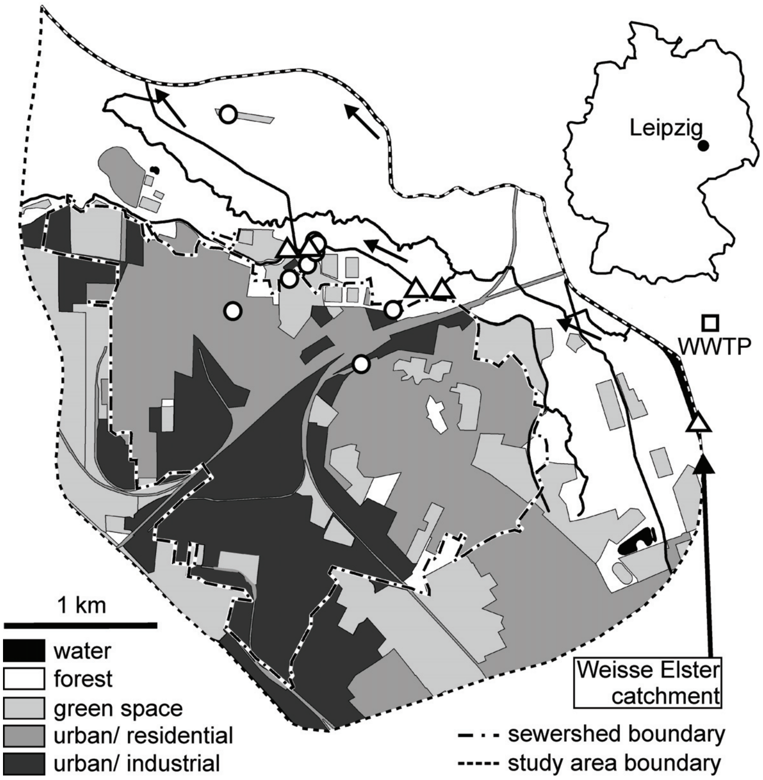

Fig. 7: Land use of the study area and position within Germany. Points refer to the sampled wells, triangles to the surface water sampling locations and arrows to the surface water flow direction. WWTP – location of the municipal wastewater treatment plant.

Analytics

The xenobiotics were analyzed without derivatization by solid-phase extraction and gas chromatography-mass spectrometry (for details see Braun et al., 2003, Einsle et al., 2006). For the quantification of CAF, HHCB, AHTN and CBZ external standards were used. Internal standards were used for NP (4-n-nonylphenol) and BPA (d_{16} bisphenol A).

Limits of detection in the surface water samples are 1 ng L^{-1} for HHCB and AHTN, 5 ng L^{-1} for CAF and CBZ and 10 ng L^{-1} for BPA and NP. In the groundwater samples limits of detection are 0.2 ng L^{-1} for HHCB and AHTN, 1 ng L^{-1} for BPA, NP and CAF, and 2 ng L^{-1} for CBZ. Concentrations below the limit of detection where set to 0 ng L^{-1}. Concentrations based on a problematical quantification (overlapping peaks in the chromatogram or low recoveries of standards) were not considered.

Statistical methods

For all statistical analyses, the software SPSS (SPSS Inc.) was used. Univariate descriptive statistics for xenobiotic concentrations in the different water compartments were applied to characterize median and variance. The Kolmogorov-Smirnov-Test (KS-test; Manly, 1998) was used to test normality of the concentrations distributions. The KS-test yields the p-value: If $p < 0.05$, the tested distribution differs significantly from a normal distribution. Most of the data had to be log-transformed to ensure normality (see Tab. 3). For the correlation and the factor analysis, concentrations were z-normalized (mean = 0; standard deviation = 1). Concentrations below the limit of detection were omitted for the correlation and factor analysis, since this set of identical values may influence the results (Reimann et al., 2002).

Two multivariate statistical methods were applied: correlation and factor analysis. Correlation analysis reveals direction and amount of a linear relationship between two variables. The factor analysis is a method of data reduction. An input of multiple variables is reduced to a few factors, describing the variance of the dataset. These factors are built as linear regression of input variables, whereby the factor loadings reflect the amount of correlation with individual input variables. The derived factors can hint to the effective dimensionality (which refers to the number of underlying processes; Lischeid and Bittersohl, 2008) and hidden structures in the dataset. Whether a factor is meaningful should be matter of discussion by the user of this method. For the factor analysis applied here, we used principle component analysis as extraction method and the varimax method for the matrix rotation to maximize the loading of each variable (Brown, 1998).

2.2.3 Results and discussion

A statistical summary of the monitoring results is given in Tab. 3.

Xenobiotics were ubiquitously found in all urban water compartments. As the main pathways are described above focus is set on the statistical characterization of the xenobiotic contamination and the interpretation of possible underlying processes.

Tab. 3: Statistical summary of xenobiotic concentrations in the different urban water compartments. NP – technical 4-nonylphenol; BPA – bisphenol A; CAF – caffeine; HHCB – galaxolide®; AHTN – tonalide®; CBZ – carbamazepine; σ – standard deviation; *p*/ *p*-ln – p-value of Kolmogorov-Smirnov-Test for normality of original data and log-normalized data; n – number of considered samples for median, range and σ; values in brackets refer to the number of samples considered for all other statistical analyses.

	Median [ng L^{-1}]	Range [ng L^{-1}]	σ [ng L^{-1}]	*p* [ ]	*p*-ln [ ]	n
Untreated wastewater						
NP	779	2211	652	0.846	0.415	12(12)
BPA	2342	21343	5911	0.550	0.731	12(12)
CAF	4487	4028	2848	-	-	2(2)
HHCB	758	3484	1146	0.176	0.960	13(13)
AHTN	112	557	159	0.407	0.998	13(13)
CBZ	19	238	68	0.338	0.861	11(9)
Treated wastewater						
NP	184	527	140	0.116	0.718	12(12)
BPA	341	911	329	0.707	0.674	12(12)
CAF	12	43	18	-	-	5(3)
HHCB	791	1255	444	0.848	0.182	13(13)
AHTN	58	73	24	0.791	0.938	13(13)
CBZ	78	369	125	0.844	0.664	13(11)
Surface water						
NP	173	814	180	0.107	0.942	32(32)
BPA	1914	5826	1822	0.551	0.109	29(29)
CAF	40	251	66	0.204	0.626	31(28)
HHCB	9	123	21	0.007	0.862	32(32)
AHTN	4	40	9	0.009	0.748	33(31)
CBZ	30	479	118	0.017	0.521	32(30)
Groundwater						
NP	56	767	142	0.000	0.188	54(54)
BPA	318	6678	1866	0.004	0.580	56(56)
CAF	3	38	8	0.008	0.655	52(38)
HHCB	1.2	2.9	0.7	0.976	0.184	56(49)
AHTN	0.9	5.6	1.2	0.061	0.616	48(38)
CBZ	2	1162	154	0.000	0.445	57(43)

Wastewater

Compared to the other water compartments, untreated wastewater was characterized by high concentrations of CAF, BPA, NP, HHCB and AHTN. The correlation analysis revealed a significant positive relationship between the HHCB and AHTN (0.872; 0.01 level), between NP and AHTN (0.632; 0.05 level) and between NP and HHCB (0.626; 0.05 level).

Compared to untreated wastewater, median concentrations of CAF, BPA, NP and AHTN were reduced in treated wastewater. Median HHCB concentrations were comparable in both compartments. The correlation analysis revealed a significant positive relationship between HHCB and AHTN (0.940; 0.01 level). Due to the number and snapshot-character of the wastewater samples, only a limited discussion is possible. Treated wastewater was a considerable contamination source for the receiving surface water with HHCB, BPA, NP, CBZ and AHTN. A typical fingerprint of treated wastewater that may also be found in the receiving surface water was only observed for HHCB and AHTN.

Surface water

Compared to the treated wastewater as a major source for surface water contaminations, the median concentrations of BPA, CAF and NP were comparable (NP) or even higher (BPA, CAF) in the study area's surface waters (Tab. 3). Reasons were additional sources of xenobiotics such as the input of untreated wastewater from sewer overflow events (Musolff et al., 2008 [Chapter 2.1]).

The correlation analysis revealed significant positive relationships between HHCB and AHTN (0.925; 0.01 level), CBZ and HHCB (0.692; 0.01 level), CBZ and CAF (0.623; 0.01 level), CBZ and BPA (0.576; 0.01 level), CBZ and NP (0.518; 0.01 level), CAF and HHCB (0.510; 0.01 level) and between CBZ and AHTN (0.506; 0.01 level). The factor analysis was applied to the xenobiotic concentrations and resulted in the formation of two factors, explaining 74.0% of the total variance (Fig. 8). The factor 1 combines HHCB, AHTN, CAF and CBZ. The factor 2 combines NP and BPA. An additional correlation analysis was carried out to test the influence of the measured in-situ-parameter on the factors. A significant negative correlation was found for the factor 1 and the water temperature (-0.519; 0.01 level). For factor 2, a significant positive correlation was found with the electrical conductivity (0.593; 0.01 level).

The correlation and the factor analysis revealed significant relationships between several xenobiotics. A comparable occurrence characteristic of xenobiotics in the surface water can be a result of input by the same source but can also be a result of comparable transport or retention characteristics such as sorption to sediments, biotransformation, water-air exchange or photolysis. As the wastewater source characteristics, exemplarily measured in the municipal WWTP effluents, were found to show no significant concentration pattern (see above), the concentration pattern in the surface water are assumed to be a result of transport and retention processes. The sorption characteristics of CAF and CBZ (low pK_{ow}; -0.07 for CAF, 2.45 for CBZ, SRC PhysProp Database, Syracuse Research Corporation) are different to the characteristics of HHCB and AHTN (high pK_{ow}; 5.9 for HHCB, 5.7 for AHTN, SRC PhysProp Database). Moreover, the water temperature (range 2.7°C-22.9°C; median 10.6°C) was found to significantly influence the occurrence of factor 1. Thus, factor 1 is assumed to be controlled by a seasonal process. When the water temperature is high, factor 1 is less pronounced. We assume temperature-dependent attenuation processes to be the reason for this concentration pattern. The occurrence of factor 2 on the other hand was found to be in agreement with the electrical conductivity (range 536 $\mu S\ cm^{-1}$-1379 $\mu S\ cm^{-1}$; median 924 $\mu S\ cm^{-1}$)/ concentrations of inorganic major ions measured in the samples. Hence, factor 2 is assumed to be controlled by the overall discharge conditions and dilution respectively. Nevertheless, more than 25% of the xenobiotic concentration variance could not be explained by the factor analysis. Here, additional and so far unknown concentration influencing processes have to be taken into account.

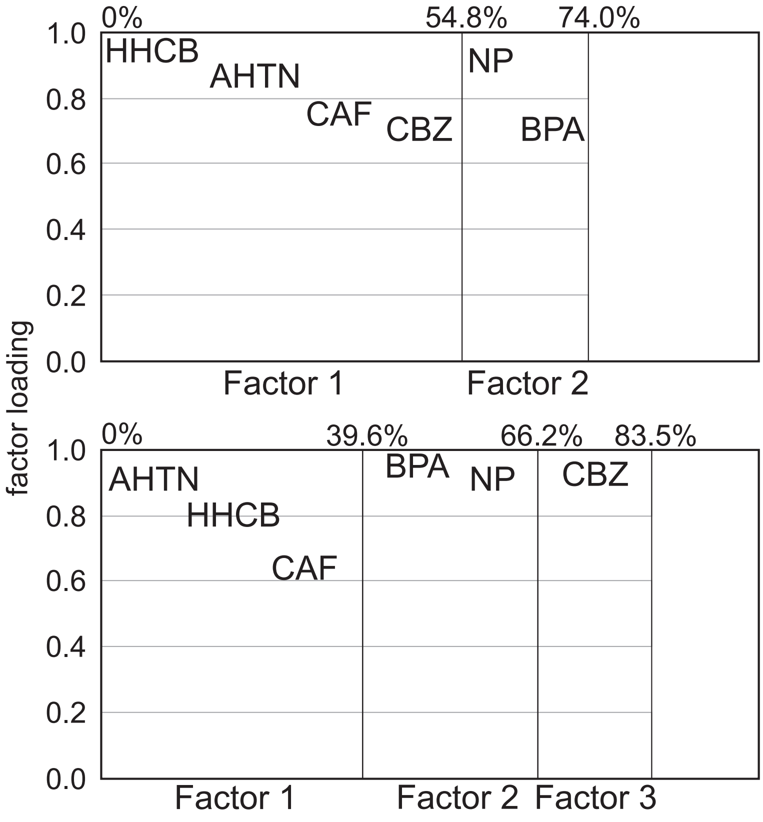

Fig. 8: Results of the factor analysis of the surface water (top) and groundwater samples (bottom). For abbreviations see Tab. 3. Grouped factors and percentage of variance explained are given on the x-axes. Factor loadings for each variable are given on the y-axes.

As all samples are characterized by the same concentration pattern, despite being taken in the Weisse Elster River or in the study area's small stream, processes controlling the occurrence of xenobiotics in the surface water samples are probably related to the entire Weisse Elster catchment. Thus, an influence of the study area's watershed-sewershed could not be delineated from the samples.

Groundwater

Compared to the other water compartments, all xenobiotics were characterized by lower concentrations (Tab. 3). The correlation analysis revealed a significant positive relationship between CAF and AHTN (0.568; 0.01 level) and weaker relationships between NP and CAF (0.329; 0.05 level), NP and HHCB (0.357; 0.05 level) and AHTN and CBZ (0.377; 0.05 level). The factor analysis took 18 valid samples with all six measured xenobiotics into account and resulted in three factors, explaining 83.5% of the total variance (Fig. 8). The factor 1 combines AHTN, HHCB and CAF; the factor 2 BPA and NP and factor 3 is only controlled by CBZ. Unlike the results of the factor analysis for surface water, groundwater factors did not show any correlations with in-situ-parameters.

Except the exclusion of CBZ from the other xenobiotics the results of the groundwater samples' factor analysis was in agreement to the findings for the surface water. This is somehow surprising, since the characteristics of input pathways to groundwater are different to the input pathways to surface waters. While groundwater is mainly polluted by spatial and temporal variable sewer leakages of untreated wastewater (Musolff, 2009 [Chapter 1.3]), surface water is continuously influenced by treated wastewater from WWTPs and additional short-term contributions of untreated runoff-related inputs. Since input characteristics are different, we assume, similarly to surface water, attenuation processes such as biodegradation to govern the concentration pattern of factor 1 in the groundwater. The processes causing the formation of factor 2 and 3 and, thus, a higher dimensionality in the groundwater's xenobiotic concentrations can so far not be delineated.

2.2.4 Conclusions

The application of univariate and multivariate statistical methods helped to characterize the xenobiotic impact on the study sites water compartment and to delineate concentration influencing processes.

In untreated and treated wastewater highly significant concentration patterns of xenobiotics were limited to the polycyclic musk fragrances HHCB and AHTN. Nevertheless, surface water samples were characterized by a typical fingerprint of xenobiotic concentrations. Here, the results of correlation and factor analysis gave valuable indications for processes controlling the environmental occurrence of xenobiotics. The significant relation of the concentrations of HCB, AHTN, CAF and CBC are most likely a result of water temperature-related attenuation processes. Furthermore, dilution of xenobiotics in surface water influences the concentration pattern of NP and BPA. Here, we conclude, that processes in the surface water have more influence on the observed xenobiotic fingerprint than the concentration pattern in the wastewater source.

For groundwater, a comparable xenobiotic fingerprint was found in the factor analysis. Taking the different sorption characteristics of similarly behaving xenobiotics into account, we also assume attenuation processes to be the most important driving force of the similarities in the occurrence of HHCB, AHTN and CAF in the groundwater. Here, the attenuation is not related to the water temperature and, thus, not seasonally pronounced. For groundwater as well as for surface water samples, variables related to the redox conditions of the water samples, such as Eh and dissolved oxygen showed no relation to the observed xenobiotic concentration patterns as for instance observed by Greskowiak et al. (2006).

The findings lead to the conclusion, that seasonal pronounced attenuation of xenobiotic should be considered, when assessing these substances in the surface water. In groundwater the assumed attenuation of xenobiotics can be seen as one part of the processes leading to the observed high spatial and temporal concentration variability.

Based on the result of this data-driven approach to xenobiotic concentrations physical process-based models should be applied to address the xenobiotic impact on the aquatic environment. Here, a better knowledge on the exact physical attenuation processes, such as water-air exchange, photolysis or biotransformation and their location on the pathways of micropollutants in the aquatic environment is necessary. The consideration of wastewater, surface water and groundwater loads as well as the temporal behavior of xenobiotic concentrations/ loads will give a deeper insight into the actual pollution of urban water resources.

Chapter 3

Temporal and spatial patterns of micropollutants in urban receiving waters

This chapter is published as:

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Abstract Based on a monitoring program over the course of a year, we characterize the temporal and spatial distribution of selected micropollutants in an urban watershed within the city of Leipzig, Germany. Micropollutants revealed a ubiquitous presence in untreated and treated wastewater, surface water and groundwater. The loads of 4-nonylphenol in the effluents of the municipal wastewater treatment plant followed a seasonal trend, whereas the loads of all other micropollutants were highly variable and not correlated to seasons. In the surface water, load seasonality of caffeine, galaxolide$^{®}$ and tonalide$^{®}$ resulted from a rapid removal with increased water temperature. The loads of 4-nonylphenol and of caffeine in the colder months increased when rainfall occurred. In the groundwater, complex spatial and temporal patterns were apparent and were related to varying input, retardation and removal processes. As a consequence, an assessment of micropollutants in urban waters should consider different micropollutants' temporal and spatial variability.

3.1 Introduction

Micropollutants are an emerging issue. All over the world pharmaceuticals and additives of personal care products (PPCPs) as well as hormones and detergents have been found in wastewater, surface water, groundwater, and drinking water (Ellis, 2006). Although present in concentrations, where acute toxicological affects are unlikely to occur, micropollutants may pose a threat to the aquatic ecosystem and the human health. Severe effects can be based on interactions of micropollutants (Luckenbach and Epel, 2005; Pomati et al., 2008) or on a long-term exposure (Fent et al., 2006b). According to Schwarzenbach et al. (2006) the scientific challenges of micropollutants are to assess the impact of these substances, to explore remediation and water treatment technologies and to minimize their inputs into the aquatic environment. Because most micropollutants have their origin in products of daily use, their occurrence in the aquatic environment is likely to correlate with population density (Schirmer and Schirmer, 2008). Thus, urban areas can be expected to be “hotspots” of such contamination (Osenbrück et al., 2007; Reinstorf et al., 2008). Numerous studies deal with the occurrence and inventory of micropollutants in the wastewater and the receiving water. Principal pathways are known to be wastewater treatment plant (WWTP) effluents (Daughton and Ternes, 1999) and combined sewer overflows (CSO; Buerge et al., 2006) for surface water. For groundwater leakages from sewers (Musolff et al., 2007), septic systems (Swartz et al., 2006) as well as bank infiltration (Heberer, 2002b) are relevant.

The key in assessing micropollutants is to understand temporal and spatial concentration variability (Musolff, 2009 [Chapter 1.3]). Due to concentration variability in the wastewater itself and the spatial distribution of sources, steady-state concentration distributions are unlikely to develop. Moreover, different physiochemical properties of micropollutants result in different transport and removal processes in the surface water and groundwater. Temporal patterns of micropollutants in the aquatic environment have been found at different time scales. For wastewater treatment plants as well as for surface water, seasonal concentration differences were described for caffeine (Buerge et al., 2003b; Conley et al., 2008), polycyclic musk fragrances (Buerge et al., 2003a; Quednow and Püttmann, 2008b), nonylphenol (Ahel et al., 1994a; Ahel et al., 1994b; Quednow and Püttmann, 2008a), and several pharmaceuticals (Vieno et al., 2005; Conley et al., 2008). On a shorter timescale, intermittent inputs of organic wastewater compounds to surface waters due to CSO are described for caffeine (Buerge et al., 2006), bisphenol A (Boyd et al., 2004) and some endocrine disrupting compounds (Jonkers et al., 2009).

So far, there is a lack of continuous monitoring of micropollutants in the aquatic environment to describe long-term trends and seasonal variations (Sacher et al., 2008). We hypothesize that a monitoring of micropollutants in urban receiving waters over one year is capable to characterize temporal and spatial concentration and load patterns.

In the study “WASSER Leipzig – Water- and Sewershed Study of Environmental Risk” we assess the impact of micropollutants on an urban watershed within the city of Leipzig, Germany. Within a holistic approach, surface water, groundwater, and wastewater are taken into account as parts of the urban water and matter balance (Schirmer et al., 2007). Previous studies gave an overview on the inventory of micropollutants and their occurrence in the aquatic environment of the study area (Musolff et al., 2007; Strauch et al., 2008). As a result, a monitoring program was conducted from April 2007 to April 2008. Based on a literature review and previous studies (Reinstorf et al., 2008) micropollutants were chosen for chemical analysis: bisphenol A (BPA), technical 4-nonylphenol (NP), caffeine (CAF), galaxolide$^{®}$ (HHCB), tonalide$^{®}$ (AHTN), and carbamazepine (CBZ). Criteria for choosing these substances were a unique origin in wastewater, different environmental persistence, a transport mainly with water flow, a potential threat for the ecosystem or the human health and a reasonable laboratory effort for the analysis. From the comparison of the first six months median concentrations of micropollutants preliminary conclusions were drawn by Musolff et al. (2008) (Chapter 2.1):

Due to the incomplete removal in the WWTP, treated wastewater was a relevant source of micropollutants for the receiving surface water. Elevated concentrations of CAF, NP, BPA and CBZ in the surface water were assumed to be originated in water from additional sources such as CSO. For the contamination of groundwater with micropollutants, principle pathways were found to be sewer leakages and the infiltration of contaminated surface water.

Here we present results of the completed 13-months monitoring program. The main objectives are (1) to characterize the overall impact of micropollutants on urban waters, (2) to describe their temporal and spatial patterns in the urban water compartments, (3) to discuss the major processes influencing micropollutant concentrations and loads, and (4) to conclude on appropriate monitoring strategies for different micropollutants.

3.2 Materials and Methods

3.2.1 Study area

This study was conducted in an urban watershed situated in the western part of the city of Leipzig. Leipzig is located in the eastern part of Germany, has a population of about 510 000 and covers an area of 300 km^2. The study area has a size of 18 km^2 with a population of approximately 20 000. In the southern part, urban land use dominates (Fig. 9). The northern part is characterized by the wooded floodplain of the river Weisse Elster. Within the study area, all watercourses are fed by the channel Elsterbecken (ELB). The ELB receives water from the river system Weisse Elster with a median daily discharge of 27.4 m^3s^{-1} (ranging from 8.6 m^3s^{-1} to 126.1 m^3s^{-1}) during the sampling period (data provided by the federal states Saxony and Saxony-Anhalt). The water discharge did not show a pronounced seasonality. The river Weisse Elster is affected by several wastewater treatment plants in the south of Leipzig. According to data from the Saxon State Ministry of the Environment and Agriculture, a discharge of 1.9 m^3s^{-1} was derived from municipal and industrial wastewater treatment plants upstream of our study area. This amounts to a mean fraction of 7% treated wastewater in the river Weisse Elster during the sampling period. The daily precipitation was provided by the Saxon State Ministry of the Environment and Agriculture from a weather station in the northeastern part of the study area. The cumulative precipitation during the sampling period was 761 mm.

The study area is underlain by Quaternary sands and gravels covering Proterozoic and Carboniferous bedrock and Tertiary sands. The Quaternary sediments form a shallow aquifer, which is covered by loamy sediments within the floodplain. Based on water table data, a catchment area was defined. Groundwater flows from south to the northern floodplain and discharges into the river Neue Luppe. The urbanized areas are drained by a combined sewage system, receiving both wastewater and storm water runoff. The total length is 64 km which results in a sewer density of 8.3 km km^{-2}. The catchment of wastewater is congruent to the catchment of groundwater. All wastewater is transported into the municipal WWTP in the eastern part of the study area (Fig. 9). The WWTP has a capacity of 463 000 population equivalents. A mean discharge of 1.27 m^3s^{-1} wastewater (ranging from 0.72 m^3s^{-1} to 3.27 m^3s^{-1}; data provided by the operator Kommunale Wasserwerke GmbH) was treated during the sampling period. WWTP effluents discharge into the river Neue Luppe and do not influence the watercourses within the study area.

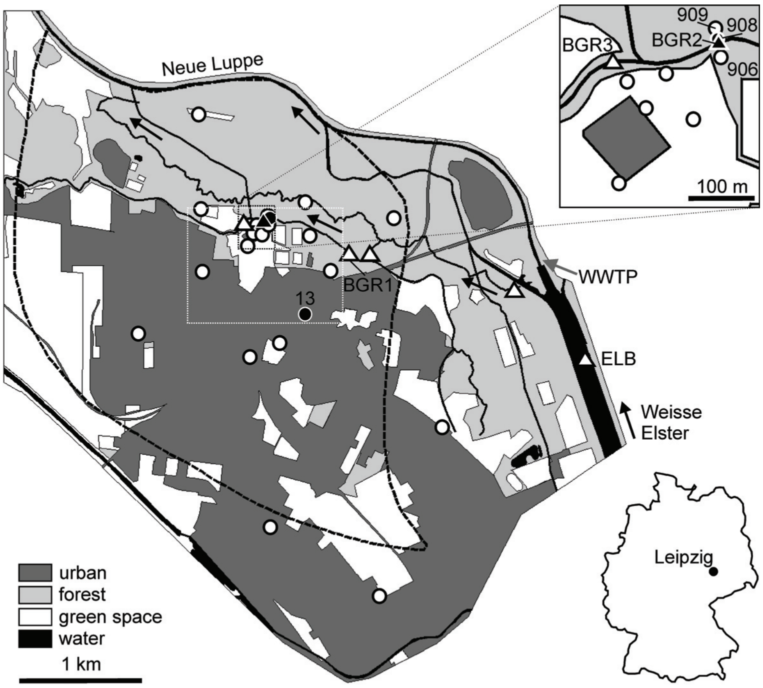


Fig. 9: Map of the study area and location within Germany. Dashed black line marks the groundwater catchment area. Dashed white rectangle marks the position of Fig. 5. △ – surface water sampling location, ○ – observation well, WWTP – wastewater treatment plant effluent, ELB – channel Elsterbecken. Filled symbols mark location with a sampling interval of one month.

3.2.2 Sampling

The monitoring program was conducted from April 2007 to April 2008 including the WWTP, 6 surface water sampling locations, and 22 groundwater observation wells (Fig. 9).

Laboratory efforts to analyze micropollutants are high. To meet laboratory and personnel requirements and observe micropollutant occurrence over the course of a year, we chose a fixed-period sampling covering the different seasons as well as different flow conditions in the surface water. Five main sampling campaigns were conducted in spring 2007 (April 3-11), summer 2007 (July 9-12), autumn 2007 (October 8-11), in winter 2008 (January 14-16), and in spring 2008 (April 7-9). This dataset was complemented with sampling every month at selected critical points (WWTP influent and effluent; observation wells 13 and 908; surface water sampling location BGR2).

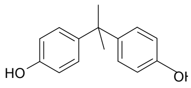
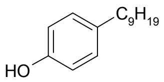
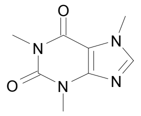
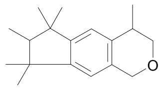
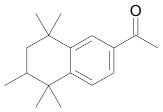
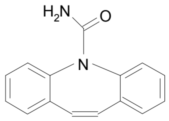
To characterize the influence of CSO on micropollutant occurrence in the surface water, three sampling locations (BGR1, BGR2, BGR3) were placed downstream of an outfall pipe, where CSO is known to occur. CSO events were registered by logging the surface water level automatically. Three observation wells (906, 908, and 909) and one surface water sampling location (BGR2) were used for the determination of interaction between surface water and groundwater. Surface water and groundwater levels were logged hourly to observe the variations of the hydraulic gradients between groundwater and surface water. Observation well 13, located at a distance of 12 m to a damaged sewer, was sampled to resolve the temporal variations of micropollutant concentrations in the groundwater due to wastewater losses from the sewage system (see Fig. 9).

Samples from the WWTP were taken as grab samples from the inflow after primary sedimentation and from the effluent. Surface water samples were taken as grab samples from the center of the watercourses. Sampling was conducted in agreement with the water flow direction from the ELB to the small streams (Fig. 9). Groundwater was sampled using submerged pumps following the German DVWK protocol. All samples where analyzed in the field for dissolved oxygen, electrical conductivity, pH, Eh, water temperature, and carbonate alkalinity. Samples for the analysis of micropollutants were collected in 1 L glass bottles and stored in dark and cool places until analysis.

3.2.3 Analysis

The micropollutants selected for analysis are characterized in Tab. 4. All samples from the WWTP, samples from five surface water sampling locations, and samples from nine groundwater observation wells were analyzed for micropollutant concentrations. For the entire monitoring program this amounts to a total number of 13 samples from the WWTP inflow, 13 samples from the WWTP effluent, 33 samples from the surface waters and 60 samples from the groundwater. Details on the micropollutant analysis are given in Braun et al. (2003) and in Einsle et al. (2006). Briefly, the target compounds were enriched by solid phase extraction at neutral conditions. Gas chromatography-mass spectrometry analyses were carried out without derivatization in accordance to Suarez et al. (2005) and Hao et al. (2007). Particularly, the thermal lability of CBZ requires a careful analysis and data processing. Different possibilities for quantification recommend the use of isotope labeled CBZ which was not available within these investigations. Alternatively, the thermal degradation product of CBZ, iminostilbene, is quantified and added to the CBZ. This process is preferred when analyzing conditions (injection temperature and/or matrix) vary. The GC-MS analyses of this monitoring program were performed at stable, optimized conditions. An external standard mixture was measured every 5 analyses to check the instrumental performance. CBZ, HHCB, AHTN, and CAF were quantified to the external standards, NP and BPA to the internal standards 4-n-NP and d_{16} BPA, respectively. Limits of quantification and recovery rates are reported in Tab. 4. Concentration, based on problematical quantification due to peak overlapping in the chromatogram or low recovereis of standards, were not considered. Concentrations below the limit of quantification were set to 0 ng L^{-1}.

Tab. 4: List of analyzed micropollutants. LOD SFW – limit of detection in surface water; LOD GW – limit of detection in groundwater; recovery rate refers to 100 ng L^{-1} of the target substance in surface water and groundwater, mean relative standard deviation (n=4): 12%; recoveries in wastewater are 10-20% lower; pK$_{ow}$ – logarithm of partitioning coefficient octanol/water (from SRC PhysProp Database, Syracuse Research Corporation).

Micropollutant	Application	Structure	CAS-Nr.	pK$_{ow}$	LOD SFW [ng L^{-1}]	LOD GW [ng L^{-1}]	Recovery rate [%]
Bisphenol A (BPA)	Educt of polycarbonate production; endocrine disrupter		80-05-7	3.32	10	1	75%
Technical 4-nonylphenol (NP)	Degradation product of industrial surfactants; endocrine disruptor		104-40-5 (4-nNP)	5.76 (4-nNP)	10	1	82%
Caffeine (CAF)	Psychomotor stimulant		58-08-2	-0.07	5	1	98%
Galaxolide® (HHCB)	Polycyclic musk fragrance; chemosensitizer		1222-05-5	5.9	1	0.2	100%
Tonalide® (AHTN)	Polycyclic musk fragrance; chemosensitizer		1506-02-1	5.7	1	0.2	100%
Carbamazepine (CBZ)	Psychoactive drug		298-46-4	2.45	5	2	73%

3.2.4 Data analysis

For statistical analyses, the software package SPSS (SPSS Inc.) was used to describe the micropollutant concentrations and influencing factors. Descriptive statistics provided concentration mean, median, standard deviation, outliers, and extremes as well as normality of distribution in the different water compartments. For the applied multivariate methods, concentrations were log-normalized to ensure normality and thus, linear relationships. Correlation analysis was used to reveal degree and direction of linear relationships of two variables. Cross-correlation was used to estimate time lags in the transport of micropollutants within the groundwater.

3.3 Results and discussion

3.3.1 Overview

The chosen micropollutants, BPA, NP, CAF, HHCB, AHTN, and CBZ, were detected in all the samples. They showed a ubiquitous presence in all the urban water compartments (Fig. 10).

3.3.2 Micropollutants in the wastewater

Monthly samples from the WWTP influent and effluent gave insight to the overall micropollutant concentration variability in untreated and treated wastewater. Correlation analysis was applied to the micropollutant concentrations in the WWTP effluent to elucidate typical signatures of micropollutant concentrations from this source. Correlation was only significant for HHCB and AHTN (correlation coefficient 0.917; 0.01 level) and thus, a concentration pattern of micropollutants was limited to the polycyclic musk fragrances.

The mean wastewater discharge during the days of sampling was used to estimate daily loads (Tab. 5). Only daily loads of NP in the WWTP effluent were characterized by a pronounced seasonality and correlated significantly negative with the wastewater temperature (-0.757; 0.01 level). Load seasonality of NP was also present in the influent with a weaker, not significant negative dependency from the water temperature (-0.435). WWTP removal of NP is a complex issue, as both the formation of NP from nonylphenol polyethoxylate degradation and the removal by sorption to sludge solids and biotransformation is known (Ahel et al., 1994a; Jin et al., 2008; Soares et al., 2008). However, from our data we hypothesize aside from sorption an enhanced removal within the sewage system and the WWTP due to biodegradation of NP during the summer months. All other micropollutants followed no seasonal pattern in the effluent and were characterized by highly variable daily loads (see standard deviations in Tab. 5). This variability can probably be led back to the temporal variable input of micropollutants into the sewage system by different domestic and industrial sources which can vary significantly over the day (e.g. Ahel et al., 1994a).

The applied sampling strategy probably did not cover the whole range of concentrations, as a sample with higher concentrations of BPA and CBZ was taken from CSO water (see section

3.3). Future research will concentrate on the analysis of robust time-integrating passive sampling devices, used simultaneously with the snapshot samples (adapted devices based on Bopp et al., 2005).

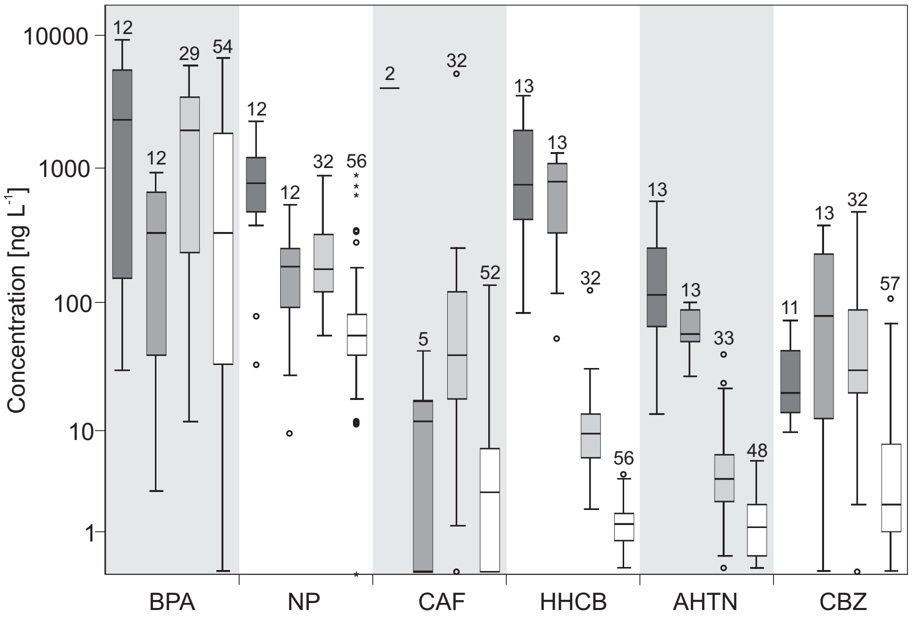


Fig. 10: Box plots of micropollutant concentrations in the untreated wastewater (■), treated wastewater (■), surface water (▨) and groundwater (□). Number of samples are given above the plots. Box plots show 25th and 75th percentile (box) and median (line within box). Outlier (○) are values that lie more than 1.5 times, extremes (*) more than 3 times lower or higher than the interquartile range (25th - 75th percentile) from the box. Whiskers connect smallest and largest values that are not outliers. For abbreviation see Tab. 4.

Tab. 5: Median micropollutant daily loads in the wastewater treatment plant (WWTP) and in the surface water (without event water). σ – standard deviation, n – number of samples.

Compartment		Bisphenol A (BPA)	Technical 4-nonylphenol (NP)	Caffeine (CAF)	Galaxolide® (HHCB)	Tonalide® (AHTN)	Carbamazepine (CBZ)
WWTP influent	median	208.4	73.5	391.6	72.5	9.5	1.5
[g d^{-1}]	σ	531.5	56.1	264.2	101.8	14.4	5.9
	n	12	12	2	13	13	11
WWTP effluent	median	40.5	17.7	1.5	65.5	5.1	7.2
[g d^{-1}]	σ	30.0	12.9	3.3	40.9	2.2	11.3
	n	12	12	5	13	13	13
Surface water	median	5319.3	387.0	143.1	21.6	9.7	109.9
[g d^{-1}]	σ	5624.8	180.6	159.0	13.5	7.9	198.0
	n	22	24	25	25	23	24

3.3.3 Micropollutants in the surface water

Micropollutants were monitored at five surface water sampling locations. The sampling was able to represent the overall flow variability of the Weisse Elster river system. Mean daily discharges on the days of sampling were compared to the discharges over the course of the entire monitoring period. The probability distribution of both data sets fits well. Only 5% of overall daily discharges were above and 3% were below the range, covered by the sampling dates.

One of the surface water samples was taken during a CSO event (April 2008, BGR3) and is interpreted separately from non-event water.

Non-event water

During each sampling (duration of 5-6 hours) all surface water samples were characterized by the same major ion composition (data not shown here) and comparable micropollutant concentrations. For each sampling, all sampling locations are thus assumed to be characterized by the same type of water. A spatial pattern of micropollutants between the sampling locations was not observed. Concentration variations between the sampling campaigns were related to the concentration variations in the ELB/river Weisse Elster.

For the correlation analysis and daily load estimation, the following samples were not taken into account: (1) samples taken a few hours after an CSO event (July 2007: BGR1, BGR2, BAG2); (2) samples from location BGR3, since the water course was blocked by wood and debris most of the year; (3) sample from location BGR2 in Mai 2007, since untreated wastewater was flowing into the surface water due to an operation fault in the sewage system.

Correlation analysis revealed a typical pattern of micropollutant concentrations in the surface water. Significant correlations were found for HHCB and AHTN (0.860; 0.01 level), CAF and CBZ (0.713; 0.01 level), AHTN and CBZ (0.669; 0.01 level), HHCB and CBZ (0.652; 0.01 level), and CAF and AHTN (0.534; 0.01 level). BPA was less significantly correlated with CBZ (0.537; 0.01 level) and HHCB (0.504; 0.01 level). NP showed no correlations with other micropollutants.

To minimize the influence of dilution, micropollutant daily loads were estimated on the basis of concentrations and the corresponding mean water discharge of the ELB at the day of sampling (Tab. 5). Daily loads of CAF, HHCB, and AHTN were characterized by a pronounced seasonality (Fig. 11). While daily loads in summer were low, loads in winter were high with a higher variability. Correlation analysis revealed a significant negative linear relationship for the daily loads of HHCB, AHTN, and CAF with the mean water temperature at the day of sampling (Fig. 12). An increase of water temperature from 10°C to 15°C resulted in a decrease of daily loads for CAF by 61.0 g d^{-1} (45.7%), for HHCB by 10.6 g d^{-1} (35.7%), and for AHTN by 5.7 g d^{-1} (39.3%). Two outliers for CAF in November 2007 and April 2008 could be led back to rain events before the sampling. It is likely that these events caused CSO into the surface water leading to high loads of CAF as previously described in Buerge et al. (2006). In times of high water temperature, the decrease of daily loads of CAF may be assigned to several processes. Buerge et al. (2003b) described photolysis and, to a minor extent, biotransformation as eliminating processes for CAF in Swiss lakes. Furthermore, Bradley et al. (2007) found biotransformation of CAF to be significant in oxic sediments. Correlation of daily loads of CAF with mean global radiance estimated for a 4-days period before sampling gave less significant relations (-0.801; 0.01 level). Since global radiance correlates with water temperature, the influence of both variables cannot be distinguished.

For HHCB and AHTN, two outliers in January 2008 and March 2008 (exceptional low loads) were determined with unknown reason. Significantly lower concentrations of polycyclic musk fragrances during the summer months compared to the winter months were also reported by Quednow and Püttmann (2008b) for small rivers in Hessen (Germany). Buerge et al. (2003a) determined direct photolysis as a main elimination process for AHTN but not HHCB in Swiss lakes in summer. Water-air exchange and sorption were found to be the main elimination processes for HHCB during the whole year and for AHTN in winter while biotransformation was neglected (Buerge et al., 2003a; Peck and Hornbuckle, 2006). Equally, Bester (2005) found no indications of biotransformation of polycyclic musks in the river Ruhr (Germany). In contrast, Martin et al. (2007) demonstrated efficient biotransformations for HHCB and AHTN by aquatic fungi. As discussed for CAF, abiotic and biotic processes such as sorption, photolysis, water-air exchange, and biotransformation can lead to a seasonality of HHCB and AHTN occurrence. The exact reason for the significant relationship between water temperature and daily loads of the CAF, HHCB and AHTN cannot be elucidated here.

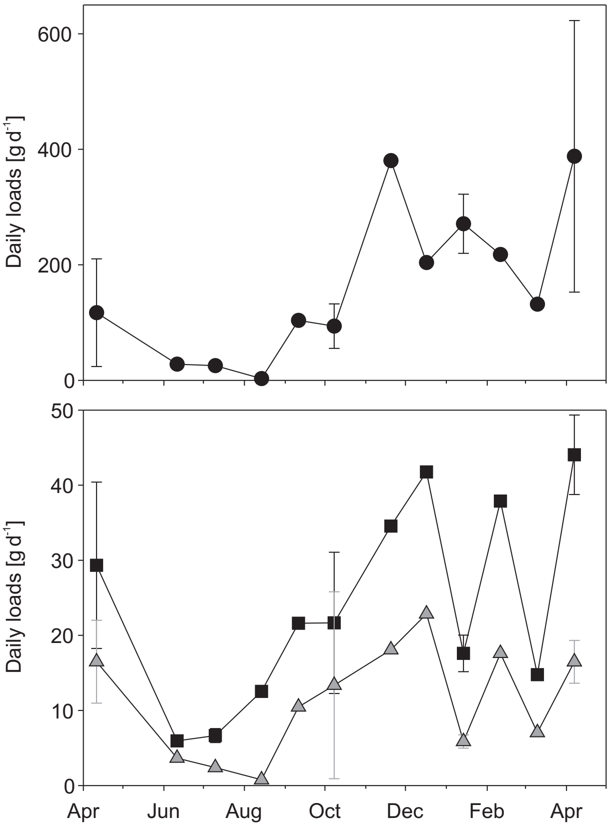


Fig. 11: Mean daily loads of caffeine (●), galaxolide® (■) and tonalide® (▲) in the surface water from April 2007 to April 2008. Error bars indicate standard deviation when more than one sample was available.

The daily loads of NP showed no seasonality. During periods without rain, the observed loads remained constant (median 315.9 g d^{-1}; standard deviation 84.2 g d^{-1}). Daily loads increased significantly when rainfall occurred in a 3-days period before sampling (median 634.7 g d^{-1}; standard deviation 347.3 g d^{-1}). Ahel et al. (1994b) reported a weakly pronounced seasonality for NP in river water in Switzerland. They assigned these variations to a lower input in summer or a more efficient elimination with higher water temperatures. Patrolecco et al. (2006) found higher loads of total NP (in water and in suspended particulate matter) from urban sources in the river Tiber (Italy) during higher flow regimes. From our data, a dependency of daily loads of NP with the flow regime of the river Weisse Elster and hints on seasonal varying removal was not observed.

Daily loads of CBZ and BPA show a high variability but no seasonality or dependencies with water temperature, precipitation prior to sampling or flow regime.

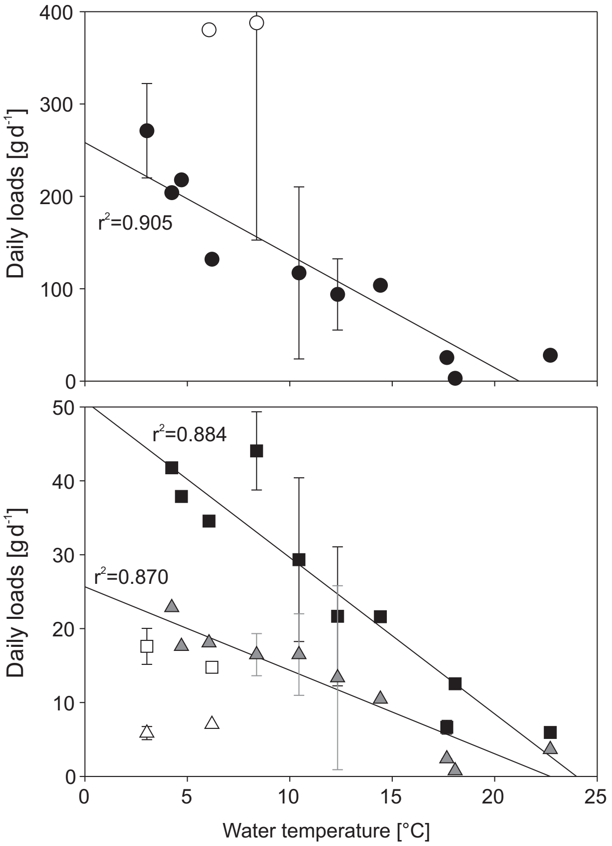


Fig. 12: Mean daily loads of caffeine (●), galaxolide® (■) and tonalide® (▲) in the surface water vs. mean water temperature at the day of sampling. Error bars indicate standard deviation when more than one sample was available. Empty symbols were omitted for regression (see text).

CSO event water

Water from a CSO event was directly sampled in April 2008 at location BGR3. The concentrations of most micropollutants were higher compared to the median of non-event surface water samples but lower compared to the median of untreated wastewater samples. A dilution of wastewater with river water and rain water thus occurred. Dilution was lowest for NP and CAF (factor 2), followed by AHTN (factor 3) and HHCB (factor 6). CBZ and BPA concentration were found to be higher than in the untreated wastewater samples. We assign these differences to the high temporal variability of micropollutants concentrations in the untreated wastewater.

Conclusions drawn from a singular snapshot sample have to be handled with care and due to the first-flush-effect, the timing of the sampling is a crucial point in the characterization of storm runoff (Lee et al., 2007). The studies on the sampling locations BGR1, BGR2 and BGR3 showed that CSO events were only of short duration (mean 4 h). Significantly elevated concentration could not be found in samples taken downstream of an outfall pipe, 12-14 hours after an event. Thus, CSO events represent short peaks in discharge with high loads of micropollutants. On the other hand CSO occurs often. Within the 13 months of monitoring 43 events were recorded at BGR2 that caused more than 0.1 m water level rise. Most events occurred between May and September, when summer rainstorms dominated the precipitation. Referring to the catchment of the Weisse Elster, CSO pulses were longer present and were likely the cause of elevated loads of NP and of CAF in autumn and spring. Buerge et al. (2006) and Jonkers et al. (2009) also showed that CSO can be a significant source of micropollutant loads to surface waters. Micropollutant concentrations are not necessarily increased by CSO, as dilution by rainwater may balance the highly concentrated input (Benotti and Brownawell, 2007).

Sources of micropollutants in the surface water

The correlation analysis of micropollutant in the surface water revealed a concentration pattern of CAF, HHCB, AHTN, and CBZ. Standley et al. (2000) described the combination of musk fragrances with CAF as unique tracer for the impact of WWTP effluents on surface waters. Thus, we assign the musk fragrances and CAF as well as the correlated CBZ to the presence of WWTP effluents in the river Weisse Elster. Nevertheless, the loads of some micropollutants where higher than expected from this source. Since the amount of treated wastewater in the river Weisse Elster is known, the causing mean micropollutant concentrations in WWTP effluents from the Weisse Elster catchment can be estimated. For CAF, these concentrations do not match with the measured concentrations from the WWTP effluent within the study area and literature data. In the winter months when no precipitation occurred prior to sampling (December 2007 to February 2008), a CAF concentration of 1370 ng L^{-1} in the treated wastewater was computed to be necessary to explain the observed loads. The WWTP effluent at the study area was characterized by concentration of CAF up to 43 ng L^{-1}. Ternes et al. (2001) reported CAF concentrations in WWTP effluents in the range of 190±90 ng L^{-1}. Consequently, an additional constant source of untreated wastewater can be the reason for the detected high surface water loads of CAF.

BPA concentrations correlated well with CBZ and HHCB, which points at WWTP effluents as a potential source. Nevertheless, BPA was also present in concentrations that cannot be explained by the sole input of treated municipal wastewater. Alternative highly concentrated constant sources have to be taken into account. After Fürhacker et al. (2000) and Fromme et al. (2002) BPA cannot be led back to municipal wastewater only and industrial wastewater or landfill leachates may be additional sources.

NP can arise from WWTP effluents, urban/suburban runoff, agricultural activities (Standley et al., 2000), and industrial wastewater (Vethaak et al., 2005). Correlation analysis did not show relations of NP concentrations to the other micropollutants and surface water loads were found to be too high to be explained by treated municipal wastewater only. There are potential constant sources of industrial wastewater such as chemical production facilities in the south of the city of Leipzig which contribute wastewater to the river Weisse Elster. Additional, intermittent sources for elevated NP loads found after rainfall periods such as CSO and runoff from urban/suburban and agricultural areas are present in the Weisse Elster catchment.

3.3.4 Micropollutants in the groundwater

Correlation analysis revealed significant dependencies only between the concentrations of CAF and AHTN (0.587; 0.01 level) and of HHCB and AHTN (0.330; 0.05 level). No correlation was found for micropollutant concentrations and physicochemical parameters such as pH, Eh and groundwater temperature. The spatial and temporal distribution of micropollutant concentrations in groundwater is illustrated in Fig. 13 for HHCB and AHTN. Highest concentrations of the musk fragrances in the groundwater were observed in the direct surrounding of the sewer network. On the other hand, short distances to potential sources did not necessarily result in high concentrations of HHCB and AHTN. The resulting spatial pattern of micropollutant in the groundwater was not consistent throughout the study area and varied significantly in time. Since principle pathways of wastewater to the groundwater are known to be sewer leakages and the infiltration of contaminated surface water (Musolff et al., 2008 [Chapter 2.1]), the focus in this study is set on the temporal variations of micropollutants within the sampling period. Two wells were sampled monthly: observation well 13 to reveal the impact of nearby leaky sewers and well 908 to reveal the impact of bank infiltration on micropollutant concentrations in the groundwater.

In well 13, compared to the median concentration in all groundwater samples, elevated concentrations of CBZ have been observed (27 ng L^{-1}). Variations of NP, CBZ, and CAF seem to follow temporal patterns (Fig. 14). Nevertheless, no dependencies of micropollutant concentrations with times of possible wastewater infiltration to the groundwater (groundwater surface below sewer section) or groundwater temperature were found. Dilution is supposed to be one of the major processes influencing the concentration. The groundwater surface in the study area varied significantly over the year and was characterized by a fast response to rain events. Changing gradients result in changing groundwater flux and thus, changing micropollutant dilution. So far, the available data do not provide a measure for the dilution of micropollutants.

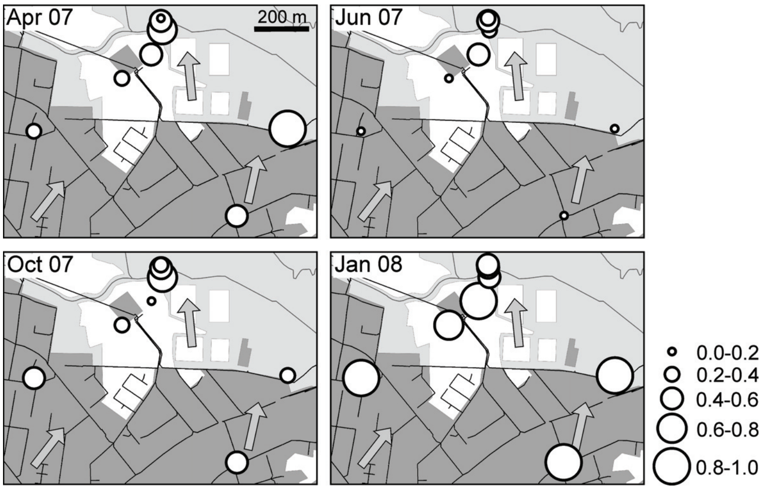


Fig. 13: Spatial distribution of galaxolide® and tonalide® in groundwater in the centre of the study area (log-normalized concentrations were normalized to the highest value, summed and again normalized). Black lines indicate the sewage system. Arrows mark the groundwater flow direction. For land use legend see Fig. 9.

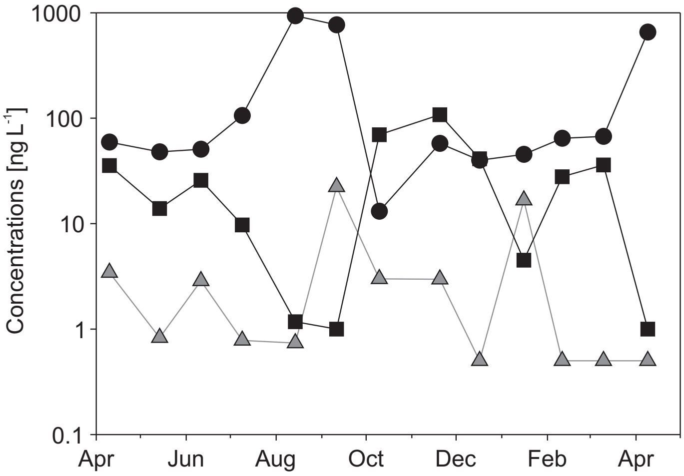


Fig. 14: Concentrations of technical 4-nonylphenol (●), carbamazepine (■) and caffeine (▲) in observation well 13 from April 2007 to April 2008.

Measurements of surface water level in BGR2 and groundwater level in 908 enable the estimation of the gradient between both water compartments. A gradient towards groundwater was observed between April and September 2007. In well 908, temporarily lower electrical conductivity (EC) in the groundwater compared to in well 906 upstream became apparent. This can be assigned to intermittent exfiltration of surface water (mean EC of 898 µS cm^{-1}) to the groundwater (mean EC upstream of 1642 µS cm^{-1}). The occurrence of decreased EC in monitoring well 908 was in coincidence with the occurrence of CAF in the groundwater. A time lag of 112 days for EC (correlation -0.593; std. error 0.316) and 109 days for CAF (correlation 0.392; std. error 0.333; Fig. 15) can be estimated by comparing the gradient of surface water to groundwater with EC and CAF concentrations by the use of cross-correlation. Retardation in the transport of EC and CAF is not assumed (see low pK_{ow} in Tab. 4). This time lag is plausible for a simple 1D Darcy-approach with the measured gradients, a distance of 3.5 m between stream and wells filter screen and an estimated hydraulic conductivity of 1×10^{-6} m s^{-1} (loamy sediments covering the aquifer at well 908). All other micropollutants did not follow this pattern. For AHTN, a correlation with water temperature was found (0.640; 0.05 level). It is not clear whether this correlation is due to enhanced degradation or sorption at higher temperatures or a highly retarded seasonal input.

Future work will focus on the estimation of water flux and differentiation of concentration-influencing processes. Furthermore, results from the application of integral pumping tests, used to quantify micropollutant loads in groundwater from different urban sources will be integrated (method adapted from Bayer-Raich et al., 2004).

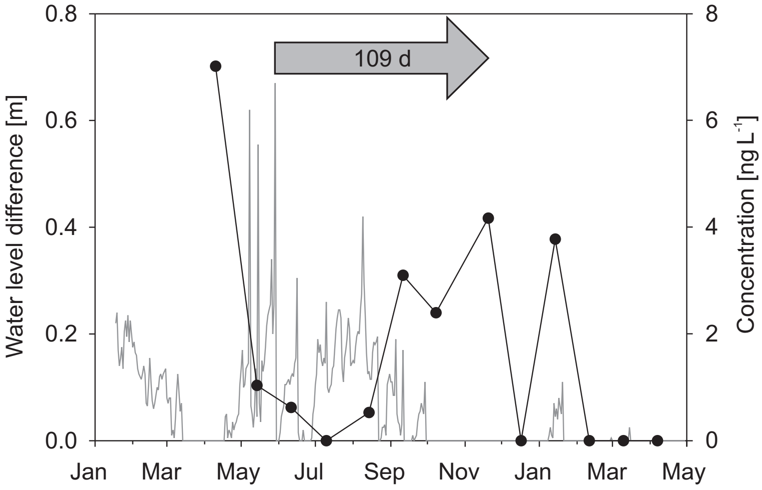


Fig. 15: Differences of surface water level and groundwater level at monitoring well 908 (grey line) and caffeine concentration (●) from January 2007 to April 2008. Arrow describes the time lag of 109 d.

3.4 Conclusions

In this paper, a data-driven holistic view on micropollutants in urban receiving waters is presented. The monitoring program was capable to reveal different micropollutants contribution to urban waters in time and space and allows a deeper insight into micropollutant sources, distribution and removal within a watershed. This knowledge contributes to micropollutant risk assessments, taking long-term and short-term exposure and thus potential chronic as well acute effects in aquatic ecosystems into account.

We conclude that time and place of sampling are crucial points in the assessment of micropollutants in the aquatic environment since concentrations are influenced by source variability, dilution, retardation, removal processes and events such as CSO. Especially in urban areas, monitoring programs with continual sampling over the year are essential to overcome heterogeneity and seasonality of micropollutants in the wastewater, surface water and groundwater. Source variability and seasonality of micropollutants can substantially differ and should be taken into account when assessing the occurrence of these substances:

- Rapid and probably site specific removal of CAF, HHCB, and AHTN in the surface water in times of high water temperature has to be considered when assessing the impact of these substances.
- An assessment of CBZ, which is often used as wastewater indicator in surface water and groundwater, should take the high variability of this drug in the wastewater into account.
- The estrogenic micropollutants NP and BPA are characterized by multiple constant sources as well as intermittent sources that need further investigation to characterize the presence and fate in the surface water and groundwater. Seasonality should to be taken into account when assessing NP from municipal WWTPs. Rain events can significantly increase NP loads in the surface water and should be considered in monitoring programs.

Chapter 4

Micropollutant loads in the urban water cycle

This chapter is submitted to Environmental Science and Technology to be potentially published as:

Musolff A, Leschik S, Reinstorf F, Strauch G, Schirmer M (2009) Micropollutant loads in the urban water cycle.

Abstract The assessment of micropollutants in the urban aquatic environment is a challenging task since both, the water balance and the contaminant concentrations are characterized by a pronounced variability in time and space. In this study the water balance of a central-European urban drainage catchment is quantified for a period of one year. Based on a concentration monitoring of several micropollutants a contaminant mass balance for the study area's wastewater, surface water and groundwater is derived. The release of micropollutants from the catchment was mainly driven by the discharge of the wastewater treatment plant. However, combined sewer overflows (CSO) released significant loads of caffeine, bisphenol A and technical 4-nonylphenol. Since a fraction of 11.5% of the wastewater's dry weather flow was lost as sewer leakages to the groundwater, considerable loads of bisphenol A and technical 4-nonylphenol were also released by the groundwater pathway. The different temporal dynamics of releases loads by CSO as an intermittent source and groundwater as well as treated wastewater as permanent sources may induce acute as well as chronic effects on the receiving aquatic ecosystem. This study points out the importance of the pollution pathways CSO and groundwater for the contamination assessments of urban water resources.

4.1 Introduction

A variety of organic compounds from wastewater sources such as pharmaceuticals, additives of personal care products (collectively PPCP) and industrial chemicals are widely recognized as a potential threat to aquatic ecosystems and to human health. Because most of these contaminants are environmentally present in low concentration ranges of pg L^{-1} to ng L^{-1} often the term micropollutant is used (Schwarzenbach et al., 2006). Major concerns regarding the risk micropollutants pose on aquatic ecosystems and on human health involve endocrine disrupting effects (Jobling et al., 1998), possible interactions of contaminant mixtures (Pomati et al., 2008), chemosensitizing effects (Luckenbach and Epel, 2005) and chronic effects by a long-term exposure (Fent et al., 2006b).

Since large amounts of wastewater are produced, transported and treated in urban agglomerations, urban water resources are known hotspots of micropollutant contaminations (Schirmer et al., 2007; Reinstorf et al., 2008). Until now, most studies deal with the occurrence of micropollutants in the effluents of wastewater treatment plants (WWTP) and in the receiving waters. This source is considered most important because often micropollutants are only partially removed during the treatment process and thus continually released into the aquatic environment (Ahel et al., 1994a; Ahel et al., 1994b; Ahel et al., 1996; Halling-Sørensen et al., 1998; Heberer et al., 1998; Ternes, 1998; Daughton and Ternes, 1999; Heberer, 2002b; Glassmeyer et al., 2005; Barber et al., 2006). Fewer studies deal with the input of micropollutants by combined sewer overflow (CSO). In areas served by combined sewage systems, storm water runoff can exceed the capacity of the sewer network and untreated wastewater can be released into surface waters. CSO is recently recognized as an important additional source for micropollutants in surface waters (Buerge et al., 2006; Benotti and Brownawell, 2007; Welker, 2007; Jonkers et al., 2009; Phillips and Chalmers, 2009). Only few studies deal with micropollutants in groundwater resources. Here, sewer leakages and the influence of contaminated surface water may deteriorate groundwater quality on a long term (Fenz et al., 2005; Greskowiak et al., 2006; Massmann et al., 2008; Musolff et al., 2008 [Chapter 2.1]; Reinstorf et al., 2008; Leschik et al., 2009).

To the best of our knowledge, so far no study shows the relevance of different wastewater pathways for the micropollutant contamination of groundwater and surface water in urban areas. Here, a comprehensive knowledge of the urban water flow as well as on the micropollutant occurrence in the different water compartments is required. Surface sealing, exfiltration of groundwater to and losses from the sewage system strongly affect the water and contaminant balance (Lerner, 2002). The resulting spatiotemporally variable distribution of water flow as well as the diffuse, line and point character of contaminant sources lead to a complex pattern of micropollutant concentrations in urban waters (Musolff, 2009 [Chapter 1.3]; Musolff et al., 2009 [Chapter 3]).

We hypothesize that for complex urban areas a holistic approach including wastewater, groundwater and surface water flow, and contamination is capable to describe micropollutant loads in all the water compartments and, thus, helps to improve the knowledge of the relevance of the different environmental pathways.

In the chosen study area the catchment of groundwater and the drainage catchment of wastewater, the sewershed, are in a matching position. Therefore, an integrative water and contaminant mass balance, including the sewage system as a source of micropollutants and groundwater and surface water as recipients is possible (Schirmer et al., 2007). So far, research was focused on a monitoring of micropollutant concentrations in the different water compartments over the course of a year and the evaluation on the basis of statistical methods (Musolff et al., 2008 [Chapter 2.1]; Musolff et al., 2009 [Chapter 3]).

This study focuses on the micropollutant loads in the urban water compartments for a sewershed within the city of Leipzig, Germany. We use the results of the monitoring program concerning micropollutant concentration probability in the treated and the untreated wastewater and in the groundwater. Numerical models of groundwater recharge and groundwater flow as well as the measured wastewater flow from the sewershed are combined with the micropollutant concentrations to estimate annual loads. Thus, we are able to (a) characterize the water flow in and between the different urban water compartments, (b) describe the micropollutant load balance, (c) specify the temporal distribution of micropollutant release to the environment and (d) discuss the relevance of different micropollutant release pathways and the potential impact on the aquatic ecosystem.

4.2 Material and methods

4.2.1 Study area

The study area is located in the north-western part of the central-European city of Leipzig (Fig. 16). We focus on a subcatchment of the sewage system – the sewershed – with a size of 5.37 km^2. Here, 24.6% of the area is fully sealed by roads and buildings, 31.8% is partly sealed. The sewershed is drained by a combined sewage system with a total length of 54.7 km. A fraction of 29% of the sewers is located beneath the average groundwater table.

Wastewater is flowing to a station that pumps all wastewater to the municipal WWTP northeast of the study area, serving most parts of the city of Leipzig. Treated wastewater from the WWTP discharges into the river system of the Weisse Elster.

A small stream, the Bauerngraben, located on the eastern and northern edge of the sewershed, receives no surface runoff except CSO water at 6 locations along the course. To ensure constant water flow within the stream Bauerngraben, river water from the Weisse Elster is bypassing through this stream. The study area is underlain by three connected Quaternary fluvial sand and gravel aquifers and one discontinuously distributed Tertiary sandy aquifer. Two discontinuously distributed boulder clay layers between the Quaternary aquifers and one distinctive floodplain loam layer in the northern part of the area act as aquitards. Groundwater flows mainly from the south to the north forming a watershed in good agreement with the sewershed. Within the sewershed, groundwater is unconfined and oxic.

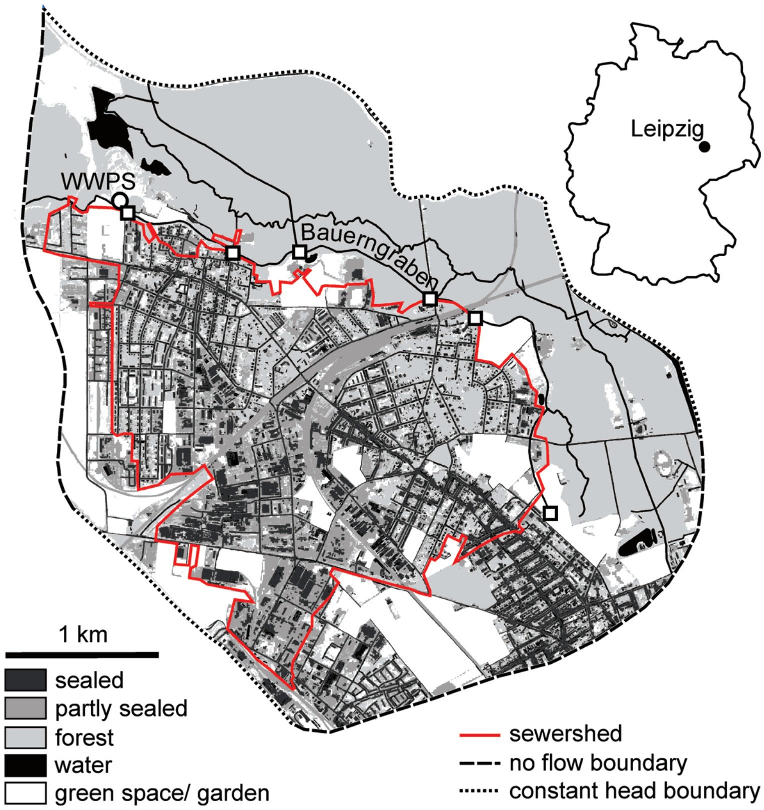


Fig. 16: Study area with boundaries of the groundwater flow model, location of the sewershed, land use and surface sealing. Upper right map shows location within Germany. WWPS – wastewater pumping station, □ – outlet of combined sewer overflow facilities.

4.2.2 Sample collection and additional field work

The monitoring of water quality and quantity was conducted from April 2007 to April 2008 and is comprehensively described in Musolff et al., (2008) (Chapter 2.1) and Musolff et al., (2009) (Chapter 3). Briefly, within the sewershed seven groundwater observation wells were sampled every three months concerning micropollutant concentrations. Furthermore, two wells, the inflow after primary sedimentation and the outflow of the municipal WWTP were sampled every month. Additional fieldwork included automatic measurements of groundwater table at eight observation wells.

4.2.3 Sample analysis and quality assessment

A total number of 13 samples from the WWTP influent, 13 samples from the effluent and 56 samples from the groundwater were considered in this study. Six micropollutants were chosen for analysis:

- Bisphenol A (BPA), a precursor of polycarbonate production with estrogenic activity (Jin et al., 2008)
- Technical 4-nonylphenol (NP), an isomer mixture from the degradation of nonylphenol polyethoxylates (used as surfactants) with estrogenic activity; restricted use in the European Union since 2005 (Höhne and Püttmann, 2008)
- Caffeine (CAF), a stimulant from beverages as well as from pharmaceuticals; established marker substance for wastewater (Buerge et al., 2003b)
- Galaxolide® (HHCB) and tonalide® (AHTN), polycyclic musk fragrances with a potential of bioaccumulation and chemosensitizing effects (Luckenbach and Epel, 2005)
- Carbamazepine (CBZ), antiepileptic drug with high persistence in the water cycle (Fenz et al., 2005)

The chemical analysis was done using solid phase extraction at neutral conditions and gas chromatography-mass spectrometry (see Braun et al., 2003; Einsle et al., 2006). Analysis was performed without derivatization and used external standards for the quantification of CAF, HHCB, AHTN and CBZ (every 5 analysis) and internal standards for NP (4-n-nonylphenol) and BPA (d_{16} bisphenol A). Recoveries in surface water and groundwater ranged from 73% (CBZ) to 100% (HHCB and AHTN). Limits of detection in groundwater were 0.2 ng L^{-1} for HHCB and AHTN; 1 ng L^{-1} for BPA, NP and CAF and 2 ng L^{-1} for CBZ.

For the load estimation, concentrations below the limit of detection where set to 0 ng L^{-1}. Micropollutant concentrations from samples with a problematical chemical analysis (e.g., low standard recovery; peak overlapping in the chromatogram) were not considered.

4.2.4 Water flow quantification

The quantification of the sewershed's water balance is based on a combination of different model and estimation approaches for the different water compartments. In the following section, water flow quantification, data basis and assumptions made will be explained briefly. An overview of the considered water flow types between the urban water compartments is given in Fig. 17.

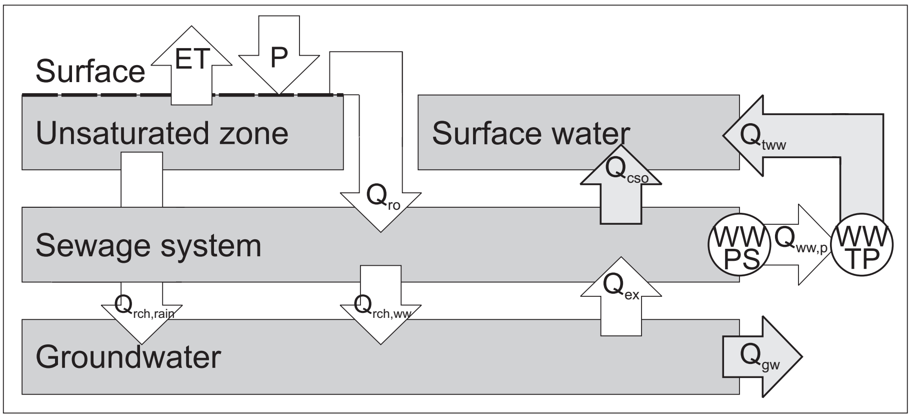


Fig. 17: Scheme of water flow between the urban water compartments. Grey arrows indicate the pathways relevant for the environmental release of micropollutants from the sewershed. WWPS – wastewater pumping station; WWTP – wastewater treatment plant; ET – evapotranspiration; P – precipitation; Q_{ro} – surface runoff to the sewage system (storm water); $Q_{rch,rain}$ – groundwater recharge from infiltrated rainwater; $Q_{rch,ww}$ – groundwater recharge from sewer leakages; Q_{cso} – combined sewer overflow to the surface water; Q_{ex} – groundwater exfiltration flow to the sewage system; Q_{gw} – groundwater discharge through the sewershed boundary; $Q_{ww,p}$ – combined wastewater pumped to the WWTP; Q_{tww} – treated wastewater from the WWTP.

Precipitation and potential evapotranspiration

The data on climate is based on a weather station of the Saxon State Ministry of the Environment and Agriculture in the north-eastern part of the study area. Air temperature, wind speed, total humidity and irradiance were obtained on a daily basis, precipitation (P) on an hourly basis. Date on daily air pressure was provided by a climate station (DWD - Deutscher Wetterdienst) 9 km north-west of the study area. We used the Penman-Montheith approach (Allen et al., 1998) to estimate potential evapotranspiration (ET) for different land use types (forest, garden, green space, urbanized areas and crops) as the basis for the numerical model of groundwater recharge. The leaf area index and plant height was taken from Breuer et al. (2003); phenology data were provided from the DWD.

Wastewater flow

Daily cumulative values of combined wastewater pumped from the sewershed ($Q_{ww,p}$) were provided by the operator of the sewage system and the WWTP (Kommunale Wasserwerke Leipzig GmbH). To estimate the storm water runoff to the sewage system, we analyzed the data corresponding to a base flow analysis in surface water. To this end, peaks of water quantity on days of precipitation were separated manually. For the precipitation days where no CSO events were registered, we applied a regression analysis of storm water runoff and rainfall. The derived linear relation was applied to the annual precipitation to estimate the total storm water runoff to the sewage system (Q_{ro}). It is hereby assumed that the surface runoff for larger rainfalls that leads to CSO follows the same linear relation.

Strict wastewater without surface runoff ($Q_{ww,ex}$) was found to be variable over the year and in positive correlation with the elevation of the groundwater table (correlation coefficient 0.84; 0.01 level). Since a constant daily wastewater input was assumed throughout the year, variability was led back to groundwater discharge to the sewer sections beneath the groundwater surface (Q_{ex}). Therefore, we used Kriging-interpolated groundwater surfaces from each of the five major sampling campaigns and GIS data of the sewage system to query the length of sewer sections underneath the groundwater table. Lengths of affected sections for each time slice were related to the amount of wastewater base flow ($Q_{ww,ex}$) at the same time by a regression analysis. From the exponential relation, the amount of strict wastewater flow (Q_{ww}) as well as the exfiltration flow from the groundwater to the sewage system (Q_{ex}) was derived.

Combined sewer overflow

Combined sewer overflow volume was estimated from the storm water runoff to the sewage system (Q_{ro}, from regression analysis) and the runoff to the sewage system from the base flow analysis of the actually pumped wastewater. The difference of both is the surface runoff, exceeding the capacity of the sewage system and the wastewater pumps and therefore was discharged into the surface water as CSO. To compute total CSO volume, incorporated wastewater had to be estimated. We assumed a complete mixture of surface runoff water with volume of wastewater produced during the CSO event plus the storage volume of wastewater in the sewage system. Timing and duration of CSO events were obtained from the water level measurements in the stream Bauerngraben. Wastewater volume produced during the CSO event was estimated by scaling Q_{ww} to the duration of the event. Storage volume was estimated on the basis of the diameter and length of all the sewers and an approximated wastewater level of 8 cm (minimum), 10 cm (mean) and 12 cm (maximum) (randomly tested in the study area’s sewer sections). Thus, we obtained a minimum, mean and maximum ratio of surface runoff water and wastewater for each CSO event. This ratio was applied to the estimated surface runoff volume discharging into the surface water to compute the volume of CSO (Q_{cso}) and the volume of wastewater in CSO ($Q_{ww,cso}$).

Groundwater

Hydrogeological model basis

A hydrogeological structural model was created by the use of GIS, geostatistical analysis and Kriging interpolations with the software Surfer (Golden Software). Geological information was derived from the borehole database of the Saxon State Ministry of Environment and Agriculture and included over 1300 boreholes. Additionally, 30 own boreholes in the uppermost quaternary aquifer were drilled with the help of Geoprobe® direct-push techniques. Hydraulic conductivity for the hydrogeological model was based on grain size analyses from the 30 boreholes and on the sediment description from the borehole database. To enhance the knowledge of anthropogenic soil types and structures at the surface, several shallow boreholes (0.5 m to 2 m) were made within the sewershed. Sediment characterization was based on the German KA5-chart (AG Boden, 2005), providing van-Genuchten-parameters for the application in the numerical groundwater recharge model. Near saturated hydraulic conductivity of the soil surface was estimated with a double ring infiltrometer at 14 locations.

Groundwater recharge

Groundwater recharge quantity on a daily basis ($Q_{rch,rain}$) was numerically modeled with Hydrus-1D (PC-Progress, Šimůnek et al., 2008). Based on a statistical evaluation of distribution and thickness of geological layers, 12 representative soil profiles were chosen. As boundary conditions, we applied an upper atmospheric boundary (daily Penman-Montheith evapotranspiration; daily precipitation) and a lower constant head boundary (four classes of mean annual groundwater table). The hydraulic parameters of the unsaturated zone were parameterized according to the van Genuchten-Mualem model (van Genuchten, 1980). The air-entry was set to -2 cm pressure head. Parameterization was based on the KA5 (AG Boden, 2005). For the uppermost 15 cm of each profile, near saturated hydraulic conductivity from the double ring infiltrometer measurements was used. Root water uptake was modeled according to Feddes et al. (1978). As initial conditions we assumed pressure heads in equilibrium with the groundwater surface. The model was run over a period of 2000 days. The resulting bottom water fluxes of the last 1000 days were considered as spatially differentiated and temporally varying boundary condition of the groundwater flow model. By modeling groundwater recharge with 1D soil profiles we assumed no significant influence of lateral water flow in the unsaturated zone.

For the urbanized areas, the calculated groundwater recharge rates did not properly reproduce the observed temporal variability of the groundwater surface in the numerical groundwater model. Fast groundwater recharge was reproduced well but the longer tailing of recharge events predicted by the model was not observed in the field. We suppose that these differences are related to the hydraulic properties of anthropogenic soils within the urbanized area and the above described fast infiltration of storm water runoff. Thus, we applied the water level fluctuation method (Crosbie et al., 2005) for two wells in the urban area. Results for the timeframe of February 2007 to March 2008 were used for an inverse model to estimate the best fit of van-Genuchten-parameters. Derived parameters were applied for urbanized areas over the entire 2000-days-period in the numerical groundwater recharge model.

Groundwater flow through sewershed boundary

The groundwater flow was numerically modeled with FEFLOW (DHI Wasy GmbH). The geometry of the four aquifers and three aquitards was taken from the hydrogeological model described above. The water levels of the river system of the Weisse Elster in the north and east and of two channels in the south were used as constant head boundaries. No-flow boundaries were applied on the basis of the interpolated groundwater surface (see Fig. 16). The daily groundwater recharge ($Q_{rch,rain}$) was applied as inflow on top of the aquifers. In the areas where the sewage system is located beneath the water table, a constant withdrawal of groundwater was implemented to account for groundwater losses (Q_{ex}). An interpolated mean annual groundwater surface was used as initial hydraulic head condition.

The model was run transient with a phreatic (free) surface over a period of 1000 days. Calibration was performed on the basis of the measured groundwater levels by varying the hydraulic conductivity. The daily discharge through the sewershed boundary was computed for the last 366 days in the post processing options.

4.2.5 Load estimation

Annual contaminant loads were estimated by multiplying the measured micropollutant concentration with the estimated annual water flow. To account for the statistical distribution of concentrations, we used the median as well as the 5th, 25th, 75th and 95th percentiles for the groundwater samples and the median, 25th and 75th percentiles for the wastewater samples:

$$M_{i,uww} = Q_{ww,p} C_{i,uww} \quad (1)$$

$$M_{i,tww} = Q_{ww,p} C_{i,tww} \quad (2)$$

$$M_{i,cso} = Q_{ww,cso} C_{i,uww} \quad (3)$$

$$M_{i,gw} = Q_{gw} C_{i,gw} \quad (4)$$

where $M_{i,uww}$ is the load of micropollutant i from the sewershed by untreated wastewater pumped to the WWTP, $C_{i,uww}$ is the micropollutant concentration percentiles in untreated wastewater; $M_{i,tww}$ is the release of micropollutant i by treated wastewater to the surface water, $C_{i,tww}$ is the micropollutant concentration percentiles in untreated wastewater; $M_{i,cso}$ is the released mass flow of micropollutant i by CSO to the surface water, $Q_{ww,cso}$ is the annual minimum, mean and maximum of wastewater discharge by CSO; $M_{i,gw}$ is the released mass flow of micropollutant i by groundwater discharge out of the sewershed boundary, $C_{i,gw}$ is the micropollutant concentration percentiles in groundwater. For other abbreviations see Fig. 17. Concentration measurements are published in Musolff et al. (2009) (Chapter 3). Groundwater samples taken outside the sewershed are not considered here. Therefore, Tab. 6 gives an overview of concentration percentiles of micropollutants used in this study.

Tab. 6: Percentiles of micropollutant concentrations measured in the WWTP influent and effluent and in the sewersheds groundwater. NP – technical 4-nonylphenol; BPA – bisphenol A; CAF – caffeine; HHCB – galaxolide®; AHTN – tonalide®; CBZ – carbamazepine; n – number of samples considered.

Percentile	NP [ng L^{-1}]	BPA [ng L^{-1}]	CAF [ng L^{-1}]	HHCB [ng L^{-1}]	AHTN [ng L^{-1}]	CBZ [ng L^{-1}]
Untreated wastewater	n = 12	n = 12	n = 2	n = 13	n = 13	n = 11
25th	429	157	-	396	62	10
median	779	2342	4487	758	112	19
75th	1373	5488	-	2206	272	46
Treated wastewater	n = 12	n = 12	n = 5	n = 13	n = 13	n = 13
25th	83	34	0	238	49	11
median	184	341	12	791	58	78
75th	256	671	30	1125	90	235
Groundwater	n = 52	n = 53	n = 52	n = 54	n = 48	n = 56
5th	12	7	0	0.0	0.0	0
25th	38	31	0	0.7	0.2	0
median	56	362	3	1.2	0.9	2
75th	80	2158	7	1.7	1.5	15
95th	460	5735	23	2.3	4.1	75

Since it was not feasible to sample wastewater in the pumping station of the sewershed, untreated wastewater samples were taken in the municipal WWTP. Thus, it was assumed that untreated wastewater from the sewershed had the same properties as the taken wastewater samples. The estimation of $M_{i,tww}$ to the surface water does not take seasonality of micropollutant concentrations in the treated wastewater into account. A seasonality of contaminant loads was limited to NP Musolff et al. (2009) (Chapter 3) but did not have influence on the annual load from the WWTP since the wastewater discharge was uniform over the year. For groundwater samples, no spatial trend of concentrations was found Musolff et al. (2009) (Chapter 3) while temporal trends were limited to an infiltration of contaminated water from the stream Bauerngraben to the groundwater outside of the sewershed. Thus, groundwater samples from inside the sewershed were assumed to be representative for all the groundwater flowing through the boundaries of the sewershed.

4.3 Results and discussion

4.3.1 Urban water balance

An overview of the major water flow to and from the sewershed is given in Tab. 7.

Precipitation (P) was the major source for water in the sewershed. Additionally, water was imported to the sewershed by water mains and released as strict wastewater flow into the sewage system (Q_{ww}, corresponds to 31% of the precipitation amount). For the part of the sewage system beneath the groundwater surface, groundwater exfiltrates into the sewer section (Q_{ex}) made up 16% of the combined wastewater pumped out of the sewershed. The amount of wastewater losses to the groundwater ($Q_{rch,ww}$) based on the measured micropollutant concentrations is matter of discussion below.

Although the sewershed is highly sealed, only 11% of the precipitation is discharging as storm water runoff (Q_{ro}) to the sewage system. Thus, a considerable amount of the sealed surface was not contributing to the sewage system or allowed water to infiltrate through cracks and joints into the subsurface. Nevertheless, the highly sealed surface reduced the evapotranspiration. This resulted in a high groundwater recharge rate ($Q_{rch,rain}$, 37% of the precipitation). The measured groundwater surface as well as the modeled groundwater recharge rates indicate a very fast response of the water table to rainfall with maxima in a time period of 18 h to 28 h. Thus, groundwater was dominantly recharged following rainfall events; a slow recharge component was not observed. The modeled annual discharge of groundwater out of the sewershed boundary (Q_{gw}) was lower than the groundwater recharge. Consequently, there was a change of groundwater storage in the aquifers through the monitored year.

In the stream Bauerngraben, CSO from the sewershed (Q_{cso}) corresponds to 16% of the annual undisturbed surface water flow. Overall, 33 events with a mean duration of 4 h were registered. The release of untreated wastewater by CSO corresponds to a median of 2.9%

(min 2.1%; max 3.4%) from the annual untreated wastewater discharge (dry weather flow) to the surface water.

Tab. 7: Major water flow of the sewershed. The estimation of sewer leakages is discussed below.

Flow type	Description	mm a^{-1}	m^3 d^{-1}
P	Precipitation	663	9721
ET	Potential evapotranspiration	364	9574
$Q_{ww,p}$	Pumped combined wastewater	307	4497
$Q_{ww,ex}$	Pumped combined wastewater without storm water	255	3733
Q_{ww}	Strict wastewater flow, without storm water and exfiltration flow from groundwater	207	3029
Q_{ex}	Groundwater exfiltration flow to the sewage system	48	704
Q_{ro}	Storm water runoff to the sewage system	73	1069
Q_{cso}	Combined sewer overflow, max>mean>min	28>26>24	403>383>354
$Q_{ww,cso}$	Wastewater in combined sewer overflow, max>mean>min	9>7>5	129>108>79
Q_{rch}	Groundwater recharge	242	3549
$Q_{rch,ww}$	Sewer leakages	33	483
Q_{gw}	Groundwater discharge through the sewershed boundary	118	1724

4.3.2 Micropollutant balance

The annual cumulative micropollutant loads are based on the cumulative water flow and the probability distribution of measured concentrations. Derived micropollutant loads are given in Fig. 18.

Micropollutants release from the sewershed was evaluated by comparing the loads from treated wastewater (M_{tww}), from CSO (M_{cso}) and by groundwater discharge out of the sewershed boundary (M_{gw}). For the total released micropollutant mass, HHCB, BPA and NP dominated over the other micropollutants. Concerning the relevance of different pathways, significant differences are apparent (Fig. 19). For the release of CBZ, AHTN, HHCB, NP and BPA, treated wastewater was the most important pathway. Nevertheless, M_{cso} is of significance. Median CAF output by CSO made up 89.0% of the total mass released to the environment. Also for BPA (10.5%) and NP (8.3%), CSO contributed significant loads to the environment. For BPA (25.9%) and NP (9.5%), a considerable amount of the total release from the sewershed can be assigned to the loads in groundwater discharge (M_{gw}).

Several authors describe the interplay of dilution by storm water and by the receiving surface water and the removal efficiency in WWTPs to be driving agents of micropollutant enrichment in surface waters following CSO (Benotti and Brownawell, 2007; Fono and

Sedlak, 2005; Welker, 2007. Loads of micropollutants with pronounced removal in the WWTP (here: CAF; BPA; NP; AHTN) were characterized by a higher fraction of CSO input than loads of more persistent contaminants (here: HHCB, CBZ). The importance of CSO-related release of micropollutants to surface waters is described in several studies. In a previous study, elevated loads of CAF and NP were found in the Weisse Elster river after rainfall, pointing at an influence of untreated wastewater inputs from CSO (Musolff et al., 2009 [Chapter 3]). Findings from Buerge et al. (2006) (in summer, 90% of CAF in a Swiss lake came from CSO inputs) and from Phillips and Chalmers (2009) (in spring and summer, 90% of CAF in a North American lake came from CSO inputs) agrees with the results presented here. In accordance to our findings of BPA release by CSO, Jonkers et al. (2009) improved a river mass flow balance for BPA by adding untreated wastewater sources during wet weather.

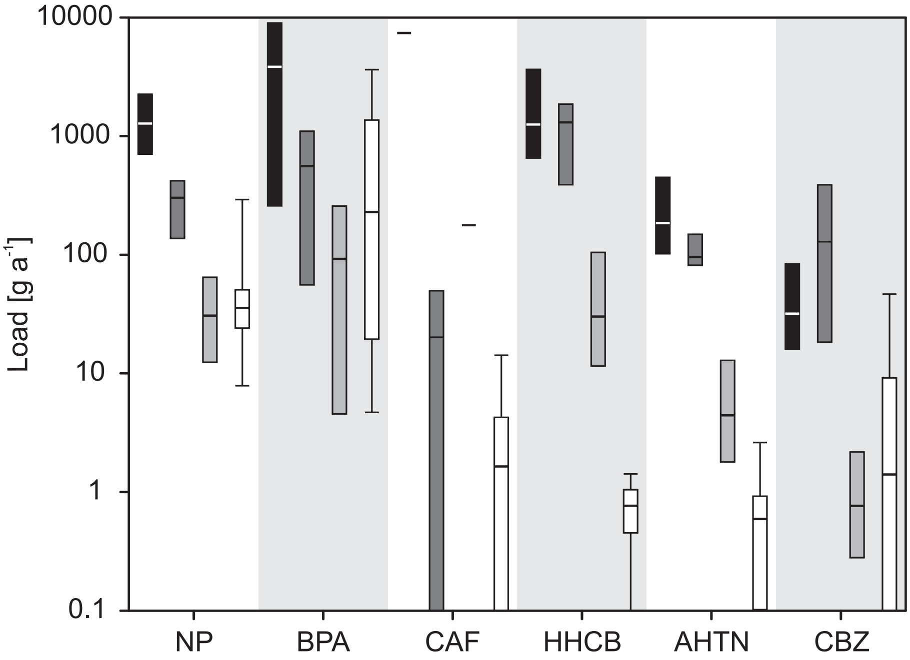


Fig. 18: Micropollutant loads from the sewershed: ■ – by untreated wastewater pumped out of the sewershed; ▓ – by treated sewage discharge into the Weisse Elster river; ░ – by combined sewer overflow (CSO) into the Bauerngraben; □ – by groundwater discharge through the sewershed boundaries. Boxes represent 25th and 75th percentile, line in the boxes represents median, vertical line for groundwater represents 5th and 95th percentile. For CSO-loads, the median from mean CSO estimation, the 25th percentile from minimum of estimation and the 75th percentile from the maximum of estimation was used (see text). For abbreviations see Tab. 6.

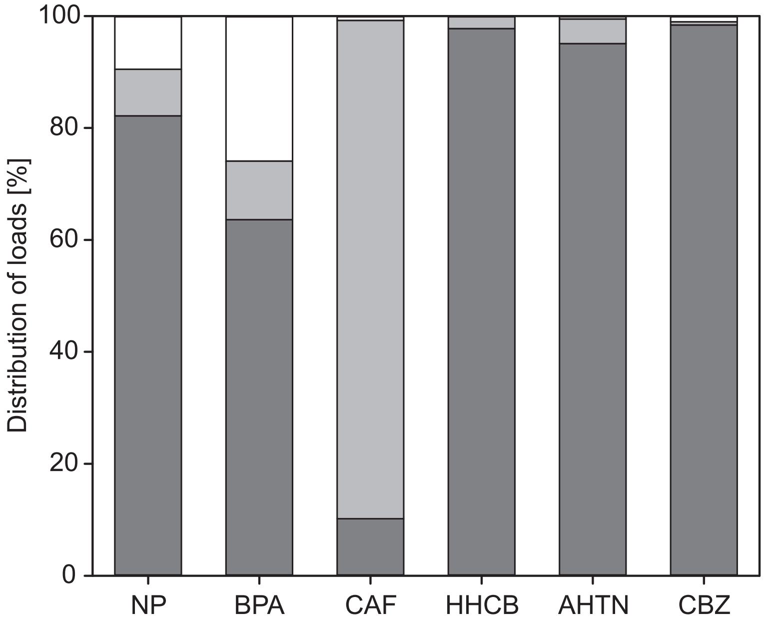


Fig. 19: Distribution of median loads concerning the environmental release of micropollutants from the sewershed ■ – by treated sewage discharge into the Weisse Elster river; ▨ – by combined sewer overflow (CSO) into the Bauerngraben; ☐ – by groundwater discharge through the sewershed boundaries. For abbreviation see Tab. 6.

4.3.3 Sewer leakages

Results of this study point at a considerable fraction of groundwater-related release of micropollutants. In previous studies (Musolff et al., 2007; Musolff et al., 2008 [Chapter 2.1]) sewer leakages were found to be the most likely reason for micropollutant occurrence in the sewershed's groundwater. The knowledge of the total groundwater recharge rate, the micropollutant concentrations in untreated wastewater as the source and in groundwater as the recipient allows for the quantification of sewer leakages. We applied the approach of Lerner (2002) for conservative contaminants with a distinct origin and steady-state conditions.

$$C_{i,gw} = \frac{1}{Q_{rch}}\left(\left(Q_{rch,ww}C_{ww}\right) + \left(Q_{rch,rain}C_{rain}\right)\right) \quad (5)$$

where $C_{i,gw}$ is the average concentration of contaminant i in groundwater; Q_{rch} is the annual amount of total groundwater recharge, $Q_{rch,ww}$ is the amount of recharge from untreated wastewater (sewer leakages), $Q_{rch,rain}$ is the amount of recharge from precipitation, $C_{i,uww}$ is the average concentration in untreated wastewater and $C_{i,rain}$ the average contaminant concentration in the groundwater recharge from precipitation. Since $C_{i,rain}$ is assumed to be zero, the equation simplifies and can be transposed to $Q_{rch,ww}$. We assume the amount of total recharge Q_{rch} to be equal to the modeled recharge $Q_{rch,rain}$ within the urbanized part of the study area. Here, the numerical groundwater recharge model was calibrated to the total recharge on the basis of the water level fluctuation method (Crosbie et al., 2005), which includes the water quantity from sewer leakages. Sewer leakages were quantified for each micropollutant (Tab. 8).

Tab. 8: Estimation of sewer leakages based on median concentrations in untreated wastewater and the receiving groundwater and a total groundwater recharge of 242 mm a^{-1}. Amount per area refers to the sewershed; percentage of dry weather flow (dwf) refers to $Q_{ww,ex}$ of 255 mm a^{-1} plus the mean amount of sewer losses (BPA and CBZ) of 33 mm a^{-1}: amount per sewer refers to the total length of sewer sections. For abbreviations see Tab. 6.

Leakage	Unit	NP	BPA	CAF	HHCB	AHTN	CBZ
Per area	[mm a^{-1}]	17.3	37.4	0.1	0.4	2.0	28.4
From dwf	[% dwf]	6.01	13.03	0.05	0.14	0.70	9.88
Per sewer	[L $s^{-1}km^{-1}$]	0.05	0.12	0.00	0.00	0.01	0.12

Due to the different persistences of the studied micropollutants, the derived leakage rates vary over two orders of magnitude. The most persistent and thus reliable of the micropollutant is CBZ (e.g. Clara et al., 2004). For BPA, biodegradation in oxic groundwater is possible (Ying et al., 2003) but studies in groundwater show comparable detection rates for CBZ and BPA (Focazio et al., 2008). Thus, we assume most reliable leakage rates from these two micropollutants. The mean leakage rate of 33 mm a^{-1} (0.10 L s^{-1} km^{-1} referring to the total length of sewer section; 11.5% from the dry weather flow of wastewater, $Q_{ww,ex}+Q_{rch,ww}$) corresponds to 14% of the total groundwater recharge rate. Results are in the same order of magnitude as found in a study by Leschik et al. (2009) on a sewer section within the sewershed by applying integral pumping tests and direct measurements in a blocked sewer sections (0.3 L $s^{-1}km^{-1}$ to 0.7 L $s^{-1}km^{-1}$). In comprehensive reviews, Rutsch et al. (2006) state leakage rates of 1% to 10% of the wastewater's dry weather flow, while Chisala and Lerner (2008) found rates of 0.01 L $s^{-1}km^{-1}$ to 0.10 L $s^{-1}km^{-1}$ to be most likely. The leakage rates estimated here represent the upper limit of this reviews' findings. For the micropollutants NP, CAF, AHTN and HHCB, we assume a pronounced removal on the leakage pathway or within groundwater, therefore, a less reliable estimation basis for leakage rates.

Since 14% of total groundwater recharge can be assigned to sewer leakages, the temporal dynamics of leakages probably follows the temporal dynamics of rain-induced groundwater recharge. The calibration of the groundwater flow model on the basis of the measured hydraulic heads was only feasible taking distinct groundwater recharge events into account. Therefore, we assume sewer leakages to occur simultaneously with natural groundwater recharge during and shortly after rainfall and to be not evenly distributed over time. This agrees with findings that the temporal dynamics of wastewater composition and of wastewater hydraulic heads may enforce the intermittent character of sewer leakages (Stögbauer et al., 2004).

4.3.4 Temporal dynamics of release to the aquatic environment

For the risk assessment of micropollutant release from urban areas, a comprehensive knowledge of concentrations and load dynamics in receiving waters is crucial. Temporal dynamics of concentrations in the surface water and in the groundwater were discussed in Musolff et al. (2009) (Chapter 3). Micropollutant load dynamics of the release by groundwater, treated wastewater and CSO are shown in Fig. 20.

Micropollutant loads from treated wastewater inputs and groundwater discharge were evenly distributed over the course of the year. Contrary, micropollutant release via CSO was distinctly distributed over 33 events, operating in only 1.5% of the monitored time of one year. Up to 17% of the annual load was released in single events. For the events, a mean fraction of 28% of untreated wastewater in the CSO water was estimated. Adding the undisturbed flow of the receiving stream Bauerngraben, during CSO a mean fraction of 18% of untreated wastewater in the stream water events was estimated. As a consequence, in the stream Bauerngraben higher micropollutant concentrations than in the effluents of the WWTP occurred.

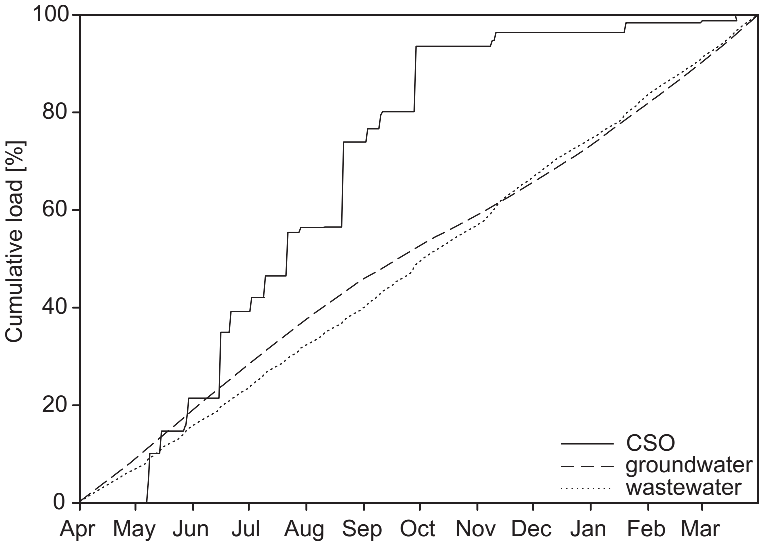


Fig. 20: Cumulative release of micropollutants from the sewershed by treated wastewater, combined sewer overflow (CSO) and groundwater discharge. Each release pathway scaled to 100%.

4.4 Conclusions

The applied holistic approach of incorporating wastewater, surface water and groundwater flow in a sewershed to reveal the related micropollutant loads enables to draw conclusions on the relevance of pathways of micropollutant releases.

Urban areas are emitter for micropollutants. Without doubt, the continuous release of treated wastewater from the sewershed is the most relevant source of micropollutants for the receiving surface waters. This results in a long-term chronic exposure of the aquatic ecosystem and a potentially sustained contamination of surface water resources. However, depending on the removal efficiency of the WWTP, CSO can contribute a significant portion of micropollutant loads to the surface waters. Here, the intermittent character with high micropollutant concentration may pose the risk of acute effects on the aquatic ecosystem. A fraction of 11.5% of the dry weather flow wastewater in the investigated sewer sections was directly lost to the groundwater. Consequently, also continuous groundwater discharge contributed to a considerable part of the micropollutant release from the sewershed.

As a result of this study, the pollution pathways of CSO as well as of groundwater should be adequately considered in assessments of micropollutant contamination of urban water resources. The micropollutant inputs to surface waters, natural attenuation by natural processes such as volatilization, photolysis or biodegradation may level part of the contamination (Gurr and Reinhard, 2006; Musolff et al., 2009 [Chapter 3]).

Micropollutant loads by urban groundwater discharge were found to be relevant and can exceed CSO loads from the same area. Here, the large volume of contaminated groundwater, the slow flow velocities and the possible persistence of micropollutants should be kept in mind. There is strong evidence that micropollutants persist in groundwater for decades (Massmann et al., 2008). As a consequence, a long-term and probably sustained contamination of groundwater with micropollutants beneath urban areas can be expected.

Chapter 5

Synthesis and perspective

5.1 Synthesis

Worldwide, more and more people are living in cities. The resulting ongoing urban land consumption has a tremendous impact on the entire water balance of the affected areas and goes along with manifold contaminations of all water compartments. Of particular relevance are contaminations from wastewater sources, since wastewater production, transport and treatment is concentrated in urban areas. Within this context, the group of micropollutants such as active compounds of pharmaceuticals and personal care products (PPCP) and industrial chemicals is a matter of growing concern (Schwarzenbach et al., 2006). Even in low concentration ranges, micropollutants can act as endocrine disruptors or chemosensitizers and, therefore, pose a potential threat to aquatic ecosystems and to human health (Schirmer and Schirmer, 2008). Beside toxicological evaluation and legal aspects, a crucial part for a micropollutant risk assessment in urban receiving waters is the knowledge of input, transport and fate of micropollutants in the aquatic environment.

So far, assessments of micropollutant occurrence and exposure scenarios frequently focus on wastewater treatment plant (WWTP) effluents as a major pathway for the contamination of surface water, since these substances are often only partially removed during the treatment process (e.g. Ternes, 1998; Heberer, 2002b). Nevertheless, wastewater can pollute surface water and groundwater by different pathways. Hence, sole assessments of WWTP effluents may not give the whole picture of micropollutant release into urban water resources.

Micropollutant occurrence in urban receiving water is characterized by a high spatial and temporal variability. This is a result of the dynamics of water flow and wastewater inputs in urban areas as well as a consequence of concentration variability in the wastewater and possibly variable retention processes. Therefore, micropollutant assessments demand measurements on different spatial and temporal scales in all urban water compartments.

In this study, a holistic approach was applied to assess micropollutant occurrence and fate, including wastewater as the source and surface water as well as groundwater as recipients. The micropollutants bisphenol A (BPA), technical 4-nonylphenol (NP), caffeine (CAF), galaxolide® (HHCB), tonalide® (AHTN) and carbamazepine (CBZ) were considered. The study area within the city of Leipzig, Germany, was carefully chosen, ensuring congruent catchments of wastewater – the sewershed – and of groundwater. This allowed for the assessment of a combined water and micropollutant mass balance for these water compartments. Micropollutant occurrence was monitored over the course of a year, accounting for possibly seasonal as well as intermittent variations. Results of this approach are synthesized here.

The monitoring of micropollutant concentrations and other water quality parameters in wastewater, surface water and groundwater yielded a multitude of data. To cope with this dataset, the first evaluation used univariate, descriptive statistical methods. Based on the micropollutant's statistical characteristics as well as on the spatial distribution in groundwater, a conceptual model of micropollutant input pathways was derived. Micropollutants in the surface water of the study area originated mainly from nearly constant WWTP effluent inputs and intermittent wastewater sources such as combined sewer overflow. The groundwater contamination was a result of sewer leakages and partly of the infiltration of contaminated surface water.

In the next step the multivariate statistical methods correlation analysis and factor analysis were applied to the micropollutant concentrations and the measured in-situ parameters pH, Eh, water temperature, electrical conductivity and dissolved oxygen. Here, conclusions were drawn concerning possible concentration influencing processes. Water temperature and dilution was found to significantly influence the concentrations of micropollutants in the surface water. In the groundwater samples factor analysis revealed statistical similarities in the occurrence of HHCB, AHTN and CAF and of NP and BPA, which was probably a result of comparable degradation processes.

Based on the findings of the statistical analysis of concentrations, the temporal and the spatial patterns of micropollutant occurrence were evaluated. The evaluation of the surface water samples showed that the major input and the concentration influencing processes can be found outside of the study area. Water from the study area's small streams originated from a bypass of the Weisse Elster river system, showing a micropollutant signature referring to the whole river catchment. The impact of the sewershed on the surface water quality was limited to the intermittent influence of combined sewer overflow (CSO). For the little, fast flowing streams this influence was found to be short in time limited to the duration of the CSO event. Thus, the integral watershed-sewershed approach of water and contaminant fluxes within the study area did not apply the way it was initially thought. Nevertheless, valuable results were derived from the river water of the Weisse Elster that was bypassing through the study area. Seasonality of surface water loads of CAF and the polycyclic musks HHCB and AHTN were found to be a result of water temperature-enhanced attenuation processes, such as biotransformation, water-air-exchange and photolysis. For CAF in the colder months and NP throughout the year, loads increased after rainfall. These loads can be assigned to the influence of contaminated surface runoff and of untreated wastewater from CSO. In the summer month, the attenuation of CAF in the warmer water compensates the higher inputs by rainstorm-induced intermittent sources. Additionally, a constant source of untreated wastewater had to be assumed to explain the high loads of CAF and BPA. This source is still not known and a further analysis would need to conduct a monitoring of the entire Weisse Elster catchment.

In the examination of surface water, timing and location of sampling is crucial, since seasonal removal, intermittent inputs of micropollutants as well as dilution controls the observed concentrations. This points to a fundamental problem, when monitoring micropollutants. The laboratory efforts for the extraction and the chemical analysis of micropollutant are high which often leads to a discrepancy between the number of samples required to solve the scientific task and number of samples that can be reasonably handled in the laboratory. The conclusions stated in Chapter 3 may help with the conceptual design of monitoring programs and, thus, an effective use of laboratory resources.

The patterns of groundwater contamination could only be explained for part of the watershed. A temporal pattern of CAF concentration downstream of a polluted stream could be related to a seasonal infiltration of contaminated surface water. All other observed concentration variability could not be assigned to a certain input or attenuation process. Nevertheless, the implications are the same as for surface water sampling. Monitoring of micropollutant concentration over a longer period of time is crucial to capture the occurrence behavior in the urban receiving groundwater. From the monitoring data it was found that concentration influencing factors are too diverse to conclude a process-based cause-effect-chain for the groundwater contamination in the study area.

As the final step in this thesis, the relevance of the micropollutant release from the sewershed via WWTP effluents, CSO discharge and groundwater discharge was discussed. For this task, the holistic watershed-sewershed approach fully applied. The basis of the micropollutant load estimation was a model of the water flow in the study area, combining balance approaches for the wastewater and CSO assessment and numerical approaches for the groundwater recharge and groundwater flow quantification. The transient 3D groundwater flow model enabled the quantification of water discharge through the sewershed boundary. Micropollutant concentration probability from the groundwater samples was assumed to be representative for the entire groundwater domain of the watershed. Thus, groundwater discharge was combined with the micropollutant concentration probability to estimate the integral release from the sewershed in relation to the other pathways. The major findings showed that groundwater contributes a significant fraction of total micropollutant load release of NP and BPA. Also CSO, especially for the CAF release, were found to contribute a significant part of the loads from the sewershed. This pattern of load release from the sewershed as well as the different temporal dynamics of release pathways has implications concerning micropollutant exposure scenarios. While WWTP effluents and groundwater discharge lead to a long-term exposure with potential chronic effects on aquatic biota, CSO can lead to highly concentrated short-time exposure in surface water with potentially acute effects.

The relation of the persistent CBZ and BPA concentration in the wastewater and in the receiving groundwater allowed the estimation of sewer leakages. The volume of sewer leakages made up 14% of the total groundwater recharge. This refers to a loss of 11.5% of the dry weather flow of wastewater into the subsurface.

The findings of this study have shown that the integral watershed-sewershed approach was feasible to allow a joint evaluation of water flow and micropollutant mass flow. The monitoring program over the course of one year was capable to account for seasonal as well as for short-term variability of micropollutant occurrence. The results also show the necessity to consider the groundwater pathway in micropollutant assessments. Of particular concern is the long-term and probably sustained pollution of this water resource. Here, the example of the estrogenic NP, one of the priority substances of the water framework directive (European Commission, 2000), can be referred to. Although, reduced in production and usage since the end of the 1980s and finally significantly restricted in the European Union since 2005 (Quednow and Püttmann, 2008a), NP is still one of the most relevant micropollutants in the watershed's groundwater. Micropollutants have shown to persist in groundwater over decades (Massmann et al., 2008). Any measure to avoid the further input of micropollutants into urban groundwater resources will need time to fulfill its purpose. Also, with regard to the ongoing introduction of new chemicals in consumer products and thus in wastewater, precautionary principles should be applied (Schirmer and Schirmer, 2008). The release of micropollutants in urban receiving waters may be reduced by a better design and a better maintenance of the sewage system as well as improved treatment technologies in WWTPs and in the drinking water production. Moreover, Schirmer and Schirmer (2008) call for a more environmentally friendly design of chemicals of the daily use and a better public awareness of this issue. Nevertheless, releases of micropollutants into the urban aquatic environment cannot be totally avoided. The today's ubiquitous presence of these substances in urban receiving waters and the possible consequences for aquatic ecosystems and for human health calls for risk assessments on the basis of a sound scientific knowledge. A profound understanding on the quantity and quality of input, transport and fate of micropollutants in urban water compartments is needed, taking surface water, groundwater, wastewater and their complex interactions into account. This study attempts to contribute to this knowledge.

5.2 Perspective

Based on this study, recommendation for future work concerning the assessments of micropollutants in urban receiving waters can be made.

The applied holistic approach relied on the major assumption that micropollutant input to surface water and to groundwater mainly resulted from wastewater sources. Sources may also exist outside wastewater, e.g. in rainwater or urban runoff water from roofs and streets. Surface runoff from urban, suburban and agricultural areas was supposed to be one of the reasons of increased loads of NP in the river water from the Weisse Elster catchment following rainfall (see Chapter 3). Within the sewershed these sources are perhaps not relevant for the micropollutants chosen here but they can be significant for other groups of substances, such as phtalates, biocides, heavy metals, or flame retardants (e.g. Vethaak et al., 2005; Schwarzenbach et al., 2006; Peters et al., 2008).

The study presented here relied on micropollutants dissolved in water. In particular hydrophobic contaminants in surface water and wastewater can also be present in suspended particulate matter and colloidal phases with consequences for the transport and bioavailability (Winkler et al., 1998; Patrolecco et al., 2006; Vignati et al., 2009). An incorporation of these particulate and colloidal phases will probably contribute valuable information for risk assessments but also implies more complex sampling and analytical workflows.

The applied monitoring strategy with monthly to quarterly sampling was found to capture seasonal and intermittent micropollutant concentration variations in the surface water and in the groundwater. However, the samples from the WWTP did most likely not fully represent the true concentration probability. For instance, median CBZ concentrations were found to be higher in the WWTP effluent than in the influent, although a formation in the treatment process can be excluded. Sampling in the wastewater treatment plant would be improved by composite flow-proportional sampling approaches, accounting for intra-day concentration variability. This sampling approach would probably also improve the robustness of surface water samples. The use of automatically sampling devices for these tasks may also allow a reliable sampling of CSO water.

The groundwater samples were assumed to be representative for micropollutant occurrence in the watersheds groundwater. It is likely that the concentration variability could be better explained with refined sampling approaches. Spatially highly resolving sampling within groundwater may account for small scale heterogeneities while integral pumping tests with large sample volumes give better average concentration results. The latter method was successfully applied by Leschik et al. (2009) within the study area. Nevertheless, both approaches are only feasible for monitoring on a smaller scale, since technical and analytical efforts are high and the number of samples is large.

To overcome temporal pollutant concentration variability, passive sampling devices can provide robust time-integrating information. In this thesis, in collaboration with toxicologists from the UFZ – Helmholtz-Centre for Environmental Research, passive sampling devices successfully applied for polycyclic aromatic hydrocarbons (Bopp et al., 2005) were adapted to the micropollutants. Results from the chemical analysis of the devices after three and six months of exposure in treated and untreated wastewater, surface water and groundwater were found to be inconsistent. Duplicate samplers did not yield comparable micropollutant concentrations. Thus, this dataset was not used in this thesis. More work on the adaption of passive sampling devices to micropollutant is needed to follow up this promising approach.

The approach of loosely coupled water flow models was sufficient to capture the study area's main water flow paths. However, results of the urban water balance indicate the importance of a good representation of surface runoff, CSO, groundwater recharge and sewer leakages. The loose coupling of models at the interfaces of groundwater and the sewage system and of the unsaturated and the saturated zone can only approximate the interactions in both directions. Further studies may rely on an integral numerical model of surface water flow, wastewater flow, surface runoff, infiltration and unsaturated flow as well as groundwater flow to provide a better insight into the flow dynamics in time and space. Furthermore, an integral model allows a more practical calibration process and sensitivity analysis. The information on uncertainty of the input parameters could be better incorporated, for example by the use of Monte-Carlo-approaches (Wolf et al., 2007).

As stated in Chapter 2.2 "Statistical methods to evaluate the impact of xenobiotics on urban receiving waters" the data-driven approach applied in this study should result in physically-based models of micropollutant flow and fate in the urban catchment. Such models can help to study micropollutant behavior under different scenarios of changing boundary conditions. So far, the micropollutant occurrence in urban receiving waters suggests several concentration influencing processes, such as biotransformation, photolysis and water-air-exchange but there is still a lack of knowledge of the exact physical meaning and the spatial location of these processes. Measurements of micropollutant metabolites may provide valuable information of the type, time and the place of transformation processes. A promising approach is to focus on interfaces between the water compartments, where steep gradients of physicochemical parameters such as oxygen and the redox potential may enhance the transformation processes. Of particular interest is the interface between wastewater and the unsaturated soil at sewer leaks, the capillary fringe at the transition between unsaturated and saturated zone and the hyporheic zone at the groundwater-surface water interface. Here, future efforts are required to study and model water and contaminant flow at these interfaces and scale the results to the catchment size.

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