Managing organic micropollutants in rivers

From monitoring to mitigation

Andrea F. Brunsch

Propositions

1. Micropollutant removal by retention soil filters can compete with classical fourth treatment steps.
   (this thesis)

2. Standardized monitoring is inadequate for organic micropollutants in the water cycle and needs to be customized to the prevalent environmental conditions.
   (this thesis)

3. The causal relation between the global spread of antibiotic resistant bacteria and traveling abroad can be explained well by infectious disease sciences.

4. Citizen science stimulates preserving and promoting global biodiversity.

5. The experience of canoeing is relevant for water researchers to understand their field of study.

6. A sustainable society cannot be achieved through individual consumption behavior.

7. Being a parent effectively improves time- and stress-management skills.

Propositions belonging to the thesis, entitled

"Managing organic micropollutants in rivers - From monitoring to mitigation"

Andrea F. Brunsch
Wageningen, 18 October 2021

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Managing organic micropollutants in rivers - From monitoring to mitigation

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Thesis

submitted in fulfilment of the requirements for the degree of doctor
at Wageningen University
by the authority of the Rector Magnificus,
Prof. Dr A.P.J. Mol,
in the presence of the
Thesis Committee
appointed by the Academic Board
to be defended in public
on Monday 18 October 2021
at 1:30 p.m. in the Aula.

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Managing organic micropollutants in rivers - From monitoring to mitigation,
192 pages.

PhD thesis, Wageningen University, Wageningen, the Netherlands (2021)
With references, with summary in English and German

ISBN: 978-94-6395-892-9

DOI: 10.18174/549910

Für meine Eltern, Monika und Herbert

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General introduction

1.1 Water quality situation (in Western Europe)

1.1.1 Anthropogenic actions affecting organic micropollutants related water quality

(Waste)water managers and researchers have to deal with the consequences of anthropogenic activities on the environment. High population density is influencing both structure and water quality of surface waters by constructional interventions in and next to the water body as well as pollutant emissions into the water. Moreover, emerging contaminants such as pathogens, microplastics and organic micropollutants (OMPs) are challenging water managers, responsible for water quality. OMPs are solely defined by their concentrations found in the aquatic environment which are ranging between ng/L to µg/L. That is why OMPs include a variety of different compound classes such as pharmaceuticals, personal care products, pesticides or compounds used during industrial processing each containing a variety of sub-classes and substances.

Studying fate and behaviour of OMPs has become a significant topic in water pollution research. OMPs have been detected in various parts of the water cycle including surface water, groundwater and drinking water. Many of them are of considerable toxicological concern, especially when present as components of complex mixtures (Schwarzenbach et al., 2006). Since the 1980s, when analytical methods for OMPs improved, it became possible to study trace levels of these pollutants in the environment. This resulted in the detection of a broad range of chemicals, several associated with diverse input pathways. These OMP inputs are now known to originate from sewage treatment plant effluent (Götz et al., 2012; Scheurer et al., 2009; Ternes et al., 1999b; Ternes Thomas A., 1998; Vieno et al., 2005), untreated sewer system overflow (Burkhardt et al., 2011; Gasperi et al., 2012; Musolff et al., 2009; Zgheib et al., 2012), surface runoff from landscape (Wittmer et al., 2010) and atmospheric deposition (Law et al., 2006).

The anthropogenic emissions as described above are influenced by climate change, leading to extreme weather conditions: in North-Western Europe long dry periods in summer are frequently occurring nowadays and these are locally intermitted by short heavy rain events (Brasseur et al., 2017). The effect is that pollutants, including OMPs, become more concentrated in the river water due to low dilution by rain water and recharging groundwater, and that sewage treatment plants are more often confronted with storm water overflows, exposing rivers to sudden untreated wastewater discharges (Delpla et al., 2009; Neumann et al., 2015; Nickel and Fuchs, 2019). Hence, the understanding of OMP emissions

to river waters and designing measures to control and mitigate these, both face the highly dynamic nature of hydrological and other processes in a river basin. Studies on the level of a river basin, giving adequate insights into OMPs fate, are rare because of the complexity of these systems. Because of this lack of understanding, it is difficult to design regulations and measures by which water authorities can monitor and mitigate OMP emissions adequately. For this reason, studying well-defined small catchment systems can offer new basic and necessary insights in OMPs fate and transport in rivers, and this was the main motivation for conducting this PhD research.

1.1.2 Relevant European and German Directives

With the establishment of Directive 2000/60/EC (Water Framework Directive) by the European Union, water protection and management of river basins became a relevant issue for local water managers. With its aim of achieving good ecological status or good ecological potential and good chemical status by the end of 2015, the Directive formulates an approach which meets the needs of sustainable development. This includes improving the ecological status of aquatic ecosystems and reducing pollution. Annex IX of Directive 2000/60/EC covers emission limit values and environmental quality standards (EQS) necessary to reach good chemical status of surface waters. Decision 2455/2001/EC of November 2001 defines 33 priority substances or groups of substances for action at community level. This Decision requires continuous reduction in their concentrations. The 33 priority substances include metals, metal compounds, pesticides, biocides and industrial chemicals. Some of them have also been identified as priority hazardous substances for which measures are required to cease or phase out use leading to reduced emissions within 20 years. Directive 2008/105/EC adopts corresponding EQS for these 33 priority substances, indicated as annual average and maximum allowable concentration. The European Commission calls for a review and update of the list of prioritised substances every four years. The clear objective in defining concentration limits for prioritised substances is to ensure good chemical status of surface waters. However, the Water Framework Directive regulates not only chemical status but also ecological status, which provides a measure of a healthy ecosystem. In order to meet this requirement, every Member State needs to control additional pollutants of national relevance.

In Germany a federal surface water ordinance (Oberflächengewässerverordnung) was adopted in 2009. For classification of chemical status, the surface water ordinance adopts the list of priority substances including environmental quality standards set down in Directive

2008/105/EC. For classification of ecological status, the surface water ordinance provides a list of 162 river basin specific substances which must be observed and controlled if there is significant pollution through discharge in the watercourse. Unlike priority substances for which the EQS must be determined by annual average and maximum allowable concentration, the EQS of the river basin specific substances need only be determined by annual average. Pharmaceuticals have not been comprised in the Directive 2008/105/EC. The same applies for the 162 river basin specific substances listed in the surface water ordinance. Although some pharmaceuticals (carbamazepine and sulfamethoxazole) were originally proposed for inclusion, they were withdrawn on the basis of a Federal Council Decision in 2011 (Drucksache 153/11). However, the Water Framework Directive calls for provision of a new list of priority substances every four years. In this context, on 31 January 2012 the European Commission proposed a Directive amending priority substances in Directive 2000/60/EC and Directive 2008/105/EC. In 2013 the list of priority substances was extended to 45 substances by Directive 2013/39/EG. In addition, a watch list was introduced. This list included three active pharmaceutical ingredients: 17α-ethinylestradiol, 17β-estradiol and diclofenac**.** In 2015 this watch list was extended by additional substances with Decision 2015/495/EU. Besides three macrolide antibiotics a natural hormone, some pesticides a UV filter and an antioxidant were included in this list. However, due to a sufficient amount of data describing occurrence of the substances in European water bodies, the pharmaceutical diclofenac, the pesticides triallat and oxidiazon, the antioxidant 2,6-ditert-butyl-4-methylphenol and the UV-filter 2-ethylhexyl-4-methoxycinnamat were withdrawn from the watch list, whereas the insecticide metaflumizon and the antibiotics amoxicillin and ciproflaxin were added to the list (2018/840/EU). A revised version of the German federal surface water ordinance (Oberflächengewässerverordnung) was released in 2016 where amendments of Directive 2013/39/EG were considered.

According to the current legislations and proposals as discussed above, it is likely that a broader range of OMPs (e. g. pharmaceutical compounds) will be added to the list of priority substances and to the list of river specific substances. The study of Barbosa et al. (2016) revealed that knowledge on the occurrence and treatment of OMPs of the watch list is compound specific including some very well-known OMPs (e.g. diclofenac) and lack of knowledge on other OMPs (e.g. pesticides), highlighting the need for additional research on OMP behaviour and removal.

In 2015, 89% and 100% of the rivers in Germany did not meet the requirements of the WFD for an ecological good status and chemical good status (BMUB and UBA, 2016) and the

presence of OMPs in surface waters is one reason for this poor result. OMPs have already been detected in every EU country (Loos et al., 2009). As they have been identified as pollutants of significant concern for surface water and drinking water quality, actions regarding measures to reduce OMP pollution are highly recommended by researchers (Hofman-Caris et al., 2019; Sousa et al., 2019). In Europe, initiatives on a nation-wide level do only exist in Switzerland, where authorities decided to implement additional sewage treatment plant steps as mitigation strategy to improve water quality (Eggen et al., 2014). This strategy seems promising for Switzerland. However, other EU countries have not yet implemented mitigation measures, or only implemented measures in individual cases. A reason for this might be, on the one hand insufficient data on the removal efficiency of (innovative) treatment technologies on full scale application and on the other hand the costs and energy consumption of such techniques. A bigger dataset of treatment technologies examined in the "real environment" could thus mitigate for the current low number of large scale solutions in wastewater treatment.

1.1.3 OMPs in rivers and their emission pathways

OMPs enter surface waters through different emission pathways (Figure 1-1). It is known from several studies that the discharge of treated effluent from sewage treatment plants (STPs) is a major pathway for the introduction of OMPs to surface waters (Daughton and Ternes, 1999; Luo et al., 2014). In the review study of Luo et al., 2014, it was shown that OMPs appear in various concentrations at STP effluent. This is not surprising since technical specifications of STPs is highly variable. Moreover, composition of the wastewater entering the STP is diverse according to the catchment area and characterised by consumer behaviour, industries, surrounding agricultural lands, health care infrastructure and the prevalent sewer system. In combined systems, both sewage and rain water are transported to STPs. In case of STPs overload due to heavy rainfall events, combined sewer overflow is entering the river directly. In contrast, separate sewer systems carry sewage and rain water in separate pipes. At heavy rain fall events, rain water is collected in storm water basins before it is discharged into the receiving river. In both, combined sewer overflows and storm water basins a variety of OMPs is present and emitted into rivers (Burkhardt et al., 2011; Gasperi et al., 2012; Launay et al., 2016; Zgheib et al., 2012). Storm water events do not only trigger for point emissions but also diffuse emissions. Surface runoff of rural and urban land use leads to elevated

background concentrations or sharp peak concentrations (i.e. as a result of pesticides use in agricultural or urban areas) of various OMPs in receiving rivers (Wittmer et al., 2010).

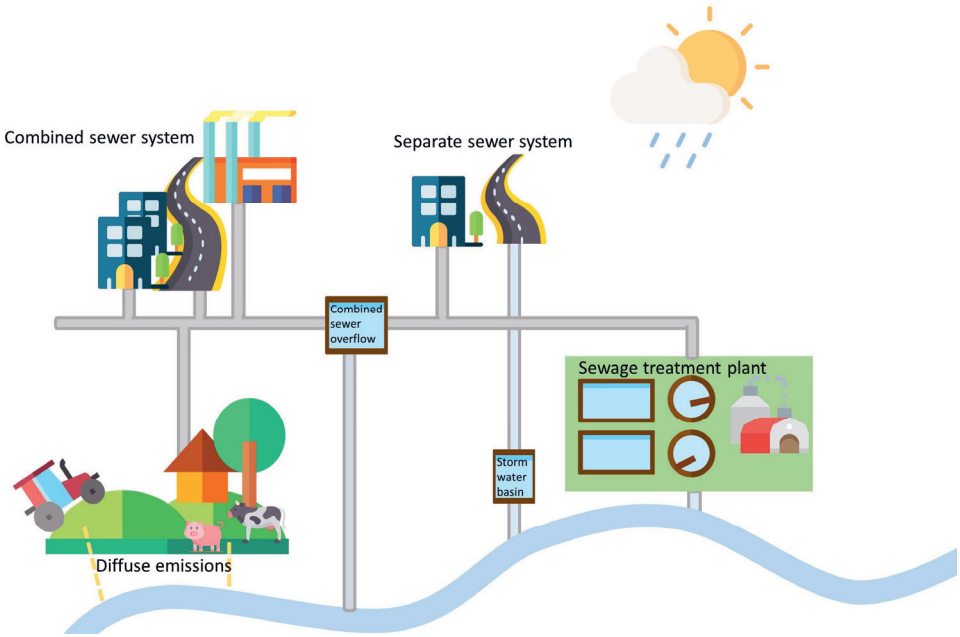


Figure 1-1: Emission pathways into surface waters

Due to climate change, it is most likely that we have to deal with more intense and frequent extreme events such as storms and hot spring and summer spells in the near future (Brasseur et al., 2017). This affects both, wastewater quality and quantity of emission entries related to rain fall intensity as discussed above. Small river systems in urbanized areas contain high wastewater loads and are affected directly by such weather changes. These rivers are most influenced by emission inputs and thus water quality changes. Larger rivers will carry the OMP contributions of all tributary catchments and will have a more averaged out quality effect, that will even be more difficult to study in terms of mechanistic understanding of OMP behaviour in rivers. Hence, smaller urban influenced catchments are of interest to study because of their sensitivity to OMP pollution and because of their better system monitoring options, offering a potential to learn more about effects of STP emissions and processes along transport in the river. The various relevant processes controlling fate of OMPs in a river catchment are described below.

1.2 Behaviour and fate of OMPs in rivers

After being emitted into rivers, OMPs are being part of the river ecosystem and therefore exposed to several natural conditions such as solar radiation, changing temperatures, microorganisms or suspended particles. These conditions can affect the removal or formation of OMPs depending on the chemical structure of the individual OMP (Figure 1-2). In the following, the most important processes, influencing the behaviour and fate of OMPs in rivers are presented.

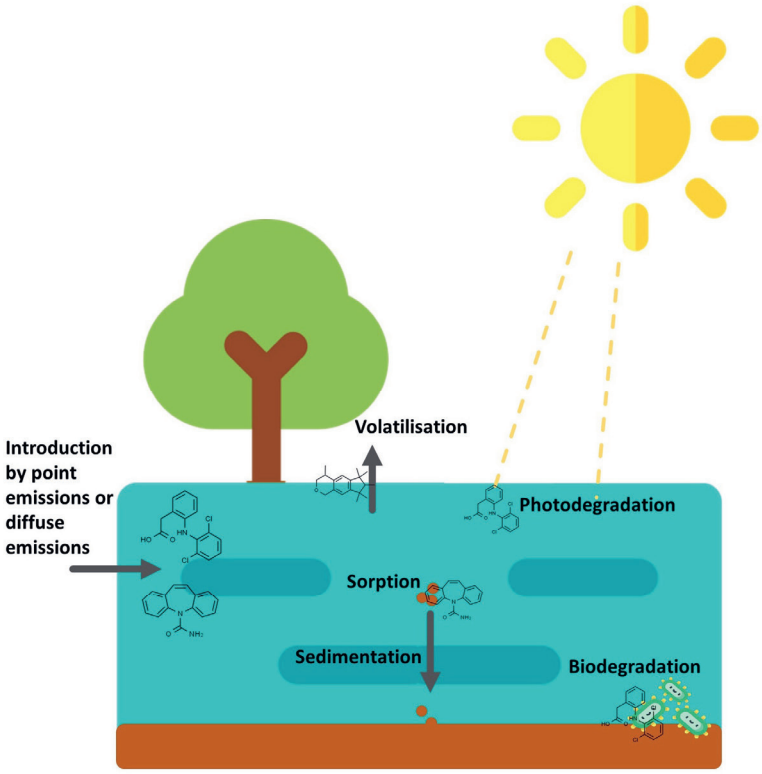


Figure 1-2: Behaviour and fate of OMPs in rivers

1.2.1 Biodegradation

It is known that most OMPs are in general not persistent against biodegradation and are potentially transformed by metabolic and in particular co-metabolic processes (Barra

Caracciolo et al., 2015). Microorganisms - metabolically diverse bacteria, archaea, protists and fungi - play the most important role in biotransformation. These microorganisms are very adaptive to prevalent environmental conditions and pursue different strategies for the transformation of OMPs. For example, different microorganisms can form associations (syntrophy) that enable each other to transform a compound that would not have been possible by a single organism (Schwarzenbach et al., 2016). In general, two approaches facilitate biotransformation. The first approach is that microorganisms use enzymes that serve as catalysts to convert OMPs. The second approach is that the microorganisms invest metabolic energy to synthesize reactive species. An example of these are white rot fungi that produce peroxide and other radical forming species, normally used to crack lignin structures to make these digestible, now attacking the OMP molecular structure (Mir-Tutusaus et al., 2018).

Many OMPs have structures that differ from the organic compounds usually processed by microorganisms in STPs at high concentrations. Hence, the microorganisms are often not equipped with suitable enzymes when they first encounter OMPs. Generally, there is no strong selective pressure on microorganisms in an STP to develop such enzymes, due to the abundance of easy degradable organic substrates other than OMPs (Majewsky et al., 2011). This makes OMPs in an STP rather persistent to biotransformation. However, enzymes that bind and catalyse reactions of particular chemicals may also have some ability to bind and induce reactions in structurally similar compounds resulting in “accidental” (co-metabolic) biotransformation of OMPs with similar structural parts like those of common substrates (Fischer and Majewsky, 2014; Schwarzenbach et al., 2016). Moreover, microorganisms seem to always have some nonspecific enzymes available for the purpose of transforming unexpected or unknown compounds. This means that OMPs which are unusual to the relevant microorganisms may be slowly degradable by the use of such nonspecific enzymes (Majewsky et al., 2011; Schwarzenbach et al., 2016).

In rivers, the conditions for biodegradation of OMPs are slightly different. Compared to an STP, the organic matter concentration in river waters is much lower (Westerhoff and Mash, 2002). Even though the OMPs are only a small part of the total organic matter content (Shon et al., 2006), microorganisms are motivated to develop enzymes for the transformation of OMPs. Hence, metabolic biodegradation is an important degradation pathway for OMPs in rivers (Vargha et al., 2005; Wang et al., 2018). Furthermore, a contribution of co-metabolic transformation, as described above for STPs, is still expected.

Degradation studies revealed that OMPs are transformed by microorganisms in the hyporheic zones of rivers (Kunkel and Radke, 2012; Schaper et al., 2018; Writer et al., 2013). Some factors enhancing biodegradation in the hyporheic zone are e.g. an intense exchange of river water and sediment pore water from the river bed (Kunkel and Radke, 2012), the residence time of the OMPs in the hyporheic zone, and the reactivity of the OMPs (Schaper et al., 2018). Moreover, the transformation of OMPs is higher in the presence of oxygen and moderate temperatures (20 °C) and lower in the absence of oxygen and cold temperatures (Burke et al., 2014; Schaper et al., 2018).

Additionally, the presence of OMPs does influence the biofilms present in rivers on stones and other materials, with changes in biofilm thickness or biofilm communities. For example, both positive and toxic effects where measured on riverine microorganisms depending on the individual OMPs and their concentrations in rivers (Lawrence et al., 2005).

1.2.2 Photodegradation

Photodegradation describes the alteration of chemicals in association with light. Two general processes can be distinguished: direct and indirect photodegradation. Direct photodegradation is the transformation of OMPs as a consequence of light absorption. Indirect photodegradation is the transformation of OMPs by reactive intermediates such as hydroxyl, carbonate and alkyl peroxy radicals, singlet oxygen and aqueous electrons, which are generated by natural water components. The adsorption of radiation by nitrate and dissolved organic matter leads to the production of most of these species (Lam and Mabury, 2005). Another indirect photodegradation reaction is photosensitization, the transformation of OMPs by energy transfer from another excited species such as dissolved organic matter (Ye et al., 2019). Accordingly, it was reported by several authors that the presence of nitrate and dissolved organic matter enhances photodegradation rates for some OMPs (Andreozzi et al., 2003; Chin et al., 2004; Lam and Mabury, 2005; Wang et al., 2017). Additionally, pH values affect photodegradation rates of OMPs, but with no clear direction. These pH initiated changes in degradation are in fact compound specific (Baena-Nogueras et al., 2017).

The prevalent solar spectrum, influencing photodegradation in natural water bodies, is depending on the geographic location, season, time of day, weather condition and air pollution. Accordingly photolabile OMPs attenuate significantly in the daytime but persist in the night time (Hanamoto et al., 2013), also photodegradation underlies a seasonal trend (at e.g. northern European latitudes) with higher rates in summer compared to winter (Poiger et

al., 2001). Within the water column, light is scattered by suspended particles and adsorbed by particles and dissolved natural organic matter. Deeper in the water column more light is already absorbed, leading to a decrease in direct photolysis of dissolved OMPs (He et al., 2016; Ye et al., 2019).

1.2.3 Sorption

The fate and impact of structurally identical molecules in the environment is very different if they are dissolved in water or sorbed onto or into solids. The dissolved OMPs may sorb to suspended solids in the river water column and subsequently settle to the river sediment floor together with these solids (Schwarzenbach et al., 2016). Moreover, sorbed OMPs become less accessible to light, less available for biodegradation, and enter a low oxygen or even anoxic environment upon ending up in the sediments at the river bed, all leading to a reduced degradation compared to dissolved chemicals (de Weert et al., 2009).

Sorption of OMPs is a complex process and dependent on compound properties, sorbent properties and environmental conditions. An important OMP property is the octanol/water distribution coefficient. OMPs with higher octanol/water distribution coefficients tend to sorb stronger (Karickhoff et al., 1979). Important sorbent properties are the organic fraction and surface area of the sorbent (soil or sediment). Higher organic fractions as well as fine particles with a high specific surface area enhance sorption capacity (Karickhoff et al., 1979). Sorption is also a matter of electrostatic interactions between OMPs and sorbent surfaces or organic matter. OMPs can be adsorbed to charged surface sites of opposite charge or repulsed when OMPs and material surfaces are both negatively charged (Moreno-Castilla, 2004).

Finally, environmental conditions such as the aqueous chemistry (pH and ionic strength, ion composition) play a significant role on the sorption behaviour of especially ionizable OMPs. It affects sorbate (OMP) speciation and sorbent surface charge. Additionally, ions in solution can compete for sorption sites with the OMP. Accordingly, sorption is also possible for hydrophilic OMPs due to additional ionic interactions, such as cation exchange processes. Hence changes in the pH caused by e.g. variations in land use or climatic conditions, might affect the predominant sorption mechanisms (hydrophobic or electrostatic interactions) (Moreno-Castilla, 2004; Schaffer et al., 2012).

In rivers, sorption occurs in biofilms and sediment particle associated surfaces in the hyporheic zone, biofilms on submerged macrophytes, suspended particles in the streaming water and biofilms in stagnant surface pockets (Riml et al., 2013).

1.2.4 Volatilisation

Volatilisation is the process where chemicals are transferred from liquid phases to gaseous phases when they are not at equilibrium. Environmental systems can be brought to disequilibrium due to natural biochemical reactions as well as processes associated with anthropogenic actions including spilling of chemicals into the environment (Schwarzenbach et al., 2016). Additionally, partition coefficients between water and air (Henry´s law coefficient) depend on temperature (Hulscher et al., 1992), which obviously varies with time and space and accordingly, adjacent air and water systems are continuously pushed out of equilibrium. Besides temperature also the area of the air-surface water interface is an important factor affecting volatilisation. This interface can be highly variable and depends on the dimensions and hydraulics of the river (Schwarzenbach et al., 2016). For example, simulations with a conceptual model indicated that volatilisation at waterfalls, with a large air-water interface, is significant for chloroform, chlorinated benzenes and PCBs (McLachlan et al., 1990). Moreover, the very hydrophobic musk fragrances AHTN and HHCB were suspected to be removed from rivers by volatilisation (Schwientek et al., 2016). However, field research on volatilisation of volatile organic contaminants in rivers is still rare.

1.3 Measures to reduce OMPs from wastewater

To enhance chemical and biological water quality and "to achieve the elimination of priority hazardous substances and contribute to achieving concentrations in the marine environment near background values for naturally occurring substances" (Directive 2000/60/EC), OMPs must be retained before entering surface waters. With this ultimate aim, the WFD points out the need of combined approaches to pollution abatement. Due to the huge number of OMPs and the variety of usages and input pathways a combination of complementary measures is required to reduce OMPs in the aquatic environment (Eggen et al., 2014). Measures must be positioned at different locations of OMPs life cycle from production over consumption (= pollution sources) to entry points to surface waters. Because OMPs are known to be present in municipal wastewater, water managers have to re-evaluate their approach to wastewater

treatment by optimising existing technologies or implementing novel technologies specifically targeting OMPs. In the following, only the so-called end of pipe solutions, means measures executed by water managers before entering surface waters are discussed.

1.3.1 Conventional wastewater treatment

Conventional municipal wastewater treatment can commonly be divided into mechanical treatment followed by primary sedimentation and biological treatment followed by secondary sedimentation. In most studies, the overall removal efficiency in STPs including primary and biological treatment is investigated (Luo et al., 2014). Reduction of OMPs is compound specific, ranging from 12.5 to 100% (data from 14 different countries/regions) (Luo et al., 2014). These numbers include large location specific elimination disparities, including a broad range of reduction rates even for the same compound (Luo et al., 2014). Mechanical treatment facilitates the removal of some OMPs, whereas most of the OMPs - out of the ones which are at least partly reduced by conventional STPS - are getting reduced during biological treatment (Carballa et al., 2004). Two mechanisms were found to be responsible for the reduction of OMPs: the biological degradation of OMPs and the adsorption onto primary and secondary sludge (Carballa et al., 2004; Joss et al., 2008). Some factors are influencing especially OMP reduction in biological treatment (mostly activated sludge treatment) such as solid retention time (Clara et al., 2005), pH (Gulde et al., 2014), redox conditions (Suarez et al., 2010) and hydraulic retention time (Gerbersdorf et al., 2015). The reason for a variability of these factors can be operational settings or varying STP inflow composition (quantity and quality). Consequently, the reduction of OMPs in conventional STPs is not only compound specific but also dependent on operational performances of the STP. Due to this only partial OMP reduction, the need for new strategies in wastewater treatment emerged (Joss et al., 2008; Suárez et al., 2008).

1.3.2 Technical post treatment steps

Conventional STPs can effectively remove organic carbon, nutrients and pathogens from wastewater. The reduction of OMPs is, depending on the compound, often insufficient (as discussed above). Therefore, different methods are currently tested or applied for the additional treatment of wastewater as a part of municipal wastewater treatment. The three most popular technical treatment processes are discussed in the following.

1.3.2.1 Degradation by advanced oxidation processes

Advanced oxidation processes (AOPs) use different reagent systems for the production of OH radicals, which have a strong impulse to react with organic compounds in wastewater. This reagent systems can be classified as photochemical degradation processes (UV/O_3 and UV/H_2O_2), photocatalysis (TiO_2/UV and photo-Fenton reactions) and chemical oxidation processes (O_3, O_3/H_2O_2 and H_2O_2/Fe^{2+}) (Poyatos et al., 2010). Following this, AOPs include a variety of treatment processes and some AOPs, especially those involving ozonation and UV irradiation, are already well established and operated in full scale in drinking water treatment and water reuse facilities (Miklos et al., 2018). In the following only these two processes should be addressed. Before using ozonation for removal of OMPs it was long used as oxidant and disinfectant (Miklos et al., 2018). An advantage of ozonation as post treatment step for OMP removal is hence the additional disinfection of STP effluent before entering surface waters.

In wastewater ozonation compounds are often directly oxidized because wastewater ozonation is already intrinsically an AOP process (Buffle et al., 2006). For this reason, ozonation is sometimes classified as AOP like process. However, at high pH, compounds are oxidised by OH radicals, because an increase in pH accelerates ozone decomposition and the generation of OH radicals (Buffle et al., 2006). Research showed, that with ozonation also persistent OMPs can be successfully degraded (Huber et al., 2003).

UV based AOPs are processes that are based on UV irradiation (mostly UV-C) and the combination of UV light and different radical promoters (mostly H_2O_2) (Miklos et al., 2018). The effectivity of phototransformation with UV is dependent on the pH value and the OMP structure. In direct comparison of ozonation and UV treatment, the ozonation did show higher effectivity in the transformation of pharmaceuticals (Gagnon et al., 2008; Kovalova et al., 2013).

The reaction with ozone and OH radicals will not result in a total mineralization of OMPs and can lead to the production of by-products (Huber et al., 2003). These transformation products of OMPs can be toxic and have thus negative effects on the aquatic environment (Richardson et al., 2007). Another disadvantage of AOPs is the relatively high energy consumption of several kwh/m^3 (Miklos et al., 2018).

1.3.2.2 Separation by membrane filtration

Membranes are physical barriers that either reject or reduce the flux of a given compound. The primary effect of membrane filtration is size exclusion and thus this process can be divided into four main groups depending on the size of particles they remain: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). MF and UF filtration are often called particular filtration because the solutes that are separated are often in the form of undissolved particles in sizes between 1 and 0.01 μm. NF and RO allow for the separation of smaller molecules. They can separate even molecular to ionic particles (0.01 – 0.0001 μm) and are therefore best suited for OMP rejection or desalination. Membrane filtration in drinking water and wastewater purification is pressure driven. Whereas MF and UF membranes are operated with relatively low pressure (0.5 – 10 bar), NF and RO require high pressure for operation (5 – 100 bar). (Madsen, 2014)

The rejection of OMPs by NF membranes is a mixture of steric hindrance and competitive diffusion, which makes the prediction of OMP rejection increasingly complicated. Accordingly, the effectivity of NF is dependent on the characteristics of the specific OMPs, the membrane and the wastewater composition (Madsen, 2014; Plakas and Karabelas, 2012).

Membrane filtration studies at real STPs revealed excellent removal (99%) of OMPs with RO in comparison to only low rejection (20%) with UF (Urtiaga et al., 2013). Other studies revealed that even so pores in UF or MF are in general too big to retain OMP, they are somehow efficient in OMP removal from wastewater. This can be explained rather by the biofilm formed on the membranes which 1) makes separation characteristics tighter related to OMPs and 2) enhances sorption of OMPs on the biofilm (Sahar et al., 2011).

For higher efficiency, membrane filtration processes are sometimes combined with each other (e. g. UF or MF with RO or NF) or with other treatment methods (e. g. with activated carbon, membrane bioreactors or AOPs) (Hartig et al., 2001; Madsen, 2014; Sahar et al., 2011).

1.3.2.3 Sorption by activated carbon

Initially mainly used in drinking water treatment, adsorption by activated carbon has great potential as post treatment step for the reduction of OMPs at STPs (Luo et al., 2014). Both powdered activated carbon (PAC) and granular activated carbon (GAC) have already been

used for this purpose. 44 studies dealing with the adsorption of OMPs on GAC on pilot and full scale were found through literature research conducted in 2017 by Benstoem et al., 2017.

The main removal mechanism of adsorption of OMPs from dilute aqueous solution on carbon is based on a complex interplay between non-electrostatic and electrostatic interactions and both interactions depend on the characteristics of the sorbent and the sorbate and the aqueous chemistry (Moreno-Castilla, 2004). The properties of a sorbate (OMP) which mainly predict the adsorption are the octanol-water distribution coefficient (Kow or Dow respectively in case of acid-based specifications), acid dissociation constant (pKa), molecular size, aromaticity and aliphaticity and the presence of special functional groups. The properties of a sorbent (activated carbon) that are influencing the adsorption are its surface area, pore size and texture, surface chemistry (functional groups, point of zero charge) and the mineral matter content (Kovalova et al., 2013; Moreno-Castilla, 2004). Even so there are various types of interactions, it was found, that compounds with logDow greater than two are getting completely removed from wastewater by activated carbon treatment (Kovalova et al., 2013). Relevant parameter in pilot or full scale studies testing the efficiency of activated carbon are the dosing of PAC, the amount of DOC in wastewater because it competes with OMPs and the contact time (Benstoem et al., 2017; Mailler et al., 2015). Moreover, it was found that the quality of activated carbon at different test sites was very heterogenic and most relevant for OMP removal (Benstoem et al., 2017). One big advantage of activated carbon treatment is that no by-products are generated (Suárez et al., 2008).

1.3.3 Constructed wetlands as natural post treatment step

Constructed wetlands (CWs) for the treatment of wastewater were first used in the late 1960s in Europe, North America and Australia, and used world-wide since the 1990s. CWs are engineered systems, designed and constructed to utilize the natural processes in a better controlled environment (Vymazal, 2011). Originally, they were designed for the removal of nutrients, in particular nitrogen and phosphorous, from municipal wastewater. They can be categorized according to hydrology (open water surface flow and subsurface flow), type of macrophytic growth (emergent, submergent, free-floating) and the flow path (horizontal and vertical) (Figure 1-3). These single-stage systems are either aerobic or anaerobic systems, with respective specialized microorganisms inducing pollutant removal. The different types of CWs are also combined with each other (i.e., hybrid or combined systems) to profit from both systems (Vymazal, 2011, 2007).

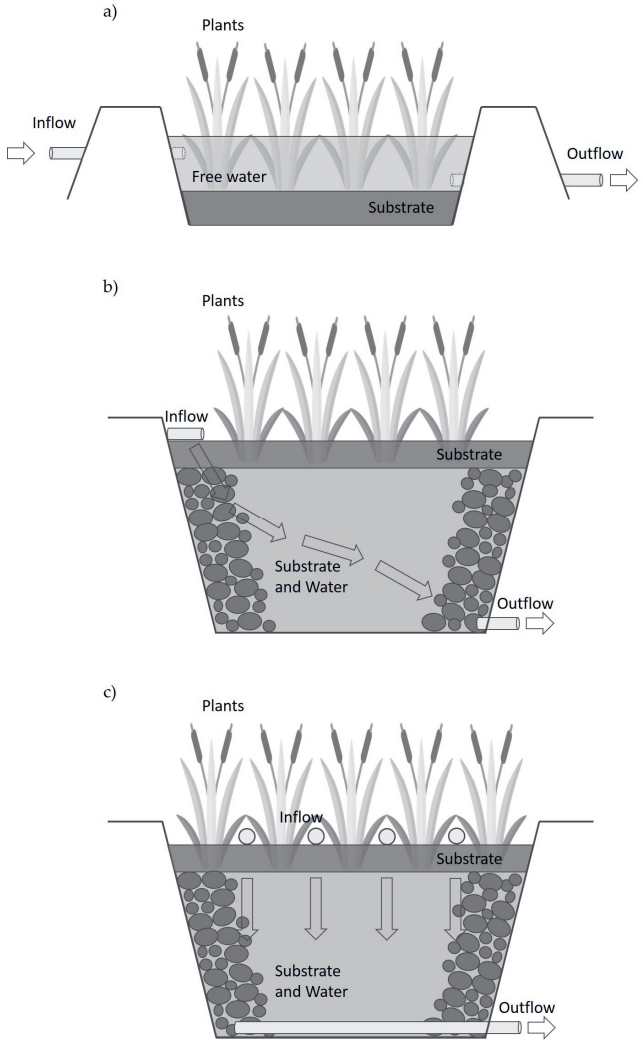


Figure 1-3: Examples of constructed wetlands for wastewater treatment: a) Surface free water CW, b) horizontal subsurface flow CW, c) vertical subsurface flow CW (adapted from Li et al., 2014)

Recently, CWs are getting increasing attention for their application in OMP removal from (pre-treated) wastewater and according to previous research in this field, CWs hold great potential as being used as an alternative post treatment system for STPs (Li et al., 2014; Matamoros et al., 2008; Verlicchi et al., 2013).

The main components responsible for OMP removal or reduction respectively are the substrate or support matrix, microorganisms and the vegetation. These three components are in fact interdependent of each other. The substrate interacts directly with the OMPs through sorption processes and is especially important for hardly biodegradable OMPs. In the past sand and gravel were the main materials used as substrate material. They were chosen according to their ability to provide adequate support for vegetation and prevent clogging. Nowadays and with the aim to remove OMPs from wastewater, research for alternative sorbent materials increased. Those materials include activated carbon, clay-based materials, zeolites and other siliceous materials as well as industrial and agricultural wastes and by-products. (Dordio and Carvalho, 2013)

Biodegradation of OMPs in the substrate can occur under either aerobic or anaerobic conditions involving the activity of various microorganisms (de Wilt et al., 2018; Li et al., 2014). However, the majority of OMPs are effectively biodegraded under aerobic conditions (Auvinen et al., 2017; Kahl et al., 2017). In addition, higher biodegradation in CWs was observed in summer season with higher temperatures (Kahl et al., 2017) and at structurally simple compounds with high water solubility and low sorption (see also 1.2.1) (Dordio and Carvalho, 2013).

Vegetation on the CWs can reduce OMPs directly via plant uptake. It was found that the common CW plant *phragmites australis* is able to degrade pharmaceuticals via phytodegradation (He et al., 2017; Sauvêtre and Schröder, 2015). Moreover, the vegetation enforces OMP reduction indirectly: in the rhizosphere larger microbial populations are present compared to the bulk soil, enhancing biodegrading activities in dense root systems. Moreover, the release of oxygen of some plants around their roots leads to the development of aerobic microorganisms, which are in general more effective in biodegradation processes (Dordio and Carvalho, 2013).

1.4 Content of the thesis

1.4.1 Research needs

As discussed above, water managers are currently confronted with new challenges: to measure and evaluate the occurrence of OMPs in surface waters and to identify adequate measures to reduce OMPs. In view of this initial situation, an application-oriented research approach is needed considering the following two issues:

- Ready-for-implementation measures to remove OMPs before entering surface waters.
- Data from field research to show the behaviour and fate of OMPs in the real environment.

Appropriate measures are essential in order to fulfil the requirements of the Water Framework Directive regarding OMPs in surface waters. The implementation of technical post treatment steps such as activated carbon treatment or ozonation seems very promising in certain areas such as Switzerland (Eggen et al., 2014). However, the implementation requires high expenses for construction, special equipment and consumables; and as the technologies are rather new, additional expert knowledge and maintenance during operation is necessary. Due to the relatively high capital and operational expenditures, technological post treatment steps are not applicable in every region (e.g. decentralised areas or non-industrialised countries). Moreover, energy demand for some technologies such as UV/H_2O_2 or membrane filtration is with > 0.5 kWh/m^3 treated water rather high (Joss et al., 2008; Miklos et al., 2018). At the same time, the current environmental developments such as climate change and a resulting increasing environmental awareness cries out for environmentally friendly technology solutions with reduced carbon footprints. Therefore, the challenge is to find measures with high removal efficiency and yet low environmental impact. Nature based solutions, like CWs, have not only the image, but also proven low environmental impact leading to an energy consumption of < 0.1 kWh/m^3 treated water (Brix, 1999).

Data on OMP behaviour and OMP removal as well as data on OMP concentration in the environment are present in literature (see sections above and Luo et al., 2014; Petrie et al., 2015). Nevertheless, a comprehensive understanding of OMPs fate during wastewater treatment in real treatment plants and within the environment is currently lacking (Petrie et al., 2015). One reason might be the shortage of number of field studies on OMPs compared to the number of studies conducted in laboratories. OMPs can react very sensitive to changes of anthropogenic or natural environmental conditions (Jaeger et al., 2019; Musolff et al., 2009), which makes the interpretation of field study results often difficult and indeterminate. In laboratory research, the factors influencing OMP behaviour can be controlled and thus results better related to initial factors. Disadvantage of such research is, that results might not be transferable to the real environment. For example, the removal of OMPs from emission pathways requires innovative techniques. These new techniques are usually first tested in laboratory scale before implemented in real environments. It is however crucial to know if results of theoretical and/or lab studies can be transferred to real river ecosystems.

Accordingly, it was shown that the efficiency of the treatment processes can decrease considerably when realistic water matrices are used instead of synthetic ones (Barbosa et al., 2016). Additionally, changing environmental conditions such as weather might influence the treatment performance. Therefore and because multiple factors can affect the efficiency of treatment measures, experiments should be performed as close as possible to the real conditions (Barbosa et al., 2016). This can be for example experiments performed with real wastewater or river water respectively, but also detecting approaches considering existing wastewater infrastructure and the anthropogenic and natural environmental conditions in the region where measures are needed. These conditions are specific for the respective on-site situation and results not necessarily transferable to different (climatic) regions. However, data on OMP treatment efficiency gained in the real environment might be of high significance for water managers who have to make decisions on implementing appropriate measures for OMP reduction. Consequently, research is needed with the approach to link between theoretical research, laboratory research and field research.

1.4.2 Objectives

This study aims in realising a holistic monitoring approach, considering the most important input pathways, as well as the fate of OMPs in rivers. This way, the "real" water quality situation in rives can be determined. The goal is to find out when and where highest emission peaks appear, how they develop in time and hence when OMP pollution pressure on the aquatic environment is highest. Another goal of this research is to elucidate how OMPs behave in rivers according to prevalent natural conditions (e. g. river ecosystem, weather and climate). To accomplish this approach, the study must be performed in a catchment with the possibility to monitor the whole river trajectory including emission entry points into the river. Therefore, a small river catchment with a limited number of well-known emission pathways is best suited for this research.

The results of this study are essential for water managers who have to decide if, when or where measures for the reduction of OMPs have to be implemented. Additionally, decisions have to be made of the kind of measure to be implemented. This leads to another important aim of this study: the determination of removal and fate of OMPs during a (cost-effective and sustainable) treatment measure, considering its likely implementation into a conventional STPs treatment train. The studied treatment measure, a retention soil filter, is novel in its idea as near natural treatment with improved sustainability and a reduced energy demand. The

goal is here to determine whether an alternative treatment technique delivers reduction rates comparable to those achieved by more technologically intensive post treatment steps at point sources, such as ozone or UV based AOP technologies. Results of this study will be taken into account as design recommendations for possible large scale implementation.

1.4.3 Outline of the thesis

The research is performed application-oriented with the possibility to integrate results directly into water management decisions. Therefore, it was conducted in cooperation with the water board Erftverband. The Erftverband is responsible for water management in the catchment area of the Erft, a part of the Rhine river catchment in North Rhine-Westphalia, Germany. The catchment of the Swist river, a tributary of the Erft, was chosen as study location. This system met the requirements for a small, well-defined catchment. The river Swist has a length of 44 km, its catchment is dominated by settlements with small to mid-sized industries (accordingly no large industry dominates pollutant emissions) and agricultural land. The local water management authority Erftverband aims in improving water quality of the Swist river by reducing pollutant emissions from point sources. This research fed into that approach, delivering a high level of science-to-impact quality, since results could be (and were) used in shaping the water management in practice.

First, a monitoring program for the investigation of emission pathways and the transport trajectory in the river was established. Second, a model was used to additionally examine behaviour of OMPs in the river. Third, retention soil filter for reducing OMP emissions from STP to river was tested. This measure should be implemented at full scale for one or more STPs feeding this river catchment if results were promising.

The outlet of the four STPs in the Swist river catchment were monitored over a period of four years to study the concentration variability of pharmaceuticals and the dependence of this variability on hydrology and other factors (Chapter 2). Subsequently, monitoring data of STP outlets and the river Swist were used to create a mass balance to study the fate of OMPs in the river. This research was complemented by the results of a water quality model, simulating the behaviour of OMPs in the Swist (Chapter 3).

A retention soil filter pilot plant was investigated for its ability to reduce OMP concentration from one large scale STP outlet. Retention soil filters are a special configuration of CWs, which were originally established to reduce nutrient input in riverine systems during storm events.

These are especially used widely in North-Rhine Westphalia, Germany. The retention soil filter has proven to demand low maintenance effort and energy costs and thus provide an environmentally friendly alternative treatment technique towards more technological treatments.

In this thesis two retention soil filters with conventional filter material and one with conventional filter material plus sorptive additives were investigated (Chapter 4). In addition, it was tested whether conventional retention soil filters are suitable for dual treatment application types: an STP outflow combined with a sewer outflow (the latter in case of storm water overflow situations) (Chapter 5).

In Chapter 6 the assets and drawbacks of application-oriented work with scientific context is discussed. Moreover, it is shown how the results of this work are implemented by the water board Erftverband, and how the results, conceptual findings and lessons learned can be translated to the wider context of OMP management and emission reductions in river basins.

Chapter 2
Pharmaceutical concentration variability at sewage treatment plant outlets dominated by hydrology and other factors

A modified version of this chapter has been published as

Brunsch, A.F., ter Laak, T.L., Rijnaarts, H., Christoffels, E., 2018. Pharmaceutical concentration variability at sewage treatment plant outlets dominated by hydrology and other factors. Environmental Pollution 235, 615–624.

Abstract

A study was conducted in which the effluent at four small to medium sized sewage treatment plants (STPs) in North Rhine-Westphalia, Germany was monitored for three pharmaceutical compounds (carbamazepine, diclofenac, metoprolol) over a period of four years. Grab sampling and auto sampling campaigns were accomplished with respect to various weather conditions in the catchment area. Flow volumes and hydraulic retention times (HRTs) from various sampling dates which provide information on processes causing emission changes were additionally taken into account. Monitoring results showed that concentration scattering in the effluent is related to HRT in the sewage treatment plants. Dilution effects following rain events in the catchment area were analysed for the three investigated substances. Short-term emission changes explained by dilution only could be well determined by the mathematical relation between discharge and concentration, and for carbamazepine to be solely determined by the dilution effects at all HRTs. For metoprolol, a clear decrease in concentrations was observed at HRTs above 80 hours, and a significant contribution of biodegradation was supported by independent biodegradation tests. For three out of the four STPs, a decrease in concentrations of diclofenac was observed at hydraulic retention times above 80 hours, indicating removal, whereas the relationship between concentration and HRT of the other STP could be explained by dilution only. The study shows that emissions can vary with weather conditions, hampering the assessment of emissions and estimation of concentrations in surface waters from generic removal rates only. Furthermore, it illustrates the importance of HRT of rather stable substances in wastewater treatment.

2.1 Introduction

Pharmaceutical compounds found in the aquatic environment enter surface waters mainly through municipal sewage treatment plant (STP) effluents (Daughton and Ternes, 1999; Ternes Thomas A., 1998). Concentrations of pharmaceuticals in STP effluents appear to be rather variable within one STP and when comparing miscellaneous STPs (Luo et al., 2014 and references therein). Changes in water quality of the effluent can have effects on ecosystems that are exposed to the substances. Varying loads from STP outlets are reflected in varying loads and concentrations measured in watercourses (Comoretto and Chiron, 2005). So, emissions into watercourses and thus the concentrations and loads at the outlets of the STPs must be considered when assessing the aquatic environment. Furthermore, for water managers it is important to know when highest emission peaks appear. This knowledge will help to find right measures for reducing micropollutant loads in STP effluents and surface waters respectively.

So far, pharmaceutical loads in rivers and lakes have been rather successfully predicted through modelling with consumption and sales data (Alder et al., 2010; Götz et al., 2012; Marx et al., 2015; Oosterhuis et al., 2013; ter Laak et al., 2014, 2010). However, predicting concentrations and their short-term dynamics appear to be more complicated because they depend on specific events and conditions. Besides varying discharges due to daily or weekly patterns of water usage of connected inhabitants and industries, hydrological conditions in the STP catchment area can lead to abrupt changes in quantity of STP inflow. Changing weather conditions with dry and rainy periods are known to influence micropollutant concentrations measured at STPs as well as in watercourses. Substance concentrations can vary depending on their sources and emission routes. For example, Bollmann et al. (2014) demonstrated that certain biocides are found in higher concentrations at STPs during rainy weather, stating that biocides were washed off by wind driven rain. Contrarily, concentrations of compounds such as pharmaceuticals that are typically in (domestic) wastewater at relatively constant loads are reduced by rain due to dilution. Several studies illustrated this dilution effect as well as additional emission through untreated sewage by combined sewer overflows (Baker and Kasprzyk-Hordern, 2013; Benotti and Brownawell, 2007; Musolff et al., 2009; Phillips et al., 2012). For pharmaceutical compounds that are well degraded in STPs, such as ibuprofen, combined sewer overflows are a more relevant emission pathway into watercourses than the effluents of STPs (Buser et al., 1999).

Changing hydrological conditions are influencing the rain water/wastewater ratio in the sewer system and also hydraulic retention times (HRT) of STPs and can thus affect

micropollutant removal (Gerbersdorf et al., 2015; Ternes Thomas A., 1998). In addition, removal can be affected by biological or chemical degradation or sorption to sludge processes (Joss et al., 2005). In many practical situations, it has remained unclear, by which factors the short term pharamceutical variability in STP effluents is dominated. Knowing these factors is as a base to develop an adequate monitoring strategy, and either develop and implement additional treatment steps or to improve STP operations.

The aim of this study is therefore, to quantify short term fluctuations in pharmaceutical concentrations from STP effluents by relating emissions of selected compounds to meteorological conditons and to conceptualize the relation between concentration and STP specific operational characteristics. It was intended to capture the broadest range that operational parameters can have on effluent concentrations. With the aim to conduct a comprehensive study, the research was carried out at four real size STPs, all within the catchment of one small river in the western part of Germany, over a period of four years. These STPs have comparable treatment steps, but vary in their design and connected sewer systems. Detailed investigations on real size STPs require an intense monitoring strategy, but are of special interest for water and wastewater manangers. The current study uses intensive monitoring of three pharmaceutical model compounds – carbamazepine, diclofenac and metoprolol – under various hydrological conditions to understand and conceptualize observed trends in data in effluent concentration as a function of HRT (Figure 2-1).

2.2 Material and methods

2.2.1 The discharge-concentration relation

The amount of precipitation as well as the length of a rain event in the catchment area of combined sewer systems largely determines the amount of inflow to the STP. The hydraulic retention time (HRT) was selected as a parameter which accounts for dilution effects in STPs. It is directly related to the volumetric flow rate (Q) of the inflow, given the fact that the volume of water in treatment plants (V) is set at a defined level. This relationship can be expressed as follows:

Equation 2-1: $$\mathrm{HRT} = \frac{\mathrm{V}}{\mathrm{Q}} \quad [\mathrm{h}]$$

for a steady inflow, with tank volume V in m³ and the flow rate Q in m³/h. A minimum daily inflow level (base flow level) is assumed to be the more or less constant and continuous

sewage flow coming from households and industry. With increasing precipitation, Q will increase and the fraction of rain water grows. The maximum inflow is defined by the maximum capacity of the individual sewage treatment plant. Inflow which contains both base flow and rain water will be referred to as storm flow in the following (see supplementary information (SI) for details on hydraulic design of German STPs).

When Q exceeds the maximum capacity of the treatment plant, water will be either stored in storm water retention tanks or directly emitted via storm water overflows. At that point STPs are not the only emission pathway of pharmaceuticals into rivers. In this study, only emissions from STPs and the associated effects of changing HRT will be considered as one reason for varying concentrations measured at STP outlets.

Concentrations are inversely related to the HRT if we assume constant loads of pharmaceuticals stemming from households and no significant or stable removal during treatment. The concentration in the STP outflow ($C_{STP\ outflow}$ in µg/L) is defined by Q and follows this relation:

Equation 2-2*:*

$$C_{STP\ outflow} = \frac{\text{Inh. spec. Load} * \text{Connected Inhabitants}}{Q} \quad [\mu g/L]$$

With the inhabitant specific load in µg/h/inh. and Q, the discharge at the STP in L/h.

Inhabitant specific loads were obtained from either literature or from measurements.

Maximum and minimum HRT are defined by operational conditions and the design of a treatment plant. Maximum HRT occurs at minimum inflow and minimum HRT occurs at maximum allowable inflow. Within this window a linear relation between concentration and HRT is expected (Figure 2-1). For substances which are partly removed within the treatment process, i.e. by biodegradation, sorption, photodegradation or volatilisation, deviations from this linear relation can be expected, since higher retention times might lead to higher removal rates (Johnson et al., 2005; Oosterhuis et al., 2013).

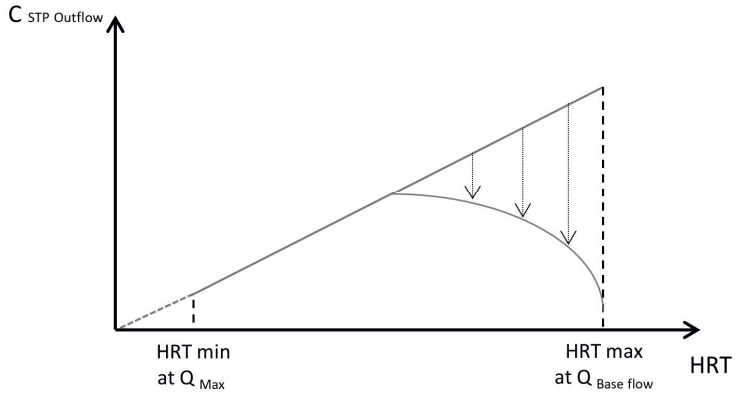


Figure 2-1: Concept for the relation between concentrations of pharmaceutical compounds at STP outflows and hydraulic retention times at STPs. The straight solid line indicates dilution effect under ideal mixing conditions and without degradation. The downward bended line with arrows indicates deviations due to degradation.

2.2.2 *Sewage treatment plants (STPs)*

The investigated STPs are located within the catchment area of the Swist river, a tributary of the Erft river and part of the greater Rhine river catchment in North Rhine-Westphalia, Germany. The catchment area has a size of 289 km². STP Flerzheim (STP F) is with 50,000 inhabitant equivalents (IE) the largest STP in the catchment, followed by STP Rheinbach (STP R), STP Miel (STP M) and STP Heimerzheim (STP H) (More information on STPs in Table 2-1).

Table 2-1: Characteristics of the investigated STPs.

	STP F	**STP R**	**STP M**	**STP H**
Inhabitant equivalents	50,000	27,000	11,000	10,700
Tank volume [m³]	25,174	12,350	4,890	4,736
Connected inhabitants	35,441	19,679	10,058	7,672
Separate sewer system [%]	36%	13%	13%	69%
Annual wastewater [m³]	4,308,241	1,963,308	817,989	523,347
Sludge retention time [d]	30 – 45	25 – 35	20 - 30	20 - 30
$Q_{Base\ flow}$ [L/s]	78	37	18	12
Q_{Max} [L/s]	400	200	110	107

STP R discharges into the Wallbach brook, a tributary of the Swist. The three other STPs discharge directly into the Swist river. Treatment processes of the four STPs include physical procedures as sieving, sedimentation, separation and in case of STPs F and R additional filtration downstream the secondary clarifier; biological procedures are nitrogen and phosphorous removal in aeration tanks and an additional trickling filter at STP H; chemical procedures are flocculation and phosphorous precipitation (Erftverband, 2014). More information on effluent quality demands of the STPs is present in SI. The amount of discharge was measured continuously at the inlet and outlet of the STPs with an ultrasonic level meter (inflow STP H and R) or a magnetic inductive flow meter (all other locations). Base flow (as shown in Table 2-1) was calculated as an average flow value of selected dry weather days within 2011 – 2015 where at least five days ahead no precipitation was measured within the STP catchment. The sewers connected to the STPs can be constructed as either combined to carry both wastewater and rain water or separate, with discrete transport of wastewater and rain water. In the latter case, the separate rain water sewer pipe is not connected to the STP but leads first to a storm water basin for hydraulic retention before discharge into the watercourse. In view of the different sewer systems, with larger percentage of separate sewer system at STPs F and H, dilution effects on the STP inflow following rain events are expected to be less intense in these two STPs. Moreover, a lower amount of rain water entering the STPs will be reflected in higher HRTs.

Data from a total of seven rain gauges distributed within the Swist catchment were taken to calculate precipitation within the specific STP catchments and compared to STP inflow volumes.

2.2.3 Sampling

Samples were taken at the outlets of the four STPs in the research catchment in 16 batches between September 2011 and August 2015. The sampling methods employed were grab sampling (13 batches) and auto sampling (3 batches).

Grab sampling was always performed around noon (between 10 AM and 2:30 PM), when inflow volumes regularly are highest during dry weather (data from 12 individual diurnal data sets per STP). This was done in order to reduce variation due to diurnal patterns of water consumption. Sampling dates throughout the year with a high variability of weather conditions were chosen. Grab sampling was the method of choice for a large part of sampling

batches because this method provides high flexibility in choosing sampling times to capture the broadest possible range of precipitation conditions.

Additionally, time proportional auto sampling campaigns were performed in series of 12 x 2-hour composite samples (6 minutes time intervals between each sub-sample). Campaigns during dry weather, a light rain event (7 mm within 3 days) and a heavy rain event (60 mm within one day; see Figure 2-2) were performed. Thereby, daily fluctuations of emissions as well as the evolution of concentrations during rain events could be monitored.

All samples collected were filled in 1 L brown glass bottles. Samples were all filtrated and acidified not later than 24 hours after sampling and kept cool in darkness at 4 °C. The conserved samples were analysed not longer than 7 days after sampling.

2.2.4 *Investigated substances & analytics*

The outcomes of the conducted study should be applicable for a broad range of pharmaceuticals and other organic micropollutants but for the detailed research three model compounds were chosen. The anti-epileptic drug carbamazepine, the anti-inflammatory drug diclofenac and the beta blocker metoprolol were best suited because they were detected in all samples above limit of quantification and all three of them are relatively well studied in their behaviour in lab scale treatment plants.

Here, the behaviour of these pharmaceuticals at the outflow of real scale treatment plants is tested and compared to results of other studies.

Analytics were performed with HPLC/DAD (carbamazepine until April 2012), LC/MS-MS (carbamazepine and metoprolol since May 2012) and GC/MS (diclofenac). More information on the methods can be found in SI. Carbamazepine and diclofenac were analysed in all 16 sampling batches. Metoprolol was analysed in 9 out of 13 grab sampling batches and all three auto sampling batches.

2.2.5 *Reliability of data*

A number of uncertainties can adversely affect results in monitoring studies. Grab sampling, for example, was found to come with higher uncertainties than time or flow proportional sampling with high sampling frequency (Ort et al., 2010). Moreover, seasonal variation in

loads of pharmaceuticals have been previously detected in the effluent of STPs as well as in receiving waters (Golovko et al., 2014; Musolff et al., 2009; ter Laak et al., 2010; Vieno et al., 2005). These variations can coincide with (seasonal) variation in consumption. This is for example observed for macrolide antibiotics that are prescribed more often in winter than in summer (Marx et al., 2015). Additionally, in summer, higher temperatures will intensify biological transformation as well as higher solar radiation will increase both direct and indirect photo degradation (Golovko et al., 2014; Musolff et al., 2009; ter Laak et al., 2010; Vieno et al., 2005). This leads to higher removal rates during wastewater treatment and higher transformation in surface waters in summer and hence a decrease in substance loads.

In this study uncertainty is mitigated by selection of three suitable pharmaceutical compounds, carbamazepine, metoprolol and diclofenac. For epileptic drugs and beta blockers no seasonal variation due to consumption behaviour is expected; although it was found out that anti-inflammatory drugs can be influenced by seasonality (Camacho-Muñoz et al., 2014). Hourly variation of pharmaceutical compounds at STP inflow can be neglected since it is known that loads sampled at STP outlets are composed of inlet loads of several preceding days (Majewsky et al., 2013). Furthermore, carbamazepine was compared to other substances in grab sampling studies and was found to occur with lower deviations (Ort et al., 2010). It is referred to as a good trace compound because of its persistence during STP treatment and in the aquatic environment (Clara et al., 2004). In this study it was used as an indicator as well as to investigate dilution effects. Also, its behaviour was compared to that of metoprolol and diclofenac.

Data of two inflow sampling campaigns, which are independent of the outflow samples, are given in SI. Differences of inflow and outflow concentrations are discussed in section 2.3.2. However, this study aims in elaborating concentration ranges of pharmaceuticals of only outflow data rather than determining a detailed mass balance. Mismatch of sampled inflow and outflow can lead to falsely interpreted mass balances (Majewsky et al., 2013). Accordingly, in- and outflow data can only be compared best, when sampling time at outflows is sampling time at inflows plus hydraulic retention time. This is a challenging approach for real size STPs since inflow volumes and HRT underlie great variability and rapid changes. In order to make a reliable statement only with outflow sampling, a large number of samples (n = 196) has been taken over a period of four years. This way, irregularities can be balanced out by the quantity of data.

2.2.6 *Hydraulic retention time (HRT) and proportion of storm flow in STPs*

In order to determine the hydraulic retention time, the time span equivalent to the time of filling the tanks of the STPs was calculated. At every sampling time, the water volume at the effluent was taken into account. In order to determine the filling time of the tanks, the water volumes measured at STP outlets were cumulated, starting at the time of sampling and adding the volumes of the past hours until the tank volume of the specific STP was reached. The loss of surplus activated sludge (< 5% of total volume) was not considered. Minor deviations are hence possible.

The following equation was applied for calculating HRT.

Equation 2-3:

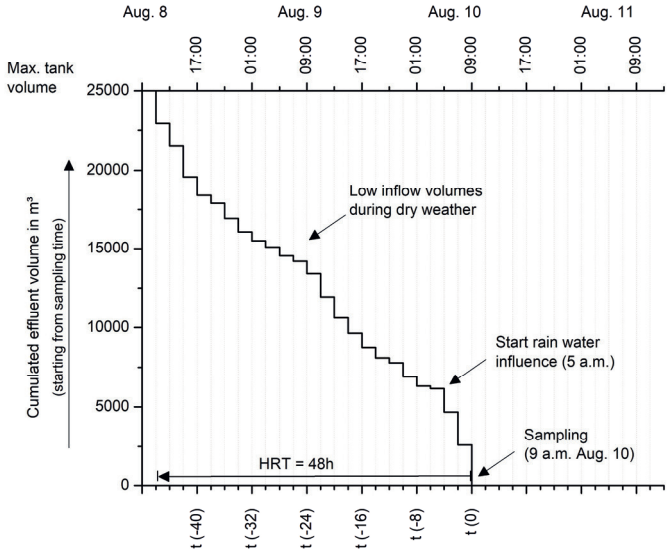
$$\sum_{i=0}^{n} V_{t_i} = V_{STP}\ [m^3]$$

$$HRT = n * \Delta t\ \ [h]$$

n represents the number of flow volume measurements. The time interval Δt between measurements is considered to be of equal length. Each measurement took place at a time t_i, and V_{ti} [m^3] being the measured corresponding value. V_{t0} is the volume at sampling time t_0. V_{STP} is the tank volume of the individual STP. An example of this calculation can be found in SI (Table SI 2-3).

With this method, the actual hydraulic retention time for the continuously measured discharge Q was calculated for each sample. Calculated HRTs range from 12 hours to 127 hours. Figure 2-2 shows exemplarily the cumulated flow volumes and calculated HRT for STP F after a heavy rain event started. At 5 AM on August 10, 2015 an abrupt change in discharge is observed. This is the point in time where maximum inflow to the STP starts. Rain water influenced discharge following the heavy rain event enters the STP. The rain water enters the STP with a certain delay after the start of the rain event. This delay depends on precipitation intensity as well as the size and the characteristics of the sewer system connected to the STP. Residence times during rain in the sewer network of the investigated STPs range from two to four hours.

a



b

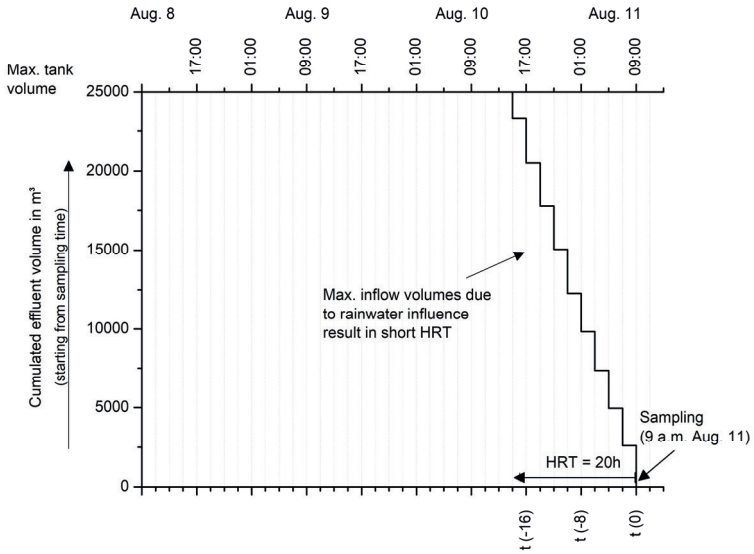


Figure 2-2: Graphical demonstration of HRT calculation by summing up STP effluent volumes. The cumulative flow volumes and calculated HRTs are shown for the example of two STP outflow samples collected at STP F at 9 AM August 10 (a) and 9 AM August 11 (b). The HRT of sample (a) is 48 hours due to both dry and rain weather influence; the HRT of sample (b) is 20 hours due to the heavy rainfall starting at 5 AM August 10.

For each point in time and for each sample during the course of a rain event, the proportion of storm flow (wastewater diluted with rain water) can be calculated (Equation 2-4). Figure SI 2-1 illustrates the ratio of storm flow in STP F starting at 5 AM on August 9 when inflow increased due to a rain event.

Equation 2-4: $$\text{Storm flow in the STP} = \frac{\sum_{i=1}^{n} V_{CS_i}}{V_{STP}} * 100 \quad [\%]$$

V_{CS_1} [m³] is the discharge at time t_1 when storm flow starts to enter the STP and V_{STP} [m³] is the volume of the STP. n represents the point in time when a 100% ratio of storm flow is reached.

2.3 Results and discussion

2.3.1 System sensitivity: the delayed response of STP outflow concentration on rainfall induced changes in inflow volumes

Real size STPs consisting of several different tanks cannot be characterised as neither a completely stirred tank reactor nor a plug flow component. For the concept shown in Figure 2-1 an instantaneous and complete mixing of dry weather base flow and combined flow of rain water and wastewater is assumed, but in reality, this mixing is not instantaneous. The incomplete mixing of storm flow with base flow within the STP results in temporal deviations from the linear relation (Figure 2-1) of HRT and concentrations. So, it was tested how fast water quality at the effluent reacts on rainfall induced changes in inflow volumes.

Shortly (< 2 hours) after the start of the rain event, the amount of inflow to the STPs increases (Figure 2-2) and HRTs drop (Equation 2-1) since the flow times in the sewer network are short and the storm water flow is five to ten times higher than the base flow.

Detailed studies involving results of the time proportional effluent monitoring during rain events had been performed to get a better insight on mixing conditions at the investigated STPs. Three parameters were considered: $C_{STP\ outflow}$; HRT; and the proportion of storm flow in the STP tanks. Figure 2-3, Figure SI 2-2 and Figure SI 2-3 show the result of the 24-h time proportional monitoring campaign during light and heavy rain weather and the incomplete mixing effect with the example of STPs F, R and H. At the light rain event, storm flow was entering the STPs continuously with the effect that, within the sampling day, HRT was

dropping from 89 to 47 hours at STP R, from 111 to 70 hours at STP H and from 70 to 40 hours at STP F. Concentrations were stable when storm flow first entered the STP inflow. At around 40 - 50% storm flow contribution in the tanks, concentrations started to drop. At the heavy rain monitoring campaign sampling started when there was already storm flow in the STP tanks. Behaviour of carbamazepine and diclofenac concentrations were in line with the first monitoring campaign, they started decreasing when there was around 50% storm flow in the tanks. Metoprolol concentrations were decreasing along with the HRT. Moreover, it was determined that also with 100% storm flow in the STP, concentrations were dropping. The ratio between base flow and rain water is then still decreasing. Reason for this are combined sewer overflows, where storm flow is discharged directly into the rivers. However, despite the sampling campaigns took place in late autumn (08-09.12.2015) and summer (10-11.08.2015), concentrations only seem to follow dilution. Concentration changes due to seasonality were not explicitly determined. Comparable results were found for all four STPs.

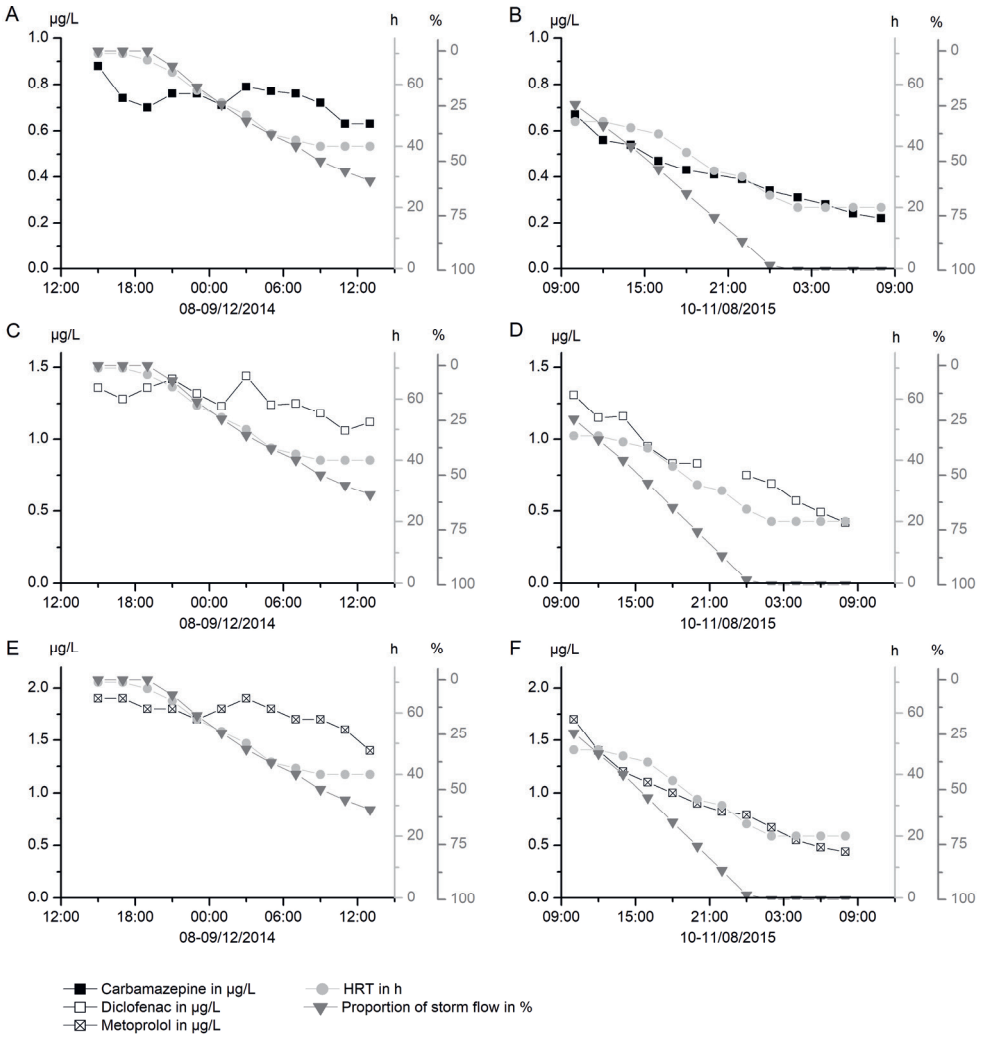


Figure 2-3: Substance effluent concentration, HRT and the proportion of storm flow in the STP tanks taken from the 24-hour sampling campaigns. Each point represents the result of a 2-hour composite sample. Shown are the examples of carbamazepine measured at light rain weather (A) and heavy rain weather (B), diclofenac measured at light rain (C) and heavy rain weather (D) as well as the example of metoprolol at light rain (E) and heavy rain weather (F) exemplarily for STP F. Figures for the STPs H and R can be found in SI.

The analysis on system sensitivity revealed that neither instantaneous mixing in the STP tanks nor plug flow can explain the hydraulic behaviour in the investigated STPs. When storm flow enters the STPs, it is not instantaneously and completely mixed with the "dry weather

sewage" present in the plant, especially when they consist of several tanks. Due to the abrupt increase in inflow volume, the dry weather sewage is pushed out of the STP faster, temporally resulting in stable "dry weather" concentrations with "rain weather" discharge, and therefore a higher load. It is assumed that the mixing process of sewage with different pollution compositions depends on the design of the STPs. However, at the four investigated STPs dilution is the factor influencing concentration scattering at the outlet when there is more than 50% storm flow in the tanks.

These findings enable the further development of the discharge-concentration concept (Figure 2-1). The incomplete mixing effect can temporally lead to deviation from the dilution and removal lines (the adapted graph can be found in SI). This should be considered when samples are taken at the beginning of rain events.

2.3.2 Variability of pharmaceutical compounds at STP outlets

Carbamazepine, diclofenac and metoprolol were detected above limits of quantification in all samples. Average inhabitant specific loads for the three investigated pharmaceuticals (Table SI 2-4) were highest at STP M with 0.42 mg/inh./d carbamazepine, 0.89 mg/inh./d diclofenac and 1.09 mg/inh./d metoprolol. Lowest average inhabitant specific loads were detected at STP R (carbamazepine: 0.25 mg/inh./d, diclofenac: 0.54 mg/inh./d, metoprolol: 0.68 mg/inh./d). These differences between the STPs did not exceed a factor of 1.7 for all compounds indicating that consumption was rather similar in the catchment of the different STPs.

Standard deviations calculated for each STP and compound of the measured concentrations of all samples range from 33 to 55% (Table SI 2-4). This result shows that there is considerable short-term variability in emissions at STP effluents. However, the variation in concentration of the 24-hour dry weather sampling campaign was much smaller (< 9% for the three pharmaceuticals at STPs H, M and F and 13 and 18% for diclofenac and metoprolol concentrations at STP R). This shows that diurnal variation is not a relevant factor affecting the variability of effluent concentrations. It was assumed that concentration varies according to rainfall and thus according to HRT, as explained in section 2.2.1, so concentrations were plotted against HRT (Figure 2-4, Table 2-2).

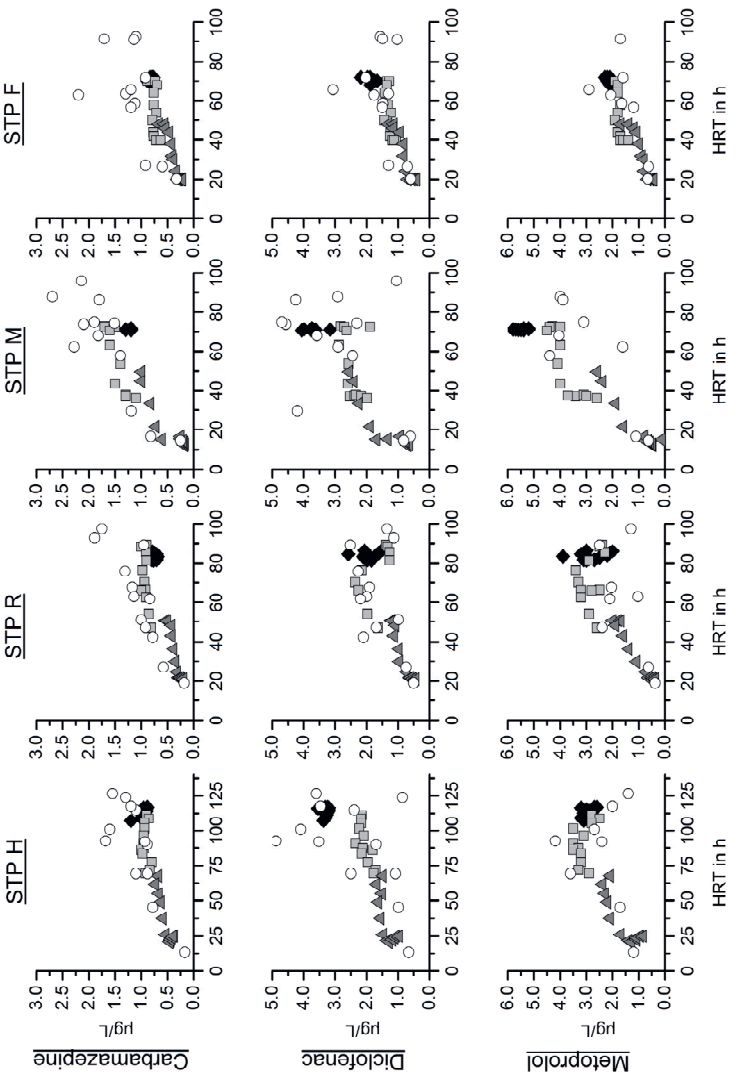


Figure 2-4: Concentrations and hydraulic retention times of 16 sampling campaigns at four sewage treatment plant outlets. 13 grab sampling campaigns and three 24-hours auto sampling campaigns (with 12 results per campaign from 12 x 2-hour composite samples).

Table 2-2: Statistical parameters of sampling results of carbamazepine (showed in). Calculated slopes are based on the linear regression of concentrations and HRT for each substance and STP.

	STP H	**STP R**	**STP M**	**STP F**
Coefficient of determination R^2	0.61	0.50	0.68	0.45
Slope of the HRT - c regression line and confidence intervals 95%-level (regression through origin)	0.010 (0.009 – 0.011)	0.012 (0.011 – 0.013)	0.022 (0.021 – 0.024)	0.014 (0.013 – 0.015)

All three substances have their minimum concentrations at shortest HRTs (12 – 20 hours) (Table SI 2-4). Minimum concentrations of carbamazepine were around 0.2 µg/L at all four STPs. Minimum concentrations for diclofenac ranged from 0.4 µg/L (STP F) to 0.7 µg/L (STP H) and for metoprolol from 0.1 µg/L (STP M) to 0.9 µg/L (STP H). Concentration ranges of the individual substances measured at STPs H, R and F are similar; concentrations at STP M are higher (see results in Figure 2-4).

Concentrations of the independent inflow studies at base flow conditions (dry weather) (Table SI 2-1) were compared to outflow concentrations from the 24 h dry weather sampling campaign (Table SI 2-2). The average ratio of out- and inflow concentrations for carbamazepine were between 0.8 (STP R) and 1.5 (STP M), leading to the assumption that carbamazepine was not removed within the STPs. The ratios for diclofenac were 0.5 for STP F and 0.6 for all other STPs. Outflow/inflow ratios for metoprolol were 0.3 at STP H, 0.6 at STPs R and F as well as 1.1 at STP M.

Moreover, an analysis of variance (ANOVA) was conducted to test if the three pharmaceuticals show a different behaviour to HRT (SPSS Inc. Version 16.0). According to the results (p-value = 0.066) it can be assumed that the interaction between the pharmaceuticals and their related HRT is not significant (more details can be found in SI).

Considering carbamazepine as a stable trace compound (section 2.2.5) and the results of the ANOVA test as well as the independent inflow- outflow studies, it is assumed that in contrast to carbamazepine, diclofenac and metoprolol are partly removed in the STPs. This is also supported by literature and will be discussed in more detail below.

2.3.3 *Variability explained by dilution dominated concentrations – carbamazepine*

Carbamazepine seems to follow the discharge concentration relation (Figure 2-1, Equation 2-1, Equation 2-2). With increasing HRT, concentrations rise. The correlation was found to be significant ($p < 0.001$). The slope of the regression line of c as function of HRT ranges from 0.010 (STP H) to 0.022 (STP M) (Table 2-2). Concentrations appear to increase linearly with HRT. Maximum concentrations appear at high HRTs. The linear correlation between HRT and concentrations explained 45 – 68% of the variation.

Dilution with rain water seems to be the main factor influencing variability in carbamazepine concentrations. There was no indication on removal by transformation at higher HRT (Table 2-2, Figure 2-4). This conclusion is supported by ~100% recovery of carbamazepine observed in the inflow/outflow assessment discussed in the previous paragraph. Furthermore, it agrees with other studies, where carbamazepine was found to be a very stable, non-sorptive and non-volatile compound in conventional STPs (Kosjek et al., 2009; Suarez et al., 2010; Sui et al., 2011). Clara et al. (2004) determined that it is neither biologically degraded nor sorbed to particles, independent of solid retention times. Only at extremely long HRT of 78 days, 73% removal in full scale conventional STPs were detected by Leclercq et al. (2009). Such high HRTs are exceptional for conventional STPs. Common removal rates of STPs are below 10% (Zhang et al., 2008).

2.3.4 *Variability explained by dilution and non-hydrology dominated concentrations – diclofenac & metoprolol*

Diclofenac effluent concentrations increase with HRT. However, at HRTs above 60-80 h concentrations start to scatter and deviate downwards from the straight line that assumes sole dilution (Equation 2-1, Equation 2-2). Especially at STP R a decrease in concentration is observed beyond 80 h HRT (Figure 2-5).

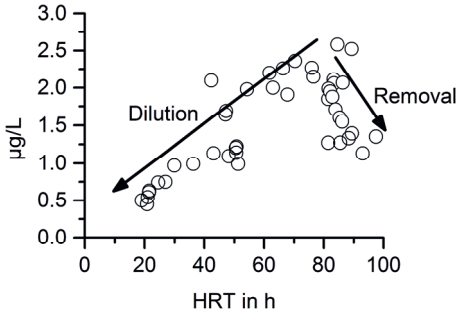


Figure 2-5: Diclofenac concentrations in relation to HRT at STP R.

At STP M and F only three grab samples were taken with an HRT above 80 h. The concentrations of these samples were all lower than the maximum concentrations, but there were insufficient data to show a clear trend. For STP H no decrease in concentration of diclofenac was observed at high HRTs, despite the fact that HRTs at this plant extended to 124 hours. Maximum concentrations of metoprolol (2.9 µg/L, 5.8 µg/L, 3.9 µg/L, 4.2 µg/L) were measured at HRTs of 66 (STP F), 71 (STP M), 83 (STP R) and 93 (STP H) hours. When the HRT is increased beyond those values, concentrations declined. At STPs H and R this decrease was most prominent. At STPs M and F there were too little data at long HRTs to clearly identify the decline. The findings indicate that the relation between the HRT and diclofenac and metoprolol concentration respectively is not solely determined by dilution, but also other, non-hydrology dominated processes are relevant at higher HRTs. A relation of HRT and pharmaceutical removal was already discussed in previous studies where lower removal rates were linked to higher flow rates and thus lower HRT following rain events (Maurer et al., 2007; Ternes Thomas A., 1998). This is in agreement with other literature sources where it was determined that both substances are partially removed in conventional STPs: Suarez et al. (2010) stated that diclofenac is removed via biological transformation in an aerobic reactor and Vieno and Sillanpää described a positive effect of nitrifying biomass (Vieno and Sillanpää, 2014). Metoprolol is biologically degradable under aerobic conditions as well, with a positive effect of higher biomass concentrations (Rubirola et al., 2014; Wick et al., 2009). Due to its positive charge, sorption was determined as significant in STPs (Torresi et al., 2017). Conversely, other studies showed that sorption to activated sludge was a minor component of the removal for both metoprolol and diclofenac (Maurer et al., 2007; Vieno and Sillanpää,

2014; Wick et al., 2009). Tests in the laboratory with original wastewater from the bioactive aeration tanks of the four STPs revealed that removal of diclofenac and metoprolol was increasing at artificially extended HRT. For more details see SI. Consequently, the decrease of concentration at high HRT is most likely a result of biotransformation. As discussed in section 2.2.5, seasonal changing external parameters such as temperature and solar radiation can affect removal capacities for pharmaceutical compounds. Higher temperatures might have a positive effect on biodegradation of metoprolol and diclofenac (Sui et al., 2011; Vieno et al., 2005) and often coincide with higher light intensity that affect photo degradation of diclofenac (Salgado et al., 2013). However, this was not determined in our study.

In conclusion, it can be stated that concentrations of diclofenac and metoprolol behave very similar at STP R and are suspected to behave similar at STPs M and F. At STP H their concentrations act differently: metoprolol shows a clear reduction with higher HRT, while diclofenac concentrations at STP H seem to be determined only by dilution (Figure 2-1).

In addition, within this study it was possible to assess the contribution of non-hydrology dominated processes and hydrology dominated processes by evaluating the concentrations of the pharmaceuticals in the STP effluent at different HRTs. Known biodegradable compounds show a reduced concentration with increasing retention times due to biological transformation while concentrations of recalcitrant compounds are only driven by dilution. This is backed up by literature studies and additional laboratory tests.

To a large extent, varying removal rates can thus be explained by different hydraulic retention times in relation to biomass in the STPs. In accordance with that knowledge, an optimization of treatment systems towards increased removal through transformation can help to reduce emissions.

2.3.5 Calculating hydrology-dominated concentration ranges

The aim was to illustrate, that concentrations for pharmaceutical compounds for individual STPs can be determined on the basis of the concentration – HRT concept (section 2.2.1) with basic STP operational data as well as literature data on inhabitant specific loads. It was intended to only describe the dilution effect and exclude other processes. The variability of concentrations to be expected at STP outlets is of special interest for water managers. Based on Equation 2-2, hydrology dominated concentrations are expected to appear in the range of:

Equation 2-5:

$$\frac{\text{Inh. spec. Load} * \text{Connected Inhabitants}}{Q_{max}} < C > \frac{\text{Inh. spec. Load} * \text{Connected Inhabitants}}{Q_{\text{Base flow}}}$$

According to Equation 2-1 and Equation 2-2 concentrations for individual HRTs can be expressed as

Equation 2-6:

$$C = \frac{\text{Inh. spec. Load} * \text{Connected Inhabitants}}{V_{STP}} * \text{HRT} \quad [\mu g/L]$$

For a comparison of measured and calculated concentrations, inhabitant specific loads (0.26, 0.49 and 0.58 mg/inh./d for carbamazepine, diclofenac and metoprolol, respectively) were taken from a study from (Götz et al., 2012). They calculated loads from monitoring data of 13 STPs in North Rhine-Westphalia, Germany. These data seemed to be especially relevant because the data collection was done within the same district as in the current study.

illustrates a cross validation with the results of the calculated predicted concentrations and the monitoring data. Concentrations were calculated for STP M, one of the two small STPs and for STP F, the largest of the investigated STPs. Diclofenac and metoprolol concentrations obtained with HRTs longer than 80 hours were excluded from this analysis, as removal was observed beyond that HRT (section 2.3.4) and the data could bias simulation results. Furthermore, three extreme outliers were excluded. They were identified because of their large Mahalanobis distance of greater 14 (SPSS Inc. Version 16.0) and excluded because the sample was influenced by the incomplete mixing effect (section 2.3.1).

Coefficients of determination ranged from 0.60 to 0.83, with the best results for diclofenac and metoprolol (Figure 2-6). The average ratio of observed to calculated values ranged from 0.90 (metoprolol, STP F) to 1.30 (diclofenac and metoprolol, STP M). Ratios closest to 1 were obtained for carbamazepine with 0.94 (STP F) and 1.08 (STP M). In general, the outcomes of the two STPs as well as the three different pharmaceuticals are comparable. Effluent concentrations can thus be determined very accurately with literature data on inhabitant specific loads. One reason for such good results is the comprehensiveness of the current study and the ability to identify outliers and which samples were affected by non-hydrology dominated processes (e.g. biotransformation). In that way, uncertainties could be kept at a minimum and results fitted very well with inhabitant specific loads from literature.

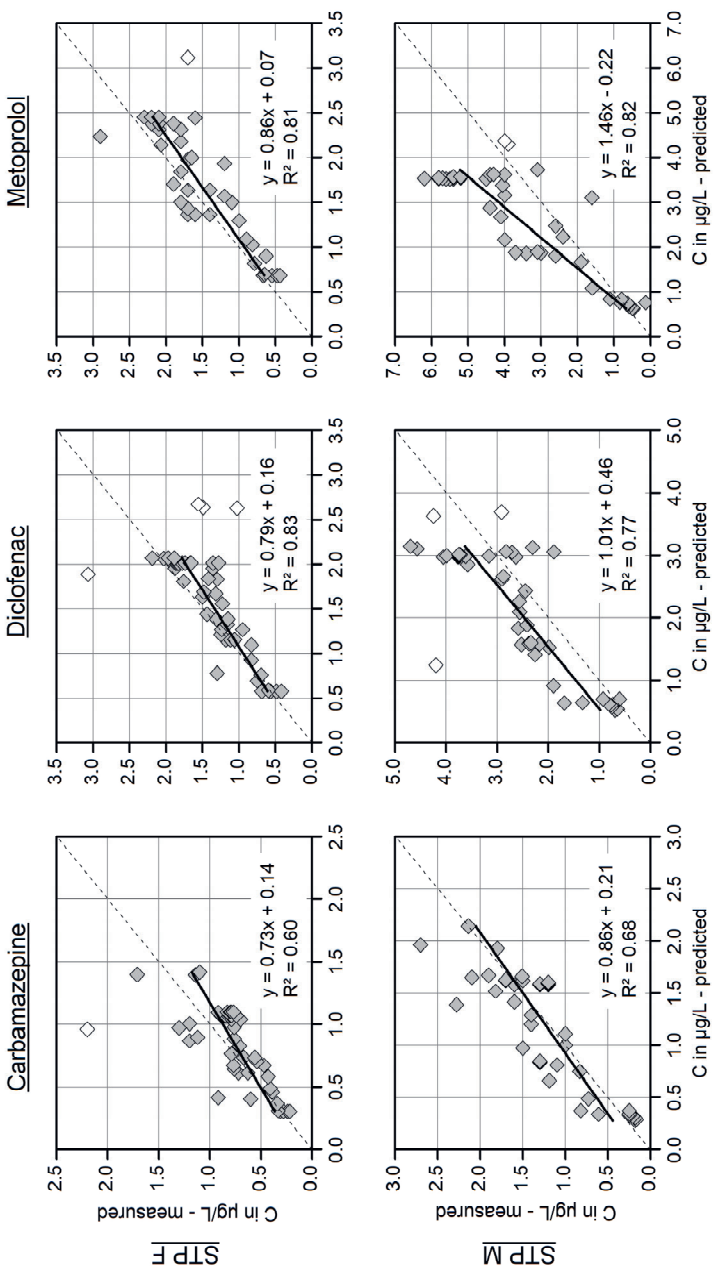


Figure 2-6: Cross validation of the predicted concentrations for the pharmaceuticals carbamazepine, diclofenac and metoprolol at STPs M and F. The equation for the linear fits as well as the coefficient of determination is shown in each graph.

2.3.6 Practical applicability of the results

Three effects could be determined which mainly influence concentration scattering in correspondence with varying HRTs:

- Dilution effect concentrations are linearly related to HRT.
- Non-dilution dominated effects (e. g. biotransformation) observed for diclofenac and metoprolol at HRTs greater than 80 hours.
- Incomplete mixing effect at the beginning of rain events which masks the dilution effect, when concentrations remain stable with decreasing HRTs.

The results of the study and therefore the concept (Figure 2-1) can be transferred to other wastewater micropollutants with steady input patterns to STPs, such as other pharmaceuticals as well as corrosion inhibitors and artificial sweeteners. Concentrations of such compounds that are stable and mobile are determined by dilution. Concentrations of less stable mobile compounds tend to be higher at short or intermediate HRTs (Phillips et al., 2012). Consequently, these substances are of greater relevance with (heavy) rain. This means that a broader range of compounds is likely to be detected under short or intermediate HRTs. The incomplete mixing effect applies to all substances and can lead to temporal deviation from the dilution dominated and both dilution and removal dominated patterns.

Results of the study can be valuable in reducing monitoring efforts. It was demonstrated that, with only little effort, dilution-induced concentration ranges can be reliably determined with inhabitant specific loads obtained from literature. Moreover, the research might be a benefit in interpreting monitoring data. With the knowledge gained through this study differences in monitoring results can be explained by varying rain intensities and thus by dilution or non-hydrology dominated processes within the STPs.

Combined sewer systems are found out to be very vulnerable regarding short-term emission changes because they have great influence on HRTs in treatment plants and removal rates of substances. Especially for small rivers with low emission buffering capacity and high wastewater load, it is important to know when highest concentrations of pharmaceuticals appear. With this knowledge, targeted measures can be applied. In separate sewer systems, rain water and wastewater is carried separately. HRTs are therefore more stable and rain is not affecting emissions.

2.4 Conclusion

- Concentrations of the investigated wastewater micropollutants diclofenac, carbamazepine and metoprolol, measured at the outlet of four STPs, are dependent on hydraulic retention times and hence hydrological conditions (precipitation) within the STP catchment.
- Three effects of varying HRTs on concentrations observed at STP outlets could be determined: Hydrology dominated processes (dilution), non-hydrology dominated processes (biotransformation) and incomplete mixing in the STP tanks. Whereas dilution could be determined for all three substances, removal at high HRTs was clearly found for metoprolol and partially for diclofenac. The incomplete mixing effect applies for all pollutants within STP tanks.
- The three effects have been integrated to a general concept which allows to transfer it to other STPs. These effects should be taken into account for hydrological modelling studies or interpretation of monitoring data.
- Large sampling campaigns require resources and time, and can hence be further optimized by integrating literature data on inhabitant specific loads.

Acknowledgement

The study presented has been funded in the framework of following projects: M³ (LIFE07 ENV/L/000540) "Application of integrated modelling and monitoring approaches for river basin management evaluation", financed by LIFE+ programme of the European Commission. The project TAPES (330J) “Transnational Action Program on Emerging Substances” has received European Regional Development Funding through INTERREG IV B. AquaNES “Demonstrating synergies in combined natural and engineered processes for water treatment systems” has received funding from the European Union´s Horizon 2020 programme (689450). The authors are grateful for the financial support of the projects. Thanks also to: F.-M. Mertens, J. Wunderlich-Pfeiffer, R. Krump, O. Altunay, M. Trimborn, S. Kindgen-Gronwald, M. Reif, A. Ahring, the staff at the STPs, D. Reyes Lastiri, C. Dobre and B. Smallberg.

Supplementary information for Chapter 2

The discharge-concentration relation

In the investigated conventional STPs, maximum inflow is five to ten times the base flow level. This base flow level is lower than average dry weather discharge, which is the basis for the dimensioning of German STP tanks. According to spreadsheet 198 of the German Association for Water, Wastewater and Waste (DWA) (ATV-DVWK, 2003) the maximum inflow of combined sewer (rainwater, domestic and industrial wastewater) is calculated as two times average dry weather discharge plus extraneous water. The latter is unwanted infiltration water.

When Q exceeds the maximum capacity of the treatment plant, water will be either stored in storm water retention tanks or directly emitted via storm water overflows. This direct discharge into rivers is strictly regulated and only possible at a few locations of the sewer system (ATV-DVWK, 1992).

There are high demands on the treatment ability of STPs in Germany. Therefore, the STPs are designed to ensure that even in high loading cases, at maximum inflow volumes and short HRT organic carbon, nutrients and pollutants can be sufficiently reduced. The performance of the aeration tanks is determined in the DWA spreadsheet 131. According to that, for example nitrate concentration at the secondary clarifier effluent should be 60 to 80% of the control value (DWA, 2016).

The emissions of individual STPs into surface waters are defined by the German Federal Water Act (WHG). For the four investigated STPs, control values between 1 and 4 mg/L for NH_4-N and between 0.4 and 1.2 mg/L for P_{total} have to be met beside others.

Inflow studies

Inflow studies were accomplished in September and November (Table SI 2-1). Samples were taken as time proportional composite samples over a period of 24 hours. Start of sampling was Monday 00:00 AM. Sampling in September was accomplished under dry weather inflow (base flow); sampling in November was accomplished during storm flow.

Inflow concentrations of these two campaigns were compared with outflow concentrations of the four year sampling period (Table SI 2-2).

Table SI 2-1: Three pharmaceutical compounds measured at four STP inlets in September and November

		Daily Flow/ Base flow	Carbamazepine	Diclofenac	Metoprolol
			µg/L	µg/L	µg/L
November	**STP H**	2.4	0.73	2.80	3.00
	STP R	3.1	0.22	1.70	1.10
	STP M	3.3	0.37	2.00	1.50
	STP F	3.2	0.29	2.10	0.95
September	**STP H**	0.8	1.10	5.70	9.90
	STP R	1.1	0.91	3.50	5.00
	STP M	0.9	0.82	6.50	5.20
	STP F	1.3	0.68	3.50	3.40

Table SI 2-2: Ratio of outflow concentrations from the 24 h dry weather campaign (12 individual samples per STP) and inflow concentrations measured in September at dry weather conditions

		STP H	STP R	STP M	STP F
Carbamazepine	**Max**	1.1	0.9	1.6	1.3
	Min	0.8	0.8	1.5	1.1
	Average	0.9	0.8	1.5	1.2
Diclofenac	**Max**	0.6	0.7	0.6	0.6
	Min	0.6	0.4	0.5	0.5
	Average	0.6	0.6	0.6	0.5
Metoprolol	**Max**	0.3	0.8	1.2	0.7
	Min	0.3	0.4	1.0	0.6
	Average	0.3	0.6	1.1	0.6

Analytics

HPLC/DAD – Carbamazepine – until April 2012

Analysis was performed after solid phase extraction by HPLC/DAD following the norm DIN EN ISO 15913: 2003-05. Reference standard was purchased from Sigma-Aldrich Co. LLC. Calibration curve was generated using the processed standard samples with the external standard calibration method. The samples were analysed by the Shimadzu LC 10 AD

followed by the diode-array detector SPD-M 10 A (Shimadzu Corporation). Limit of quantification is 50 ng/L.

LC/MS-MS – Carbamazepine. Metoprolol – since May 2012

Metoprolol and carbamazepine were analysed using the Agilent HPLC 1260 followed by the Agilent Triple-Quadrupol 6460 (Agilent Technologies Inc.). After adding the internal standards, the samples can be injected directly into the HPLC. Reference standards were purchased from Dr. Ehrenstorfer GmbH (metoprolol) and Sigma-Aldrich Co. LLC. (carbamazepine). Limits of quantification: metoprolol: 50 ng/L, carbamazepine: 100 ng/L.

GC/MS – Diclofenac

Analysis of diclofenac was performed after solid phase extraction and derivatisation by GC-MS following the norm DIN EN ISO 15913: 2003-05. The overall method was calibrated using internal standards with each measurement sequence. Reference standard was purchased from Sigma-Aldrich Co. LLC. Samples were analysed by the TRACE GC/TSQ8000 (Thermo Fisher Scientific Inc.). Limit of quantification is 50 ng/L.

Analytical uncertainties

Uncertainties were calculated at the laboratory internally through control samples as well as through ring tests. With the latter procedure, the performance of different laboratories was compared to each other. For the in-house control the relative standard uncertainty for each presented pharmaceutical compound measured with HPLC/DAD, LC/MS-MS and GC/MS 90 was less or equal 5%. The overall combined standard uncertainty including in-house control and the ring test was less than 20% for carbamazepine, metoprolol and diclofenac measured with LC/MS-MS and GC-MS. No ring test results for carbamazepine measured with the HPLC/DAD method were present. Accordingly, the results of the in-house control tests and/or the ring test show that analytical data presented are reliable.

Hydraulic retention time (HRT) and proportion of storm flow in STPs

Table SI 2-3: Fictitious example of HRT calculation.

	Time t_i	Volume V_i at time t_i	Cumulated volume V_{t0+i}	
		m^3/h	m^3	
	01:00 - 01:59	360		Total tank volume STP =
	02:00 - 02:59	432		V_{STP} = 2500 m^3
	03:00 - 03:59	396	2502	
	04:00 - 04:59	378	2106	
	05:00 - 05:59	540	1728	
	06:00 - 06:59	360	1188	
sampling time: 8:59 →	07:00 - 07:59	396	828	$Vt_0 + V_{t0-1}$
	08:00 - 08:59	432	432	Vt_0
	09:00 - 09:59	378		

From 03:00 till 08:59 water in the STP tanks was completely exchanged; HRT is therefore 6 hours.

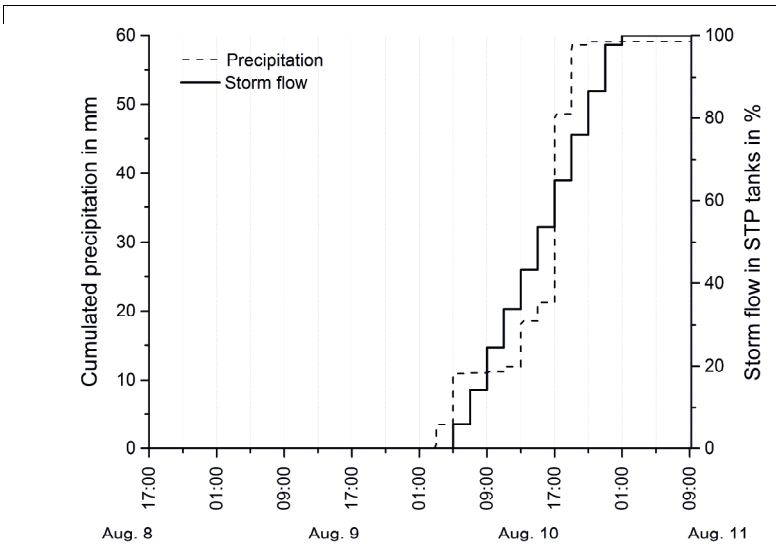


Figure SI 2-1: Amount of precipitation as an average value of data from three gauges in the STP catchment (dashed line). Proportion of storm flow (wastewater diluted with rainwater) to dry weather flow (wastewater undiluted) within the STP (solid line). Due to the rainfall, the amount of storm flow in the STPs is increasing from 5 AM August 10 until 1 AM August 11, when storm flow in the STPs reached 100%. By this time, HRTs are at their minimum.

System sensitivity: the delayed response of STP outflow concentration on rainfall induced changes in inflow volumes

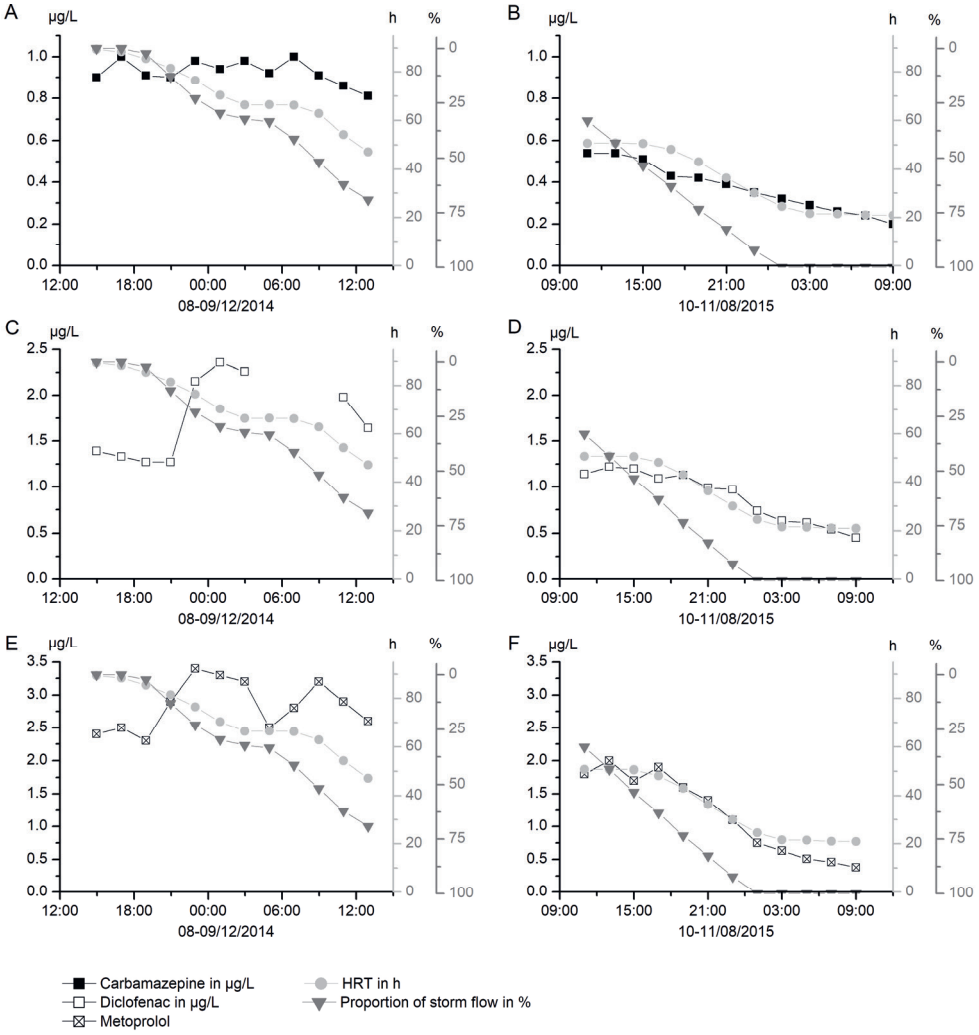


Figure SI 2-2: Substance effluent concentration, HRT and the proportion of storm flow in the STP tanks taken from the 24-hour sampling campaigns. Each point represents the result of a 2-hour composite sample. Shown are the examples of carbamazepine measured at light rain weather (A) and heavy rain weather (B), diclofenac measured at light rain (C) and heavy rain weather (D) as well as the example of metoprolol at light rain (E) and heavy rain weather (F) for STP R.

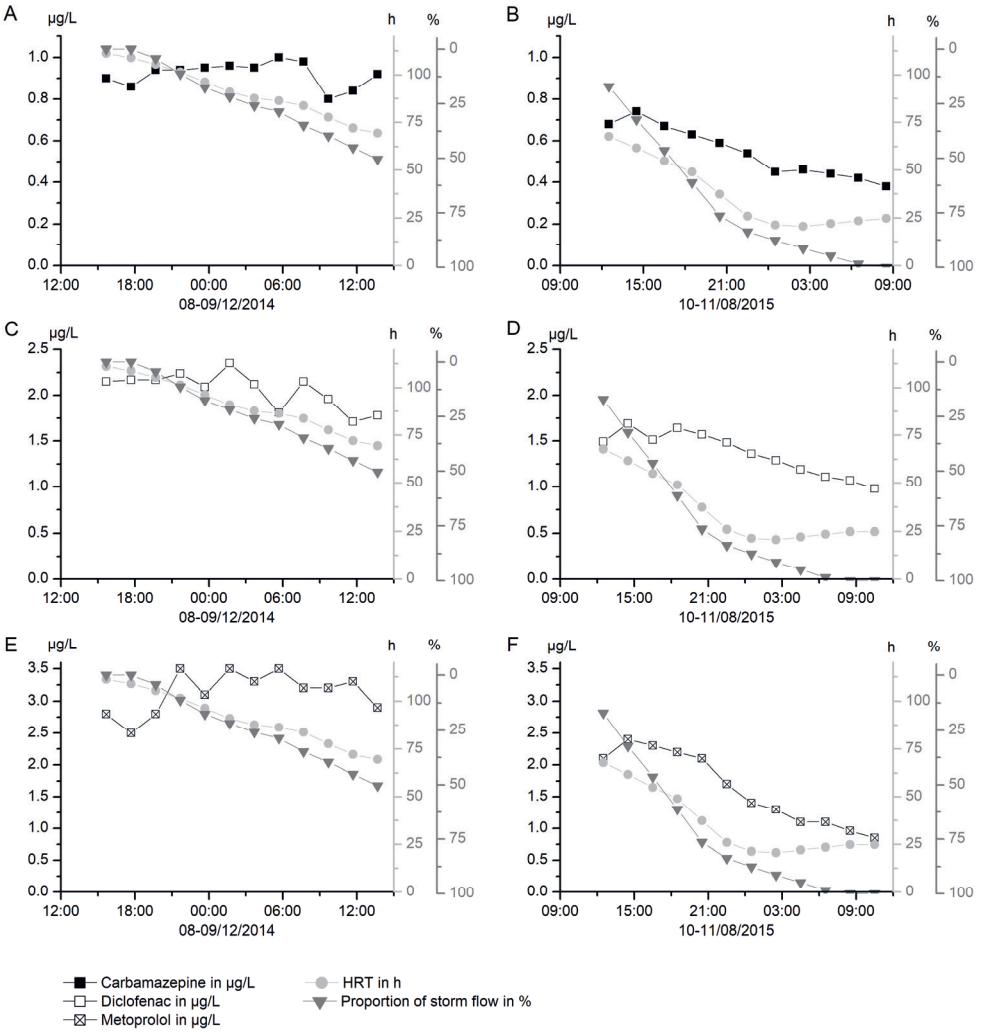


Figure SI 2-3: Substance effluent concentration, HRT and the proportion of storm flow in the STP tanks taken from the 24-hour sampling campaigns. Each point represents the result of a 2-hour composite sample. Shown are the examples of carbamazepine measured at light rain weather (A) and heavy rain weather (B), diclofenac measured at light rain (C) and heavy rain weather (D) as well as the example of metoprolol at light rain (E) and heavy rain weather (F) for STP H.

No graph for system sensitivity is presented for STP M for the following reason: during the heavy rain event, the effluent of STP M was influenced by surface water. Due to the high

water level in the receiving river, surface water from the river was entering the STP outlet. Therefore, some data points had to be excluded from the study.

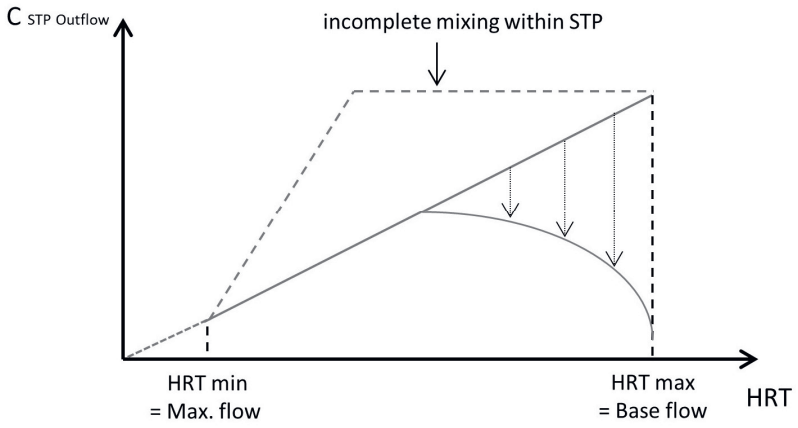


Figure SI 2-4: HRT - concentration concept including the incomplete mixing effect. The straight solid line indicates dilution effect under ideal mixing conditions and without degradation. The dashed line above indicates deviations due to non-ideal mixing in the STP tanks. The downward bended line with arrows indicates deviations due to degradation.

Variability of pharmaceutical compounds at STP outlets

Table SI 2-4: Parameters for the three pharmaceutical compounds based on all sampling campaigns

			STP H	STP R	STP M	STP F
Carbamazepine	**n**		49	49	48	49
	Max	µg/L	1.68	1.89	2.70	2.20
	Min	µg/L	0.17	0.18	0.17	0.22
	Median	µg/L	0.90	0.78	1.25	0.77
	Average	µg/L	0.87	0.77	1.21	0.77
	Standard deviation	%	35	46	48	47
	Average inh. spec. load	mg/inh./day	0.27	0.25	0.42	0.37
Diclofenac	**n**		49	46	48	48
	Max	µg/L	4.88	2.58	4.70	3.07
	Min	µg/L	0.66	0.45	0.61	0.42
	Median	µg/L	2.15	1.58	2.58	1.32
	Average	µg/L	2.30	1.53	2.63	1.37
	Standard deviation	%	43	38	44	37
	Average inh. spec. load	mg/inh./day	0.65	0.54	0.89	0.65
Metoprolol	**n**		45	45	44	45
	Max	µg/L	4.19	3.90	6.20	2.90
	Min	µg/L	0.85	0.38	0.13	0.44
	Median	µg/L	2.70	2.30	3.95	1.70
	Average	µg/L	2.51	2.12	3.37	1.57
	Standard deviation	%	33	45	55	39
	Average inh. spec. load	mg/inh./day	0.86	0.68	1.09	0.77

The inhabitant specific loads presented in Table SI 2-4 were higher during rainy weather compared to dry weather conditions. A reason for this might be:

- The incomplete mixing effect: at the beginning of rain events, flow volumes in the STPs are increasing. At the same time higher dry weather concentrations at the outlet are pushed out of the STP in higher quantity, resulting in temporarily higher loads.
- The removal of compounds at higher HRT.
- First flush effects in the beginning of rain events: the release of solid deposits and sorbed pollutants in the sewer system can be the reason for higher STP inflow concentrations.

Table SI 2-5: Result of the analysis of variance. Dependent variable is the logarithmic concentration. F is the value of the test statistic (F-value); df are the degrees of freedom.

Between-Subjects Factors

		Value Label	N
Pharmaceutical	1	Carbamazepine	195
	2	Diclofenac	191
	3	Metoprolol	179

Tests of Between-Subjects Effects

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Pharmaceutical * HRT	1	2	0.538	3	0.066
Error	110	559	0.197		
Total	348	565			
Corrected Total	291	564			

Laboratory test on biological degradation

A test was conducted to verify the results of the real scale STP monitoring campaigns and the statement that biological transformation in STPs is reliant on higher HRTs. Therefore, samples were taken at the effluent of activated sludge tanks of STPs H, R, M and F. Samples were brought to the laboratory where one part was filtrated and analysed immediately and a second part was autoclaved at 120 °C for 15 minutes in order to prevent biological activity. The third untreated part as well as the autoclaved samples were filled in glass bottles, aerated and kept dark for the duration of the experiment at a temperature of 19 °C. Oxygen content in the biological active samples was around 6 – 7 mg/L and in the autoclaved, biological inactive samples 9 mg/L. Samples were analysed after two days and after seven days.

Results (Figure SI 2-5) reveal best removal rates for metoprolol in the activated sludge samples after seven days of aeration. That leads to the assumption that conditions in the lab were very good for metoprolol removal. Removal is as well suggested for diclofenac, since after two and seven days the concentrations were lower than in the fresh and in the autoclaved samples. Reason for the difference of metoprolol and diclofenac removal is presumably the experiment

conditions which had influence on the biological activity in the sludge samples. Samples in the experiment were kept dark and have been aerated continuously, which is in contrast to large scale activated sludge tanks. Concentrations of carbamazepine were lower in the samples after two days and seven days in the artificial aeration tank but as well in the autoclaved samples. This indicates no biological removal of carbamazepine.

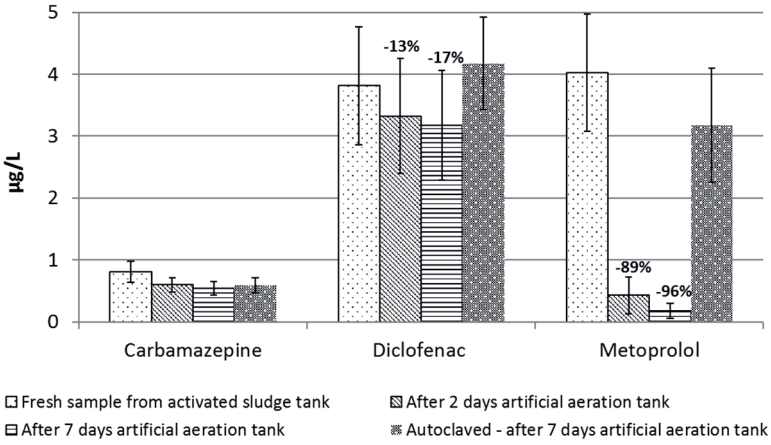


Figure SI 2-5: Average values, standard deviation bars and removal rates of samples from activated sludge tanks.

Chapter 3

In situ removal of four organic micropollutants in a small river determined by monitoring and modelling

A modified version of this chapter has been published as

Brunsch, A.F., Langenhoff, A.A.M., Rijnaarts. H.H.M., Ahring. A., ter Laak. T.L., 2019. In situ removal of four organic micropollutants in a small river determined by monitoring and modelling. Environmental Pollution 252. 758–766.

Abstract

Organic micropollutants (OMPs) are widely detected in surface waters. So far, the removal processes of these compounds *in situ* in river systems are not yet totally revealed. In this study, a combined monitoring and modelling approach was applied to determine the behaviour of 1H-benzotriazole, carbamazepine, diclofenac and galaxolide in a small river system. Sewage treatment plant effluents and the receiving waters of the river Swist were monitored in 9 dry weather sampling campaigns (precipitation < 1 mm on the sampling day itself and < 5 mm total precipitation two days before the sampling) during different seasons over a period of three years. With the results gained through monitoring, mass balances have been calculated to assess fate in the river. With the DWA Water Quality Model, OMP concentrations in the river were successfully simulated with OMP characteristics gained through literature studies. No removal was determined for 1H-benzotriazole and carbamazepine, whereas diclofenac showed removal that coincided with light intensity. Moreover, modelling based on light sensitivity of diclofenac also suggested relevant degradation at natural light conditions. These two approaches suggest removal by photodegradation. The highest removal in the river was detected for galaxolide, presumably due to volatilisation, sorption and biodegradation. Furthermore, short-term concentration variability in the river was determined, showing that daily concentration patterns are influenced by dynamics of sewage treatment plant effluent volumes and removal processes in the river.

3.1 Introduction

Organic micropollutants (OMPs) stemming from domestic or industrial wastewater are only partially removed in conventional sewage treatment plants (STPs) and are emitted into surface waters (Daughton and Ternes, 1999; Ternes, 2007) where they are widely detected (Luo et al., 2014). An extensive exposure assessment of OMPs in rivers is therefore necessary. This implies not only monitoring emission and input pathways, but also behaviour and fate of OMPs in surface waters. Compound specific physico-chemical properties influence the behaviour of OMPs in the water cycle and have to be taken into account together with the characteristics of the studied environment.

Behaviour of OMPs is often investigated in laboratory studies and/or water treatment processes (Luo et al., 2014; Onesios et al., 2009; Zhang et al., 2008). There are only limited studies testing and evaluating environmental behaviour *in situ*, since sampling, controlling and accounting for varying conditions is difficult or not feasible. A mass balance approach according to the Lagrangian sampling scheme (correct timing of sampling suited to fully encompass a mass of water along its way downstream) to determine OMP behaviour in rivers was introduced by Schwientek et al. (2016). They calculated net removal of OMPs with samples taken over 24 hours on two representative river locations. A reactive tracer test along a small river in Sweden revealed the *in situ* removal of ibuprofen and clofibric acid (Kunkel and Radke, 2011). Moreover, removal of pharmaceutical compounds (ibuprofen, ketoprofen, naproxen, diclofenac), musk fragrances (tonalide, galaxolide) and caffeine concentration along a river have already been determined (Bendz et al., 2005; Musolff et al., 2009; Osorio et al., 2012; Poiger et al., 2003), but the various removal mechanisms potentially responsible for this are not easy to reveal.

Both emission data and environmental monitoring data do not give an exhaustive picture of the OMP situation in the river as there are data-gaps on temporal and spatial scales. Models can be applied to fill these data-gaps. By combining modelling with dedicated sampling and monitoring strategies under specified conditions and with a high temporal resolution enables to unravel *in situ* fate and behaviour of OMPs in surface waters, thereby giving the highest confidence in exposure assessment to enable better risk assessment (Johnson et al., 2008).

A number of Geographic Referenced Point Source Water Quality Models (e.g. PhATE, GREAT-ER, and LF2000-WQX) predict concentrations of "down the drain chemicals" in catchments, starting from the moment they enter the sewage pipe until they reach the tidal limit, or the end of the catchment, as defined by the model (Johnson et al., 2008). LF2000-WQX

and GREAT-ER predict effluent concentrations according to public consumption data. Removal in STPs or rivers is predicted by removal constants and/or first order removal kinetics, which can be applied to the resulting chemical concentrations. OMP concentrations (μg/L) or loads (g/d) for e. g. propranolol and diclofenac with LF2000-WQX and various beta blockers as well as sulfamethoxazole with GREAT-ER could be well described (Alder et al., 2010; Archundia et al., 2018; Johnson et al., 2007).

The DWA Water Quality Model is specialised in predicting concentrations in rivers by distinguishing various removal processes. In contrast to GREAT-ER or LF2000-WQX, STP effluent concentrations are not predicted but given as input information by the user from e. g. monitoring results. Behaviour of OMPs is predicted in consideration of interaction processes with various conditions such as global radiation, shadowing, temperature or concentrations of suspended solids, each influencing removal processes. Under incorporation of these processes, it is possible to predict the evolution of concentration for OMPs over defined time windows. Simulation time steps can be chosen individually by the user. For example, the DWA Water Quality Model has been used to successfully simulate short term behaviour of bentazone and diclofenac in the river Main in Germany (Bach et al., 2010; Letzel et al., 2009). However, larger rivers exhibit a complex set of tributaries, with various point sources and diffuse sources that complicate quantitative *in situ* assessment of OMP behaviour. Hence, smaller rivers, with defined system monitoring transects and a limited set of (point) sources offer a better model for such *in situ* assessments. Therefore, we selected the river Swist, with a 44 km transect and 4 discharging STPs, in this study. Its mouth ends in the river Erft, a tributary of the river Rhine in western part of Germany.

The aim of this study is to determine concentration variability of four OMPs (1H-benzotriazole, galaxolide, carbamazepine and diclofenac) in a small river catchment with a high temporal resolution and to identify the processes responsible for their persistence or *in situ* removal in the river. We used two approaches: first, a monitoring study was performed, covering OMP input sources such as STP effluent discharge points and the monitoring OMP concentrations and loads in the river itself. Second, a water quality model was used with a removal part that distinguishes between the different potential processes. By a mass balance analysis approach, we aim to quantify *in situ* persistence and removal and relate these to relevant environmental conditions (such as solar radiation and temperature) controlling these processes. This unique detailed monitoring and modelling effort in a real river system enables better understanding of mechanisms for selected substances as well as model evaluation.

3.2 Materials and methods

3.2.1 Sampling

Samples were taken at the STP effluent and the water quality station at the river Swist close to the mouth (Figure 3-1). The four STPs are described in Brunsch et al. (2018b). All samples were taken by autosamplers that produced composite samples for the individual sampling duration. 1-hour or 2-hour composite samples over one whole day (b, c) were taken for daily concentration variability assessment. With the aim to calculate daily mass balances for a broad variety of dry weather scenarios, 24-h composite samples were taken (a and c) in addition to the composite samples of shorter time windows (b and c). In more detail, the following samplings were taken:

a. Seven samplings were performed in 2016/2017, three in winter and four in summer with 24-hour composite samples, taken time proportionally at the STPs and the river (5 minutes time intervals between each sub-sample). Sampling start was 12 AM for both the STP effluent and the river.

b. One sampling was performed on March 20/21, 2015 with 2-hour composite samples, taken time proportionally over a period of 24-hours at the STPs (6 minutes time intervals between each sub-sample) and correspondingly 1-hour composite samples taken at the river (12 minutes time intervals between each sub-sample). Sampling at STPs started at 10 AM and at the river at 2 PM to cover the average hydraulic retention at dry weather time between the sampling points.

c. One additional sampling was performed on August 07/08, 2018 with 24-hour composite samples, taken time proportionally at the STPs (5 minutes time intervals between each sub-sample) and 2-hour composite samples taken correspondingly at the river (5 minutes time intervals between each sub-sample). Here, sampling at the STPs started at 2 PM and at the river at 4 PM.

Samples were stored in the autosampler in glass vessels and refilled in brown glass bottles before transport and stored at 4°C until analysis (within seven days).

Sampling was accomplished during dry weather conditions with precipitation < 1 mm on the sampling day itself and < 5 mm total precipitation two days before the sampling. Hence, no direct influence of storm water e.g. through combined sewer overflows, storm water basin effluent or surface runoff is expected in the river.

The more detailed sampling on March 20/21, 2015 represents a typical dry weather scenario, with < 1 mm precipitation on 16 days before sampling and maximum air temperatures of 20 °C. The campaign on August 07/08, 2018 represents an exceptional dry weather scenario with maximum air temperatures of 38 °C and a dry river bed upstream STP F due to the high temperatures and the lack of precipitation during the summer of 2018 (sum of precipitation in June and July 2018 was 32 mm which is 4.4 times lower than the average of the last 12 years for this period). The conditions found during that sampling session, are similar to situations found in arid regions such as southern Europe. However, in the sampling night on August 8, there was an approximately 2-hour rain event with around 5 mm of precipitation, which did result in increasing STP inflow and outflow and consequently an increasing water volume in the river.

The daily average water flow, measured at gauge W (Figure 3-1), was 0.29 – 0.43 m^3/s for the 2016/2017 samplings and 0.58 and 0.27 m^3/s respectively for the sampling in 2015 and 2018. The sampling events in 2015 and 2018 represent two different dry weather scenarios; with around 32% (2015) and 71% (2018) of the water volume in the river at the mouth stemming from STP discharges.

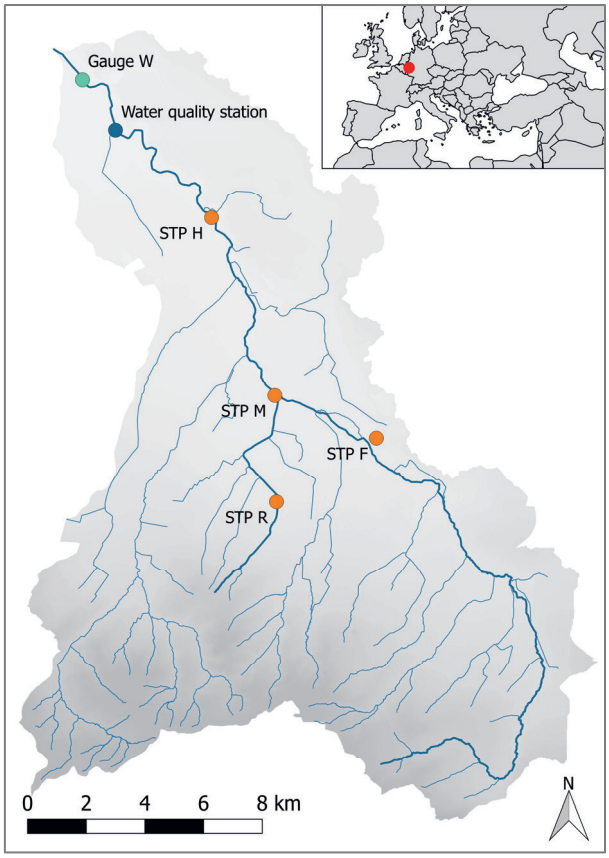


Figure 3-1: Swist catchment area with the gauge for water level measurement (gauge W), sewage treatment plants (STP H, STP M, STP F, STP R) and the water quality station. Flow direction from south to north.

3.2.2 *Analyses*

Four OMPs have been analysed, the corrosion inhibitor 1H-benzotriazole (1HB), the musk fragrance galaxolide (HHCB), the anti-epileptic drug carbamazepine (CBZ) and the anti-inflammatory drug diclofenac (DCF). Different behaviour in the river is expected for these four OMPs, e. g. CBZ is known to be persistent (Clara et al., 2004), 1HB and DCF are possibly transformed by photodegradation (Andreozzi et al., 1998; Moore et al., 1990) and HHCB is expected to have higher tendency to sorb to the organic fractions by hydrophobic interactions related to its hydrophobicity expressed by its high K_{OW} (Table 3-2).

The chemical analysis was performed according to Brunsch et al. (2018a). In short: a HPLC (1260, Agilent, USA) with a triple quad mass spectrometer (6460, Agilent, USA) was used to determine the concentrations of 1HB, CBZ. The limit of quantification was 0.05 µg/L for 1HB and 0.10 µg/L for CBZ. A GC (Trace GC, Thermo, USA) with a triple quad mass spectrometer (TSQ 8000, Thermo, USA) was used to determine concentrations of DCF and HHCB. Limit of quantification was 0.05 µg/L for HHCB and 0.02 µg/L for DCF.

Non-detectable values were set to the limit of quantification. 123 samples were analysed in total. Thereof 72 in 2015 (12 x 4 at the STPs and 24 in the river), 35 in 2016/2017 (7 x 4 at the STPs and 7 at the river) and 16 in 2018 (1 x 4 at the 4 STPs and 12 in the river). The number of non-detectable OMPs were 12 (HHCB) and 1 (CBZ); DCF and 1HB were always measured above limit of quantification.

Based on the chemical analyses, the daily loads (g/d) from STP effluents and the river water were calculated based on analysed concentrations (µg/L) and discharges (m^3/d). For the 24-hour composite samples, the concentration was therefore multiplied with the daily discharges (m^3/d). These daily discharges represent the sum of hourly or two-hour discharge values (m^3/h). For time proportional 1-hour or 2-hour composite samples, first the hourly or two-hour loads were calculated before these loads were summed up to daily loads. Subsequently, mass balances were calculated from daily loads.

3.2.3 The DWA Water Quality Model

OMP concentrations were simulated with the DWA Water Quality Model (former ATV Water Quality Model, DWA – German Association for Water Wastewater and Waste) (Christoffels, 2001). Daily loads were calculated from simulated river flow data and simulated OMP concentration. The model describes the physico-chemical processes in the river with a deterministic approach. The discharge simulation is one-dimensional and based on the Saint-Vernant-Equation (Müller, 2001). Water quality parameters are calculated in 20 individual modules, that simulate parameters such as temperature, oxygen, solar radiation, phosphorous, nitrogen, biological and chemical oxygen demand, pH, metals but also OMPs. The modules can be used individually, but simulations of some of these modules depend on input from other modules (e.g. data from the oxygen module are needed for the simulation of nitrate in the nitrogen module). We used the module for OMP simulation. Input data from emission sources – both non-point and point sources - can be either fixed values or diurnal concentration curves. In our study, we simulated dry weather scenarios (precipitation < 1 mm

on the sampling day itself and < 5 mm total precipitation two days before the sampling) exclusively and OMP emissions were limited to the effluent from the four STPs in the catchment. The input data for STP emissions such as effluent discharge, water temperature and pH, were taken directly from STP effluent measurements. Input parameters were based on independent data and not on model calibration data except for the discharge, which was manually calibrated for river sections with a very low water level. The spatial resolution of the simulation was approximately 100 m and the temporal resolution was one hour.

Relevant characteristics of the DWA Water Quality Model in OMP simulation are:

- Photodegradation is calculated from a specific radiation absorption and quantum yield.
- The calculation of sorption to suspended solids is based on the octanol water partition coefficient with $K_{OC} = K_{OW} * 0.41$ (Karickhoff, 1981).
- Ionisation of molecules is not taken into account.
- Sorption is assumed to be independent of the concentration of the OMP and amount of sorbent; sorption equilibrium happens instantaneous compared to other substance conversion processes.
- The biodegradation calculation is based on a single first order rate constant for the full river transect, and this rate is independent of e. g. hydraulics or biocenosis.
- The exchange processes between pore water from the river sediment and the river water are not considered. (Müller, 2001)

Monitoring data were used to validate simulation results. One flow gauge and one water quality station in the catchment (Figure 3-1) were measuring continuously water level and quality parameters such as temperature amongst other. For the plausibility analysis measured data were compared to simulation results: river discharge to validate the basic hydraulic model, water temperature because it influences most OMP removal processes and OMP concentration to validate OMP removal processes.

3.3 Results and discussion

3.3.1 Monitoring of OMPs

3.3.1.1 OMP concentration

Concentrations measured during the four years of sampling at STP effluents and the river are variable (Table 3-1). Median HHCB concentrations decreased over the sampling years in contrast to the other investigated OMPs. This is possibly due to a decrease in HHCB consumption in the Swist catchment area. In general, the reason for concentration variability for the four OMPs might also be related to the different sampling years with different environmental conditions, and different sampling intervals (e. g. 24-hour and 2-hour composite sampling). Nevertheless, STP outflow concentrations in 2015 and 218 of 1HB, CBZ and DCF were similar. In 2015 and 2018, samples were taken in higher temporal resolution and thus diurnal variation is taken into account when data were statistically evaluated in contrast to the 2016/2017 samplings.

Table 3-1: Concentrations (µg/L) incl. median values and standard deviation measured at outflows of STP F, STP R, STP M and STP H as well as in the Swist at the water quality station.

Year		**Sampling strategy**	**n**	**1HB**	**CBZ**	**HHCB**	**DCF**
				Median (Stand.Dev.)	Median (Stand.Dev.)	Median (Stand.Dev.)	Median (Stand.Dev.)
2015	STP	2-h composite	48	5.40 (3.24)	0.89 (0.19)	1.33 (0.17)	2.87 (0.85)
	River	1-h composite	24	1.70 (0.29)	0.31 (0.03)	0.14 (0.07)	0.48 (0.14)
2016 /2017	STP	24-h composite	28	3.35 (2.31)	0.64 (0.23)	0.79 (0.23)	2.50 (1.53)
	River	24-h composite	7	1.90 (0.81)	0.28 (0.13)	0.22 (0.06)	0.88 (0.36)
2018	STP	24-h composite	4	4.95 (1.25)	1.00 (0.05)	0.36 (0.11)	3.35 (2.84)
	River	2-h composite	12	3.00 (0.34)	0.73 (0.05)	< 0.05 (0.00)	0.40 (0.08)

In the following, river concentrations from the two samplings in 2015 (normal dry weather) and 2018 (exceptional dry weather) were compared (Figure 3-2) for evaluating short-term concentration variability in the Swist river. The data show that diurnal concentration patterns

vary amongst the OMPs. Concentrations of 1HB and CBZ were highest in 2018, presumably due to the lack of dilution of STP effluent with groundwater, surface runoff or water discharged by tributaries. CBZ and 1HB concentrations have been compared with each other and show a good correlation (coefficient of correlation 0.91). This shows that the diurnal variability of these two compounds is comparable. In contrast to CBZ and 1HB, concentrations of DCF were similar in 2015 and 2018. This indicates removal of DCF in the river, since concentrations of STP outflow were similar in both years (Table 3-1) and dilution effects in 2015 as found for CBZ and 1HB, not noticeable. HHCB was not detectable in the river in 2018 and thus not comparable with 2015 data. The variation of the concentration of HHCB in 2015 with highest values of 0.46 µg/L at 14:00 is remarkable but cannot be explained. The concentration decreases measured in 2018 at 11:00 for 1HB, CBZ and DCF is presumably due to a short rain event (see section 3.2.1) and subsequent dilution with rain water in the river. Diurnal concentration variabilities of DCF and HHCB show completely different patterns compared to 1HB and CBZ. This illustrates that concentration variability over the day and amongst the samplings is influenced by several factors. For persistent OMPs we can assume that concentration variability in the river (Figure 3-2) originates from variable STP effluent volumes. This is a result of, first, typical diurnal variation of STP effluent volumes due to greater water usage during day time and second, steady STP effluent concentration during dry weather (within the 24-hour samplings) (Brunsch et al., 2018b). This diurnal concentration pattern of stable compounds in the river can also vary amongst the different samplings as shown by the concentrations and individual effluent volumes of the four STPs observed at the individual sampling day campaign. Another reason for short term concentration variability is removal processes in the river such as sorption, volatilisation, biodegradation or photodegradation. The lowest DCF concentrations were measured between 15:00 and 2:00 in both 2015 and 2018. Given the flow time of 4 to 5 hours from STP R and STP F to the water quality station the water during this time period was mainly influenced by sunlight that promotes photodegradation. The photodegradability of DCF in natural surface waters was already determined by several authors (Bartels and von Tümpling, 2007; Buser et al., 1998; Kunkel and Radke, 2012).

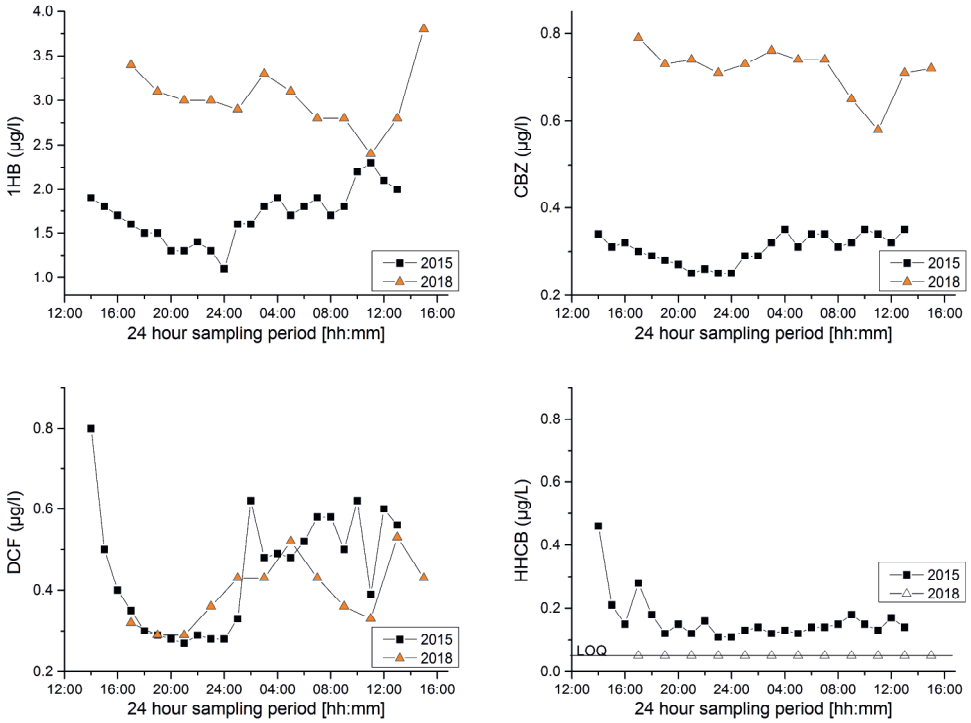


Figure 3-2: Daily OMP concentrations measured at the water quality station at the river Swist in 2015 and 2018. Colour-filled symbols = measured above limit of quantification (LOQ); transparent symbols = measured below LOQ.

3.3.1.2 OMP load and mass balance

The load in the river (L_{River}) was compared to the total load from the four STPs (L_{STP}) to be able to create a mass balance and identify removal of OMPs in the river or additional emission sources (Figure 3-3). A ratio of 1 would imply neither additional input nor removal.

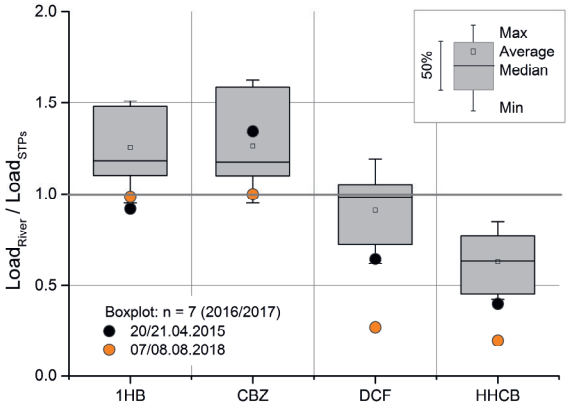


Figure 3-3: Ratio of loads in the river to loads from the sewage treatment plant for the three different samplings (indicated by boxplot and two filled circles).

L_{River}/L_{STP} for 1HB and CBZ and the 2016/2017 campaigns was approximately 1 or higher, which potentially implies that there is additional emission input, for example from diffuse sources or unknown point sources. During the exceptional dry weather campaign in 2018 with no or limited discharge from tributaries and only little influence by groundwater, loads from STPs and river were found to be the same. This suggests that there is no removal of 1HB and CBZ in the river. Persistence of CBZ in rivers was shown in several studies (Kasprzyk-Hordern et al., 2009; Kunkel and Radke, 2012; Lam et al., 2004). The stability of 1HB in rivers was also shown by Reemtsma et al. (2010) and Wolschke et al. (2011). Similarly to our study, these authors also detected increasing 1HB concentrations along the rivers. However, in these studies also large rivers were investigated and it was argued that additional emissions were possibly stemming from water discharges from industries (Wolschke et al., 2011). Moreover, increasing mass flows of 1HB along a river stretch in the Glatt river in Switzerland were identified to originate not only from STPs but also from an airport, where 1HB was used as a de-icing agent (Giger et al., 2006). This shows that 1HB has many applications, and other input pathways besides STPs are possible. However, in our catchment, emissions from direct dischargers such as big industries and airports can be neglected. Moreover, the L_{River}/L_{STP} ratio of loads in the river of both 1HB and CBZ frequently exceeds 1, suggesting additional input of wastewater and need to be further investigated. Another reason for higher CBZ loads in the river might be back transformation of carbamazepine-N-glucuronide to CBZ as determined in STPs by Vieno et al. (2007).

Lower loads in the river compared to that of the STPs have been found for DCF. L_{River}/L_{STP} values were around 1 at four samplings and smaller than 1 at five samplings, demonstrating that occasionally removal occurred in the river. As previously mentioned, in section 3.3.1.1, sunlight and photodegradation do have influence on DCF concentrations in the Swist river. Here, data of global radiation, i.e. total short-wave radiation, were compared with our DCF mass balance results. The maximum global radiation was greater than 700 W/m² on days with $L_{river}/L_{STP} < 1$, whereas on days with $L_{river}/L_{STP} >/= 1$ the global maximum radiation was below 400 W/m² (Figure 3-4). This reinforces the assumption that removal of DCF in the Swist river is influenced by solar radiation triggering photodegradation. The lowest L_{river}/L_{STP} ratio value (0.27) was detected in 2018 during exceptional dry and hot weather with high solar irradiation combined with an exceptionally low flow (0.27 m³/s at the mouth), leading to shallow water, high water temperature and optimal UV exposure. Additionally, high water temperatures and biodegradation may have contributed to the removal of DCF. Schaper et al. (2018) found a half-live of 0.09 d for 1HB and 0.16 d for DCF in the hyporheic zone (i.e. the sediment zone beneath the stream bed with which stream water easily exchanges) of a river in Berlin, Germany. According to these findings, it is likely that removal, and mainly biodegradation, is related to specific conditions of the hyporheic zone. We hypothesize that biodegradation in the hyporheic zone in the Swist river does not contribute significantly to removal, since 1HB was persistent and removal of DCF mainly related to photodegradation with the exception of the data in 2018.

HHCB load in the river was in all samplings lower than load from STPs, implying constant removal of this compound. The underlying process associated to this could not be identified, but did not correlate to variations in temperatures. Musolff et al. (2009) and Lange et al. (2015) showed increased removal of HHCB in surface water with increasing water temperature. Whereas Musolff et al. (2009) could not assign this result to a specific removal process, Lange et al. (2015) concluded that HHCB removal is due to oxidation caused by chemical or microbiological processes. Biodegradation as a contribution to removal of HHCB in rivers was also determined by Schwientek et al. (2016) In contrast to this, Bester (2005) showed that biodegradation of HHCB in the river Ruhr in Germany is negligible. For HHCB volatilisation and sorption are suspected removal processes because of its volatility and hydrophobicity (see Henry constant and *K*ow values in Table 3-2). These air-water and water-sediment exchange processes are both related to temperature and flow turbulence. The latter was not part of our study, however, the lower load ratio values in the warmer summer of 2018 with warmer water temperatures in the river thus contribute volatilisation, whereas colder water temperatures induce sorption. Therefore, a combination of both volatilisation and sorption is

most likely the reason for the good removal of HHCB in the Swist river. Nonetheless, biodegradation as a possible removal process cannot be excluded, but in order to make a reliable statement, behaviour of transformation products such as HHCB-lactone must be investigated as well. This might be subject of future studies.

A study conducted by Schwientek et al. (2016), determined mass balances for OMPs - as we did in this Swist study - in another small river in Germany. Their results reported for HHCB, DCF and CBZ removal in that river (net removal 32%, 17%, 2.5%) were in very good agreement with our results.

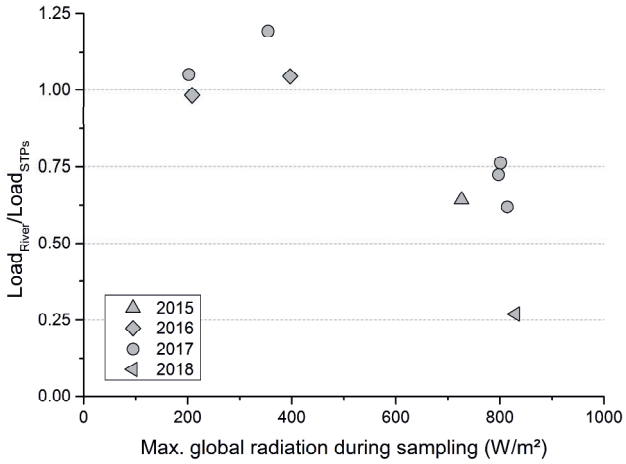


Figure 3-4: The ratio of DCF loads in the river Swist to loads from the four STPs, related to global radiation measured at the water quality station.

3.3.2 OMP behaviour determined by modelling

3.3.2.1 Model input data

To simulate the behaviour of OMPs in the river profile and diurnal variation with the DWA Water Quality Model, input parameters for OMP removal are essential. The most important input parameters for OMP simulation used are presented in Table 3-2.

Table 3-2: Input parameter for the DWA Water Quality Model.

	Biodegradation	Photodegradation	Volatilisation	Sorption
	Removal factor	Quantum yield	Henry constant[6]	*Kow*[7]
	1/d	mol/Einstein	Pa*m^3/µmol	
1HB	0.00; 0.03; 0.30	0.0294[1]; 0.0123[2]; 0.00472[2]	1.49E-08	20
CBZ	0.00	0.0000	1.09E-11	589
DCF	0.00; 0.03; 0.30	0.22[3]; 0.094[4]; 0.0375[5]	4.79E-06	18197
HHCB	0.00; 0.03; 0.30	0.0000	1.34E-05	794328

([1]Benitez et al, 2013, [2]Andreozzi et al 1998, [3]Moore et al, 1990, [4]Packer et al, 2003, [5]Andreozzi et al, 2003, [6]www.norman-network.net, [7]www.chemicalize.com)

For the calculation of sorption and volatilisation the *Kow* value and the Henry constant were used by the model. Both parameters are constants and hence not variable. DCF and 1HB are often described as photodegradable OMPs which is related to their high quantum yield values. Several quantum yield values that were determined under different conditions such as pH, light wavelength and light intensity have been collected (for DCF: Andreozzi et al., 2003; Buser et al., 1998; Keen et al., 2013; Moore et al., 1990; Packer et al., 2003 for 1HB: Andreozzi et al., 1998; Benitez et al., 2013; Borowska et al., 2016; Wang et al., 2000). Three quantum yield values for each DCF and 1HB, representing a minimum, maximum and intermediate value representative for the study conditions were used in our simulations (Table 3-2). It is known that under laboratory conditions, photodegradation can only occur at water depths up to 100 cm due to UV quenching (He et al., 2016), hence it is likely that deeper waters with high turbidity do not show significant DCF photodegradation. The river Swist is shallow, especially at dry weather discharges as studied here, with large transects having depths of a few decimetres. Hence, photodegradation is a potential contributor to removal. For biodegradation, data on rates in rivers are rarely reported. Kunkel and Radke (2008) stated that half-live for DCF in the river sediment is 5.5 and 18.6 days at slow and high flow rates. Buser et al. (1998) found out that biodegradation of DCF in a lake (Greifensee) is minimal. Biodegradation of 1HB was detected in activated sludge with a half-live of 23-45 hours by Mazioti et al. (2015). According to these data and in consideration of the high uncertainties in biodegradation rate constants adopted from literature to modelling (Greskowiak et al., 2017), a variety of removal factors [1/d] (0.00, 0.03 and 0.30) for biodegradation was used for

simulating 1HB and DCF. CBZ is known as a stable compound (Clara et al., 2004), with neither photodegradation (Baena-Nogueras et al., 2017) nor biodegradation to be significant in the river water, river sediment respectively (Löffler et al., 2005). HHCB was detected to be recalcitrant against biodegradation (Bester, 2005) and photodegradation (Buerge et al., 2003) in rivers (see also section 3.3.1.2). On the other hand, degradation of HHCB was determined in an STP under nitrifying conditions (Suarez et al., 2010). According to that, the removal factors adapted for DCF and 1HB (0.00, 0.03 and 0.30 1/d) have also been applied for the simulation of HHCB.

3.3.2.2 Simulation results

Two different dry weather scenarios were simulated with the model. In order to validate the simulation results with monitoring data, we selected April 20/21 2015 and August 07 2018 as simulation periods, representing one normal dry weather and one extreme dry weather scenario. The short rain event at August 8 (see section 3.2.1) was excluded in the simulation to reduce uncertainties due to surface runoff and dilution. The Nash-Sutcliff model Efficiency coefficient (NSE) (Nash and Sutcliffe, 1970) and the coefficient of determination (R^2) were calculated to compare simulated and measured discharge and temperature data. The NSE for discharge at gauge W was 0.58 for the 2015 campaign and 0.25 for the 2018 campaign. R^2 was calculated with 0.69 and 0.63 respectively. The 2018 campaign data showed higher differences between measured and simulated discharge data. The reason is presumably the extremely low water level and discharge in the river. However, in consideration of the high temporal resolution of the simulation, results for both years are accounted to be satisfactory and the model to be well validated in regard to basic hydrology. Moreover, the measured temperature data validate well the simulated temperature values for the 2015 campaign (R^2 = 0.81), whereas the measured temperature data of 2018 did not match the simulated data (R^2 = 0.39). This is in accordance to the discharge values and illustrates that the extreme dry weather scenario (2018) is more difficult to describe with the model in small rivers in contrast to the normal dry weather scenario (2015). The accuracy of the parameterization of the model i.e. the description of the real conditions of the river and the surrounding environment is most important under extreme conditions with very low water level and consequently uncertainties in simulating such scenarios are growing.

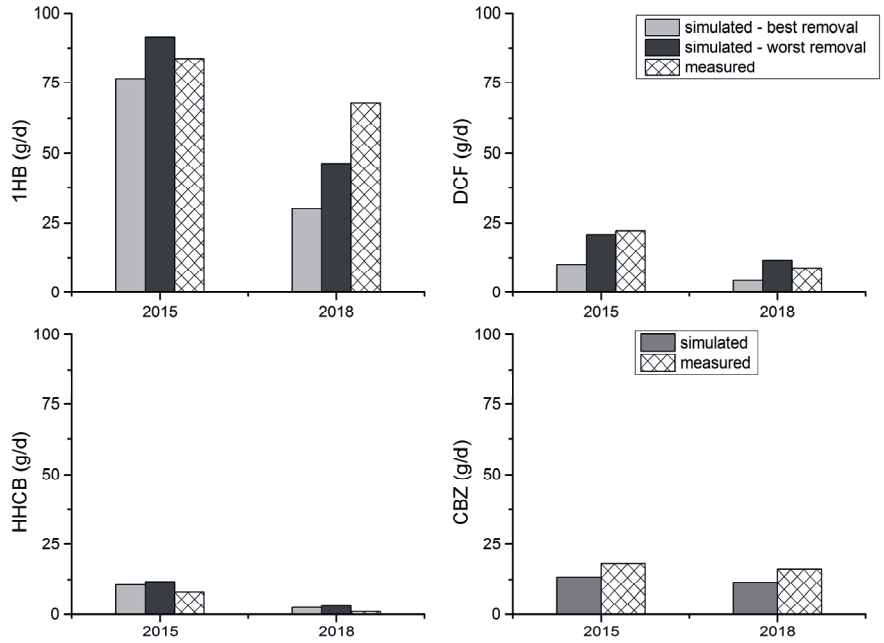


Figure 3-5: Daily loads in the river Swist calculated with monitoring data and simulated data for April 2015 and August 2018. Simulated best removal is based on highest quantum yield and biodegradation input data and worst removal is based on lowest quantum yield and biodegradation input data as shown in Table 3-2.

A range of loads in the river was simulated for 1HB and DCF using different input parameters for biodegradation and photodegradation (Table 3-2). In Figure 3-5 simulated and measured loads are presented. A minimum and maximum load were simulated for DCF, 1HB and HHCB, while for CBZ only a single load is simulated. For DCF, 1HB and HHCB, worst removal represents a simulation with the lowest biodegradation rate and quantum yield values, and best removal represents the simulation with the highest biodegradation rates and quantum yields as shown in Table 3-2. 1HB load in the river could be well described by the model for the campaign in 2015, with a L_{sim}/L_{mon} of 0.9 – 1.1. In 2018, measured loads are higher than the simulated values (L_{sim}/L_{mon} 0.4 – 0.7). CBZ loads were slightly underestimated by the model in both years (L_{sim}/L_{mon} ~0.7 in 2015 and 2018 respectively). Reason for higher CBZ and 1HB monitoring loads could be additional unknown sources of emission as discussed in section 3.3.1.2 that were not considered in the model. Alternatively, photodegradation and biodegradation for 1HB might have been overestimated with modelling. This is in accordance with the results as discussed in section 3.3.1.2, showing that 1HB is recalcitrant in rivers.

DCF loads from monitoring were both years in the range of the simulated loads (L_{sim}/L_{mon} in 2015 0.5 – 0.9 and in 2018 0.5 – 1.3), showing that quantum yields from literature and a biodegradation removal factor of up to 0.3 1/d are able to explain observed losses of DCF loads in the Swist river. Given the fact that the flow time from the two main dischargers, STP F and STP R to the mouth of the river is 4 – 5 h, the biodegradation factor of 0.3 1/d might have a much lower contribution to the simulated loads in comparison to photodegradation. Moreover, both quantum yield and the biodegradation factor are fixed values in the model, despite their sensitivity to external factors. Subsequently, in real surface waters these factors might vary, due to redox conditions, conditions in the hyporheic zone, flow properties, or the biocenosis characteristics in different river segments. HHCB loads were slightly overestimated in 2015 with a L_{sim}/L_{mon} of 1.3 - 1.5 and considerably overestimated in 2018 with a L_{sim}/L_{mon} of 2.5 - 3.1. Differences in simulated daily loads for worst and best removal with biodegradation removal factor from 0.0 – 0.3 1/d were low (3.1 and 2.5 g/d 2018, 11.7 and 11.6 g/d 2015), leading to the conclusion that sorption and volatilisation were the most relevant removal processes for HHCB as determined by the model. However, it is possible that these processes were underestimated, possibly by inadequate determination of amounts of suspended solids enhancing sorption and removal by sedimentation out of the water column, inadequate determination of sorption to sediment, or higher biodegradation rate that may have occurred. Moreover, uncertainties and variabilities in comparing simulation and field observations are considered to be higher for volatile and hydrophobic compounds, sensitive to temperature variation and flow dynamics than for stable or photodegradable compounds (when known regional lux data are available). As an overall result, OMP behaviour can be reasonably well described with the DWA Water Quality Model, especially at "normal" dry weather conditions as in our example in 2015.

3.4 Conclusion

Studying the behaviour of OMPs in a real river system, by monitoring OMP concentrations is challenging, due to influences of "uncontrollable" environmental conditions such as weather, varying compositions of microbial communities or hydraulics in the river. For this reason, modelling is a suitable additional approach to the field monitoring results. We combined high resolution monitoring of a river, and a model with a deterministic mechanistic basis that includes a variety of removal processes. This enables to better understand the processes that occur in a river, and to determine the effects of environmental conditions on removal. This

combined approach fills the gap between laboratory and mesocosm studies of diverse OMP emissions, and the fate and behaviour of OMPs in river systems.

Generally, our monitoring data revealed that short term concentration variability in a river is at first a result of varying STP effluent volumes and subsequent dilution, and secondly, by action or absence of diverse removal processes occurring in the river. With the DWA Water Quality Model, it was possible to simulate OMP concentration profiles as observed in the river, using a variety of kinetic rate constants for various OMP removal processes as reported in the literature. Modelling results showed, that data on photodegradation as well on sorption and volatilisation, which were determined in laboratory studies, were transferable to the conditions in a shallow natural river system. It can be concluded that the DWA Water Quality Model is well suited for simulating OMP concentrations and loads in rivers as well as for secondary identification of *in situ* removal process for some compounds in rivers. We recommend this model, and included micropollutant module, to be further developed for other conditions and compounds to enhance its use for managing river water quality with respect to OMPs.

In this study different dry weather scenarios were compared, all valuable to determine the behaviour of OMPs in small rivers. Extreme dry weather scenarios, with lowest input on diffuse or other unknown sources, were ideal for studying OMP *in situ* behaviour in rivers through only monitoring data. For modelling hydraulic as well as reactive processes, the "normal" dry weather scenarios appear to be most suitable.

Diclofenac removal was mainly related to high global radiation triggering photolysis. Accordingly, in central Europe's latitudes diclofenac is well removed by photodegradation during summer time. In areas with higher global radiation and/or more hours of sunshine diclofenac removal in rivers can be expected to be better. Galaxolide showed the highest removal, presumably due to a variety of processes working simultaneously such as volatilisation, sorption and biodegradation whereas carbamazepine and 1H-benzotriazole were persistent in the river.

Acknowledgement

The study presented has been funded in the framework of following projects: the project TAPES (330J) "Transnational Action Program on Emerging Substances" has received European Regional Development Funding through INTERREG IV B. The project AquaNES

"Demonstrating synergies in combined natural and engineered processes for water treatment systems" has received funding from the European Union´s Horizon 2020 programme (689450). The project "Hyreka" (02WRS1377H) has received funding from the Federal Ministry of Education and Research (Germany). The authors are grateful for the financial support of the projects. Thanks also to S. Kindgen-Gronwald, M. Reif for chemical analysis, to E. Christoffels, C. Gattke for input on the research, M. Rosellen for support with the model and to R. Krump, O. Altunay for technical support.

Chapter 4
Retention soil filter as post-treatment step to remove micropollutants from sewage treatment plant effluent

A modified version of this chapter has been published as

Brunsch, A.F., ter Laak, T.L., Christoffels, E., Rijnaarts, H.H.M., Langenhoff, A.A.M., 2018. Retention soil filter as post-treatment step to remove micropollutants from sewage treatment plant effluent. Science of the Total Environment 637–638. 1098–1107.

Abstract

Retention soil filters (RSFs) are a specific form of vertical flow constructed wetlands for the treatment of rain water and/or wastewater. We have tested three pilot RSFs to investigate removal of dissolved organic carbon (DOC) and 14 different organic micropollutants (OMPs) from the effluent of a large scale sewage treatment plant (STP). Two of them were operated as conventional RSFs with material (sand with $CaCO_3$ and organic matter) from two different full scale RSFs. The third pilot RSF contained filter material (sand with $CaCO_3$) with additional biochar in the upper layer (0-10 cm) and granulated activated carbon (GAC) in the lower layer (60-90 cm). The filters were planted with *Phragmites australis*. The RSFs were operated and monitored for three years, and water samples were taken regularly at inflow, outflows and in three depths within the filters. In total 523 samples were taken. In the conventional RSF, best median removal was detected for galaxolide, diclofenac 4-hydroxy, metoprolol and clarithromycin (75-79%). No removal was seen for sulfamethoxazole and carbamazepine. The DOC and OMP removal in the conventional RSFs was best in the upper layer with highest organic matter content, increased in time over the three years of operation and also with extended contact time. In the effluent of the RSF with GAC, 10 out of the 14 OMPs could not be detected; four OMPs were detected, but only metformin with removal < 80%, thus showing a more efficient removal than the conventional RSF. A decrease in DOC removal was detected in the GAC layer (> 88% to 60%) over the 2.5 years of operation. Biochar was most effective in OMP removal in the first operational year. It can be concluded that the increasing removal efficiency of the conventional RSF material – also present in the RSF with biochar and GAC – might mitigate the reduced efficiency of the sorbent additives biochar and GAC. This enables to extend the operational lifetime of the filters with acceptable removal rates. Finally, our study demonstrates that an RSF with GAC shows an enhanced removal of OMPs, which is a suitable post treatment step for STPs.

4.1 Introduction

Organic micropollutants (OMPs), mainly originating from domestic households, are present in surface water (Daughton and Ternes, 1999; Gerbersdorf et al., 2015). They are found in the order of ng or μg per litres in rivers, and many of them are considered to be a risk for the aquatic environment, due to their toxicity at these concentrations (Schwarzenbach et al., 2006). Current sewage treatment plants (STPs) are not effective in removing those compounds from the sewage water, and thus OMP containing effluent is discharged to the surface water. As a result, surface water downstream an STP is receiving higher concentrations of OMPs, possibly resulting in higher toxic effects on aquatic organisms compared to surface water upstream of an STP (Neale et al., 2017). An enhanced treatment of STP effluent is essential for small river stretches with high wastewater load in order to achieve the aims of the European Union Water Framework Directive (Directive 2000/60/EC). Water managers are currently facing the challenge of reducing emissions to surface water. Post-treatment technologies such as ozonation, activated carbon treatment and membrane filtration may be effective for removal of even the most recalcitrant OMPs, such as diclofenac or carbamazepine (Suárez et al., 2008). Powdered and granulated activated carbon and ozonation are widely used in treatment processes not only for cleaning drinking water but also for secondary effluent. Powdered activated carbon treatment and ozonation has shown best OMP removal, however, the effectivity of activated carbon treatment is determined by the properties of both adsorbate and adsorbent (Kovalova et al., 2013). The disadvantage of ozonation treatment is the production of possible toxic by-products (Deeb et al., 2017; Kovalova et al., 2013; Ternes et al., 2017). Another technology that is used in drinking water production is membrane filtration. The retention of OMPs in membrane processes is versatile and depends on size exclusion, adsorption onto membrane, and charge repulsion (Luo et al., 2014; Verliefde et al., 2008). Finally, reversed osmosis is often used in water treatment, and showed the highest removal among the various treatments applied (Luo et al., 2014). Accordingly, several measures to reduce OMPs from STP effluent have been tested, however these technical solutions come along with relatively high energy consumption and additional costs that range from € 0.05 to 0.20 per m^3 of treated water (Joss et al., 2008).

The above-mentioned treatment technologies all need a high energy input when implemented for wastewater treatment, and alternative techniques are desired (Jones et al., 2007). This has resulted in various studies to the removal of OMPs in natural treatment techniques such as constructed wetlands. A review by Verlicchi and Zambello (2014) on pharmaceutical removal with constructed wetlands (CW) showed that wetlands are very diverse in their usage (first,

second, tertiary treatment of wastewater and other), implementation (surface flow, horizontal-subsurface flow, vertical-subsurface flow, hydroponic bed), construction (filter material, vegetation) and operation (e.g. hydraulic retention times). A broad range of removal was determined, ranging from 0-100% removal, depending on the type of wetland and the investigated OMPs.

Retention soil filters (RSFs) are a German specification of vertical flow CWs and widely used for almost 30 years. A description of RSFs as well as design and dimensioning comparison to CWs were published by Frechen et al. (2006) and Meyer et al. (2013). RSFs are operated in Germany downstream combined sewer overflows or storm water basins to protect surface water from pollution. Currently, 34 RSFs are in use in the Erft catchment (Rhine region, North-Rhine Westphalia, Germany), and operated by the local water board Erftverband. The set-up of the RSFs in the federal state of North-Rhine Westphalia Germany is standardized according to the recommendations in the RSF Handbook (MKULNV, 2015). The RSFs were initially build to reduce chemical oxygen demand COD, nutrients, heavy metals and suspended solids and to increase dissolved oxygen content (Frechen et al., 2006). Now, these are tested for their removal capacity of various compounds, including OMPs.

A few studies are published on OMP removal in RSFs for combined sewer overflow treatment and show effective retention of microorganisms and highly variable removal efficiencies among the individual OMPs (Christoffels et al., 2014; Tondera et al., 2013). Nevertheless, the determined efficiencies of OMP removal were similar to activated sludge treatment at STPs (Scheurer et al., 2015). This shows that RSFs are a useful measure to reduce pollutants from combined sewer overflows before entering surface water.

In order to test the applicability of RSFs downstream STP outflows, a pilot plant with three different columns was installed at STP Rheinbach, and the effectivity of different RSF material under the influence of different operational parameters and external conditions was investigated. The goal was to evaluate the application of RSFs for effluent polishing and optimized treatment efficiency as a basis for future implementation of such a RSF at full scale. The pilot RSFs were fed with STP effluent to cover real-life conditions and variations in water quantities and OMP concentrations. The OMP removal by the three RSFs was studied over a period of three years with and without the addition of granular activated carbon (GAC) as part of the filter bed. To our knowledge, this long-term real-life monitoring of RSFs has never been done before.

4.2 Materials and methods

4.2.1 Pilot filter plant

The pilot RSFs are installed at a medium size STP that treats wastewater for 27,000 inhabitant equivalents at the city of Rheinbach in the federal state of North Rhine-Westphalia in Germany. The STP is equipped with a sand trap with aeration, a primary clarifier, biological phosphorous elimination, denitrification, nitrification, a secondary clarifier and an additional filtration unit. An overview of water quality parameters of the STP effluent that are routinely measured is given in Table SI 4-1. Effluent of the STP is pumped to three pilot RSF columns (Figure 4-1).

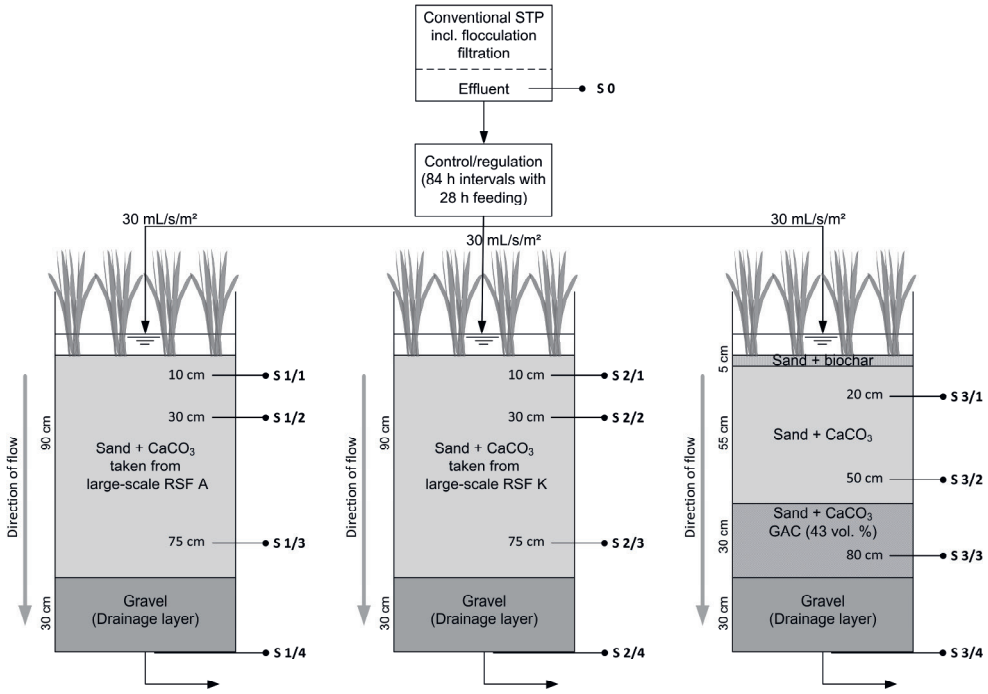


Figure 4-1: Schematic design of the pilot RSF. From left to right: RSF A, RSF K, RSF G. Sampling locations: S0-S3/4.

Each RSF column has a filter surface of 1.5 m² and a volume of 1.4 m³. The configuration of the pilot RSF is in accordance with the RSF guideline of North Rhine-Westphalia, Germany

(MKULNV, 2015). Thickness of the filter layers is 0.9 m and of the gravel drainage layers is 0.3 m. Drainage pipes are embedded in the gravel. All filters are planted with reed (*Phragmites australis*), and rhizomes taken from existing full scale RSFs were planted at the top layers. Two filters contain conventional RSF material, taken from a full scale RSF in Altendorf (700 m² filter surface) (RSF A) and an RSF in Kaster (1500 m² filter surface) (RSF K) that are in operation since 2005. Details on RSF Altendorf are described in Christoffels et al. (2014). Sand supplemented with $CaCO_3$ is used as filter material. $CaCO_3$ is added to maintain a constant pH in the RSF material. The used organic matter of the conventional RSFs has accumulated over the operational years and was highest in the upper 5 cm, respectively 3% (RSF A) and 4% (RSF K). The third column (RSF G) contains sand with 22% $CaCO_3$, and two extra additives: 13 vol.-% biochar in the upper layer (0-10 cm) and 43 vol.-% GAC in the lower layer (60-90 cm). There was no initial organic matter content in the filter sand material. More details on filter material characteristics are shown in Table 4-1.

Table 4-1: Filter material characteristics of the pilot RSFs measured in December 2016 (n. m. = not measured).

	RSF A			**RSF K**			**RSF G**			
Sampling depth	Organic matter	Carbonate ($CaCO_3$)	Clay & Silt	Organic matter	Carbonate ($CaCO_3$)	Clay & Silt	Sampling depth	Organic matter	Carbonate ($CaCO_3$)	Clay & Silt
cm	%	%	%	%	%	%	cm	%	%	%
0-10	3.4	26.2	12.8	3.9	20.6	22.1	0-10	4.2	15.9	5.5
10-30	1.1	29.2	6.4	2.6	22.2	3.0	10-20	0.7	20.2	3.3
30-75	0.8	30.1	7.4	1.0	30.2	6.9	20-50	0.5	22.1	2.6
75-90	0.7	29.7	3.9	0.8	27.0	5.6	50-90	n. m.	n. m.	n. m.

Operation of RSF A and K started in September 2014, and RSF G in April 2015. Feeding is set in alternating cycles of 28 h feeding and 56 h non-feeding. The feeding rate is set at 30 ml/s/m² (according to MKULNV, 2015), to have a similar hydraulic retention time (HRT) as the full scale RSFs. The water level in the RSFs was kept above filter surface according to the principle of communicating vessels (Figure SI 4-1). Water filling level during feeding phases is around 10-15 cm above the filter material surface. HRT is 3.25 h (flow rate 0.5 cm/min). Total feeding volumes until July 2017 were 1360 m³ for RSF A and K (972 bed volumes) and 1052 m³ for RSF G (752 bed volumes). The GAC in RSF G was treated with ~5300 bed volumes. Dead reed

parts were harvested in winter 2016. Some of these plant residues remained on top of the filter surface.

Three L-shaped sampling tubes with perforated horizontal parts were placed in each filter (Figure SI 1). The tubes were placed at 10 cm, 30 cm, and 75 cm depth in RSF A and K. In RSF G, the sampling tubes were placed at 20 cm, 50 cm and 80 cm depth from the surface, to make sampling in the different layers possible.

4.2.2 *Sampling*

Grab samples were taken from the outlet of the STP (S0), the sampling tubes within the filters and the outflow of each filter (Figure 4-1). Samples were taken according to the flow direction from inflow to outflow at weekly intervals during the first three operational months and at monthly intervals thereafter.

Samples for OMP analysis were stored in brown glass bottles at 4°C until analysis (within 7 days). Samples for DOC/TOC analysis were acidified immediately with 2 mL HCl (25%) to a sample volume of 250 mL.

Selected OPMs were the corrosion inhibitor 1H-benzotriazole (1HB) and one transformation product 1H-benzotriazole-4-methyl (1HB-4M), the musk fragrance galaxolide (HHCB), the flame retardant tris(2-chlorisopropyl)phosphate (TCPP), the anti-epileptic drugs gabapentin (GBP) and carbamazepine (CBZ) and its metabolite carbamazepine-dihydro-dihydroxy (CBZ-Di), the anti-inflammatory drug diclofenac (DCF) and its metabolite 4-hydroxy-diclofenac (DCF-4H), the anti-diabetic drug metformin (MTF), the beta blockers metoprolol (MTP) and sotalol (STL) and the antibiotic drugs clarithromycin (CLM) and sulfamethoxazole (SMX).

4.2.3 *Effect of extended contact time by impounding*

Two tests were conducted in summer and winter 2016 to study the influence of seasonality and longer contact time on the removal capacities. Therefore, water was impounded in the individual filter columns. Influent temperatures were 19.0 °C and 9.6 °C, respectively during summer and winter and average daily air temperature respectively 18.5 °C and 1.2 °C. Inflow and outflow were stopped for 7 hours directly after a regular sampling campaign. During this

impounding time, samples were taken 3 and 6 hours after flow stop in 4 depths per RSF (S 1/1-1/4; S 2/1-2/4).

4.2.4 Chemical analyses of OMPs

4.2.4.1 Chemicals

All reference standards had a purity of > 96%: 1HB, CLM, MTP tartrate and STL hydrochloride were purchased from Dr. Ehrenstorfer; 1HB-4M DCF, DCF-4H, GBP, HHCB, SMX and TCPP were purchased from Neochema; MTF Hydrochloride and CBZ were purchased from Sigma Aldrich and CBZ-Di was purchased from TRC Toronto Research Chemicals.

The internal standards had a purity of > 98%: DCF-d4 acid, Isoproturon-d6 and STL hydrochloride-d6 were purchased from Dr. Ehrenstorfer, CBZ-d10 was purchased from Neochema and MTF-d6 hydrochlorid was purchased from TRC Toronto Research Chemicals.

Deionized water (DI) from a Barnsted Nanopure Diamond water purification system (Werner Reinstwassersysteme, Germany) was used to prepare all solutions. Acetonitrile lichrosolv, methanol lichrosolv and toluene suprasolv (Merck, Germany) as well as acetone and formic acid (99%) hiPerSolv chromanorm (VWR, Germany) were used for performance of liquid chromatography and gas chromatography analysis.

4.2.4.2 HPLC/MS/MS analysis

HPLC (1260, Agilent, USA) with a triple quad mass spectrometer (6460, Agilent, USA) was used to determine the concentrations of 1HB, 1HB-4M, CBZ, CBZ-Di, GBP, MTF, MTP, STL, CLM and SMX. The injection volume was 75 µL and the chromatographic separation was achieved using ZORBAX® Eclipse Plus C-18 columns (4.6x100 mm, 3.5 µm). The mobile phase was a mixture of A (water with 0.1% formic acid) and B (acetonitrile with 0.1% formic acid). The flow rate was set with 0.4 mL/min from 95% A to 100% B. The limit of detection was 0.05 µg/L, except for CBZ 0.1 µg/L and for CLM 0.2 µg/L. The detection results were acquired and analysed automatically by software.

4.2.4.3 GC/MS/MS analysis

GC (Trace GC, Thermo, USA) with a triple quad mass spectrometer (TSQ 8000, Thermo, USA) was used to determine concentrations of DCF, DCF-4H, TCPP and HHCB. 500 mL of the sample were extracted with Oasis HLB cartridges. The extracts were derivatized by adding 50 µL of trimethylsilyldiazomethane in hexane and 250 µL of methanol. After a reaction time of around 12 hours the solution was evaporated to dryness by a nitrogen stream and dissolved in 250 µL of toluene. Column used was CS 54®, 30 m, 0.25 mm ID, df 0.25 µm. The injection volume was 2 µl. Temperature was 90 °C to 280 °C and the flow rate in helium 1mL/min (constant flow). Limit of detection was 0.05 µg/L for HHCB and 0.02 µg/L for DCF, DCF-4H and TCPP. The detection results were acquired and analysed automatically by software. Further details on analysis can be found in Table SI 4-2.

4.2.5 Data analysis

Removal [%] was calculated for each individual sampling campaign, either for the whole RSF, or per layer

Equation 4-1 $$\text{Removal per layer} = \frac{\Delta c}{c_{\text{inflow}}} * 100$$

With *c* as measured concentration and *Δc* as the concentration difference of the different layer.

An analysis of variance was conducted with Origin 9.0.0 for comparison of removal of the investigated compounds for the three pilot RSF.

Removal [%/cm filter material] is calculated as:

Equation 4-2 $$\text{Removal per unit filter material} = \frac{\Delta c}{c_{\text{overlying layer}}} * 100$$

and by dividing the result through layer thickness [cm] we calculated the removal [%] per layer [cm].

The individual limit of quantification (LOQ) was used for the calculations when OMPs were not detected in the water samples (Haas and Scheff, 1990).

4.3 Results and discussion

The pilot RSFs are operated at real life conditions. This approach required extensive monitoring to cover varying composition and conditions of STP effluent. A total of 523 samples was analysed and evaluated for this study. The high number of samples provides reliable insight in treatment performance of RSFs. Within the short time frame of the RSF HRT of 3.25 h the variation of concentration at RSF inflow is considered negligible due to the long HRT of 1-4 days and homogenisation of OMP concentration in the STP tanks. Therefore, in and outflow concentrations of samples, taken with a time difference of 1.5 hours (+/- 15 min), could be compared to determine removal efficiencies. Calculated removal corresponds to minimum removal because the individual LOQ was used for non-detects at the outflow.

Removal capacities of RSF A and K have been compared by the analysis of variance. The results showed that the removal of 12 OMPs was not significantly different in the two conventional RSF. A significant difference was only observed for MTF and STL, and that might be attributed to the minor differences in composition of the two RSFs (Table 4-1). Due to the similar removal data for the two RSFs, only the results of RSF A, representing a conventional RSF, and RSF G, representing an adapted RSF, will be discussed in the following.

4.3.1 Overall removal in RSFs

The RSFs are fed with real STP effluent; accordingly, OMP concentrations of RSF inflow did show some variation over the three years of investigation. CLM and SMX were found in 52% and 96% of the inflow samples above LOQ. All other OMPs were detected in 100% inflow samples. RSF inflow concentrations show a large variation for individual OMPs (e. g. HHCB 0.26-3.5 µg/L; MTF 0.12-2.7 µg/L; GBP 1-7.5 µg/L; SMX < 0.05-1.3 µg/L; CLM < 0.2-5.9 µg/L) and also amongst the OMPs (e. g. median concentrations for 1HB 3.9 µg/L and for CLM < 0.2 µg/L) (Figure SI 4-2). At the outflow of RSF A (conventional), the majority of OMPs were detected in contrast to the outflow of RSF G (with GAC), where most OMPs were not detected in 30 samples (Figure 4-2 - Table below the graph).

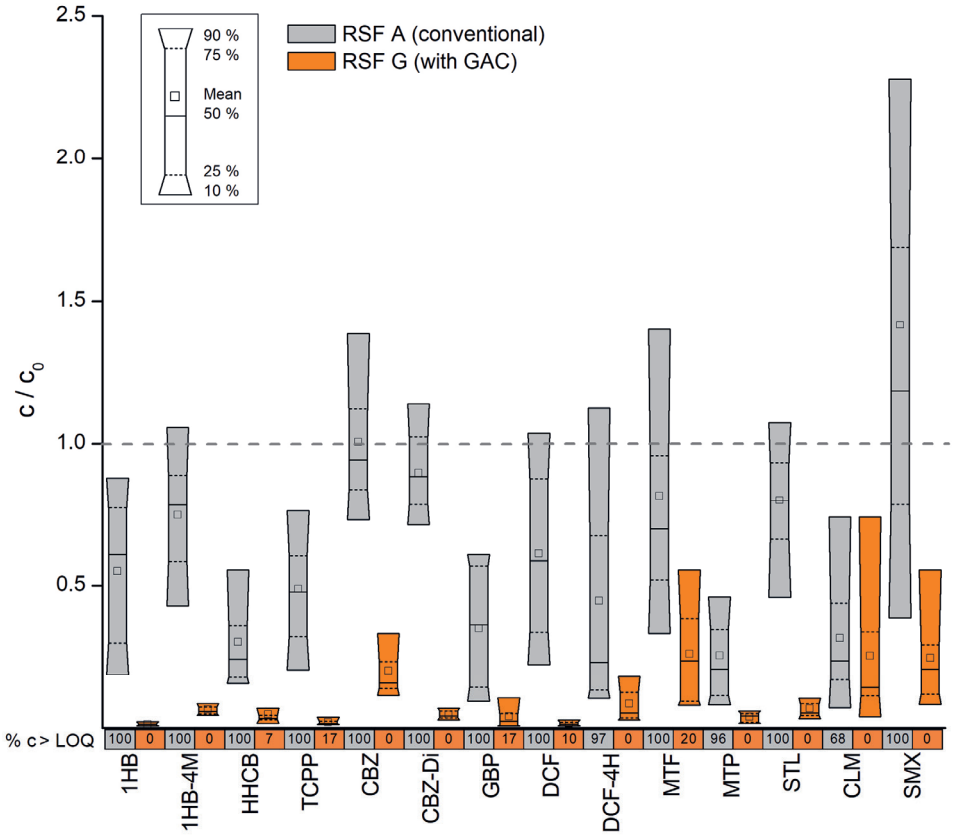


Figure 4-2: Factor of concentrations at inflow (S 0) and outflow of RSF A (S 1/4) and RSF G (S 3/4). Numbers given in the table below the graph are the percentage of samples analysed that yielded results above LOQ at the outflows in relation to analysed samples at inflows.

The removal of OMPs in the RSFs is shown in Figure 4-2. The RSF A data show limited removal, whereas RSF G shows high removal of the measured OMPs, illustrating the different removal capacities of the RSFs. Within the 27 investigated operational months, the RSF with GAC shows a median OMP removal of 95%. The calculated removal (c/c_0) is affected by using the LOQ as non-detected OMPs. Hence, the calculated removal with non-detects at the outflow is minimum removal. At the conventional RSF A, DOC was removed by 22%, which is similar to treatment efficiencies of reported sand filter columns (Reungoat et al., 2011). The removal of the investigated OMPs in RSF A was 40% and varies widely among the compounds. Best median removal for RSF A (75-79%) was detected for HHCB, DCF-4H, MTP and CLM. Medium removal for RSF A (30-64%) was detected for TCPP, DCF, MTF, GBP and

1HB and low removal (11-22%) for CBZ-Di, STL and 1HB-4M. No removal is seen for SMX (-18%) and CBZ (4%) at RSF A. Concentrations at the effluent were to some extent higher than inflow concentrations for both compounds. CBZ is known to be very persistent in conventional STP treatment and the environment (Clara et al., 2004). The appearance of negative removal was already found by other authors in activated sludge treatment. They explained it by conversion of CBZ glucuronides and other conjugated metabolites to the parent compound (Leclercq et al., 2009; Vieno et al., 2007). The metabolite CBZ-Di was detected in higher concentrations in the inflow than the outflow (median removal 11%) implying that removal of this metabolite is higher than potential conversion of glucuronides. Accordingly, glucuronidase activity, which was confirmed in activated sludge systems by Ternes et al. (1999a), might also be influencing transformation processes in RSFs. Back-transformation from metabolites to parent compound was also detected for SMX (Bonvin et al., 2013; Radke et al., 2009) and might be an explanation for negative removal of SMX determined in our study.

4.3.2 Correlation of removal and physico-chemical properties of OMPs

As shown in section 4.3.1 the removal of the individual OMPs in a conventional RSF varied per compound. Therefore, physico-chemical properties of the OMPs were taken into account to find a relation between the removal, and the hydrophobicity or charge of the OMP.

The relation between hydrophobicity and removal is given in Figure 4-3, and does not show a trend between these two parameters. If sorption was the dominant process in OMP removal, a positive linear relation between hydrophobicity and removal percentage would have been expected. Beside the hydrophobicity, also the charge of the compound can influence sorption capacities (Schwarzenbach et al., 2016). Possibly, the positively charged MTP and CLM are sorbed to the negatively charged soil material (Bertelkamp et al., 2014). Moreover, sorption is likely for the two hydrophobic and neutral OMPs TCPP and HHCB. However, there are neutral OMPs (GBP, 1HB) and negative charged OMPs (DCF, DCF-4H) which can be removed by the RSF. As a consequence, potential sorption of neutral compounds by hydrophobic interactions and positively charged compounds by electrostatic interactions cannot explain observed removal. So, other processes such as biodegradation or plant uptake likely occur in the investigated RSFs. Similar results were obtained by Bester and Schäfer (2009) in activated soil filters. First, they showed that HHCB is removed by sorption and second, they determined higher removal of hydrophilic and hydrophobic OMPs than can be explained by sorption

only. Aerobic conditions in the RSF might encourage biodegradation for some compounds. The oxygen content in RSF A is 5 mg/L in the upper layer and 8 mg/L in the lower layer (standard deviation 2 mg/L). The influence of redox conditions on the removal of aerobically degradable compounds in subsurface flow constructed wetlands was shown by Rühmland et al. (2015). For aerobically degradable OMPs such as MTP (Rubirola et al., 2014), biotransformation might thus likely occur in RSFs. Volatilisation as removal process can be neglected for the investigated compounds because even HHCB with the highest Henry constant (4.5 * 10^{-3} µg*m^3 air/µg*m^3 wastewater) volatilization in wastewater treatment processes was found to be almost negligible (< 5%) (Suárez et al., 2008).

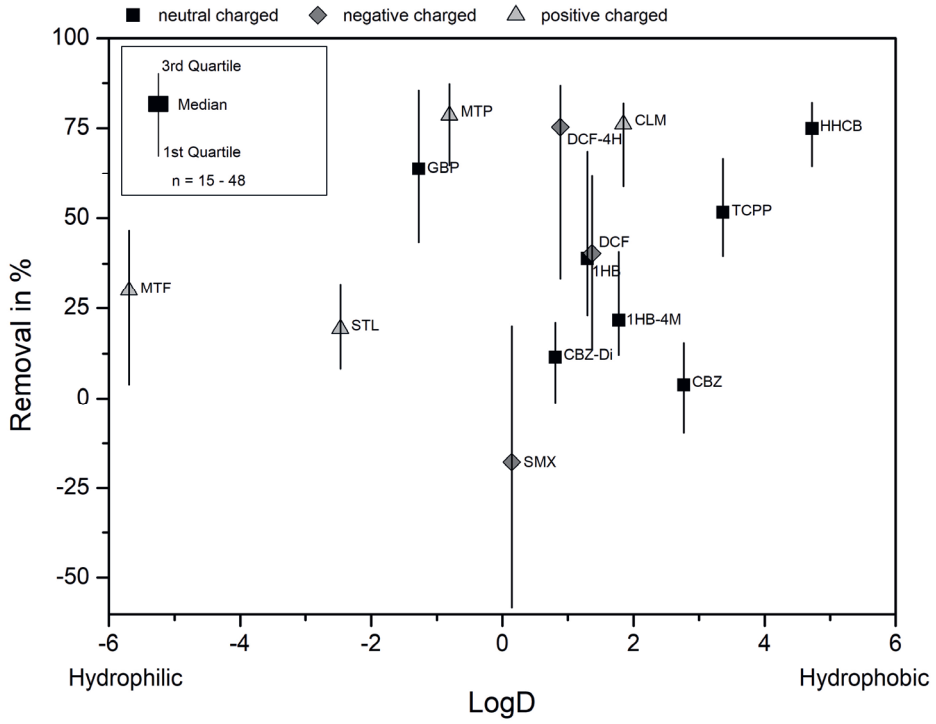


Figure 4-3: Reduction rates of RSF A in relation to logD values. The black or grey shaded symbols show the different charges of the compounds. (LogD values and charges taken from https://chemicalize.com)

4.3.3 Removal per layer

The sample tubes allowed us to take samples within the different layers of the RSF, and calculate the removal %/cm filter material. The study focuses on the difference between "fresh" (RSF G) and "used" (RSF A) filter material and the effectivity of the different sorbent materials in the individual RSF layers. Removal of the individual layers is presented in Table 4-2. The removal %/cm of OMPs is decreasing with RSF depth and organic matter content in RSF A. In RSF G the removal %/cm is highest in the upper and especially the lower layer with added biochar and GAC, respectively.

Table 4-2: Median removal %/cm filter material for each RSF layer. One layer is located between two sampling points. Highlight groups from dark to bright are (in %): ≥ 2, 1.5-1.9, 1-1.4, 0.5-0.9, < 0.5

	RSF A (conventional)				**RSF G (GAC)**			
Layer depth in cm	0- 10	10-30	30-75	75-120	0-20	20-50	50-80	80-120
Organic matter in % or additive	3.4	1.1	0.8	0.7	Bio-char		GAC	GAC
DOC	0.9	0.3	0.2	0.1	0.4	0.2	2.6	1.9
1HB	1.8	0.3	0.4	0.4	1.5	0.2	3.3	n. a.
1HB-4M	1.5	-0.1	0.2	0.6	0.5	0.2	3.1	n. a.
HHCB	4.5	1.2	0.6	0.8	2.2	0.3	3.1	n. a.
TCPP	2.8	0.5	0.4	0.3	1.6	0.4	3.2	n. a.
CBZ	0.0	0.0	0.0	0.1	0.4	0.1	2.7	n. a.
CBZ-Di	0.8	0.0	0.1	0.0	0.5	0.1	3.2	n. a.
GBP	4.3	1.0	0.4	-0.5	1.3	0.7	3.1	n. a.
DCF	2.0	0.4	0.2	0.5	1.3	0.2	3.3	n. a.
DCF-4H	3.5	0.6	0.6	1.4	1.9	0.2	3.1	n. a.
MTF	0.7	0.1	0.1	0.2	0.0	0.3	2.4	n. a.
MTP	4.3	1.1	0.8	1.0	2.3	1.0	3.0	n. a.
STL	0.6	0.0	0.1	0.6	1.0	0.2	3.1	n. a.
CLM	2.6	0.9	1.1	0.3	2.3	2.0	1.3	n. a.
SMX	-0.6	-0.1	-0.2	0.2	-0.4	0.0	2.7	n. a.

The highest reduction of OMPs in conventional RSF A was detected in the first layer. This layer has a higher organic matter, silt and clay content compared to the lower layers.

Therefore, adsorption might be responsible for the removal of OMPs, as both organic matter and clay minerals are good sorbent materials. However, organics may also function as substrates for microbial activity that may have affected OMP biodegradation. As most of the detected OMPs are not expected to sorb strongly (section 4.3.2), we hypothesize that biological transformation might have attributed also to the removal of a number of the compounds.

The addition of biochar had positive effects on RSF G with "fresh" filter material. The layer with biochar (0-10 cm) achieved better removal per cm for DOC and most OMPs, except MTF and SMX, compared to the sand layer (20-50 cm) without sorbent additives. The biochar containing upper layer of RSF G thus helps to reduce the amount of OMPs and other organic material before reaching the GAC layer. According to Summers et al., (2013) and Zietzschmann et al. (2016) GAC OMP adsorption is influenced by background organic matter concentration and competition of compounds to the GAC surface. An effective upper layer can thus improve the performance of the final GAC layer in the RSF, as there is less competition for adsorption. This was also shown in our RSF, as the OMPs that were not removed by the first 60 cm were removed by the GAC layer.

Additionally, the performance of biochar was compared to "used" material with high organic matter content by looking at the removal in the upper layers of RSF A and RSF G. OMPs with the highest removal in conventional RSF, also showed the best removal in the RSF G biochar layer (HHCB, MTP, CLM). In addition, compounds such as CBZ and STL that are persistent in the conventional RSF, were removed partly in the upper layer of RSF G. Nevertheless, despite of the higher organic carbon content of the layer with biochar compared to the naturally aged top layer of RSFs, the organic rich "used" material is in most cases more effective in removing OMPs.

The addition of GAC in a RSF is innovative and turned out to be effective. Therefore, the performance of this specific RSF layer was studied in more detail, and the relative effluent concentrations (c/c_0) in the GAC layer were related to the throughput, expressed as treated bed volumes (BV) of the GAC (Figure 4-4). Below 2500 BV the removal exceeds 88%. After that, the removal reduced to ~60%. Removal capacity of the GAC is thus decreasing with increasing treated bed volumes. However, a uniform conclusion cannot be drawn because of outliers appearing, as can be seen in Figure 4-4. The specific throughput of DOC (fed mass DOC, and not adsorbed mass) after 5300 treated BV was 53.9 mg DOC/g GAC. Compared to a GAC test study with 400 mg DOC fed per g GAC, a 90% breakthrough for poorly adsorbing OMPs was observed (Zietzschmann et al., 2016), showing that the GAC in the RSF system might still have good adsorption capacity for OMPs. In a study with DOC fed rates more than

twice as high as in our investigated system, a relative breakthrough for DOC of 50% at ~3000 BV was determined (Altmann et al., 2016). In the same study, GBP was found to be a weakly adsorbing OMP with almost complete breakthrough at 5000 BV (Altmann et al., 2016). In our study, removal of GBP was above 80%.

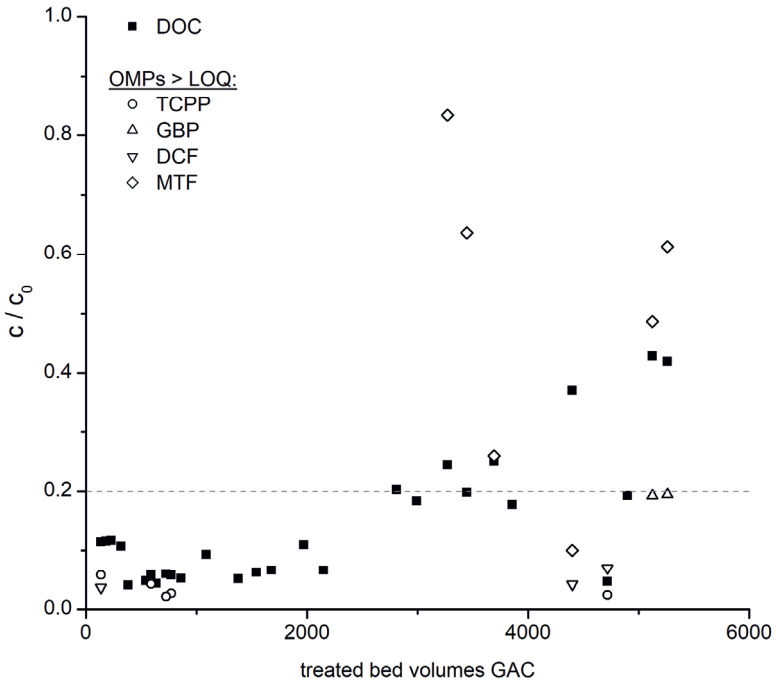


Figure 4-4: Relative effluent concentration and treated BV for DOC and OMPs. Results below LOQ are excluded and only OMPs with positive findings ≥ 10% in RSF G effluent are shown (TCPP, GBP, DCF, MTF).

There are numerous studies describing the performance of DOC and OMP removal from STP effluent through GAC (Benstoem et al., 2017 and references therein). However, a very broad spectrum was found for the treated bed volumes until the breakthrough criterion of $c/c_0 = 0.2$ was reached (e. g. for DCF from 800- > 20000 BV) (Benstoem et al., 2017). Moreover, it was found that even after a complete breakthrough for DOC, CBZ and DCF were still removed by 80% (Benstoem et al., 2017). In 95% of our samples, the OMP concentrations in the effluent of RSF G were below LOQ (Figure 4-2) and only MTF reached $c/c_0 = 0.2$ (Figure 4-4). MTF has

low sorption capacities as shown in a small scale GAC test by Scheurer et al. (2012), fed with 500 µg/L. They identified a relative breakthrough of 90% at 1250 BV. The reduction of MTF in the RSF GAC layer was lowest at 3270 treated BV in August 2016 (17%) and increased afterwards, showing a discontinuing removal for this compound. In general, it is possible that varying removal is related to background organic matter concentration. It was found by Summers et al. (2013) and Zietzschmann et al. (2016) that the level of background organic matter in the feeding water is inversely related to GAC adsorption properties. This means OMP adsorption capacities decrease with increasing TOC or DOC concentrations. However, the measured DOC of 4.9 mg/L is relatively low for STP effluents and with a standard deviation of 24% considered to be steady. A DOC of 4.1 mg/L was measured in August 2016, when MTF removal was lowest. Accordingly, MTF removal seems not to be influenced by background organic matter. Taken literature studies on GAC breakthrough and the non-consistent progress of GAC saturation into account, it seems that the RSF system cannot be compared to conventional GAC filters as sorption is presumably not the only removal process. Most likely, the GAC serves as a medium for biofilm colonization (Imai et al., 1995) and biodegradation is stimulated by the relatively long retention time and the aerobic conditions due to the feeding/non-feeding cycle. Biological activated carbon filters show steady performances for OMP removal, which implies that they can be used for many years without replacing the GAC (Reungoat et al., 2011).

4.3.4 Removal and seasonality

The RSFs were operated outdoors, and thus, seasonal effects might influence the removal efficiency. Therefore, average removal was calculated for four summer and three winter seasons by using data of the individual sampling campaigns with feeding water temperatures ≤ 11.5 °C (winter) or ≥ 17.5 °C (summer) respectively, to compare distinct cold and warm conditions. Inflow concentrations in summer and winter seasons were not significantly different for DOC and OMPs with the exception of SMX and GBP. The removal for the RSF A is shown in Table 4-3. The removal in layer 1 and 2 of RSF A and removal in layer 1 of RSF G are shown in Figure 4-5, as these layers showed the best removal capacities.

Table 4-3: Overall removal of RSF A in winter and summer. Colour grouping from dark to bright (in %): ≥ 75, 50-74, 25-49, < 25. (not measured = n. m.; not sufficient data = n. s. d.)

	RSF A (conventional)						
	2014 Sum	2015/ 2014 Win	2015 Sum	2016/ 2015 Win	2016 Sum	2017/ 2016 Win	2017 Sum
DOC	n. s. d.	21	18	23	22	36	27
1HB	25	19	48	54	65	82	42
1HB-4M	n. m.	n. m.	n. m.	n. m.	22	54	16
HHCB	n. m.	n. m.	66	63	78	72	79
TCPP	13	58	46	59	75	69	52
CBZ	21	-19	-5	-2	3	29	12
CBZ-Di	n. m.	n. m.	7	13	12	18	10
GBP	n. m.	n. m.	n. m.	n. m.	57	78	55
DCF	22	21	46	20	71	59	56
DCF-4H	n. m.	n. m.	65	53	77	60	15
MTF	33	-12	22	-28	45	11	25
MTP	68	46	83	74	88	87	79
STL	22	8	30	8	36	49	23
CLM	n. s. d.	n. s. d.	n. s. d.	n. s. d.	n. s. d.	n. s. d.	n. s. d.
SMX	-76	-180	-20	-34	36	11	72

Removal variability and trends according to seasons and with advances of operation could be determined over the three operational years. At RSF A, DOC is better removed in winter periods with lower temperatures compared to the following summer periods. Here, sorption seems to be the most relevant process, as sorption is inversely related with temperature while biodegradation is expected to be higher at high temperatures. In contrast, no clear seasonal trend could be determined for most OMPs. DCF, MTP and HHCB have a tendency to better removal in the summer period. A better removal of OMPs in summer in subsurface flow constructed and other wetlands was also detected by Reyes-Contreras et al. (2012). They explained it by biodegradation and plant-mediated processes which are favoured under summer conditions. Higher removal in summer is thus another indication for biological activity and biological transformation of OMPs in RSFs.

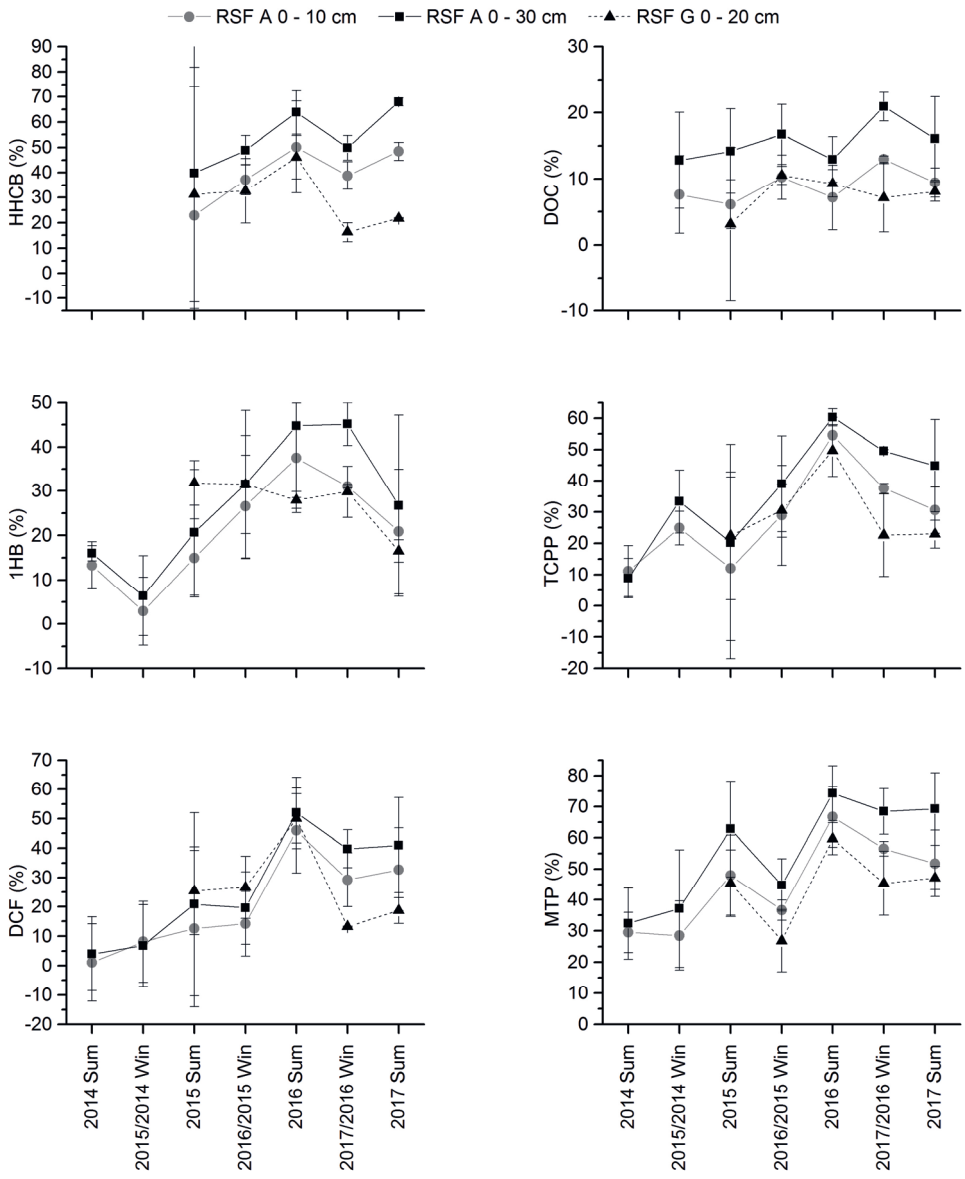


Figure 4-5: Removal (average values and error bars) for the upper layers of RSF A (conventional) and G (with GAC), for summer and winter periods from 2014-2017

Most OMPs show the best removal in summer 2016, compared to the other summers. A reason for this could not be identified, as the temperature in 2016 was not significantly different from the previous and following summer, and operational parameters of the STP were as usual.

This indicates that these systems, operated outside and fed with real STP effluent, can show variable treatment efficiency. It is important to study dynamics, and find factors that affect treatment efficiency and control these conditions to optimize performance.

Changes in organic matter content or microbiology over the operational years make it difficult to determine seasonal differences in removal. Organic matter content is changing due to constant input of STP effluent and plant residues and microorganisms getting adapted to particular conditions in the RSF, following enhanced biological removal (Bertelkamp et al., 2016). Therefore, changes over the whole operational period must be considered. Besides the removal in summer 2016 a trend towards better removal with longer operation time was obtained. For example, 29% removal was measured in winter 2017/2016 for CBZ. Also, DCF removal was in the first three seasonal periods was always below 50% and increased in the following seasons above 50%. A statistically significant relation could not be obtained between seasonality and removal for OMPs, but a correlation of the behaviour between the individual OMPs in the upper layer was found. Coefficients of correlation greater 0.8 have been detected between 1HB, MTP and DCF; between HHCB, 1HB and DCF and between TCPP and DCF. This shows that even without an obvious trend in seasonal removal, the OMP removal capacities might be less coincidentally or independent from each other.

Biochar was more effective in OMP removal during the first operational year when comparing layer 1 of RSF G with biochar to layer 1 and 2 of RSF A (Figure 4-5). Subsequently, the removal due to biochar is decreasing in the following seasons along with sorption capacities of this material. However, biological activation of the biochar is expected and along with that increasing biological transformation of OMPs as shown before for biological activated carbon filters (Reungoat et al., 2011).

4.3.5 Removal at extended contact time

The HRT in the RSFs was 3.25 h. A test was conducted in summer and winter 2016 to examine the effect of the retention time on the removal. With this test the water in the RSF was impounded and contact time increased. Data of the upper layer are shown in Figure 4-6, as this upper layer showed the best removal capacities. CLM, CBZ, CBZ-Di and DCF-4H were excluded due to non-detection (< LOQ), low removal (< 25%) or to large variation between the two test campaigns (ratio ≥10).

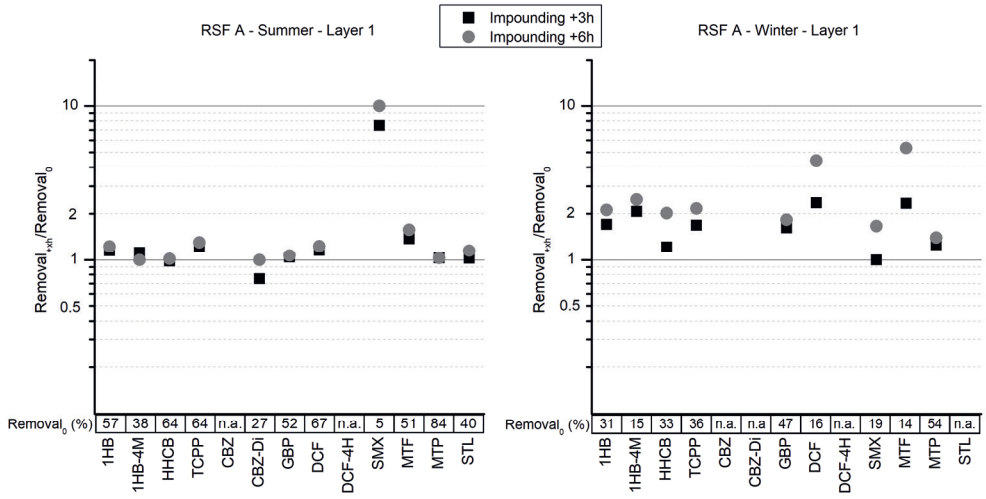


Figure 4-6: Factor of removal with impounding time of 3 and 6 hours and initial removal of RSF A in the upper layer during summer 2016 and winter 2016. Numbers for initial removal are given in the table below the graph (not applicable = n. a.).

As discussed in section 4.3.4, the summer 2016 removal was above average. Consequently, the increased contact time had no or limited effect on the removal. Except for SMX, removal with an additional contact time of 3 and 6 hours respectively was marginally better than initial removal. SMX was already described as biodegradable in river sediment (Radke et al., 2009). So, with enhanced contact time in RSFs, removal of this compound possibly exceeds back-transformation from metabolites (as described in section 4.3.1)

In winter, initial removal ($removal_0$) was lower compared to summer. The ratio $removal_0$ summer to $removal_0$ winter was respectively 0.9 for DOC 0.9 and 3.3 for OMPs. Longer retention time in winter affected all OMPs with the lowest effect on MTP ($removal_0$ 54% and $removal_{+6h}$ 76%). The ratio $removal_{+6h}$ summer to $removal_{+6h}$ winter for OMPs was on average 1.1. This shows that removal in winter at longer HRT is comparable to removal in summer under normal flow rates. Possibly, the removal is close to maximum removal in summer. However, in winter time it reached its probable maximum removal after 6 hours additional contact time.

In summer, our feeding rates of 0.03 L/s/m² proved to be suitable. On the other hand, lower feeding rates in winter, and therefore a longer contact time, is recommended for best removal.

4.4 Conclusion

Conventional retention soil filters:

- Conventional retention soil filters can remove organic micropollutants.
- The upper retention soil filter layer containing most organic matter showed best removal. This indicates that the organic matter content enhances organic micropollutant removal. This means that this conventional retention soil filter, the natural system, needs a longer start up period compared to technical treatment systems such as activated carbon filtration or ozonation.
- Contact time influences removal of organic micropollutants with better removal at longer impounding in winter. Operational conditions adapted to removal kinetics would lead to optimal utilisation of retention soil filters.
- In contrast to technical post treatment steps, the cleaning capacity for organic micropollutants of the conventional retention soil filter is not decreasing within time but increasing. This shows the robustness of this natural system. Possibly sorption and biodegradation are enhanced in organic enriched layers in the retention soil filter.
- A tendency of better removal in summer time was observed, also indicating biodegradation contributions to the removal.

Retention soil filter with GAC:

- Removal for organic micropollutants of the retention soil filter with GAC was always better than in the conventional retention soil filter.
- A slight decrease in DOC removal was detected, but at this time no conclusion on breakthrough or life time can be made.
- Additional long-term studies are necessary to demonstrate the long-term removal efficiency.
- The addition of biochar and GAC showed good results over the first 2.5 operational years.
- The positive results of this study and a GAC treatment of 45 bed volumes per week, shows that long operational life time can be expected at full scale application.

Conventional retention soil filters showed to be effective in removing several organic micropollutans from sewage treatment plant effluent. Removal was, depending on the organic micropollutant, 0-79%. The behaviour of GAC in a retention soil filter system with low feeding rates and aeration periods was not studied before, and the removal of organic micropollutant in retention soil filters for the investigated period containing GAC is more efficient than conventional retention soil filters. With our knowledge we can state that the addition of GAC into retention soil filter material is very efficient for removal of organic micropollutants from sewage treatment plant effluent. If, after a certain operational time of the retention soil filter with GAC, the efficiency of the GAC is decreasing, the cleaning capacity of the natural retention soil filter system will have an additional positive impact on the treatment efficiency. Therefore, the retention soil filter with GAC as a combination of technical and near natural treatment technique seems to be a valid alternative post treatment step for sewage treatment plants.

Acknowledgement

The study presented has been funded in the framework of following projects: the project TAPES (330J) "Transnational Action Program on Emerging Substances" has received European Regional Development Funding through INTERREG IV B. The project AquaNES "Demonstrating synergies in combined natural and engineered processes for water treatment systems" has received funding from the European Union´s Horizon 2020 programme (689450). The project "Retention soil filter Rheinbach" has received funding from the Ministry for Climate Protection, Environment, Agriculture, Conservation and Consumer Protection of North Rhine-Westphalia, Germany. The authors are grateful for the financial support of the projects. Thanks also to S. Kindgen-Gronwald, M. Reif and M. Trimborn for chemical analysis, to K. Knorz, L. Beyerle and F. M. Mertens for input on the research and to R. Krump, O. Altunay, G. Hofmann, K. Schnitzler, S. Gasse, R. Wolff, N. Viethen and W. Schwarz for technical support.

Supplementary information for Chapter 4

Table SI 4-1: Water quality parameters of STP Rheinbach effluent. Average values of 13 grab sampling campaigns accomplished during different weather conditions and seasons.

Parameter	Average value	Unit
Conductivity	710	µS/cm
Total suspended solids	2.0	mg/l
Total organic carbon	8.2	mg/l
Acidity kS 4.3	2.1	mmol/l
NH4-N	<0.1	mg/l
NO2-N	<0.1	mg/l
NO3-N	8.7	mg/l
P. total	0.28	mg/l
o-PO4-P. soluble	0.16	mg/l
Cl	96.2	mg/l
SO4	63.7	mg/l
Ca. total	41.4	mg/l
Mg. total	11.2	mg/l
Na	72.7	mg/l
K	18.1	mg/l
Fe. total	0.18	mg/l
Mn. total	0.03	mg/l
Al. total	0.09	mg/l
Zn. total	0.07	mg/l

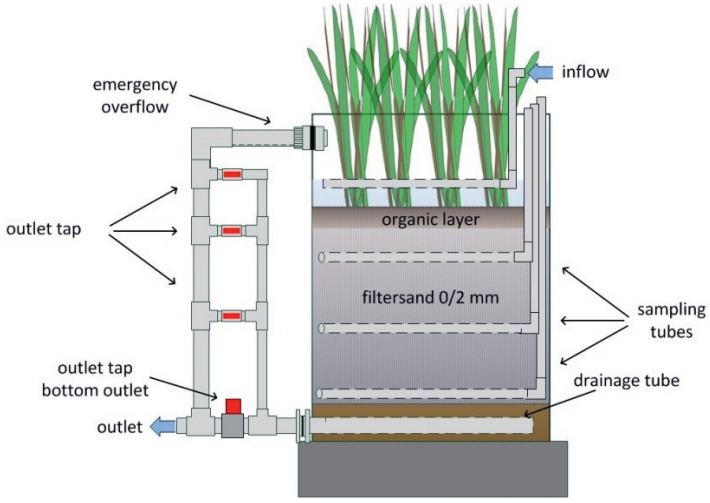


Figure SI 4-1: Schematic cross section of a pilot RSF (adapted from Beyerle, 2014)

Table SI 4-2: Applied analytical methods and limits of quantification.

OMP	Application	Analytical method	Method according to DIN-standard	Limit of quantification	Analysed since	No of analysed samples RSF A/K	No of analysed samples RSF G
TOC		Catalytic combustion. IR detection	DIN EN 1484	0.5 mg/L	SEP 2014	47	30
DOC		Catalytic combustion. IR detection	DIN EN 1484	0.5 mg/L	NOV 2014	38	28
1HB	Corrosion inhibitor	HPLC-MS-MS	DIN 38407-36	0.05 µg/L	SEP 2014	48	30
1HB-4M	Transformation product 1H-Benzotriazol	HPLC-MS-MS	DIN 38407-36	0.05 µg/L	APR 2016	15	12
HHCB	Musk	GC-MS after derivatisation	DIN EN ISO 15898	0.05 µg/L	MAR 2015	34	30
TCPP	Flame retardant	GC-MS	DIN EN ISO 15913	0.02 µg/L	SEP 2014	48	30
CBZ	Anti-epileptic drug	HPLC-MS-MS	DIN 38407-36	0.1 µg/L	SEP 2014	48	30
CBZ-Di	Transformation product Carbamazepine	HPLC-MS-MS	DIN 38407-36	0.05 µg/L	JUN 2015	27	24
GBP	Anti-epileptic drug	HPLC-MS-MS	DIN 38407-36	0.05 µg/L	APR 2016	15	12
DCF	Anti-inflammatory drug	GC-MS after derivatisation	DIN EN ISO 15888	0.02 µg/L	SEP 2014	48	30
DCF-4H	Transformation product Dicofenac	GC-MS after derivatisation	DIN EN ISO 15870	0.02 µg/L	MAR 2015	34	30
MTF	Anti-diabetic drug	HPLC-MS-MS	DIN 38407-36	0.1. 0.05 µg/L	SEP 2014	48	30

MTP	Beta blocker	HPLC-MS-MS	DIN 38407-36	0.05 µg/L	SEP 2014	48	30
STL	Beta blocker	HPLC-MS-MS	DIN 38407-36	0.05 µg/L	SEP 2014	48	30
CLM	Anti-biotic drug	HPLC-MS-MS	DIN 38407-36	0.2 µg/L	SEP 2014	48	30
SMX	Anti-biotic drug	HPLC-MS-MS	DIN 38407-36	0.05 µg/L	SEP 2014	48	30

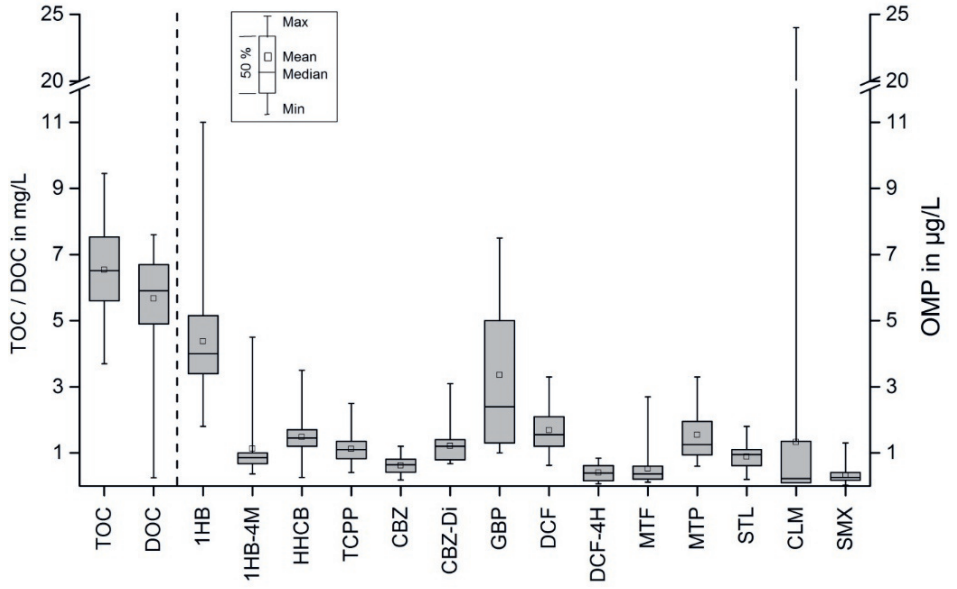


Figure SI 4-2: Inflow concentrations to the RSF pilot plant (Sept. 2014 – July 2017)

Chapter 5
Retention soil filters for the treatment of sewage treatment plant effluent and combined sewer overflow

A modified version of this chapter has been published as

Brunsch, A.F., Zubieta Florez, P., Langenhoff, A.A.M., ter Laak, T.L., Rijnaarts, H.H.M., 2020. Retention soil filters for the treatment of sewage treatment plant effluent and combined sewer overflow. Science of the Total Environment 699. 134426

Abstract

Retention soil filters (RSFs) are vertical flow constructed wetlands. They are mainly used for the treatment of combined sewer overflow or stormwater, and not operated during dry weather conditions. However, RSFs have been successfully tested as continuous post treatment for sewage treatment plant effluents. In this paper we present a new approach, namely dual usage of the retention soil filter. During dry weather the RSF is used for the polishing treatment of sewage treatment plant effluent and during overflow events, the retention soil filter treats the combined sewer overflow. This study was conducted at two pilot RSFs that were fed with sewage treatment effluent for four years. Removal of TOC, DOC, nutrients and 21 organic micropollutants was determined during six months at different sequences of regular effluent and overflow treatment conditions. TOC, DOC and nutrients, appearing in high concentration in combined sewer overflow, were effectively removed, and metformin and caffeine micropollutants showed > 99% removal. Residues from this combined sewer treatment that were sorbed on filter material or stored in pore water were washed out directly after treatment when STP effluent infiltration was initiated. This effect declined within 20 hours after combined sewer overflow treatment. Dry periods of 18 hours between combined sewer and sewage treatment plant effluent feeding counteracted the wash out effects. The highest removal efficiency was found in the beginning of the feeding time of 28 hours, indicating that shorter feeding cycles enhance the overall efficiency of the RSF. Finally, the results show that a single RSF system can successfully reduce emissions of TOC, DOC, nutrients and micropollutants to surface waters from two different emission pathways, i.e. from regular treated effluents and storm related sewer overflows. In conclusion, the dual usage of RSF is a promising approach and ready for upscaling and implementation.

5.1 Introduction

In our anthropogenically influenced environment, surface waters are affected by a great variety of pollutant sources. Nowadays the focus is on the presence and behaviour of organic micropollutants (OMPs). These OMPs enter surface waters through point and non-point sources, where they can have a negative influence on chemical and biological water quality (Neale et al., 2017). Both sewage treatment plant (STP) effluent (Daughton and Ternes, 1999; Glassmeyer et al., 2005) and combined sewer overflow (CSO) (Buerge et al., 2006; Launay et al., 2016) have been identified as relevant point pathways for OMP emissions into surface waters. STPs are designed to remove oxygen demanding compounds and nutrients, and are not specifically designed to remove OMPs. Consequently, many OMPs are barely removed within the STP and have been measured in concentrations up to 10 µg/L in STP effluents that are emitted to surface waters (Luo et al., 2014). Hence, there is a strong need for post treatment to reduce OMP load from STP effluents.

In Germany, around 54% of the sewer systems are combined systems and 46% are separate systems (Brombach and Dettmar, 2016). Combined systems transport both stormwater runoff and wastewater to STPs. In case of heavy rain fall events, the volume of combined sewerage might exceed the capacity of the STP. Then, the combined sewer discharges into a retention tank, and if completely impounded, the water overflows directly into the receiving river. The pollutant concentration in CSOs, the resulting concentration peaks in surface waters as well as associating potential environmental risk are already extensively studied for pathogens (Passerat et al., 2011; Rechenburg et al., 2006) and OMPs (Buerge et al., 2006; Gasperi et al., 2012; Launay et al., 2016; Munro et al., 2019). Compounds that are well removed in STPs were found in higher concentrations in surface water during CSO, while the concentration of compounds that are poorly removed in STPs decreased in CSO-influenced samples due to dilution with large volumes of stormwater (Weyrauch et al., 2010). Compounds from CSO were found to represent a risk for the environment due to I) a direct impact on chemical water quality by exceeding environmental quality standards (Gasperi et al., 2012) and II) an indirect impact on water quality, such as oxygen depletion as a result of enhanced biodegradation caused by the high loads of organic matter after CSO (Seidl et al., 1998).

Constructed wetlands are widely used to reduce pollutant loads from CSO, such as oxygen demanding compounds, nutrients and pathogens, before entering surface waters. The design of such constructed wetlands is customised according to the region of use and the composition of the sewage (Meyer et al., 2013; Tao et al., 2014). Vertical flow constructed wetlands have shown to be able to remove OMPs to some extent (Matamoros et al., 2007). In Germany,

retention soil filters (RSFs), a special configuration of vertical flow constructed wetlands, are constructed and operated mainly according to the recommendations of national guidelines, and (DWA, 2019; MKULNV, 2015). These RSFs are effective in removing COD, BOD, suspended solids, nutrients (Frechen et al., 2006), OMPs and pathogens including antibiotic resistant bacteria (Christoffels et al., 2014; Scheurer et al., 2015; Schreiber et al., 2016; Tondera et al., 2019, 2013). Most recently, RSFs have been shown effective for micropollutant removal in STP effluent representing a near natural alternative to engineered post treatment steps at STPs (Brunsch et al., 2018a).

RSFs for CSO treatment are solely used during storm events. As a result, the RSFs are not in operation most of the year. To make optimal usage of the treatment capacity of RSFs, we are testing a novel approach; the usage of RSFs for the treatment of both CSO and STP effluent in one system. The RSF is used to treat STP effluent in dry periods, and to treat CSO in case of storm events. As there are no practical experiences on this approach so far, our focus was to test different scenarios of operational conditions and to evaluate these scenarios according to the removal of TOC, DOC, nutrients and OMPs.

For this study, we used a RSF pilot plant with two different RSFs operated for four years for treating STP effluent. We tested different sequences of regular STP effluent polishing and artificially created CSO treatment events. The aim was to find best possible operational conditions for a broad range of compounds. During RSF feeding sequences, RSF influents and effluents were monitored for DOC, TOC, nutrient and OMP concentrations. Thus, we elucidated the application potential of dual functional RSFs in mitigating pollutant emissions to surface waters.

5.2 Materials and methods

5.2.1 Experiment set up

The RSF pilot plant consists of two individual, conventional RSFs with a filter surface of 1.5 m^2 and a filter volume of 1.4 m^3, which are installed at the Rheinbach STP in Germany. The details of this pilot plant are described in Brunsch et al. (2018). For this study, one RSF was used to treat only the STP effluent (RSF_{STP}) and the other RSF to treat CSO and STP effluent ($RSF_{CSO+STP}$) (Figure 5-1).

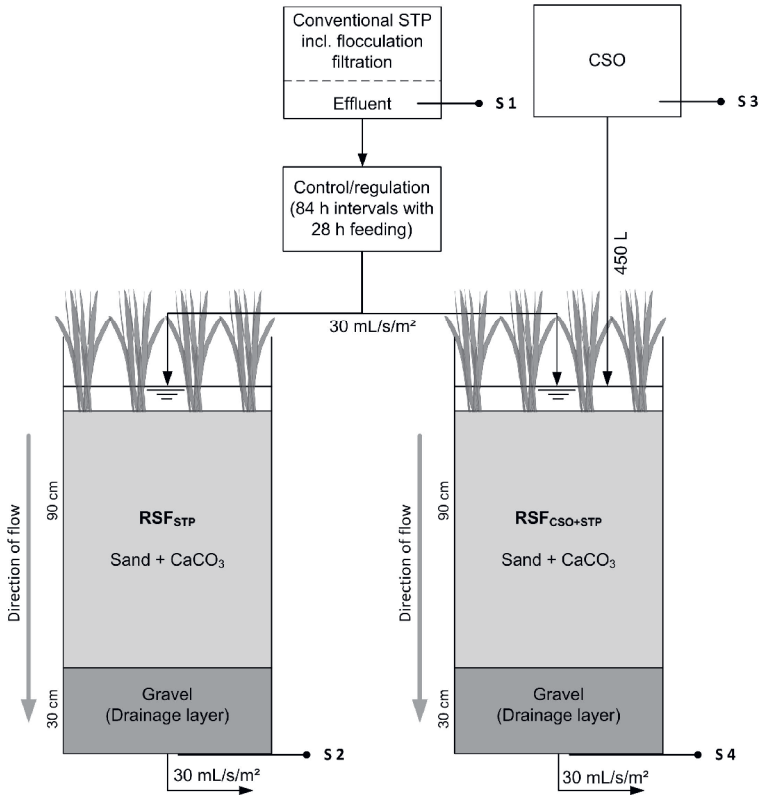


Figure 5-1: Experimental set up with RSF$_{STP}$ and RSF$_{CSO+STP}$ and STP and CSO feeding. S1 – S4 represent the sampling locations.

Both RSFs are filled with sand and calcium carbonate. The upper 10 cm are rich in (self-grown) organic matter. The RSFs are planted with common reed (*Phragmites australis*) and are in operation since 2014 for the treatment of STP effluent. Further details of the RSFs are described in Brunsch et al. (2018).The intermitting, regular feeding intervals with STP effluent have a duration of 28 h with a feeding volume of 30 mL/s/m² followed by a dry phase of 56 h. Nine CSO events were simulated at RSF$_{CSO+STP}$ during the dry phases of the regular STP effluent feeding intervals, while RSF$_{STP}$ received only STP effluent. The experiments were performed from May 2018 to November 2018. For RSF$_{CSO+STP}$, two scenarios were tested with different dry phase durations between CSO and STP effluent feeding. Scenario 1 had a dry phase of 18 h (n=4), and scenario 2 had no dry phase after the CSO event (n=5) (Figure 5-2).

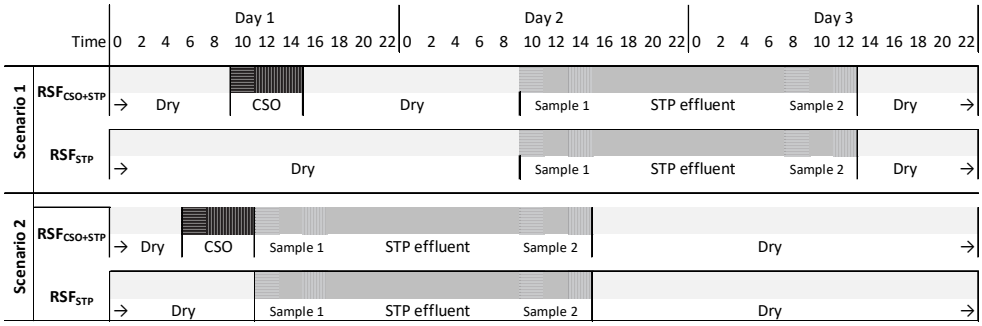


Figure 5-2: Time intervals of the feeding and sampling scheme of $RSF_{CSO+STP}$ and RSF_{STP}. Time in hours, black = CSO feeding, grey = STP feeding, light grey = dry period, horizontally striped boxes = RSF inflow sampling, vertically striped boxes = RSF outflow sampling.

At CSO feeding, 450 L artificial CSO was mixed in a container and stored for maximum 16 h before feeding start, which was always on Mondays. The artificial CSO consisted of STP influent that was taken after the coarse screen which prevents large components from entering the STP, and subsequently diluted with tap water. A CSO with a proportion of 88% tap or rain water respectively to raw sewage was mixed. This is in accordance to the amount of stormwater determined in CSO events in France (69-95%) (Gasperi et al., 2012) and Germany (73-95%) (Launay et al., 2016).

The RSF feeding duration of the CSO simulation lasted 15 min, the retaining lasted 2.5 h and drainage between 2.5 and 3 h (at 30 mL/s/m²). Time intervals between two CSO events were at least two weeks with normal STP feeding mode.

5.2.2 Sampling

Grab samples of RSF inflow and outflow were taken at $RSF_{CSO+STP}$ during CSO feeding and at $RSF_{CSO+STP}$ and RSF_{STP} during subsequent STP effluent feeding (Figure 2). CSO samples were taken directly from the container within 30 min before CSO simulation started. During CSO feeding, a composite sample over 2 h with 10 min between each sub-sample was taken at the outflow of $RSF_{CSO+STP}$. During STP effluent feeding, composite samples over 1.5 h with 10 min between each sub-sample were taken at RSF inflow and 3.25 h later at RSF outflow. 3.25h equals the hydraulic retention time of the RSF (Brunsch et al., 2018a) of both $RSF_{CSO+STP}$ and RSF_{STP}. Sampling during STP effluent feeding was performed at the beginning and at the end

of the 28 h feeding period (Figure 5-1). Samples were analysed for TOC, DOC, nutrients and OMPs. Samples for OMP analysis were stored in brown glass bottles, samples for TOC and DOC were stored in white glass bottles and acidified, immediately cooled with thermal packs and stored at 4 °C in the laboratory before analysis. The samples were stored for a maximum of four days before analysis.

5.2.3 Analysis

Water temperature was measured in a 20 min interval during sampling. TOC and DOC were analysed by catalytic oxidation and infrared detection (according to DIN EN 1484), ammonia nitrogen (NH_4-N) by acidimetric determination (according to DIN 38406 - 5-2), nitrate nitrogen (NO_3-N) by ion chromatography (according to DIN EN ISO 10304 – 1/2), total phosphorous (P_{tot}) by inductively coupled plasma optical emission spectrometry (ICP-OES) (according to DIN EN ISO 11885) and ortho-phosphate phosphorous ($O\text{-}PO_4\text{-}P$) by flow injection analysis (FIA) (according to DIN EN ISO 15681-1).

Furthermore, 21 OMPs were analysed; corrosion inhibitor 1H-benzotriazole (1HB) and its transformation product 1H-benzotriazole-4-methyl (1HB-4M), caffeine (CAF), the sweetener acesulfame (ACF), the pharmaceuticals sotalol (STL), metoprolol (MTP), bisoprolol (BSP), candesartan (CAS) and valsartan (VAS) to treat high blood pressure, metformin (MTF) for diabetes treatment, the anti-epileptic drugs gabapentin (GBP), carbamazepine (CBZ) and its transformation product carbamazepine-dihydro-dihydroxy (CBZ-Di), the antibiotic drug sulfamethoxazole (SMX), the anti-inflammatory drugs naproxen (NPX), diclofenac (DCF) and its transformation product 4-hydroxy-diclofenac (DCF-4H), the musk compound galaxolide (HHCB), the flame retardants Tris(2-chlorisopropyl)phosphate (TCPP) and Tris(2-chlorethyl)phosphate (TCEP) as well as DEET, the active ingredient in insect repellent.

MTF, GBP, CAF, CBZ, CBZ-Di, SMX, STL, 1HB, 1HB-4M, MTP, BSP, DTA, VAS, CAS and ACF were analysed by liquid chromatography with mass spectrometry; a 1260 Infinity LC (Agilent, USA) system with 6460 Triple Quad MS (Agilent).

DCF, DCF-4H, NPX, HHCB, TCPP, TCEP and DEET were analysed by gas chromatography with mass spectrometry (GC-MS) on a GC Trace 1310 (Thermo, USA) with a TSQ 8000 (Thermo, USA) Triple Quad MS. More detailed information on OMP analyses has been given in Brunsch et al. (2018).

Most investigated compounds were detected in at least eight out of nine samples in both CSO and STP effluent. Exceptions are NH_4-N, which was not detected in STP effluent, CAF which was detected only once in STP effluent, and ACF, which was detected in four out of nine STP effluent samples. SMX on the other hand was detected in nine out of nine STP effluent samples but only in three out of nine CSO-samples. For data evaluation, non-detectable values were set to the limit of quantification.

The effect of CSO events on the treatment efficiency of RSF was tested by comparing removal at STP effluent treatment of $RSF_{CSO+STP}$ to removal of RSF_{STP}. Therefore, the results of $RSF_{CSO+STP}$ and RSF_{STP} are compared by applying two different approaches to the removal data, I) a statistical theory motivated paired T-test and II) a practically motivated assumption, that removals of the two tested RSFs can be considered comparable for cases where the deviation in removal does not exceed 20%, i.e. meeting the condition 0.80 * removal RSF_{STP} < removal $RSF_{CSO+STP}$ < 1.20 * removal RSF_{STP} (OMPs with a median removal of +/- 20% are considered as not removable to cover for potential analytical and sampling inaccuracies). The two approaches were compared.

5.3 Results and discussion

5.3.1 Single CSO or STP effluent treatment

5.3.1.1 CSO and STP effluent characteristics

The RSFs were fed with STP effluent and diluted STP inflow (artificial CSO) respectively. We used artificial CSO as we wanted to demonstrate the proof of principle of dual usage of the RSF for CSO and STP effluent. Accordingly, inflow concentrations to the RSF for STP effluent and CSO treatment show some variation (Table 1). Concentrations of TOC, DOC, NH_4-N, P_{tot} and O-PO_4-P in CSO exceeded STP effluent concentrations by a factor three or more. This is in accordance with the well-known high removal of these in conventional STPs. Similarly, seven OMPs (VAS, MTF, ACF, GBP, CAF, NPX, TCPP) were detected in CSO at higher concentrations (by a factor of three or more) compared to STP effluent. This indicates removal of those OMPs in STPs as well. The other 14 OMPs appear in comparable concentrations in STP effluent and CSO. Concentrations of NO_3-N and SMX in STP effluent were higher (factor 45 and > 3.8) as in CSO. Higher NO_3-N concentrations can be explained by nitrification processes (Ottová et al., 1997). Back transformation of metabolites to the parent compound

SMX (Radke et al., 2009) during STP treatment might explain the > 3.8 fold higher SMX concentrations in STP effluent.

Finally, the higher concentration of TOC, DOC, nutrients and OMPs in the artificial CSO compared to the STP effluent could result in adsorption competition of additional compounds as they occur in real CSO, thus justifying the use of artificial CSO in our experiments.

Table 5-1: CSO concentrations and STP effluent (sample 1) concentration as measured at RSF inflow (n = 9). Units are mg/L for TOC, DOC and nutrients and μg/L for OMPs. Bold = median concentration that exceed the neighbouring value by a factor of >/= 2. Light grey= Median is equal to limit of quantification.

	Artificial CSO	STP effluent (S1)
	Median (Stand.Dev.)	Median (Stand.Dev.)
TOC	**59.20** (31.36)	6.47 (0.84)
DOC	**17.00** (5.70)	5.40 (0.90)
NH_4-N	**11.40** (4.10)	0.10 (0.00)
P_{tot}	**2.70** (0.82)	0.25 (0.04)
O-PO_4-P	**1.15** (0.56)	0.17 (0.04)
NO_3-N	0.20 (2.44)	**9.00** (2.90)
MTF	**55.00** (39.27)	0.41 (1.00)
CAF	**43.00** (19.04)	0.10 (0.03)
GBP	**6.30** (3.45)	2.20 (0.94)
ACF	**5.70** (5.33)	0.20 (0.30)
1HB	5.50 (1.05)	3.30 (0.50)
VAS	**4.10** (5.60)	0.30 (0.89)
CAS	2.90 (0.79)	2.90 (1.09)
DCF	2.50 (1.83)	2.40 (1.35)
MTP	1.40 (0.39)	0.94 (0.20)
TCPP	**1.30** (0.69)	0.43 (0.39)
CBZ-Di	1.10 (0.59)	1.00 (0.31)
STL	0.76 (0.25)	0.75 (0.30)
1HB-4M	0.76 (0.25)	0.71 (0.17)
HHCB	0.70 (0.41)	0.59 (0.48)
CBZ	0.68 (0.26)	0.70 (0.24)
NPX	**0.64** (0.89)	0.10 (0.09)
BSP	0.63 (0.20)	0.69 (0.19)
DCF-4H	0.41 (0.36)	0.65 (0.29)
DEET	0.22 (0.26)	0.13 (0.19)
TCEP	0.12 (0.06)	0.09 (0.04)
SMX	0.05 (0.07)	**0.19** (0.16)

Concentrations measured in our artificial CSO were compared to levels observed in real CSO in Germany. Even though the ratio of wastewater and tap water (artificial stormwater) was according to literature (5.2.1), concentrations of our CSO exceeded those from literature. TOC, P_{tot} and NH_4-N were measured to be two to six times higher in our CSO as in data represented by Brombach et al. (2005). Moreover, concentrations of 13 OMPs measured from our CSO were compared to concentrations determined by Launay et al. (2016). In our CSO, concentrations were higher by a factor two (ACF, 1HB-4M, TCPP) to 17 (DCF). CBZ was nine times higher and CAF six times higher. TCEP was the only OMP that was detected in higher concentrations (factor two) by Launay et al. (2016). This can be explained by different wastewater composition of individual sewer system catchment areas. As a consequence, due the high concentrations of OMPs in our CSO, our CSO simulation can be considered as close to worst-case pollutant concentration levels entering RSFs.

5.3.1.2 CSO and STP effluent removal efficiency

Removal was compared for CSO treatment ($RSF_{CSO+STP}$) and STP effluent treatment (RSF_{STP}) (Figure 5-3). For the latter, only removal from sample 1 (beginning of RSF feeding) was employed in order to have comparable feeding durations (Figure 5-2). Removal for DOC, TOC, NH_4-N, P_{tot} and O-PO_4-P was 74-99% at CSO treatment ($RSF_{CSO+STP}$) and 32-50% at STP effluent treatment (RSF_{STP}). For these particular parameters, higher removal during CSO treatment was observed compared to STP effluents treatment. These results show that the repetitive dual application does not affect the removal of these macro parameters by the CSO treatment. The difference between CSO treatment and STP effluent treatment appears related to the higher concentration of the CSO compared to wastewater that was already purified in the STP by a range of physical (e.g. sedimentation, filtration) biological (nitrification, denitrification) and chemical (e.g. phosphate precipitation) treatment steps. Apparently, the residual fractions of these macroparameters in STP effluent are more difficult to reduce further. Yet the results show that RSF are an effective post-treatment step for typical wastewater compounds. The negative removal of NO_3-N during CSO treatment is due to nitrification of ammonium and is an intended transformation process during the treatment. Nitrifying bacteria were already found in aerobic vertical flow constructed wetlands (Ottová et al., 1997). The presence of nitrifying bacteria also enhances biodegradation of several OMPs in RSFs (Rattier et al., 2014). OMP removal was -7 (CAS) to 100% (MTF) for CSO and 2 (CBZ) to 93% (DCF, DCF-4H) for STP effluent treatment. Deviations of median removal at CSO and STP effluent treatment is below 15% for most OMPs (except CAS, SMX, CBZ and CBZ-Di) and

therefore considered to be comparable. This demonstrates (compound specific) stable treatment by RSF under various conditions.

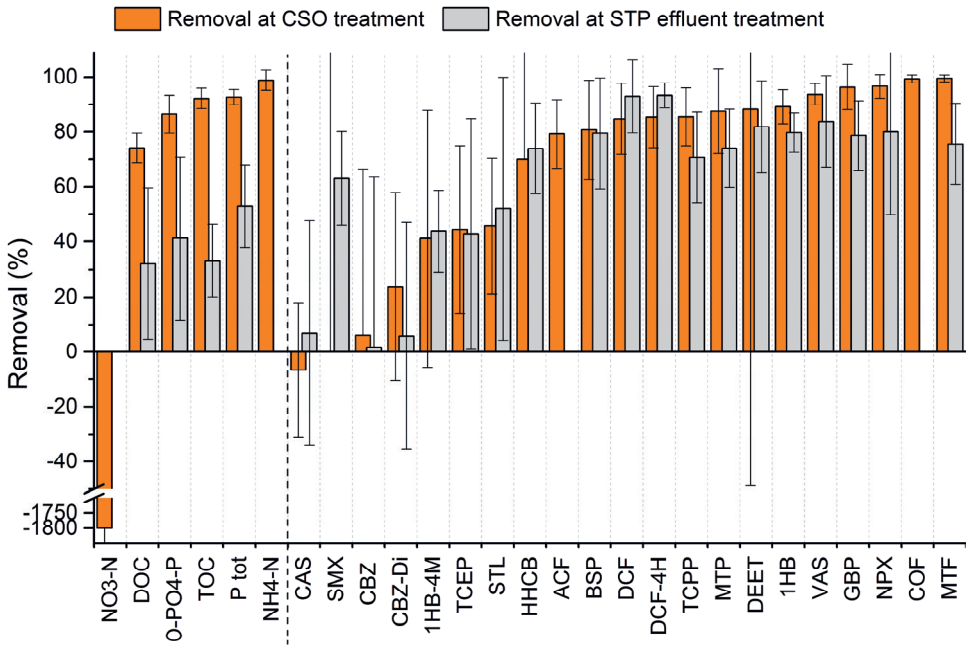


Figure 5-3: Removal for CSO treatment ($RSF_{CSO+STP}$) and STP effluent treatment (RSF_{STP}) in sample 1 (n = 9). Removal STP effluent for NH_4-N, CAF, ACF and removal CSO for SMX not applicable due to non-detectable concentrations.

Additionally, the impact of temperature on removal was tested. Biologically induced removal such as biodegradation would be expected to increase with temperature, whereas sorption would be negatively correlated to temperature (Schwarzenbach et al., 2016). For this approach only results of CSO treatment were considered. Temperature of the water samples varied from 12-27 °C with 19 °C as the average temperature. A correlation ($R^2 > 0.56$, $p = 0.004$) between temperature and removal could only be detected for 1HB, where lower temperatures led to higher removal. This indicates the dominance of sorption processes in removal, since sorption is generally more effective at lower temperatures (Schwarzenbach et al., 2016). No correlations were calculated for CAF and MTF because of their constant high removal (> 94%). For all other compounds R^2 was < 0.50 (and at the same time $p > 0.05$), which indicates I) that

there is no dominant effect of temperature on removal with suggests that sorption is not the main removal process for most compounds and II) that effects as induced by seasonal temperature variations are expected to be limited at RSF treatment. This is accordance to the result of previous RSF studies as shown in Brunsch et al. (2018).

5.3.2 CSO and STP effluent treatment – dual usage of RSF

5.3.2.1 Short term impact of CSO on RSF treatment efficiency

The impact of CSO operation on RSF treatment in different feeding sequences is shown by comparing removal at STP effluent treatment of $RSF_{CSO+STP}$ to removal of RSF_{STP}. It was found that operational conditions such as length of feeding sequences and dry phases affect compound removal by RSFs. In Figure 5-4 the removal at the two scenarios with 18 h (4 A, C) dry and 0 h dry period (4 B, D) between CSO and STP effluent feeding, and removal at the beginning (4 A, B) and end (4 C, D) of the feeding of both scenarios are presented.

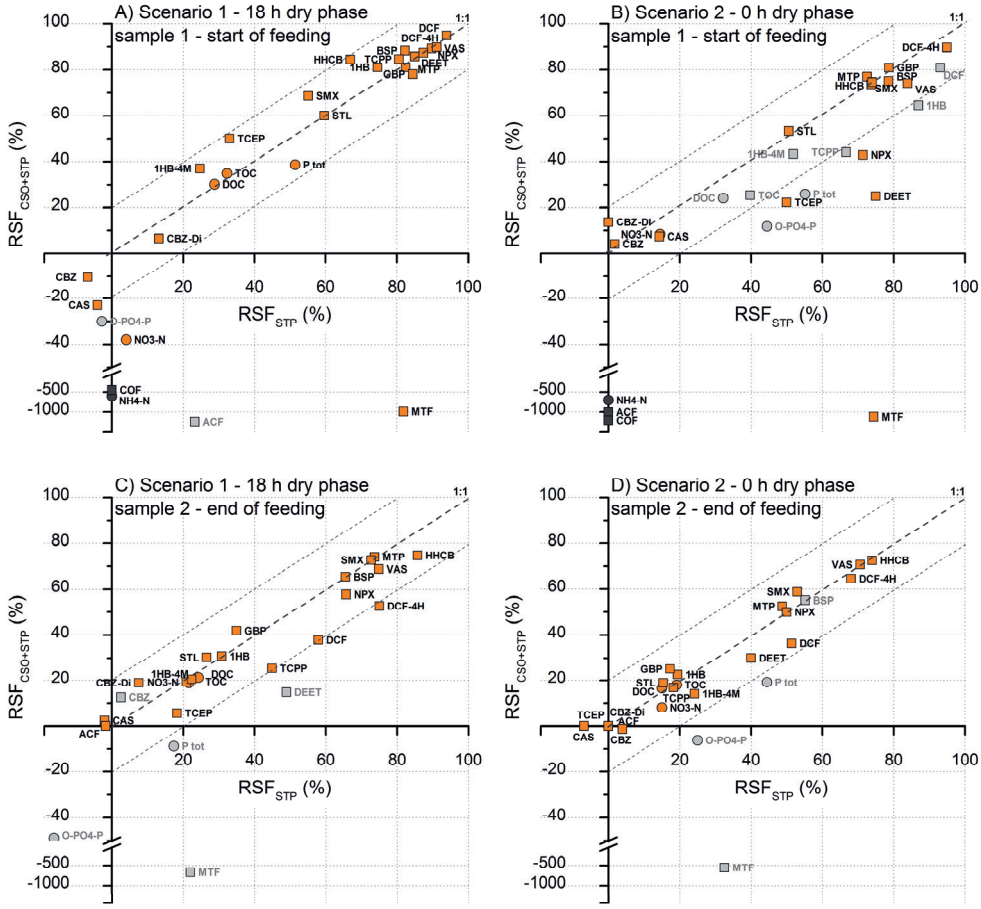


Figure 5-4: Median removal of $RSF_{CSO+STP}$ and RSF_{STP} at STP effluent treatment periods: circles: generic water quality compounds; squares: OMPs; dark grey symbols: non-detectable in RSF_{STP} inflow scenarios. A) Removal of sample 1 at scenario 1 = 18 h dry period, B) Removal of sample 1 at scenario 2 = 0 h dry period, C) Removal of sample 2 at scenario 1 = 18 h dry period, D) Removal of sample 2 at scenario 2 = 0 h dry period. Two methods of testing difference in RSF removal: 1. T-test; grey symbols: removal of $RSF_{CSO+STP}$ and RSF_{STP} is significantly ($p < 0.05$) different; orange symbols: removal is significantly ($p > 0.05$) not different: 2. Practical 20% deviation assumption: all points between the dotted lines representing +/-0.2 range along the 1:1 ratio diagonal (dashed) of $RSF_{CSO+STP}$ and RSF_{STP} are considered indifferent (no further colour indication).

Evaluation RSF removal performances

Results of the two different methods used for the comparison of $RSF_{CSO+STP}$ and RSF_{STP} showed significantly different removal according to the T-test, while the overall difference in median

removal was < 20% (Figure 5-4) for some compounds. This illustrates that the results of some compounds have a high accuracy enabling to distinguish significant differences within a narrow range. Nevertheless, the 20% threshold was used as the T-test method is based on average values and standard deviation of four (scenario 1) and five (scenario 2) values that showed high variations for several compounds. Moreover, Table 1 and Brunsch et al. (2018) show that removal in natural systems can be associated with variation and unexplained outliers in our RSF supporting this threshold. Consequently, a significantly different removal was detected by the T-test for some compounds that were identified as similar median removal by the practical 20% assumption. On the other hand, differences of compounds with a high deviation in median removal were considered not significantly different by the T test, such as for MTF in Figure 4 A and B. By considering both methods - the T-test and the practical 20% deviation from 1:1 diagonal by the median removal - we were able to evaluate differences in removal of $RSF_{CSO+STP}$ and RSF_{STP}. In fact, for three cases (A, C, D) both methods gave very similar results, and for case B most predominant differences were found when applying the T test and 20% deviation method to the data, which we discuss further below.

Scenario 1 – 18 h dry period between feeding; sample 1 – start of feeding, (Figure 5-4 A)
Removal efficiency of $RSF_{CSO+STP}$ and RSF_{STP} with 18 h dry periods between CSO and STP at the beginning of feeding is comparable. The median removal for all 21 OMPs was 78% for $RSF_{CSO+STP}$ and 75% for RSF_{STP}. A significantly different removal in both RSFs was determined for only ACF and $O\text{-}PO_4\text{-}P$. Moreover, a negative removal in $RSF_{CSO+STP}$ was detected for CAF, $NH_4\text{-}N$, ACF, MTF, $O\text{-}PO_4\text{-}P$ and $NO_3\text{-}N$. In RSF_{STP}, these compounds were either not detected in both RSF inflow and outflow or showed no or positive removal in RSF_{STP}. This negative removal is presumably due to the desorption of sorbed compounds or/and the leaching of compounds stored in pore water of the RSF. Both processes lead to a temporal concentration increase in the vertical RSF profile.

Scenario 2 – 0 h dry period between feeding; sample 1 – start of feeding, (Figure 5-4 B)
Omitting the dry period between CSO and STP feeding resulted in a median removal for all OMPs of 44% for $RSF_{CSO+STP}$ and 73% for RSF_{STP}. The removal for RSF_{STP} in scenario 2 is similar to scenario 1, sample 1, whereas removal for $RSF_{CSO+STP}$ showed 33% less removal in scenario 2 as compared to scenario 1. A significantly different removal for $RSF_{CSO+STP}$ and RSF_{STP} was found for 4 OMPs (DCF, 1HB, 1HB-4M, TCPP), whereas the median removal of 1HB and TCPP did show more than 20% deviation. TOC and DOC showed similar behaviour as most OMPs, with significantly less removal of $RSF_{CSO+STP}$ with no dry phase between CSO and STP effluent feeding then RSF_{STP}. However, the differences in median removal between $RSF_{CSO+STP}$

and RSF_{STP} did not exceed 20%. The wash out of compounds resulting in negative removal was also detected for CAF, NH_4-N ACF and MTF, but not for O-PO_4-P and NO_3-N as in the previous scenario.

Scenario 1 – 18 h dry period between feeding; sample 2 – end of feeding, (Figure 5-4 C)

The removal for both $RSF_{CSO+STP}$ and RSF_{STP} at the end of feeding was generally lower than at the beginning of feeding. Median removal for OMPs was 30 and 35% at the end of feeding for $RSF_{CSO+STP}$ and RSF_{STP}, respectively. This is approximately half of the initial removal observed at the beginning of feeding. DEET and P_{tot} were better removed in sample 2 in RSF_{STP} compared to $RSF_{CSO+STP}$. Wash out of NO_3-N, CAF, NH_4-N, and ACF could not be detected in sample 2 in contrast to sample 1 of the same scenario (Figure 4 A, B). Only MTF and O-PO_4-P were detected in higher concentrations in RSF outflow in both samples.

Scenario 2 – 0 h dry period between feeding; sample 2 – end of feeding, (Figure 5-4 D)

Removal without a dry period between CSO feeding and STP effluent feeding was also lower compared to sample 1 with 23% and 24% median removal for $RSF_{CSO+STP}$ and RSF_{STP}, respectively (sample 1: 44 and 73%, respectively). Additionally, the initial difference between $RSF_{CSO+STP}$ and RSF_{STP} diminished after 20h of STP feeding. The removal of BSP, O-PO_4-P and P_{tot} for both RSFs differed significantly from each other, whereas the median removal of BSP in the two RSFs was exactly the same (55%). MTF was the only substance were wash out was also observed in sample 2, although the magnitude of wash out was lower than in sample 1 (-550% in sample 2 removal compared to -1120% removal in sample 1).

Overall assessment of operational performance

By applying a dry period of 18 h between CSO and STP effluent feeding, the dual use of RSF with CSO and STP effluent treatment was most effective. The differences between $RSF_{CSO+STP}$ and RSF_{STP} were least pronounced for sample 1 when a dry period of 18 h was applied between CSO and STP effluent feeding (scenario 1), and most pronounced in sample 1 when the dry period was omitted (scenario 2). In general, best removal was observed for both RSFs with 18 h dry period between CSO and STP effluent feeding and in the beginning of the feeding phase. This dry phase is apparently important for more optimal treatment efficiency and prevents to a great extent washout of compounds that originate from previous CSO events. The treatment efficiency after approximately 20 hour of feeding STP effluent (sample 2) showed a decrease in removal efficiency for both RSFs in both scenarios. Besides that, the apparent differences between the two scenarios (with and without a dry period between CSO and effluent feeding) seem to diminish after approximately 20 h of operation. This proves that

effects of feeding CSO on removal efficiency of STP effluent treatment are only temporal. The $RSF_{CSO+STP}$ restores its treatment capacity within the 28 h STP feeding period.

For OMPs with a median removal of > 20% those with the lowest and highest standard deviations of median removal among the different scenarios (Figure 5-4 A – D) were assessed: the five OMPs with the highest deviations (and lowest robustness in RSF removal) were 1HB, GBP, TCPP, TCEP and DEET. The five OMPs with lowest deviation (and the highest robustness concerning RSF treatment) and median removal of > 50% in all compared scenarios and samples were: DCF-4H, BSP, SMX, VAS and HHCB.

In all four options (Figure 5-4 A, B, C, D), removal of MTF, O-PO_4-P and P_{tot} is higher in RSF_{STP}. A positive removal of O-PO_4-P was only observed in scenario 2 with 0 h dry period, which we cannot explain. The wash out of compounds and resulting negative removal was observed for MTF in every sample at $RSF_{CSO+STP}$. CAF, ACF, NO_3-N and NH_4-N were only washed out in the beginning of the feeding but seemed perished towards the end of feeding, approximately 20 h later. CAF, MTF and NH_4-N were completely removed during CSO treatment (Figure 5-3). CAF is known for its very good biodegradability in constructed wetlands (He et al., 2018). Additionally, all these compounds were found in much higher concentrations in CSO compared to STP effluent (Table 5-1). So, the leaching of small fractions CAF, MTF and NH_4-N originating from CSO itself already have a large impact on concentrations measured after the CSO event. The loads of these compounds to the environment are however limited when compared to emitted loads during the CSO. Furthermore, and most important, the loads of NH_4-N from CSO and STP effluent were reduced tremendously. The negative removal of NO_3-N in scenario 1 is most likely the result of nitrification of NH_4-N in the dry phases and desorption in the subsequent feeding hours (Dittmer, 2006). So for these compounds, small residues that were either sorbed to the filter material or stored in pore water could significantly affect the ratios between influent and effluent concentrations during STP effluent feeding.

5.3.2.2 Long-term impact of CSO on RSF treatment efficiency

The performance of $RSF_{CSO+STP}$ and RSF_{STP} 14 weeks before and 12 weeks after the CSO simulation tests was compared in order to test the long-term impact on RSF treatment efficiency (Figure 5-5).

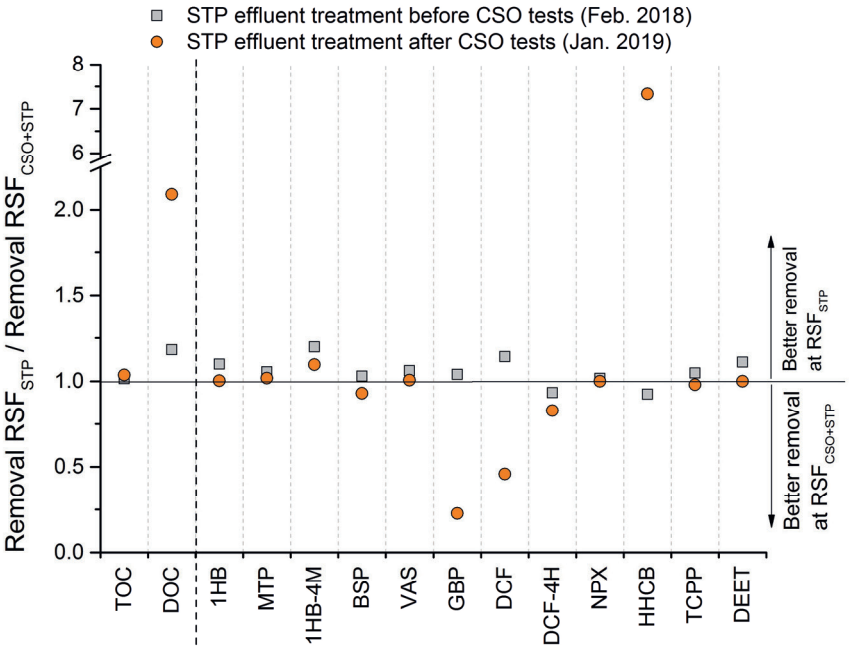


Figure 5-5: Treatment efficiency of RSF_{STP} and $RSF_{CSO+STP}$ before and after CSO simulation tests expressed in ratio removal RSF_{STP} to removal $RSF_{CSO+STP}$ for February 2018 (14 weeks before experiment start) and for January 2018 (12 weeks after experiment end). Compounds that were non-detectable or non-removable (removal < 0.2) in both RSFs were excluded.

DOC, TOC and 12 OMPs were studied for this comparison, as other compounds that were either non-detectable or non-removable cannot be used to determine differences. Before CSO simulation tests (February 2018, 8 °C water temperature), the removal ratio of the two test systems (removal RSF_{STP} / removal $RSF_{CSO+STP}$) was between 0.8 and 1.2 for all compounds. After CSO simulation tests (January 2019, 7 °C water temperature), the removal ratio RSF_{STP} / removal $RSF_{CSO+STP}$ remained between 0.8 and 1.2 for TOC and nine out of the 12 investigated OMPs (1HB, MTP, 1HB-4M, BSP, VAS, DCF-4H, NPX, TCPP, DEET). A better removal at RSF_{STP} was determined in January 2019 for DOC (62% removal at RSF_{STP}, 30% removal at $RSF_{CSO+STP}$) and HHCB (46% removal at RSF_{STP}, 6% removal at $RSF_{CSO+STP}$). However, the removal of DOC at $RSF_{CSO+STP}$ in January 2019 is in agreement with median removal for DOC shown in Figure 5-2 for RSF_{STP} (32%). HHCB removal of 6% at $RSF_{CSO+STP}$ on the other hand is below average while, better removal at $RSF_{CSO+STP}$ was determined in January 2019 for GBP (10% removal at RSF_{STP}, 45% removal at $RSF_{CSO+STP}$) and DCF (18% removal at RSF_{STP}, 40%

removal at $RSF_{CSO+STP}$). Here, both removal values for GBP and DCF at RSF_{STP} are below average compared to the results in section 5.3.1. Finally, we can state that removal of both RSFs are equal for all investigated compounds in February 2018 and are equal for 10 out of the 14 investigated compounds in January 2019. In some cases, the CSO treatment experiments lead to a lower treatment efficiency and in other cases to a higher treatment efficiency. Therefore, in general no relevant difference in treatment performance between the systems could be observed, and observed (minor) differences were likely due to the variability in removal of such natural systems. Consequently, a negative (or positive) impact of the CSO event does not have a negative impact on long term RSF treatment efficiency for degradable and/or absorbable compounds under regular STP effluent treatment conditions.

5.4 Conclusion

Retention soil filters have so far been used to treat solely combined sewer at overflow events and have additionally been tested as post treatment step, i.e. polishing for STPs effluents. The concept of the combined use, treating both CSO and STP effluent in one RSF, is innovative and had not been studied before. During dry weather, the RSF is used for the treatment of STP effluent, and the RSF is used to treat CSO in cases of CSO, triggered by heavy rainfall.

The research was conducted at a RSF pilot plant under real conditions over a period of six months. The results show that the dual approach is promising and feasible to full scale implementation. Generic compounds that indicate water quality such as TOC, DOC and nutrients that can occur in high concentrations in CSO can be effectively removed in RSFs, including biological transformation of ammonia under nitrifying conditions. Additionally, the effective removal of several OMPs from CSO was shown, with best removal for OMPs with highest inflow concentrations such as MTF and CAF. Generic water quality compounds and some of the investigated OMPs appear in STP effluent in lower concentrations as in CSO. In addition, the RSF turned out to further remove residues found in the STP effluent.

Treating CSO between regular STP effluent treatment periods has only a short-term impact on the RSF performance. Compounds found in CSO at high concentration such as MTF, CAF and NH_4-N were partially washed out with the subsequent STP effluent feeding following a CSO event. This effect attenuates fast, and after ~20 h, no negative impacts on STP effluent treatment of previous CSO treatment were noticeable. To minimize the washout of compounds, we recommend, when possible- a dry phase between CSO and STP effluent feeding of 18 hours or more. Additionally, we found that the removal efficiency is the highest

in the beginning of one RSF feeding phase and decreases only after 20 hours. Shorter cycle of feeding and dry periods might improve the overall treatment efficiency and reduce OMP emissions to surface waters. Finding the optimal duration of subsequent feeding and dry periods for optimal OMP removal is recommended for further studies. In conclusion, our results show that the dual use of RSFs at STPs at moderate climate conditions, typical for Western Europe, is a very good approach to make optimal use of treatment infrastructure and reduce contamination of surface waters. Thereby, the dual use of RSF is very promising for full scale application.

Acknowledgement

The project AquaNES "Demonstrating synergies in combined natural and engineered processes for water treatment systems" has received funding from the European Union´s Horizon 2020 programme (689450). The authors are grateful for the financial support of the project. Thanks also to S. Kindgen-Gronwald, M. Reif for chemical analysis, to K. Knorz for input on the research. R. Krump and the staff of the Rheinbach sewage treatment plant for technical support and T. Wagner for constructive criticism on the manuscript.

Chapter 6

General discussion

6.1 From theory to practice – the adoption of monitoring, modelling and measures

6.1.1 The Swist catchment as study site

The motivation of this study was to understand the origin, transport and fate of wastewater associated organic micropollutants (OMPs) in a real river system and to explore an innovative measure to reduce OMP emissions to the environment. The catchment of the Swist river was chosen for this research. The Swist is a tributary of the Erft river and part of the Rhine river catchment, close to the city of Bonn in North Rhine-Westphalia. Management of the Swist river catchment is accomplished by the local water board Erftverband. Following properties made the Swist catchment most ideal for this research:

- The river Swist has a relatively high wastewater load of up to about 70% during dry weather conditions, enhancing especially the loads of pollutants in the Swist which are persistent during sewage treatment. This high pollutant load makes the river relevant in terms of achieving the Water Framework Directive (WFD) goals to get a good chemical water quality. For this reason, the water board Erftverband also fostered the idea of upgrading sewage treatment plants (STPs) for additional wastewater purification. Furthermore, the high wastewater load promotes high expected OMP concentrations and less findings below limit of quantification in analytics.

- The four STPs in the Swist catchment present the only continuous input pathways for wastewater associated OMPs in the catchment during dry weather. With no storm driven emission inputs (e. g. combined sewer overflow, separate sewer outlets, landscape runoff), it was possible to measure all OMP emissions in this catchment.

- The discharge of the Swist is not heavily affected by additional emission inputs such as direct discharge from large industries or groundwater discharge, extracted due to mining activities from mining industries (as it is the case in the Erft river).

- The relatively short river course of 44 km from source to mouth makes sampling and simulation of the river best possible. With a flow time of max. 5 h from the STPs to the river mouth, the fate of OMPs in the river and the diurnal concentration variability could be studied. Moreover, the settings of the water quality model as applied in Chapter 3 could be accomplished in great detail (e. g. type and proportion

of vegetation along the river bed responsible for exposure to sunlight) and thus the simulation results are more reliable with a lower number of uncertainties compared to larger catchments.

- The Swist was already well studied in terms of emission inputs and the water quality situation in the river (Christoffels, 2008). The research on OMPs is a continuation of this work. Preceding research and monitoring results were helpful to understand the character of the river. The existing monitoring infrastructures (e. g. such as in the water quality station) was used and adapted to the special needs for OMP monitoring.
- The Erftverband is operating about 32 conventional retention soil filters (RSFs) for the treatment of combined sewer overflow or separate sewer outflows. The research presented here could build on the extended knowledge and experiences of the Erftverband with RSFs.

Chapter 2 and 3 showed that the appearance and concentrations of OMPs in the STPs and the river is highly variable. Sampling of all input pathways (STPs) and the river itself was successful during dry weather. By relating the results of STP samplings to results of river samplings, a diurnal mass balance was accomplished, showing OMPs fate in the river (Chapter 3). However, during storm weather, the Swist received additional emissions through combined sewer overflows, storm water basins and landscape runoff. Despite the small size of the catchment, sampling campaigns including all emission inputs during storm weather was not possible.

This means that in the small Swist catchment the number of emission inputs during dry weather was manageable for monitoring and transport studies, however during storm weather the system became very complex and thus many uncertainties are introduced, preventing successful mass balance studies under such situations. This needs to be taken into account when interpreting OMP monitoring data from this and similar catchments.

6.1.2 The importance of integrative research

The goal of the research was to gain appropriate findings on OMP origin, transport and fate in river catchments with a high relevance for management decisions. To meet this goal, we intended to perform an application-oriented approach focusing on field research. Nevertheless, it was apparent that field research alone would not result in the aspired goals

and hence the research was conducted according to the principles of a more holistic concept, extending field research with theory, modelling and laboratory research (Figure 6-1).

Figure 6-1: The four important keystones in research, theoretical research, laboratory research, computer modelling and field research, leading to successful field application

Initially starting with the theoretical study of OMP characteristics, behaviour and occurrence, „field experiments" were performed subsequently. The so-called field experiments were dedicated field monitoring studies that were designed and timed in such a way that environmental conditions could be evaluated and the question of how they affect OMP concentrations be answered. Thereby, conceptualisations taken from relevant literature were used to unravel the mechanisms behind the observed results and trends.

First, the outlets of the four STPs in the catchment were studied according to their OMP emission variability. OMP monitoring data in combination with hydrological data as well as

STP specific data revealed the dependency of OMP emissions on the hydraulic retention times of the STPs (Chapter 2). Changes in hydrological conditions (precipitation) could be directly related to dilution effects measured at STP effluents. The biodegradation effect at extended hydraulic retention times could only be confirmed with additional laboratory tests. Results gained under laboratory settings were crucial for this finding, because naturally varying factors (e. g. temperature, light intensity) influencing degradation processes, could only be controlled in laboratory tests. However, the performance of laboratory experiments in this research was limited, keeping in mind that they are time consuming and the results in the laboratory also might unravel mechanisms but are not representative of the situation in the field.

Second, the Swist river was studied for the occurrence, transport and fate of four OMPs (Chapter 3). Here, short-term concentration variability in rivers as determined through monitoring campaigns was presented and related to emission changes from STPs and removal processes in the river. Photodegradation was supposed to be the main removal process for diclofenac in the Swist river determined by the evaluation of river monitoring data and global radiation data. The simulation results of a water quality model verified this outcome. This is another example illustrating, that results of field research solely do not give full explanation of OMP behaviour in the real environment. Field research, and in this particular case OMP monitoring, has its limitations and thus modelling was used as a tool to close the knowledge gaps. In river basin research, modelling is a popular method to create mass balances for greater river catchments and/or catchments with divers OMP input pathways. Implementing a mass balance for the Swist river with the influence of storm water driven emission inputs is a recommended continuation of this research.

Putting the above-mentioned aspects in a broader context this means that:

- Temporal and spatial data gaps from monitoring programs can be filled by the application of computer models.
- The use of computer models, laboratory test results and literature data can effectively help in interpreting field research results.
- The other way around, data and findings from field research are used as input data for models or form the base for further laboratory test settings.
- By means of field experiments the results of theory and laboratory experiments can be tested or transferred to real life systems.

Findings as described in Chapter 2 and 3 on OMP concentrations in the environment show the need for measures to reduce OMPs. Accordingly, in Chapter 4 and 5 the efficiency of retention soil filters in OMP removal was demonstrated by long-term investigation of a pilot plant located at a real STP. Results of this research paved the way for large scale field application of a measure that seems promising in the removal of OMPs from the aquatic environment.

In conclusion, the methods and outcomes of this research exemplify the interdependency of four important keystones in research: theoretical research, laboratory research, computer modelling and field research. The integrative use of these four research keystones enables best possible approaches in field application including the detection of solutions to mitigate pollution in rivers and is thus is essential for environmental research.

6.1.3 OMP concentration variability and the challenge of designing a monitoring program

OMP monitoring data are required by many actors in the water sector such as water managers, environmental authorities, policy makers, scientists, hydraulic engineers. While the overarching goal is to better understand OMPs in the aquatic environment and to reduce environmental risks, the specific requirements of users can vary. This will affect the monitoring approach. Information on different time scales and spatial dimensions are required. This can comprise for example the determination of annual OMP loads or the determination of OMP dynamics (short-term and long-term) or the investigation of e. g. one OMP input pathway or a whole greater river basin. This makes the monitoring approach dependent on the special information needs of its users as well as the system (catchment) in which it is applied. Therefore, the monitoring program needs to be customized to fulfil the users' needs and system characteristics.

In this research a method to determine short-term concentration variability in STPs and rivers is presented. Planning such a monitoring campaign as was done in this research and in general, requires a comprehensive knowledge of possible factors influencing concentration variability. In the following, the reason for such short- and long-term concentration variabilities are discussed.

The temporal concentration variability in rivers is caused by emissions from input pathways (including the indirect influence of OMP usage) and removal processes in the river. These

factors are affected by changes temperature, light intensity and precipitation on a short-term level (weather changes) or seasonally (Figure 6-2).

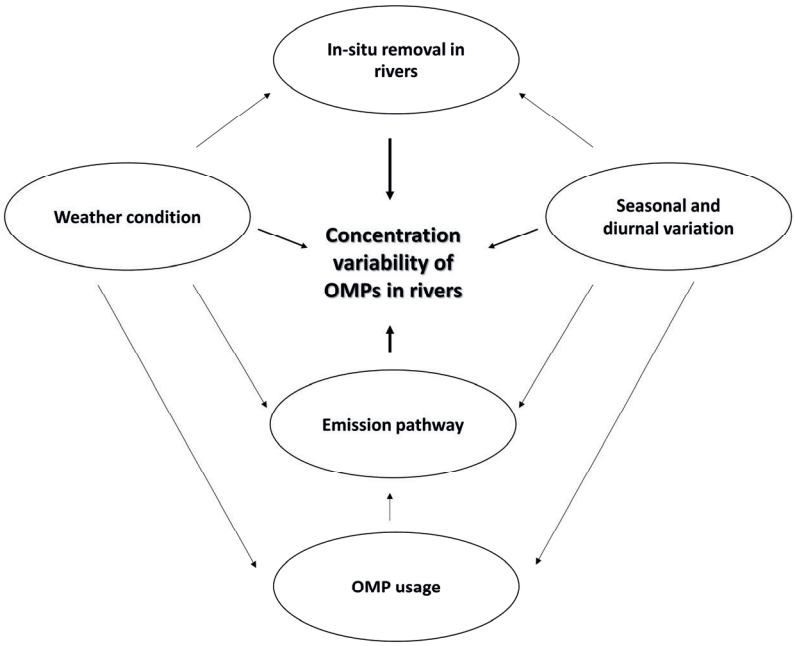


Figure 6-2: Factors triggering temporal concentration variability of OMPs in rivers

Changes in hydrological conditions either due to weather, seasons or water consumption affect water volumes stemming from STPs, landscape runoff or groundwater. Precipitation events and inflowing groundwater shape the natural flow regime of rivers and have a direct influence on concentration variability due to dilution effects. It was determined by Bai et al. (2018) that higher runoff during spring, which was induced by snow melt, facilitate the dilution of OMPs and thus a decrease in concentrations compared to the baseflow season. In Chapter 2 it was shown that hydrology (amount of rain fall and thus inflow volumes to the STP) influence OMP concentration variability at STP effluent, presumably affecting OMP concentration in the river. Additionally, in Chapter 3 it was shown that diurnal fluctuation in water consumption leading to variable STP effluent volumes and thus affecting concentration variability in the river. Furthermore, storm events cause additional emission inputs other than STPs, such as combined sewer overflow, separate sewer outlets and landscape runoff (see section 1.1.3) affecting not only river hydraulics but also the composition and concentration of OMPs in rivers. For example, special rain driven OMPs such as specific biocides, herbicides

or PAHs – washed out from building materials or deposited on the road due to traffic activities and transported together with rainwater – are found in higher concentration in the rivers during and after storm events (Launay et al., 2016; Wittmer et al., 2010).

The OMPs found in the river, are reflecting the *consumption* of such OMPs in the river catchment (Boulard et al., 2020; ter Laak et al., 2010). Therefore, changes in consumption patterns are another reason for temporal and spatial concentration variability in rivers. This consumption can change over longer time frames (years to decades) as a result of new products entering the market and phasing out of other products. In addition, consumption changes seasonally due to seasonal uses such as pesticide application (Comoretto and Chiron, 2005) or seasonal variation on pharmaceutical use. This was observed by Christoffels et al. (2016) when high concentrations of antibiotic pharmaceuticals were measured in the river during flue outbreaks in winter.

Moreover, differences in temperature and solar radiation such as in seasons and daytime will have an effect on *OMP removal processes* in both STPs and the river. In STPs, enhanced temperatures are promoting higher removal of OMPs in STPs, leading to lower concentrations in STP effluents (Musolff et al., 2009). In a river, the situation is similar. Increasing water temperatures result in higher *in situ* removal, in particular for biodegradable and volatile OMPs (Jaeger et al., 2019; Musolff et al., 2009). The transformation of photosensitive OMPs is dependent on the degree of solar radiation resulting in potentially higher photodegradation rates in summer compared to winter season as well as diurnal fluctuations (day-night rhythm) and thus short-term concentration variability (Jaeger et al., 2019; Chapter 3).

Consequently, the factors influencing concentration variability are diverse and the knowledge about this concentration ranges and their causes are essential for the interpretation of measurement results. Otherwise, single measurement results can easily be misinterpreted. The challenge is to reflect water quality situation in a river with all its variations. In order to meet this objective and depending on the goal of the research, a customized monitoring approach is needed. In the following, the primary aspects of such a monitoring approach - sampling frequency, sampling location, accompanying data, sampling method - are described.

In general, and in accordance to the research goals, a monitoring can be continuous or discrete over a certain time period. Monitoring regulated by law (e.g. monitoring of the chemical water quality status according to the WFD, Directive 2000/60/EC) might be continuous whereas monitoring in research is often discrete and limited to the period of the research project. The

factors as described earlier in this chapter can be categorised according to their *temporal appearance*. Hence, concentration variability occurs on short-term (due to e.g. weather changes or incidents), seasonal (due to e.g. temperature changes or pesticide application) or long-term (due to e.g. changes in consumer use). Accordingly, the monitoring duration and the *sampling frequency* can be adjusted (Figure 6-3).

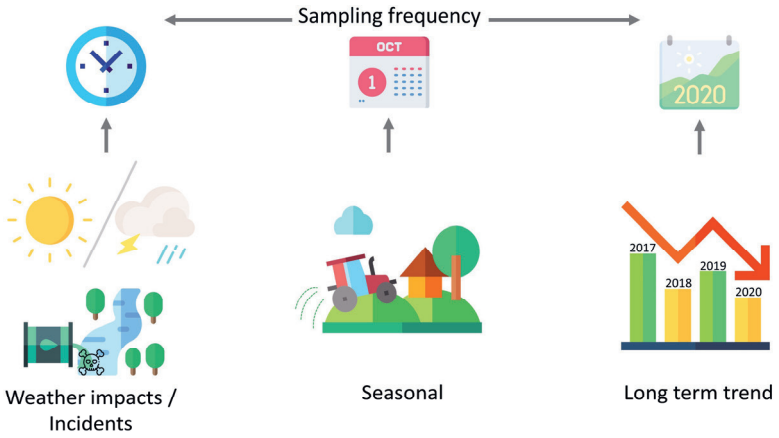


Figure 6-3: Concentration variability in rivers on different time scales and corresponding sampling frequencies

By choosing the *sampling location*, again the two factors input pathways and *in situ* removal should be taken into account in order to capture their influence on concentration dynamics in the river trajectory. As an example, sampling upstream and downstream an STP is recommended to capture influence of an STP on the OMP concentration in the river. Since temperature and solar radiation are relevant for *in situ* removal (as discussed above), one important factor is the light penetration into the river water (Jaeger et al., 2019). Hence, for instance sampling on sun exposed locations and shaded location are a method to study photodegradation in the river trajectory.

A*ccompanying data,* describing for example environmental conditions at the time of sampling, is crucial for the interpretation of monitoring data. In this research it was used in order to understand the fate and behaviour of OMPs in STPs, RSFs and the river. In Chapter 3 and 4 *in situ* removal processes were evaluated by correlating monitoring results with environmental data such as temperature or global radiation. With data of catchment

hydrology and river hydraulics (precipitation, water volume, etc.) dilution as well as OMP loads in the river were determined. In Chapter 2 precipitation data were used to categorize different sampling scenarios and in Chapter 4 temperature data were used to identify biodegradation in RSF during summer season.

In addition, when planning a monitoring campaign, the *sampling method* needs to be chosen. The two most common sampling methods are grab sampling and auto sampling. A higher sampling frequency require automated sampling. Also, the creation of individual composite samples – taken time proportional or flow proportional in the river – can be programmed and performed by autosamplers. The advantages of grab sampling are its higher flexibility and less expenses. A disadvantage might be the higher uncertainties (Ort et al., 2010). It was discussed in Chapter 2 and 4 that, within the frame of a representative sampling strategy, a higher number of grab samples or long-term research, respectively, can compensate for high uncertainties. In general, grab sampling is recommended if environmental or technical conditions of the investigated waters environment are either stable and/or well-known and thus data can be interpreted properly.

Finally, a well-planned monitoring will deliver best possible quality of data, which pose the base for research outcomes and water management decisions.

6.1.4 Mitigating OMP in the Swist river

The variety and the concentrations of OMPs found in surface waters in Europe (Loos et al., 2009) and in the Swist (Christoffels et al., 2016); Chapter 3), together with the European and German legislations, exemplify the need for the reduction of OMPs in rivers towards an enhanced water quality.

Within this research, retention soil filters (RSFs) were studied for their ability as treatment measure for OMPs. RSFs are especially widely used in Germany and are known for the reduction of a broad range of pollutants from storm water overflows. This traditional and well-known treatment method was taken and adapted to the new and special needs, in particular OMP mitigation, resulting in an innovative configuration of constructed wetlands. By means of a pilot plant study the relevance of RSFs as post-treatment for STP effluent was investigated. The performance of RSFs with conventional filter material was compared to a RSF with granular activated carbon (GAC) as additive. In a further step, it was tested whether

RSFs can be used for the dual treatment application by combining the new RSF application (STP post-treatment step) with the traditional RSF application (combined sewer treatment).

It was found that, within the research period, the removal rates for OMPs in the RSF with GAC were very good (> 80%, with the exception of metformin) (Chapter 4) and are thus comparable with technical treatment solutions such as advanced oxidation processes or activated carbon treatment. In Chapter 5 it was shown that RSFs for dual treatment are apparently capable for successfully reducing OMPs and other relevant water quality parameters from two different emission input pathways.

The investigated RSFs are a combination of technical and natural treatment techniques. The technical part is defined by the throttled in- and outflow, the possibility to control the feeding and dry phases and the GAC as special additive in the RSF material. This part allows for changes in settings and thus an optimised operation, whereas a disadvantage is that it is also a driver for carbon footprint with additional energy demand and highly processed construction and filter material for example. The natural part of the RSF (sand and organic filter material as well as vegetation) is more sustainable but the establishment of the vegetation and biomass needs time and appropriate removal cannot be achieved immediately after implementation. Moreover, removal efficiencies are for some OMPs dependent on environmental conditions such as temperature (Chapter 4) and are thus, especially in the start-up phase of operation, more unstable. However, the microbial community in the natural system will adapt itself to the prevalent (natural and operational) conditions and the biomass in the RSF grows with the operational years, resulting in more robust performance and potentially higher removal efficiencies after the start-up phase (Chapter 4; Brunsch et al., 2020).

Besides mitigating emissions into rivers, *additional advantages of RSFs can be found in monetary expenditures and sustainability.* The cost profile of RSFs is lower compared to purely technical post-treatment solutions. With regard to the annual wastewater load of an STP, the costs for RSF for dual treatment incl. GAC are up to 50% less than the costs of technical post-treatment steps such as ozonation or GAC treatment (Table 6-1). Especially the costs for operation, meaning energy consumption, personal costs and operating material, are about 40% lower in RSF treatment than for technical treatment (Brunsch et al., 2020).

Table 6-1: Specific annual costs in relation to the annual wastewater load: comparison of RSF and technical post-treatment methods (Brunsch et al., 2020)

STP size [population equivalents]	RSF for dual treatment with GAC [€/m³]	Ozon or GAC [€/m³]
27000	0.07 - 0.14	0.14 - 0.19
9000	0.12 - 0.20	0.23 - 0.27
3000	0.25 - 0.35	0.36 - 0.39

Besides the primary purpose of the purification of treated wastewater, the RSFs have an additional positive effect on the environment and this makes them more sustainable than technical post-treatment steps. Ecosystem studies on the study site revealed a positive effect in carbon storage and pollination service (Zawadzka et al., 2019). For the general public the RSFs looks like ponds, densely overgrown with reed and thus people's perception on the aesthetic value of the RSFs as compared to their engineered equivalents are largely positive (Zawadzka et al., 2019). However, the RSFs require a high amount of space and thus the available space at the specific location where water purification is needed, is one major limiting factor for their implementation.

The study on RSF with GAC for the treatment of solely STP effluent and/or the dual treatment system were the first of its kind and thus motivated for *additional research questions*. It is recommended to make this treatment method "greener" and more effective regarding RSFs construction costs while at the same time optimise the removal of a broad range of OMPs.

This can be done by:

- Optimizing the treatment cycle regarding dry phases and feeding.
- Optimizing the amount of GAC with the aim to have the best removal efficiencies and lowest carbon footprint.
- Determining the long-term efficiency and life time of GAC in RSFs and potential of bioregeneration of the GAC present in the RSFs.
- Determining degradation processes responsible of OMP removal in RSFs and potentially verify the theory on biodegradation and sorption processes as shown in Chapter 4 and 5.

- Investigating the role of reed or possible alternative plants in the context of phytodegradation.
- Examining possibilities to promote biodiversity in RSFs (e.g. through diverse plants) and thus enhance ecosystem services.

6.1.5 *Field research – the challenge of interpreting data*

This research was assessed under real environmental conditions under the principle of "bridging science to practice". The occurrence, fate and behaviour for a broad range of OMPs were studied under real life conditions with wastewater and river water, "spiked" with OMPs by the complete community and affected by the local climate conditions. These uncontrollable conditions make the interpretation of data of field experiments challenging. Therefore, it is essential to determine the advantages and limitations of field research outcomes and how to interpret them in a scientific context. Here, research outcomes are linked to the research location. One main issue of field research is that the environmental conditions are dynamic in time and space. Factors characterising the ecosystems studied in this research and influencing the behaviour of OMPs within these systems are:

- Climatologic specifics such as hydrology, radiation intensity, temperature.
- River basin specifics: the nature of the river bed and the river meadow.
- Retention soil filter specifics: initial material and plants; operational conditions.
- Physico-chemical specifics of the water and soil matrices such as the totality and diversity of organic and inorganic compounds, pH, oxygen.
- Biological specifics in the water and soil matrices: the presence or absence of micro- and macroorganisms affecting the fate and removal of OMPs.

The interaction and the variability of these factors result in very complex systems. Knowing and measuring all these factors is (to a great extend) impossible. This is the main difference to laboratory research, where conditions are controlled. Following this, it is essential to know what can be expected from field and laboratory research. In Figure 6-4 these aspects are presented with regard to this research.

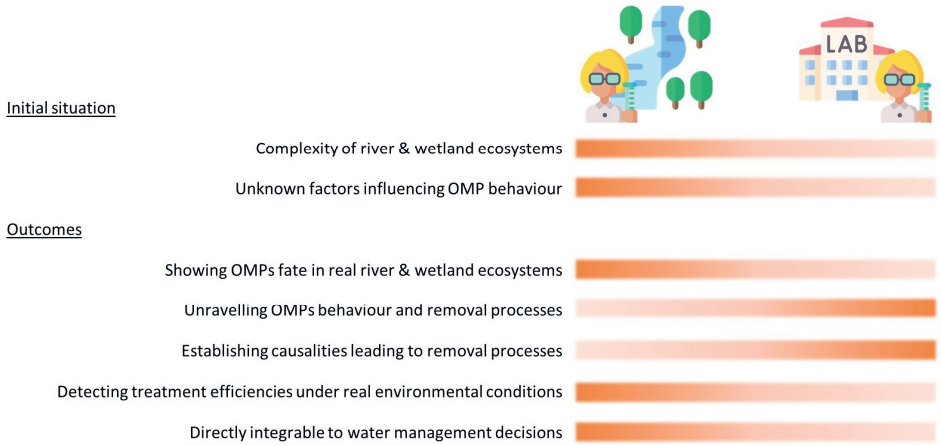


Figure 6-4: Comparative presentation of field and laboratory research characteristics. A higher colour intensity represents a higher significance.

Within this study it was possible to determine OMPs fate in STP effluents (Chapter 2), in a river (Chapter 3) and in RSFs (Chapter 4 and 5) by the calculation of removal rates for example. It was, however, impossible to give statements on the behaviour of OMPs with solely the results of field research, for instance the contribution of one removal process on the overall removal rate. Nevertheless, a system investigated under (near) natural conditions and with a long duration of operation says more about its use and benefits under environmental conditions. Therefore, the results are significant for implementation and thus for water managers.

6.2 Science for impact

6.2.1 Application of RSFs – Implementation on large scale

The positive outcomes of the RSF pilot plant study promoted the large scale implementation within the Swist river catchment. STP Rheinbach is discharging treated wastewater and combined sewer in cases of overflow situation into a small tributary of the Swist river, the Wallbach creek. This creek receives high wastewater loads during dry weather (up to 100%) as well as high hydraulic loading and additional pollution load during storm events and

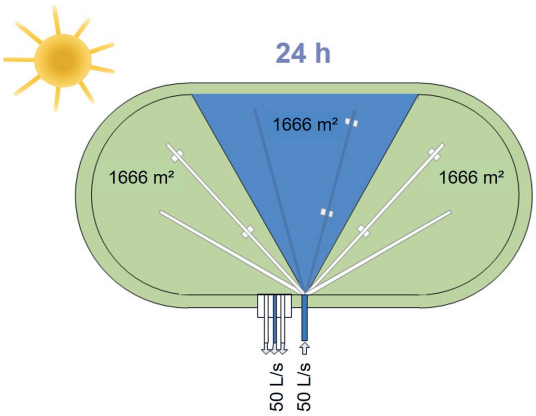
subsequent overflows. Therefore, it was initially planned to build a conventional RSF for CSO treatment as already applied in 32 locations in the Erft catchment.

The results of this study showed the need for further water purification and additionally presented the good removal efficiencies through RSFs. These findings paved the way for an individually designed large scale pilot plant for the dual treatment of STP effluent and combined sewer overflow. This new treatment technology in Rheinbach is named the RSF^{plus} (Figure 6-5). In 2018/2019 the RSF^{plus} was constructed. In spring 2019 the construction was completed and in autumn 2019 – after the reed (*phragmites australis*) was established – operation started. One special aspect of the RSF^{plus} is that the filter area of 5,000 m² is divided into three equally sized segments. During dry weather the segments are alternatingly fed with STP effluent (50 L/s) (Figure 6-6). This way, the dry phase can be guaranteed, which was found to be important for OMP removal efficiency. In case of storm water and full utilization of the STP, the RSF is used to clean combined sewer before entering the river. The STP effluent is then discharged directly and without post-treatment to the river.

The vertical set up of the filter material and the hydraulic loading (in dry weather) is in conformity to the settings of the pilot plant (Chapter 4). Here as well GAC is used as additive for the removal of persistent OMPs. The volume of GAC varies in the three segments of the RSF^{plus} with 0% (reference segment), 30% and 40% and is placed in 70 – 100 cm depths within the filter. Reason for this set up is due to further research intentions where the removal efficiencies of the three segments will be compared. Furthermore, biochar as used in the pilot plant in the upper layer was replaced by GAC. The two segments with GAC in the mid-layer have an additional upper GAC layer (20% of the filter volume) in 0 – 10 cm filter depths.

Figure 6-5: The RSF^{plus} under construction (left) (source: Ralf Eppinger, www.rheinbacher.de) and during the reed growth period (right) (source: Katharina Knorz, Erftverband)

Dry weather (regular) mode:



Storm water mode:

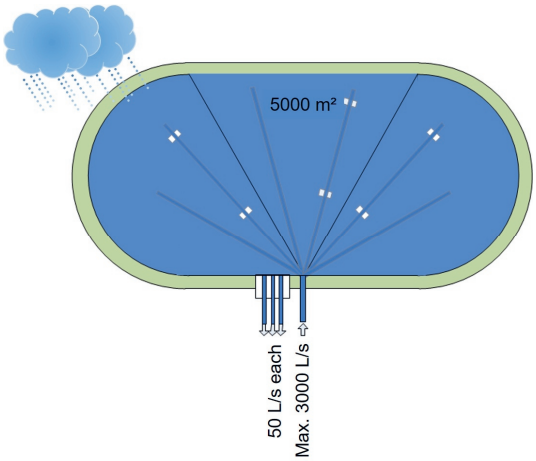


Figure 6-6: Operation mode of the RSF^{plus}: dry/regular weather mode, 1/3 of the filter area is used (treatment capacity Rheinbach RSF^{plus} = 50 L/s); storm water mode, full filter area is used (treatment capacity Rheinbach RSF^{plus} = 3,000 L/s).

Is the RSF^{plus} concept applicable in other regions?

The implementation of the RSF^{plus} is recommended for application in other regions due to the good results in pollutant removal, its robustness as well as the low maintenance effort. However, two factors must be considered: first, the number of suspended particles in the water entering the RSF is limited to max. 7 kg/m² per year in order to avoid clogging of the

RSF material (MKULNV, 2015). Second, the ground for the construction of such RSFs must be available. In the example of the RSF^{plus} in Rheinbach an area of 5,000 m² was needed to treat 50 L/s of STP effluent and 3,000 L/s combined sewer overflow. Accordingly, the RSFs might be best suited for small to midsize STPs.

In addition, operating RSFs in warmer regions might have a positive effect on OMP removal. The reason is that biodegradation is suspected to be an important degradation pathway for OMPs and this process is dependent on temperature. Hence, higher average air temperatures and a low temperature amplitude throughout the whole year might enhance removal capacities.

6.2.2 OMP management in rivers

This study was conducted under an approach following two main aspects: first, to fulfil the work in a scientific context and second, in an application-oriented context and thus generate an additional value for the water board Erftverband in particular, and for water managers in general. Within this approach, a strategy was developed to determine OMP pollution with its variabilities in a river catchment and to find explanations for this concentration variabilities. Moreover, an environmentally friendly way of how to mitigate this pollution in rivers was presented. Besides these aspects (as discussed in the previous chapters) this research had *impact on the Erftverbands OMP management* in the following manner:

- Awareness of the error susceptibility and the uncertainties which can appear during OMP sampling was raised and measures were implemented to keep these uncertainties to a minimum.
- The implementation of new methods in OMP analytics was facilitated and the number of OMPs in (standard) monitoring programs extended.
- With the experience of this study, the interpretation of results of (other) monitoring programs were supported by giving explanations on the sources and/or input pathways of OMPs in rivers.
- Results of this research were used in the application of new research projects.
- The monitoring infrastructure of this research was used and further development for additional research on OMPs or other emerging contaminants. For example, research projects on antibiotic resistant genes from STPs and in RSFs.

- The DWA water quality model (Christoffels, 2001) was used to simulate fate of different OMPs in the Swist and Erft river in order to predict future scenarios such as the impact of implementation of different measures.
- The positive results of the RSF pilot plant studies contributed for receiving funding for the construction of the large sale RSF^{plus}.
- The RSF^{plus} special sorptive material (GAC) was chosen according to results of this study.
- The operation mode of the large scale RSF^{plus} have been set according to the findings during pilot plant studies.

The benefit for OMP management in other river basins than the Swist lies in the *transferability* of this research's outcomes. The strategy as presented in this work is most relevant for water managers as this can be adapted in different locations, whereas the results of the study (e.g. the individual removal rates) might be specific for the investigated catchment area. It was presented in the previous section, that the concept of the RSF for wastewater treatment is applicable in different river catchments. Moreover, a general approach was shown in Chapter 2 to predict hydrology induced concentration ranges for persistent OMPs at STP outlets. Effluent concentrations could be determined very accurately with literature data on inhabitant specific loads. This approach is transferable to other river catchments and STPs respectively. The same applies for the approach of using a combination of mass balances and modelling. In Chapter 3 monitoring of a river with a high temporal resolution is combined with a model with a deterministic mechanistic basis of a variety of removal processes. With this approach, processes in the river could be unravelled and effects on environmental conditions on removal could be determined.

This study showed that the holistic approach (see 6.1.2) gives a systemic and science-based insight in the origin, transport and fate of OMPs in a river catchment, and provides information needed for OMP water management decisions. The results show, that a strategy as presented in this work is most relevant for water managers as this can be adapted to different locations, catchments and STPs. Since OMPs can vary in their behaviour, including removal rates during water treatment, under the influence of different conditions (e.g. light, temperature, water matrix composition), it is recommended to always include a number of laboratory and field tests to accommodate for catchment specific effects on OMP behaviour.

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Summary / Zusammenfassung

Summary

The occurrence of organic micropollutants in the aquatic environment is ubiquitous. They comprise compounds from diverse application areas such as pharmaceuticals, personal care products, pesticides or compounds used during industrial processing each containing a variety of sub-classes and substances. They are released into surface waters through point sources such as sewage treatment plant outlets, combined sewer overflow and storm water basin outlets and diffuse sources such as atmospheric deposition and surface or subsurface runoff.

Several micropollutants have negative impact on the environment due to their toxicity, persistence and bioaccumulation potential. For this reason, European legislations such as the Water Framework Directive require the observation of such harmful micropollutants. For some of them, environmental quality standards (legal thresholds) are already in place and it is expected that the number of micropollutants that will require monitoring and have environmental quality standards will grow in the near future.

Therefore, water managers are confronted with new challenges: to measure and evaluate the occurrence of organic micropollutants in surface waters and to find adequate measures to mitigate them in the water cycle. Thus, an application-oriented research was accomplished with the aim to understand the origin, transport and fate of wastewater associated organic micropollutants and moreover to find a "ready-for-implementation" measure to reduce these emissions to the environment.

The research was conducted in the Swist basin, a small and well-defined catchment area within the greater rhine river catchment, close to the city of Bonn in North Rhine-Westphalia, Germany.

In Chapter 2, emissions entering the river are assessed. Concentrations of carbamazepine, diclofenac and metoprolol were studied in the effluent of the four sewage treatment plants within the Swist river catchment. It is found that the concentrations of these pharmaceuticals vary a lot within (and between) the treatment plants (33 – 55% standard deviation). This is related to the hydraulic retention time of the wastewater in the sewage treatment plants. The hydraulic retention time in turn is dependent on the amount of sewage treatment plant inflow and thus the hydraulic situation which is heavily affected by the precipitation in the catchment area. A linear relation of concentrations and hydraulic retention time is observed, showing the dilution effect which increases at high sewage treatment plant inflow volumes. Additionally, it was demonstrated that these dilution-induced concentration ranges can be

reliably determined with inhabitant specific loads obtained from literature. At hydraulic retention times greater than 80 hours, the concentrations of biodegradable micropollutants (in this case metoprolol and diclofenac) are decreasing due to enhanced removal in the treatment plant. After dry periods and during subsequent storm events with high inflow volumes, it was revealed, that the dilution effect is delayed. This can be explained by incomplete mixing of wastewater in the tanks of the sewage treatment plant.

In Chapter 3, micropollutants in the river are assessed. Besides the effluent of the four sewage treatment plants (Chapter 2), the river Swist was investigated for the occurrence and short-term concentration variability of carbamazepine, diclofenac, 1H-benzotriazole and galaxolide. It was found that during dry weather conditions, with stable emission input concentrations, the concentrations in the river are fluctuating within the course of a day. Reasons for these diurnal concentration variations are varying sewage treatment plant effluent volumes and *in situ* removal in the river trajectory. The fate of micropollutants is described by combining mass balances studies and water quality modelling. By applying this method, it is demonstrated that carbamazepine and 1H-benzotriazole are persistent in the river, whereas diclofenac is removed mainly by photodegradation process and galaxolide is removed by diverse removal processes.

In Chapter 4 and 5 retention soil filters, a mitigation measure to remove micropollutants from the effluent of a sewage treatment plant is presented. Retention soil filters are a special configuration of vertical flow constructed wetlands, and widely used in Germany and in particular in North Rhine-Westphalia for the treatment of combined sewer overflow and separate sewer outlets. Two kinds of retention soil filter have been investigated for a period of three years for their potential in micropollutant removal from a sewage treatment plant effluent: a conventional retention soil filters with sand, calcium carbonate, planted with reed and a retention soil filter with granular activated carbon as additive. In Chapter 4 it is demonstrated that retention soil filters with granular activated carbon can reduce concentrations of a broad range of different organic micropollutants from sewage treatment plant effluent to below limits of quantification (95% median removal). The conventional retention soil filters can remove micropollutants as well, with best results for galaxolide, diclofenac 4-hydroxy, metoprolol and clarithromycin (75 – 79%). By monitoring the different layers of the retention soil filters individually, it is revealed that the upper layer with highest organic matter content is most effective.

In Chapter 5 the effluent polishing as studied in Chapter 4 is combined with the treatment of combined sewer overflow. These represents the intended application of a new generation of

constructed wetlands: the retention soil filter for the combined usage of sewage treatment plant effluent treatment during dry weather and of combined sewer treatment in case of storm and overflow events. It is shown that total organic carbon, dissolved organic carbon, nutrients and several micropollutants can be efficiently removed from combined sewer. After the treatment with combined sewer, some compounds (e.g. metformin) were washed out from the filter material at subsequent treatment with sewage treatment plant effluent. It is determined that with a dry period of 18 h between the two treatment cycles, this wash out effect can be prevented. Finally, it is concluded that both combined sewer overflow and sewage treatment plant effluent can be treated with the same retention soil filter without any negative long-term effects on its performance.

In Chapter 6 the advantages and challenges of combining scientific and application-oriented work is discussed with regard to monitoring, pilot plant studies and environmental fate research conducted at a whole river basin, all under the influence of uncontrollable environmental conditions. It is shown how the results of this work are implemented by the water board Erftverband, and how the results and conceptual findings can be translated to the wider context of the "science for impact" approach and more specifically the organic micropollutant management in river basins.

Zusammenfassung

Organische Spurenstoffe sind in der aquatischen Umwelt weit verbreitet. Zu ihnen gehören eine Vielzahl von Stoffen aus verschiedenen Stoffgruppen wie z. B. Arzneistoffe, Pflegeprodukte, Pestizide oder Stoffe aus dem verarbeitenden Gewerbe. Spurenstoffe gelangen durch Punkteintragspfade und/oder diffuse Eintragspfade in die Oberflächengewässer. Zu den Punkteintragspfaden gehören Einleitungen aus Kläranlagen und Regenrückhaltebecken sowie Mischwasserabschläge. Einträge aus dem Oberflächen- und Zwischenabfluss zählen, wie die atmosphärische Direktdeposition, zu den diffusen Eintragspfaden.

Einige Spurenstoffe haben aufgrund ihrer Toxizität, Persistenz oder ihrem Bioakkumulationspotenzial negative Auswirkungen auf die Umwelt. In der Wasserrahmenrichtlinie der Europäischen Kommission (EG-WRRL) wird unter anderem die Überwachung umweltschädlicher Stoffe geregelt. Für einige dieser Stoffe existieren zudem Umweltqualitätsnormen (legale Grenzwerte), die nicht überschritten werden dürfen. Einzelne Spurenstoffe sind in der EG-WRRL bereits aufgeführt; es ist jedoch zu erwarten, dass zukünftig weitere Spurenstoffe in die Liste der zu überwachenden umweltschädlichen Stoffe aufgenommen werden.

Die Entscheidungsträger der Wasserwirtschaft sind schon heute mit neuen Herausforderungen konfrontiert: Das Auftreten von organischen Spurenstoffen in Oberflächengewässern zu messen und zu bewerten sowie passende Maßnahmen zu finden, um die Emissionen in die aquatische Umwelt zu minimieren. Vor diesem Hintergrund wurde eine anwendungsbezogene Studie durchgeführt, mit dem Ziel, die Emissionen, den Transport und den Verbleib von abwasserbürtigen Spurenstoffen zu verstehen, sowie umsetzungsreife Maßnahmen zu finden, mit welchen die Spurenstoffemissionen reduziert werden können.

Diese Studie wurde in einem kleinen und übersichtlichen Flusseinzugsgebiet, dem Swisteinzugsgebiet in Nordrhein-Westfalen nahe der Stadt Bonn, durchgeführt. Im Swistgebiet erfolgt die Siedlungsentwässerung von Abwasser und Regenwasser vorwiegend gemeinsam über das Mischsystem.

In Kapitel 2 wurden die Konzentrationen der Arzneistoffe Carbamazepin, Diclofenac und Metoprolol in den Abläufen der vier Kläranlagen im Swisteinzugsgebiet untersucht. Im Ergebnis variieren diese Konzentrationen sehr stark; Konzentrationsschwankungen wurden sowohl innerhalb der einzelnen Kläranlagen, als auch im Vergleich der vier Kläranlagen untereinander festgestellt (33 – 55% Standardabweichung). Diese Schwankungen stehen im

Zusammenhang mit der hydraulischen Aufenthaltszeit des Abwassers in den Kläranlagen. Die hydraulische Aufenthaltszeit ist abhängig von der Zulaufmenge der Kläranlagen, welche wiederum von den Niederschlagsmengen im Einzugsgebiet beeinflusst wird. Es wurde eine lineare Korrelation von Spurenstoffkonzentrationen und der hydraulischen Aufenthaltszeit festgestellt, welcher den Verdünnungseffekt bei hohen Zulaufmengen (in diesem Fall Abwasser mit Regenwasser) zeigt. Basierend auf diesem Ergebnis wird eine Methode vorgestellt, mit der die durch Verdünnung initiierten Konzentrationsschwankungen in den Kläranlagenabläufen ohne Monitoringaufwand ermittelt werden können. Der lineare Zusammenhang von Stoffkonzentrationen und hydraulischen Aufenthaltszeiten kann von zwei Effekten überprägt werden: Während Starkregenereignissen, welche auf eine längere Trockenperiode folgen, wurde eine Verzögerung des sog. Verdünnungseffektes nachgewiesen, bedingt durch eine unvollständige Durchmischung des Abwassers in den Becken der Kläranlagen. Weiterhin wurde bei Trockenwetter und einer hydraulischen Aufenthaltszeit von mehr als 80 Stunden ein Rückgang der Konzentrationen von Metoprolol und Diclofenac festgestellt, was auf einen erhöhten biologischen Abbau dieser Stoffe zurückzuführen ist.

In Kapitel 3 wurden kurzfristige Konzentrationsschwankungen der Spurenstoffe Carbamazepin, Diclofenac, 1-H Benzotriazol und Galaxolid in der Swist durch spezifisches Monitoring von Tagesgängen untersucht. Der Verbleib dieser Spurenstoffe im Gewässer wurde durch die Kombination der Methoden Stoffstrombilanzierung und Wasserqualitätsmodellierung erforscht. Es wird gezeigt, dass während Trockenperioden mit gleichbleibenden Stoffkonzentrationen aus den Kläranlagenabläufen (Emissionen) die Konzentrationen im Gewässer tagesbedingten Schwankungen unterliegen. Grund dafür sind variable Ablaufmengen aus den Kläranlagen sowie *in situ* Abbauprozesse der Spurenstoffe im Gewässer. Durch die Methodenkombination Stoffstrombilanzierung und Wasserqualitätsmodellierung wurde festgestellt, dass Carbamazepin und 1-H Benzotriazol in der Swist persistent sind, Diclofenac jedoch hauptsächlich durch photolytische Prozesse und Galaxolid durch verschiedene Prozesse abgebaut wird.

Kapitel 4 befasst sich mit Retentionsbodenfilter zur Reduktion von Spurenstoffen aus Kläranlagenabläufen. Retentionsbodenfilter sind ein besonderer Typ von vertikal durchströmten bepflanzten Bodenfiltern (constructed wetlands) und besonders in Nordrhein-Westfalen für die Behandlung von Mischwasser und Regenwasser weit verbreitet. Zwei verschiedene Konfigurationen von Retentionsbodenfiltern wurden über einen Zeitraum von drei Jahren auf ihre Fähigkeit zum Spurenstoffrückhalt aus Kläranlagenabläufen hin

untersucht: Ein konventioneller Retentionsbodenfilter mit Sand, Calciumcarbonat, bepflanzt mit Schilf, sowie ein Retentionsbodenfilter mit dem gleichen Aufbau inklusive granulierter Aktivkohle als speziellen Zuschlagstoff. Es wurde festgestellt, dass Retentionsbodenfilter mit granulierter Aktivkohle viele verschiedene Spurenstoffe aus dem Kläranlagenablauf sehr gut zurückhalten; sie konnten im Ablauf der Retentionsbodenfilter analytisch nicht mehr nachgewiesen werden. Ferner sind auch die konventionellen Retentionsbodenfilter in der Lage Spurenstoffe zurückzuhalten. Die besten Rückhalteraten (75 – 79%) wurden für Galaxolid, Diclofenac-4-Hydroxy, Metoprolol und Clarithromycin ermittelt. Durch gezielte Beprobung der verschiedenen Schichten der Retentionsbodenfilter stellte sich heraus, dass bei konventionellen Retentionsbodenfiltern die obersten Schichten mit dem höchsten Anteil an organischer Substanz die Spurenstoffe am Effektivsten zurückhalten.

In Kapitel 5 wird die Eignung und Effektivität eines neuen innovativen Retentionsbodenfilters untersucht: Ein Retentionsbodenfilter für die duale Nutzung, welcher sowohl für die Reinigung von Kläranlagenabläufen (bei Trockenwetter) als auch für die Reinigung von Mischwasser (bei Abschlagsereignissen während Starkniederschlägen) eingesetzt wird. Aus den Studien resultiert, dass die Konzentrationen von verschiedenen Wasserqualitätsparametern aus dem Mischwasser (z. B. gelöster und gesamter organischer Kohlenstoff, Nährstoffe und diverse Spurenstoffe) effektiv minimiert werden. Manche Stoffe aus den Mischwasserabschlägen (z. B. Metformin) wurden jedoch kurz nach ihrem Eintrag und während der Trockenwetternutzung der Retentionsbodenfilter zum Teil wieder ausgewaschen. Ruhephasen von mindestens 18 Stunden zwischen zwei Beschickungszyklen wirken diesen Auswaschungseffekten allerdings entgegen. Negative Langzeiteffekte auf die Reinigungsleistung der Retentionsbodenfilter durch die zusätzliche Reinigung von Mischwasser konnten nicht nachgewiesen werden.

Die Kombination von wissenschaftlichen und anwendungsbezogenen Studien bieten einerseits Vorteile, wie z.B. eine einfachere Übertragbarkeit von Ergebnissen in die Praxis, andererseits stellen die diversen (unkontrollierbaren) Umwelteinflüsse eine Herausforderung für die empirische Forschung dar. Dies wird in Kapitel 6 in Bezug auf Monitoring, Pilotanlagenstudien und Umweltverhaltensstudien diskutiert. Abschließend wird gezeigt, wie die Ergebnisse und konzeptionellen Ansätze dieser Arbeit in die angewandte Wasserwirtschaft, respektive in das Spurenstoffmanagement in Flusseinzugsgebieten, eingegliedert werden können.

Acknowledgements

Until a few years ago, I had never thought of being in the position in which I am right now – writing the acknowledgments for my PhD thesis. It was a lucky coincidence that I met the right people who paved the way towards my PhD graduation. It would not have been possible without the help and support of you and so many others. So, thank you all (and I hope I will not forget anyone in the following).

Herr Christoffels, Sie haben den Keim für diese Arbeit gelegt und mich immer wieder ermutigt, weiter zu machen. Ich habe sehr viel von Ihrem umfangreichen Wissen über die Wasserwirtschaft profitiert und viel von Ihnen gelernt. Danke für alles.

Thomas, you introduced me to ETE and Huub. Thank you for believing in me and initiating this collaboration. From the beginning on, you helped me in composing a scientific work out of a huge amount of data. You supported me in defining my research questions and showed me how to bring single results into a broader context, relevant for the scientific community.

Huub, no matter how lost I sometimes got during my research - whilst talking to you, the fog in my head became even thicker. But after sorting and digesting the new impressions and inputs that I got during meetings with you, things were always much clearer and better organised afterwards. I truly admire your genius. Thank you for the great ideas you had for my research.

Alette, you joined the party last, but you didn´t have less impact on me in becoming an independent scientist. You provided new impulse to me and this research. You were always so perfectly well organised, reminded me to remain on track and concentrate on the purpose and intent of the research. Your tips on scientific writing were tremendously helpful.

Thomas, Alette and Huub, I really enjoyed our collaboration. Coming to ETE, in this inspiring and warm atmosphere was always a pleasure for me. I genuinely enjoyed the meetings with you, they were an enormous motivation boost for my work. I benefited from your huge pool of knowledge on micropollutants and because of each of you I have improved in scientific thinking and scientific working.

A big thank you to the ETE micropollutant team – Nora, Arnoud, Yujie, Wenbo, Azie, Laura and Thomas – for sharing your research with me, giving me ideas for my work and, not to forget, the nice talking in the corridors of the ETE department. A special thanks goes to Laura, who supported me with the completion of this work.

Vielen Dank an Herrn Engelhardt, Herrn Bucher, Herrn Schäfer, Ulrich Kern und Christian Gattke vom Erftverband, dass Sie diese Arbeit ermöglicht und unterstützt haben. Mein Dank

gilt allen Kolleginnen und Kollegen des Erftverbands für die schöne und für mich unvergessliche Zeit.

Danke an das Gewässergüteteam. Osman, Robert, Jens, Franz-Michael, Alex, Katharina, Dorothee, Marvin, Vera, ihr wart die besten Arbeitskollegen. Wir haben zusammen Wasser- und Bodenproben geholt, Messstationen geplant, aufgebaut, gewartet, Versuche im Feld und im Labor durchgeführt. Wir haben Daten ausgewertet, Ergebnisse diskutiert, an Präsentationen gearbeitet und Veröffentlichungen geschrieben. Egal ob im Feld, im Labor oder am Schreibtisch, ich hatte viel Spaß mit euch und jede/r hat auf seine Weise einen großen Beitrag für diese Arbeit geleitstet.

Lieben Dank auch an die vielen Studenten, Praktikanten und Bundesfreiwilligendienstler, die mit so viel Einsatz und Engagement an der Umsetzung der Forschungsarbeiten beteiligt waren.

Vielen Dank an Tilo, Helge und Eva für das Bereitstellen der hydrologischen Daten und die vielen Diskussionen über Abfluss und Niederschlag. Danke an Guido, für die Unterstützung rund ums Thema GIS. Danke an Andrea für die organisatorischen Arbeiten und deine gute Laune.

Während der schönen und geselligen Mittagspausen konnte ich wieder neue Energie tanken. Danke an Volker, Heather, Sascha und das Güte-Team dafür.

Danke an Herrn Trimborn und das ganze Team des Labors. Ich habe jede/n von euch mindestens einmal mit meinen Fragen und Sonderwünschen beansprucht. Ihr wart immer verständnisvoll und habt mich bei meinen Vorhaben unterstützt. Besonders bedanken will ich mich bei Sibylle und Martin. Ihr habt mir die Basis für diese Arbeit geliefert. Vielen Dank für die vielen Diskussionen, die netten Gespräche, und dass ihr immer offen dafür wart, Neues auszuprobieren. Danke, dass ihr mich über eure eigentlichen Aufgaben hinaus unterstützt habt. Die Zusammenarbeit mit euch hat mir viel Spaß gemacht und ich vermisse sie. Danke auch an Paul, der nicht nur immer die passenden Bausätze für die Versuchsaufbauten, sondern obendrein noch den richtigen Spruch auf Lager hatte.

Luk, du hast im Rahmen deiner Masterarbeit die Versuchsanlage gebaut, welche uns so tolle Dienste geleistet hat. Danke dafür, und danke auch an dich und Herrn Dahmen für den regen Informationsaustausch zum Thema Retentionsbodenfilter.

Danke an Herrn Hakenes und alle Mitarbeiter der Kläranlagen im Swistgebiet für die Unterstützung bei den Probenahmen und die Bereitstellung der Betriebsdaten. Danke an

Günther, Klaus, Steven, Richard, Nico und Herrn Schwartz von der Kläranlage Rheinbach für die vielen Kaffees, die netten Pausenrunden und die Hilfe bei der Instandhaltung der Bodenfilter.

Herr Rosellen, vielen Dank für ihre Unterstützung bei der Gütemodellierung. Vera, deine Masterarbeit und die vielen Diskussionen mit dir haben mir die Arbeit am Modell sehr erleichtert.

Simone, wir haben uns an unserem ersten Studientag kennengelernt. Nun hilfst du mir bei der Fertigstellung meiner Doktorarbeit. Danke für deine Freundschaft und Unterstützung.

Danke an Mama und Papa, dass ihr immer an mich geglaubt und mich auf all meinen Wegen gefördert und begleitet habt.

Darius, du bist der Grund für die verzögerte Abgabe dieser Arbeit. Ich bin sehr dankbar für die wundervolle Zeit die wir zusammen verbringen. Ali, du hast es mir dennoch ermöglicht die Arbeit fertig zu stellen. Danke!

About the author

Andrea Franziska Brunsch was born on June 8th, 1982, in Landshut, Germany. In 2003 she started her diploma studies in Geography at the University of Regensburg which she completed in 2006 with the intermediate diploma. Subsequently she moved to Karlsruhe to continue her academic education by studying Geoecology at the Karlsruhe Institute of Technology. In the frame of this study and during student works and internships she already set her focus on water management. Andrea completed her diploma program with a thesis on hydrology in the karst region of Gunung Kidul, Java, Indonesia, as part of an Integrated Water Resources Management project. After graduation in 2011, she started to work at the water board Erftverband in Bergheim as research assistant, where she was responsible for the scientific handling and project management for several regional, national and international research projects. Her work was focusing on surface water quality and, in particular, organic micropollutants as well as retention soil filters. In 2015, Andrea started her PhD at the Environmental Technology group at Wageningen University as external PhD student under the supervision of Prof. Dr Huub Rijnaarts, Dr Thomas ter Laak and Dr Alette Langenhoff, while at the same time continuing her work at Erftverband. She will proceed her career in the field of water management at the city administration of Bergisch Gladbach

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This research received financial support from Erftverband (Bergheim, Germany), the LIFE+ programme of the European Commission, the European Regional Development Funding through INTERREG IV B, the European Union´s Horizon 2020 programme and the Ministry for Climate Protection, Environment, Agriculture, Nature Conservation and Consumer Protection of the German State of North Rhine-Westphalia.

Financial support from Wageningen University for printing this dissertation is gratefully acknowledged.