# Field-based assessment of in-stream contaminant fate

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# ABSTRACT

Water quality of rivers worldwide is affected by the increasing use of organic micropollutants for human purposes. Most pollutants enter rivers via urban areas and wastewater treatment plants either freely dissolved, or attached to particles and may undergo transformation processes during their transport in rivers. There is still a lack of a holistic assessment of relevant processes, as well as comprehensive and representative field-based studies that describe and quantify the attenuation of these compounds in rivers. This thesis tackles this knowledge gap and aims to better understand processes that determine the in-stream contaminant fate.

Processes potentially relevant for the fate of organic micropollutants under field-conditions are summarized in this thesis in an integrated way including on the one hand hydrological aspects such as transport processes, groundwater and tributary inflow, and hyporheic exchange, as well as reactive processes comprising sorption, biodegradation, volatilisation and photodegradation. State of the art measurement approaches to capture these processes are compiled. The abundance of relevant processes under field-conditions and the fact that they take place simultaneously clearly shows the need for an appropriate sampling strategy to disentangle attenuation processes of pollutants in rivers.

For this purpose, a field study was conducted aiming at the identification of relevant water fluxes that contribute to the river discharge since they may lead either to an in-stream dilution or concentration increase of pollutants. Different potentially useful groundwater tracers were methodologically compared for this purpose. The results illustrate that the proper choice of tracer is crucial to quantify and localize groundwater inflows. In addition, these results clearly evidence the need for a holistic understanding of water fluxes in catchments, with respect to the water quality of inflowing water especially in terms of the in-stream chemical status and thus pollutant turnover processes in rivers.

On this basis, the goal of a following field study was the quantification of representative transformation rate constants of selected organic micropollutants as they are transported downstream from the wastewater treatment plant (selected indicator substances). The same water parcels were compared at two sequential reaches to investigate relevant environmental factors that may differ between both reaches and thus influence the fate. The results demonstrate the important role of photolysis for the attenuation of dissolved organic pollutants despite the generally comparably low reactivity in the selected river system. The latter is, inter alia, attributed to the anthropogenic character of the river that leads to a fast travel time.

A holistic assessment of organic micropollutant transport in rivers compiles equally the dissolved and particle-bound pollutants which is the reason why selected hydrophobic compounds associated to suspended particles were traced through the catchment during high discharge conditions. The hydrophobic character of these compounds allows the identification of particle origin in the river. Moreover, the interaction between particle transport and the sediment storage is identified as important mechanism for particle associated pollutant transport in rivers.

In summary, the holistic approach of this thesis gives insights into relevant processes that determine the fate of organic micropollutants in fluvial systems. This work provides a sound basis for future field-based fate studies that aim to quantify attenuation processes in rivers.

# ZUSAMMENFASSUNG

Der zunehmende Einsatz von organischen Mikroschadstoffen für menschliche Zwecke beeinflusst die weltweite Wasserqualität von Flüssen. Die meisten Schadstoffe gelangen über städtische Flächen und Klärwässer in gelöster Form oder an Partikel gebunden in Flüsse und können während des Transportes in Fließgewässern Transformationsprozessen unterliegen. Eine ganzheitliche Bewertung relevanter Prozesse, sowie umfassende und repräsentative Feldstudien zu dem Verbleib dieser Stoffe in Flüssen fehlt bislang. Diese Arbeit setzt an dieser Wissenslücke an und soll zu einem verbesserten Verständnis von Abbauprozessen von Schadstoffen in Flüssen führen.

Unter Feldbedingungen potenziell für den Abbau organischer Mikroschadstoffe relevante Prozesse sind in dieser Arbeit ganzheitlich zusammengefasst. Dafür sind sowohl hydrologische Aspekte wie Transportprozesse, Grundwasser- und Nebenflusszuflüsse und hyporheischer Austausch, als auch reaktive Prozesse wie Sorption, Biodegradation, Volatilisierung und Fotodegradation berücksichtigt. Aktuelle Messmethoden zur Erfassung besagter Prozesse sind zusammengestellt. Die Fülle relevanter Prozesse im Feld und die Tatsache, dass diese gleichzeitig stattfinden, zeigt deutlich die Notwendigkeit einer geeigneten Beprobungsstrategie zur eindeutigen Differenzierung von Schadstoff Abbauprozessen in Flüssen.

Zu diesem Zweck wurde eine Feldstudie durchgeführt. Die Feldstudie zielte darauf ab für den Gesamtabfluss von Flüssen relevante Wasserzuflüsse zu erfassen, da diese zu einer Verdünnung oder einer Konzentrationserhöhung von Schadstoffen führen können. Dafür wurden verschiedene potenziell geeignete Grundwassertracer methodisch verglichen. Die Ergebnisse veranschaulichen, dass die Wahl des richtigen Tracers entscheidend für die Quantifizierung und Lokalisierung von Grundwasserzuflüssen ist. Zusätzlich zeigen die Ergebnisse deutlich die Notwendigkeit eines ganzheitlichen Verständnisses von Wasserflüssen in Einzugsgebieten im Hinblick auf die Wasserqualität des zufließenden Wassers, vor allem in Bezug auf den chemischen Zustand im Fluss und damit der darin stattfindenden Schadstoffumsatzprozesse.

Auf dieser Grundlage war das Ziel einer daran anschließenden Feldstudie die Quantifizierung von repräsentativen Umsatzraten-Konstanten von aus der Kläranlage stammenden und im Fluss transportierten organischen Mikroschadstoffen (ausgewählte Indikator-Arzneimittel). Dafür wurden dieselben Wasserpakete an zwei aufeinanderfolgenden Flussabschnitten verglichen. Durch den Vergleich der Flussabschnitte wurden die Umweltfaktoren untersucht, die sich zwischen den Abschnitten unterscheidenden und den Abbau beeinflussen können. Die Ergebnisse zeigen die wichtige Rolle des Fotoabbaus für den Rückgang gelöster organischer Schadstoffe trotz der allgemein vergleichsweise geringen Reaktivität im ausgewählten Flusssystem. Letzteres wird u.a. auf den anthropogenen Charakter und der damit einhergehenden schnellen Laufzeit des Flusswassers zurückgeführt.

Eine ganzheitliche Beurteilung des Transports organischer Mikroschadstoffe in Flüssen umfasst gleichermaßen gelöste als auch partikelgebundene Schadstoffe, weshalb ausgewählte hydrophobe und an Schwebstoffen assoziierte Verbindungen während hohen Abflussbedingungen im Einzugsgebiet nachverfolgt wurden. Der hydrophobe Charakter dieser Verbindungen erlaubt Rückschlüsse auf den Partikelursprung im Fluss. Darüber hinaus wird die Interaktion zwischen suspendierten

Partikeln und dem Sedimentspeicher als wichtiger Mechanismus für die an Partikel assoziierten Schadstofftransport in Flüssen identifiziert.
Zusammenfassend liefert der ganzheitliche Ansatz dieser Dissertation Einblicke zu relevanten Aspekten, die den Verbleib organischer Mikroschadstoffe in Fließgewässern beeinflussen. Diese Arbeit stellt eine fundierte Grundlage für zukünftige feldbasierte Studien dar, die darauf abzielen, Abbauprozesse von organischen Mikroschadstoffen in Flüssen unter Feldbedingungen zu quantifizieren.

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# THESIS

# 1 INTRODUCTION AND BACKGROUND

Freshwater demand is predicted to increase significantly in the coming decades due to the growing number of anthropogenic activities and population increase (Unesco 2017). Especially the growth in agricultural, industrial and domestic use contribute to the increased demand and most of these activities entail water contamination with a broad range of different anthropogenic and natural chemical compounds (Schwarzenbach et al. 2006). Many of these organic compounds are present at trace concentrations (ng $L^{-1}$ to µg $L^{-1}$; known as 'micropollutants') and comprise e.g. pharmaceuticals, pesticides, hormones, or hydrophobic organic compounds such as polycyclic aromatic hydrocarbons (PAHs) (Luo et al. 2014). Despite the low concentrations, micropollutants can raise a significant toxicological concern due to their detrimental effects for aquatic ecosystems and human health (Escher and Leusch 2012; Poongothai et al. 2007). In recent decades, attention has been directed to pollutants in rivers since they integrate water, suspended matter and pollutant emissions of the whole catchment. For a holistic understanding of pollutants in rivers, both the dissolved and the particle-associated transport has to be considered depending on the physiochemical properties of the selected pollutants. In general, sources of micropollutants into rivers are diverse and include e.g. agricultural runoff, urban areas or (domestic) wastewater (Luo et al. 2014). A broad range of studies demonstrated a concentration decrease along the longitudinal profile of the rivers due to turnover processes for dissolved compounds that entered the fluvial system via wastewater treatment plants (WWTP) (Acuña et al. 2015; Barber et al. 2011; Guillet et al. 2019; Kunkel and Radke 2012; Li et al. 2016; Writer et al. 2013a), but also for particle-attached pollutants during high-discharge conditions (Liu et al. 2019). Turnover processes in nature do no only rely on the chemicals themselves, but also on processes specific for a selected ecosystem. Rivers consist not only of the water body as seen at a first glance, but also include adjoining compartments such as the river bed sediment (Schwientek et al. 2017) or the hyporheic zone as transition zone between groundwater and surface water (Boano et al. 2014). All these compartments and especially the respective influence on turnover processes have to be considered for an improved understanding of in-river chemical fate of reactive compounds and for assessing their environmental impact. These transformation processes include for instance photo- or biodegradation and their kinetics are a measure for the river-specific self-purification capacity and thus for the water quality. Processes and their kinetics obtained from controlled laboratory settings benefit from extremely controlled and comparably easy to handle boundary conditions such as a small experimental setup, constant temperatures or precisely defined compounds' concentrations when measuring degradation rate constants. However, these obtained rates and processes are hardly comparable to natural systems (Acuña et al. 2015). Therefore, field-based investigations are indispensable for deepened knowledge on chemicals behaviour under natural conditions.

## 1.1 HYDROLOGICAL ASPECTS

Water and particle fluxes of catchments are shaped and influenced by the catchment and the river characteristics/ settings. From a catchment perspective, this includes e.g. the (hydro-) geology of the catchment, the river network or the river valley type, while the river settings includes e.g. the interaction with adjoining aquifers such as the losing river water conditions (Payn et al. 2009), the river morphology (e.g. in-stream riffle-pool sequences as indicator for partly infiltrating conditions (Pittroff et al. 2017) or the riverbed substrate and availability of (suspended) riverbed sediment. The latter is especially a relevant feature with respect to the role of suspended particles as transport vector for hydrophobic pollutants during high-discharge conditions (Schwientek et al. 2017). These hydrological aspects are directly related to in-stream hydrological processes such as e.g. transport processes or dilution of pollutants caused by inflowing water. Hydrological processes occur simultaneously to substance-specific processes which is why these two aspects are strongly coupled to each other in field-based investigations. Thus, knowledge on hydrology is fundamental for all further investigations on reactive processes, especially since both physical and biogeochemical process signatures are integrated at the catchment outlet and have to be disentangled based on one mass flux signal of dissolved (Mallard et al. 2014) and particle-bound pollutants (Schwientek et al. 2013b).

### 1.1.1 POLLUTANT MASS FLUXES AND PROCESSES DURING BASEFLOW CONDITIONS

Pollutant mass flux in rivers is classically measured via concentration specifications of dissolved compounds in water parcels (e.g. ng $L^{-1}$). Thus, concentration changes are not only due to changes in pollutant mass following additional inputs or loss processes, but are influenced by hydrological processes during baseflow conditions. These processes may disperse, dilute or even enrich compounds' mass and thus constitute attenuation processes that occur, in contrast to laboratory studies, only under field conditions. During baseflow conditions, the majority of organic pollutants in rivers is transported freely dissolved and mainly comes from point sources such as WWTPs (Müller et al. 2018) since traditional WWTP remove the pollutants only partly during the treatment process (Pal et al. 2010). The chemical concentration, as well as the volume of the inflow in comparison to the river discharge determine the contamination of the river water. The water from the WWTP effluent blends with the river water which leads, due to the temporal dynamic input, to water parcel specific concentrations of pollutants. This necessitates the comparison of the same water parcel as the water is transported downstream (so-called Lagrangian parcel). Downstream of these point sources, hydrological processes that may influence the Lagrangian parcel comprise transport processes (advection + dispersion) (Ji 2017), hyporheic exchange (Schaper et al. 2018), dilution caused by tributaries (Julien 2002) and groundwater inflow (Manamsa et al. 2016). Transport processes are crucial to consider when comparing the same water parcel (Antweiler et al. 2014). Dispersion of water along the longitudinal profile hampers comparability between water parcels (Guillet et al. 2019), and also hyporheic exchange of water (Schaper et al. 2018) can have a delaying effect for water parcels due to the different residence time in this zone in comparison to the flow in the open river channel. Tributaries, as well as inflowing groundwater significantly can influence the pollutant mass flux within the river in case of a contamination of inflowing water and therefore have to be considered separately.

### 1.1.2 POLLUTANT MASS FLUXES AND PROCESSES DURING HIGH DISCHARGE CONDITIONS

High discharge conditions may lead to a dilution effect of compounds emitted from the WWTP as main inflow pathway, whereas other chemical inputs such as surface runoff from urban areas introduced via e.g. sewer systems are highly important for the water quality in the river (DiBlasi et al. 2009; Luo et al. 2014). In contrast to baseflow conditions, particle-associated pollutant transport becomes more important due to the high concentrations of suspended particles and attached pollutants during these conditions (Rügner et al. 2019). Especially hydrophobic compounds are attached to particles and are, depending on the compound-specific distribution coefficient, known to contribute significantly to the annual chemical flux in catchments (Schwientek et al. 2017). The pollutant mass flux is thus controlled by the (introduced) suspended particle concentrations (e.g. in mg $L^{-1}$) during high discharge (Herrero et al. 2018) and mass of particle-attached pollutants (e.g. mg pollutant $g^{-1}$ particles) both in comparison to the concentration and contamination of prevailing or additionally introduced (cleaner) particles in the river (Schwientek et al. 2017). Origin of suspended particles may be surface erosion, bank erosion, the (re-) suspension of river bed sediments (Liu et al. 2018) and additional input of suspended particles from urban areas (DiBlasi et al. 2009). During high discharge conditions and associated turbulence, the resuspension of river sediment can make historical pollutions available again (Hamers et al. 2015). As particle-associated pollutants are transport downstream of the input source, an important process that influences the mass flux of pollutants in rivers is particle exchange which consists of deposition and (re-) mobilisation (Marttila et al. 2013) of suspended particles.

## 1.2 REACTIVE PROCESSES

Reactive processes influence the pollutant mass, i.e. the numerator in the concentration specification (e.g. ng $L^{-1}$). Within the river, either a (re)distribution to another compartment or a transformation to another compound can occur. Volatilisation and sorption are examples of distribution processes and describe the transfer from the water to the air in case of volatilisation (Schwarzenbach et al. 2003) and for sorption the transfer from the water to the particle-bound phase like e.g. (suspended) sediment (Rügner et al. 2019; Radke and Maier 2014). Reactive processes leading to a structure alteration of a compound (transformation processes) have been studied intensively for the last decades and mainly rely on the intrinsic physicochemical properties and the structure of each compound (Kümmerer 2009). Transformation processes comprise photodegradation, biodegradation or chemical transformation such as hydrolysis (Schwarzenbach et al. 2003). Photochemical degradation is an important attenuation process for many pharmaceuticals and pesticides and exclusively occurs in surface water (e.g., Jaeger et al. 2019; Kunkel and Radke 2012; Lin et al. 2006). Biodegradation is influenced by microbial activities whereas the hyporheic zone is one hotspot of this process due to the high density of microorganisms in this compartment (Kunkel and Radke 2008). Stream biofilms were also described as relevant compartment for biodegradation (Writer et al. 2013a) and recent investigations discuss the role of macrophytes for biodegradation due to the covering epiphytic biofilm (Jaeger et al. 2019).

## 1.3 MICROPOLLUTANTS AS PROCESS INDICATORS

Hydrological and reactive processes are strongly coupled to each other. Organic micropollutants originating from WWTPs have already been used for hydrological characterizations such as e.g. as indicators for surface water and groundwater interaction in the hyporheic zone (Banzhaf et al. 2012). This is possible since continuous improvements in analytical methods allow the detection of organic micropollutants even at low concentrations (Clara et al. 2004). Thus, despite the adverse impacts of these compounds on freshwater ecosystems, they can also serve for scientific purposes. As an example, in rivers, conservative organic micropollutants are frequently applied e.g. to consider dilution by GW inflow as concentrations of organic micropollutants are typically not detected in the groundwater (Dickenson et al. 2011; Li et al. 2016; Müller et al. 2018; Radke et al. 2010). A prominent example, among many other soluble compounds, is carbamazepine due to its long half-live compared to the travel time of river water and thus conservative character (Guillet et al. 2019; Kunkel and Radke 2012; Pal et al. 2010; Schwientek et al. 2016). The main advantage of organic micropollutants as tracers in comparison to especially geogenic compounds is the exact allocation to their source, which allows tracing back the origin of water during the mixing process of different water in aquatic systems. Thus, organic micropollutants constitute a complementary tool as process indicators to classical hydrological process indicator tracers such as conservative ions.

# 2 OBJECTIVES AND STRUCTURE OF THIS THESIS

The overall objective of the present thesis was to improve the understanding of the environmental fate of micropollutants in rivers directly in the field. More specifically, this thesis provides new insights into hydrological and reactive attenuation processes in rivers that influence the overall water quality at the outlet of catchments. Both dissolved and particle-attached contaminants have to be considered for a holistic understanding of the water quality of rivers which is why baseflow and high discharge conditions are examined. The major work packages are presented in **Fig. 1** starting with a conceptualization of relevant processes that influence pollutant attenuation under field conditions (**paper I**), characterisation of the general hydrological fluxes within a catchment during baseflow by comparing different environmental tracers to understand the role of the groundwater inflow (**paper II**) on the basis of which reactive processes of selected organic compounds can be quantified (**paper III**). Particle-associated pollutant transport is more important during high discharge conditions in comparison to dissolved pollutant transport which is why particle and associated contaminant dynamics was evaluated for the high-discharge scenario by tracing conservative organic micropollutants (**paper IV**).

In detail, this thesis aims to answer the following research questions:

- (i) What attenuation processes (reactive + hydrological) are conceptually relevant to comprehensively describe the fate of reactive pollutants in rivers and how can these processes be measured in the field?
- (ii) What is the role of water fluxes in catchments for the in-stream dilution or concentration increase of pollutants?
- (iii) Can representative transformation rate constants be quantified in the field by measuring indicator substances?
- (iv) What is the role of particles in rivers for the associated pollutant transport during high discharge conditions?

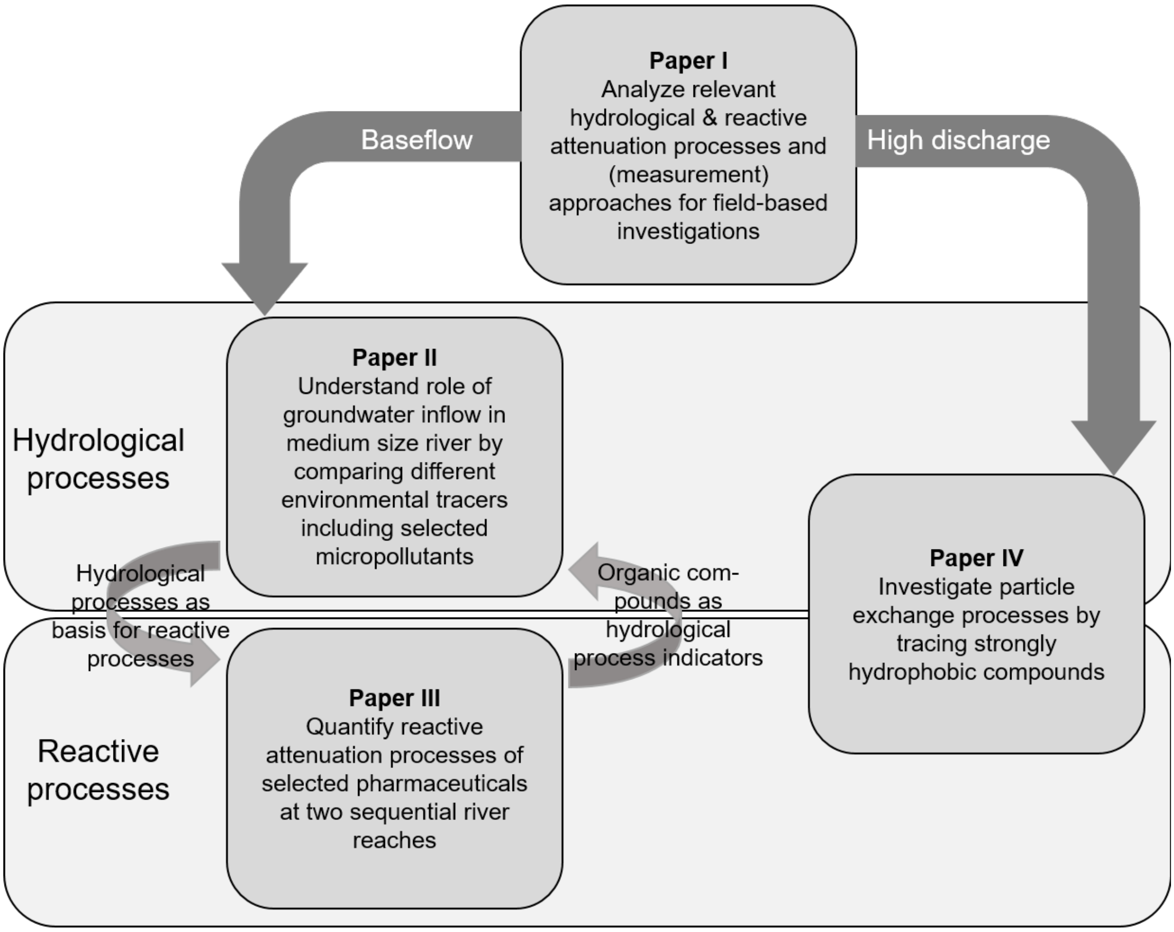

***Fig. 1:*** *Field based assessment of in-stream contaminant fate*

In **paper I** (chapter three), all processes potentially relevant for the fate of organic micropollutants under field-conditions are summarized including hydrological aspects on the one hand, as well as reactive processes on the other hand. Potential state of the art measurement approaches are presented. Based on the outcome of this publication, the gained knowledge was applied in a case study for the Ammer River (**paper II**) aiming in identifying hydrological settings of the river. The key findings are discussed in chapter four. With this understanding on the hydrological settings and water fluxes in the catchment, quantification of attenuation processes of organic micropollutants and process drivers was conducted (**paper III**) and is shown in chapter five. Hydrological settings and transport of pollutants during baseflow are hardly transferable to rain events, especially since a broad range of hydrophobic compounds is associated to suspended particles that are mobilised during high discharge. Chapter six (**paper IV**) presents results of relevant in-stream sediment and particle exchange processes in rivers traced by hydrophobic organic micropollutants. In chapter seven, I put the key findings of the previous sections in a broader context with a special focus on the interaction between hydrological aspects and reactive processes.

# 3 DESIGNING FIELD-BASED INVESTIGATIONS OF ORGANIC MICROPOLLUTANT FATE IN RIVERS

## 3.1 ABSTRACT

Organic micropollutants in rivers are emitted via diffuse and point sources like from agricultural practice or wastewater treatment plants (WWTP). Extensive laboratory and field experiments have been conducted to understand emissions and fate of these pollutants in freshwaters. Nevertheless, data is often difficult to compare since common protocols for appropriate approaches are largely missing. Thus, interpretation of the observed changes in substance concentrations and of the underlying fate of these compounds downstream of the chemical input into the river is still challenging. To narrow this research gap, (1) process understanding and (2) measurement approaches for field-based investigations are critically reviewed in this article. The review includes, on the one hand, processes that change the volume of the water (hydrological processes) and, on the other hand, processes that affect the substance mass within the water (distribution and transformation). Environmental boundary conditions for the purpose of better comparability of different attenuation studies, as well as promising state-of-the-art measurement approaches from different disciplines, are presented. This overview helps to develop a tailored procedure to assess turnover mechanisms of organic micropollutants under field conditions. In this respect, further research needs to standardize interdisciplinary approaches to increase the informative value of collected data.

## 3.2 INTRODUCTION

Micropollutants comprise anthropogenic and natural substances like industrial chemicals, daily care and consumer products, pharmaceuticals, hormones, pesticides, and their transformation products (Barbosa et al. 2016). Recent attention has been directed to organic micropollutants in rivers due to their environmental concern. They arise from diffuse and point sources in agricultural or urban areas. Especially wastewater treatment plants (WWTP) are a major emission source into rivers (Loos et al. 2009; Schwarzenbach et al. 2006). Regulations aim to reduce production and use of dangerous chemicals and thus ensure water quality (Brack et al. 2017). To assess the environmental impact of organic micropollutants in rivers, their general behavior and turnover processes have to be described and quantified. Former investigations focused on this topic and characterized the observed attenuation and underlying fate of selected organic micropollutants, mixtures, and toxicity in rivers all over the world (Acuña et al. 2015; Banjac et al. 2015; Kunkel and Radke 2012; Neale et al. 2017; Paíga et al. 2016; Radke et al. 2009; Riml et al. 2013; Zha et al. 2017). Due to the interdisciplinary character, many reviews already exist and go deep into detail of the single hydrological and reactive processes depending on the selected discipline. Groundwater-surface water interactions were recently presented by Brunner et al. (2017), and related measurement approaches were summarized by Kalbus et al. (2006). Flow and transport processes within the hyporheic zone and the relevance for biogeochemical mechanisms were discussed by Boano et al. (2014). Schwarzenbach et al. (2003) gave a detailed view into all reactive processes like sorption, photolysis, biodegradation, and chemical reactions (e.g., hydrolysis and redox reactions). The general occurrence of organic micropollutants in the overall aquatic system was described by Luo et al. (2014), and pollutant-specific processes such as thermolysis or hydrolysis for antibiotics were studied in detail by Kümmerer (2009). Despite these detailed studies, there is still a gap in knowledge regarding the overall, integrative process understanding and the linkage of different disciplines. This is especially relevant for field-based investigations, since they provide data that are essential for a more appropriate picture of the fate of organic micropollutants in rivers. However, fate investigations are often still difficult to compare. A comprehensive knowledge in respect of all relevant processes of the surrounding environmental compartments and properties of the chemical itself as well as the quality of the data determine comparability and explanatory power of investigations. Controlled laboratory settings are useful to study single processes and mechanisms in isolation but are hardly transferable to natural conditions due to the complexity and interaction of both reactive and hydrological processes in the field (Li et al. 2016; Writer et al. 2013a). Under field conditions, comparisons between different studies might end up in different results for the same chemical compound. Compilation of appropriate measurement approaches for all relevant field-based attenuation processes is still missing in literature. A systematic concept for achieving an integrative character of field-based attenuation studies and to consider and/or measure the main processes for a broad range of chemicals are necessary. In detail, the aims of this study are (1) to give an overview of all relevant processes from different disciplines, which may cause attenuation of organic micropollutants in the river water, and (2) to highlight promising state-of-the art field-based (sampling) approaches from different disciplines (e.g., hydrology or meteorology and environmental chemistry). We associated established field-based (sampling) approaches with introduced processes for proper designing of field investigations. A detailed description of single processes is beyond the scope of this study. However, we hope to establish a base for scientists with different backgrounds to analyse the interactions of relevant attenuation and transformation processes of organic micropollutants in river systems and thus give a guideline on how to assess them in the field. This will allow gaining meaningful data and developing appropriate model approaches to describe the fate of organic micropollutants comprehensively.

## 3.3 ATTENUATION PROCESSES

Attenuation processes in rivers take place in the river water body, but also in adjoining compartments. In general, attenuation may result from a decrease or transformation of compounds into one or multiple transformation products. As such, a single compound already leads to chemical mixtures with complexity even increasing, if a broad range of parent compounds and additional inflows of chemicals along the flow path contribute (**Fig. 2**). River water is connected and influenced by groundwater, the hyporheic zone (HZ), tributaries, and the water-sediment and water-atmosphere interfaces (**Fig. 2**). Two categories of processes determine the concentration of organic micropollutants: those that affect the substance mass within the water (distribution and transformation) and such that change the volume of the water (hydrological processes). Only by including both sides, it is possible to gain comprehensive knowledge and quantify the fate of micropollutants in the environment (**Fig. 3**). Hydrological processes play a particular role in river systems, since they are not compound specific, but relevant for all substances and create respective boundary conditions at the same time. Therefore, river-based fate investigations should take understanding and quantification of this aspect as a base (**Fig. 3(2)**). Quantification of the fate of organic micropollutants in river systems requires the specification of boundary conditions, especially for dynamic input via WWTPs into rivers (emission patterns) and dynamics of the natural environment (catchment dynamics). Both aspects may influence hydrological and reactive processes. WWTPs are the major point sources of organic micropollutants in rivers impacted by humans besides diffuse inputs from, e.g., industry and agriculture (**Fig. 2**) and thus alter surface water chemistry significantly (Schwarzenbach et al. 2006). WWTPs vary in discharge and chemistry due to the inhabitants' consumption behaviour (e.g., usage patterns of pharmaceuticals or per-capita water consumption) and the treatment process of the WWTP (Dickenson et al. 2011). WWTP discharge can vary over different magnitudes and time scales (Ort et al. 2010b; Ort et al. 2010a). Additionally, dynamics of the chemical input into river systems is caused by temporally changing removal efficiency in the treatment process of the WWTP (Loos et al. 2009; Ternes 1998; Zhang et al. 2008). WTP-delivered pollutants show a diurnal cycle. Further, compound concentrations typically differ among days (Majewsky et al. 2011; Majewsky et al. 2013; Salgado et al. 2011; Schwientek et al. 2016). Consequently, not only the chemical load of single chemicals but also the mixtures vary in time.

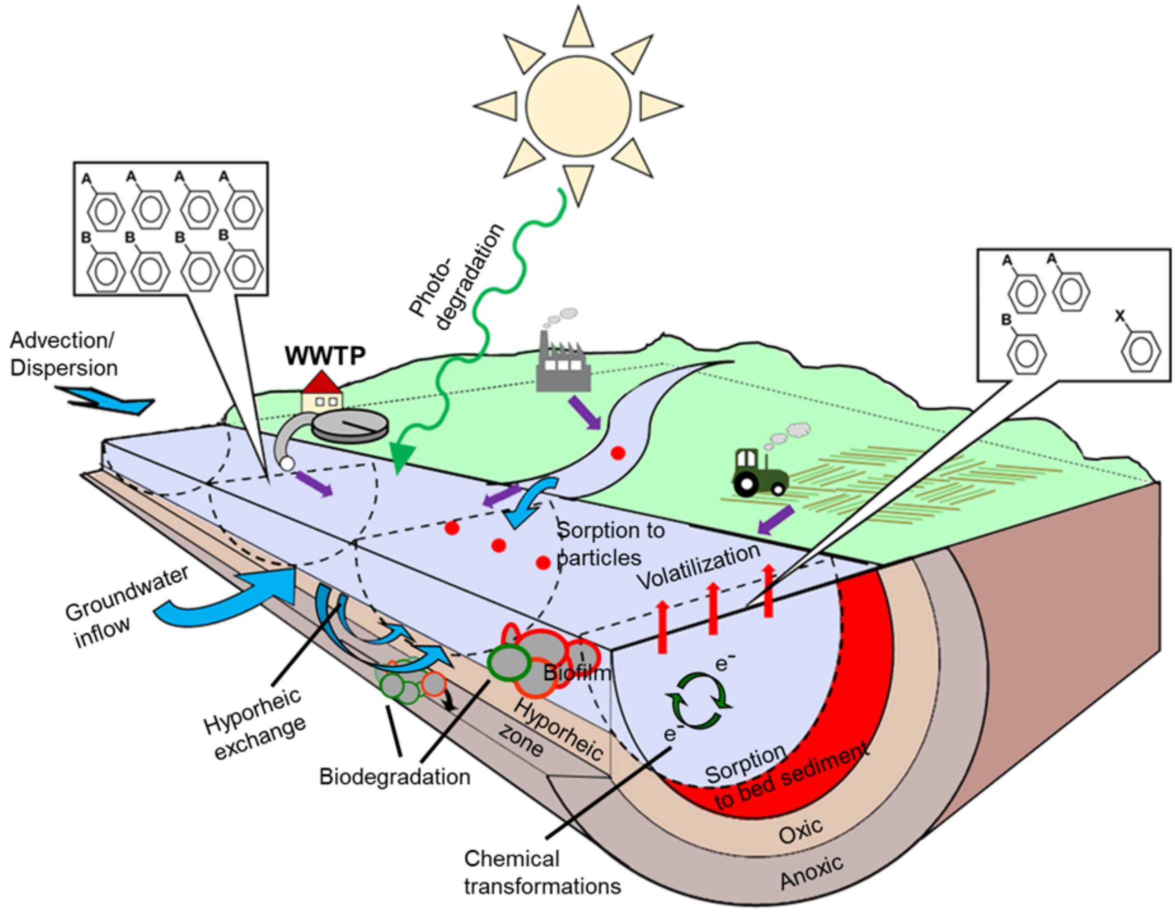

***Fig. 2**: River and adjoining compartments relevant for attenuation processes of organic micropollutants. These compartments can be mainly involved in hydrological (blue), distribution (red), and transformation (dark green) processes. Possible sources of organic micropollutants in the river system are wastewater treatment plants (WWTP), industrial discharge and diffuse anthropogenic emissions, e.g., from surface runoff from urban or agricultural areas (purple). Processes within these compartments may lead to a reduction and transformation of chemical compounds downstream of a certain chemical input into a river (inserts; schematic illustration of organic compounds), thus leading to a shift of composition regarding the overall chemical mixture. Besides transformation, additional inflow may be the reason for a different chemical concentration pattern further downstream*

## 3.3.1 ATTENUATION CAUSED BY HYDROLOGICAL PROCESSES

The mass and volume of the flowing water in rivers changes due to tributaries, groundwater inflow, and hyporheic exchange and dispersion (**Fig. 3(2)**).

### *3.3.1.1 Tributary inflow*

Tributaries play a significant role for the water and matter budgets of river segments and, thus, change water chemistry and geomorphology, increase physical heterogeneity, and alter biodiversity in the main stem river (Benda et al. 2004; Best 1988; Jones and Schmidt 2018; Rice et al. 2001). Especially dilution can be caused by water inflow from tributaries (Palmer et al. 2011; Yu and Heo 2001). Complete mixing of the main stem with a tributary particularly in lateral direction (lateral dispersion) is difficult to predict and depends on the heterogeneity of the river bed (Gualtieri 2010). The mixing rate is increased by bed discordances (Gaudet and Roy 1995). The significance of confluence effects may be determined by the confluence symmetry ratio (CSR), which describes the tributary basin size relative to the main stem river basin upstream of the confluence (Jones and Schmidt 2018). A bigger ratio increases the effect of the tributary (Benda et al. 2004). Chemical point sources like WWTPs have an influence on rivers comparable to tributaries.

#### *3.3.1.2 Transport processes in the river channel*

The most important processes of matter transport in rivers are advection and dispersion. Both hydrological processes require travel time–based attenuation investigations (Barber et al. 2011; Brown et al. 2009). In this context, advection describes the horizontal transport of matter with the mean cross-sectional velocity of the river water; dispersion corresponds to local deviations from that (Ji 2017). Longitudinal dispersion describes horizontal spreading and mixing of water mass and solutes in the water body, which is caused by molecular diffusion and heterogeneous velocity distribution in a river cross section (Ji 2017). Consequently, dispersion distributes sediments, particles, and solutes in the water body and between adjacent water parcels. Hydraulic reach characteristics like length, sinuosity, width, depth, geometry, and channel resistance govern advection and dispersion (Schmadel et al. 2016). For transport, lateral advection and dispersion in rivers are less relevant (except for additional inflows like tributaries) and can in many cases be negligible (Julien 2002).

#### *3.3.1.3 Groundwater inflow*

Perennial rivers arise from groundwater springs. As rivers move downstream, both compartments remain coupled reservoirs and influence each other, either diffusely or selectively (Atkinson et al. 2015). Thus, groundwater–river exchange fluxes have to be known since they can alter river water composition and volume (Manamsa et al. 2016). Groundwater inflow together with an absence of organic micropollutants or lower concentrations in the groundwater than in the surface water causes dilution in the river. Dilution by groundwater was considered in former attenuation studies by calculating dilution factors (Acuña et al. 2015; Antweiler et al. 2014; Radke et al. 2010). A broad range of organic micropollutants like pesticides, pharmaceuticals, or their transformation products may occur in groundwater systems, for instance reviewed by Díaz-Cruz and Barceló (2008). The contaminant load of groundwater depends, besides other factors, on the anthropogenic use of chemicals in the catchment area of the groundwater and arises from point or diffuse sources like agriculture or industrial leakages (Barth et al. 2007; McManus et al. 2017; Sacher et al. 2001; Verstraeten et al. 2002; Yang et al. 2017). Chemically reducing conditions and stable temperatures characterize groundwater, while the contact of this water with the atmosphere leads to an equilibration with atmospheric gases and temperature (Boano et al. 2014; Wawrzyniak et al. 2017). Oxygen content and temperature changes may either enhance or reduce micropollutant transformations depending on the characteristics of the specific compound (Burke et al. 2014; Díaz-Cruz and Barceló 2008; Grünheid et al. 2005).

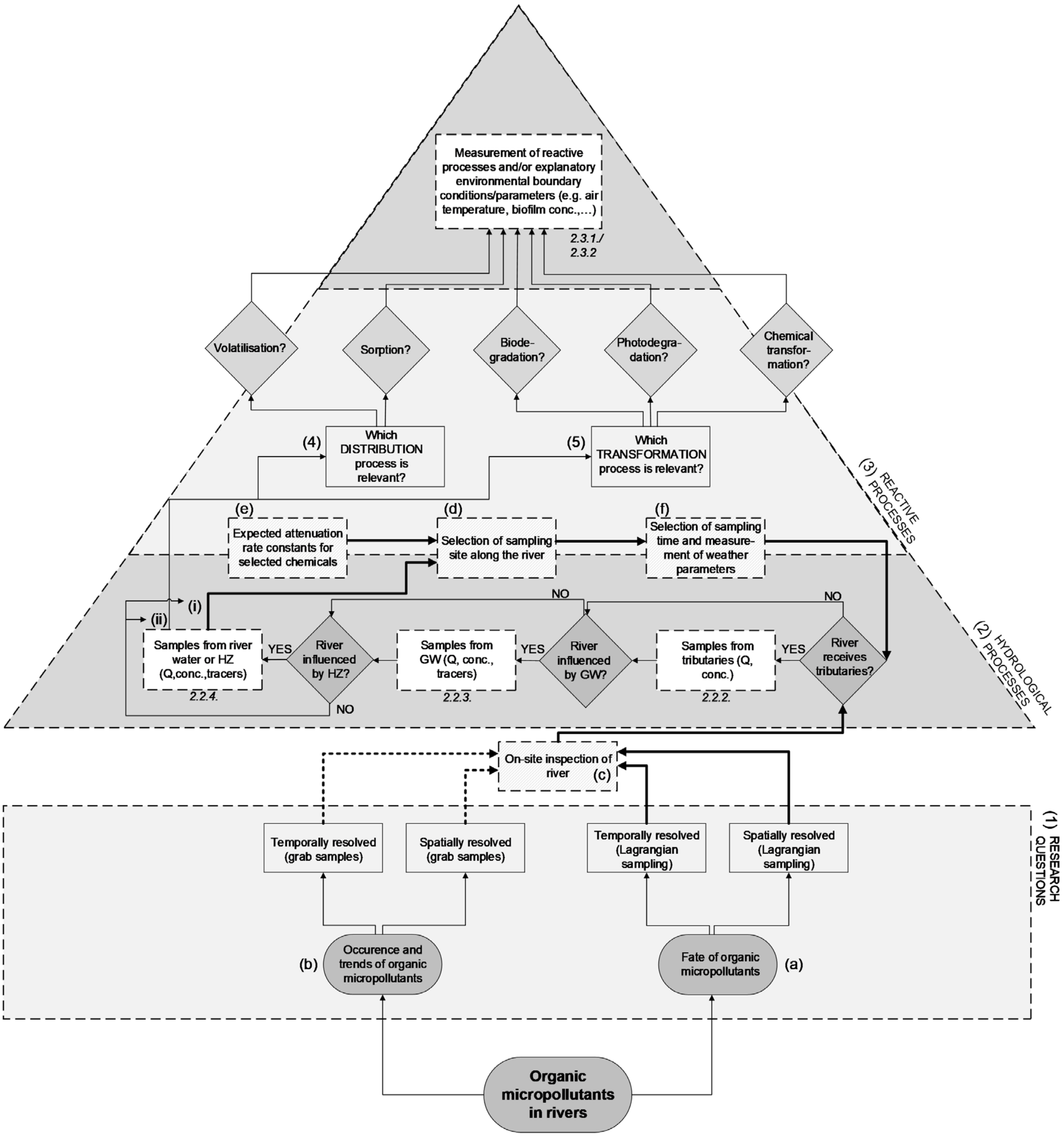

***Fig. 3***: *Theoretical basis for field-based sampling to describe the fate (a) and occurrence (b) of organic micropollutants in rivers.*

*Striped boxes highlight steps necessary for the definition of environmental boundary conditions ((c) to (f)) preceding the actual sampling campaign, whereby white boxes indicate sampling recommendations with the corresponding chapter in italics beneath the boxes. Bright grey areas display the underlying research questions ((1), (4) and (5)). A proceeding aiming to stake environmental boundary conditions is displayed with bold arrows, compound specific decisions on relevant processes with arrows associated with the "Yes" and "No" option. Order of arrows is represented by (i) and (ii). Occurrence and trends of organic micropollutants is displayed for the sake of completeness regarding organic micropollutants in rivers (b), but sampling approaches are not explained in detail, even though the on-site inspection of the river would be the following step (dashed arrows) after defining the specific research question*

#### *3.3.1.4 Hyporheic exchange*

The hyporheic zone (HZ) constitutes the interface between groundwater and river water. River water infiltrates into the river bed sediment, mixes with groundwater, and re-exfiltrates into the river at a different location with the "signature" of the HZ. This zone is concomitantly influenced by physicochemical parameters of the river (highly variable flow velocities and water depths, high oxygen and organic carbon contents, variable temperatures), the river bed (substrate, distribution of substrates, permeability, particle size, biota,) and the groundwater (groundwater flux, low oxygen and organic carbon contents, stable temperatures) (e.g., Boulton et al. 1998; Lawrence et al. 2013). Consequently, "the" hyporheic zone is a highly diverse compartment in space and time, also due to spatially and temporally altering upwelling and downwelling zones (Cranswick et al. 2014; Peralta-Maraver et al. 2018). Especially permeability of the bed sediment and stream flow velocity are dominant parameters for the hyporheic/ surface water exchange, but also river bed morphology, geometry, slope, and depth of sediment govern the exchange (Boano et al. 2014; Buffington and Tonina 2009; Packman and Salehin 2003). Residence time in the HZ is mainly influenced by the length of the hyporheic flow path, thickness of the HZ, river bed slope, streambed permeability, turbulence, wave pumping, and bioturbation. A minor important parameter is the length of roughness features of the streambed (Boano et al. 2014). Some authors claim this part of the river as the most significant removal compartment and award this aspect of river hydrology a high attenuation capacity for contaminants in the river (Lawrence et al. 2013; Lewandowski et al. 2011; Li et al. 2015; Nogaro et al. 2013; Schaper et al. 2018). The parameters residence time, temperature-/ redox-zonation, and microbial activity influence the attenuation in this compartment. Residence time is the main factor to distinguish between different flow paths of the HZ.

### 3.3.2 REACTIVE PROCESSES OF THE POLLUTANTS IN RIVERS

Reactive processes (**Fig. 3(3)**) in rivers can be differentiated into distribution (shift from water to another phase or reverse) and transformation of the chemical structure. Both aspects lead to a change of the dissolved concentration of compounds in rivers.

#### *3.3.2.1 Distribution processes*

Volatilization describes the transfer from the water to the air phase of the chemical compound (Schwarzenbach et al. 2003). It depends on the dimensionless Henry's gas-water partitioning coefficient of the single compound. Different organic micropollutants show a volatile behaviour, e.g., selected pesticides, musk fragrances, and polycyclic aromatic hydrocarbons (PAHs) (Gómez et al. 2012; Murschell et al. 2017; Peck and Hornbuckle 2004; Schwientek et al. 2016; Wombacher and Hornbuckle 2009 and references therein). However, stripping efficiency of musk fragrances in WWTPs was in most experiments smaller than 10% (Joss et al. 2006). Low Henry's law constants and acidic properties make volatilization unlikely (Lin et al. 2006). Similarly, for polar, anionic compounds (e.g., diclofenac) volatilization is unlikely, depending on the pH of the river (Buser et al. 1998). No direct measurements of such processes in combination with river attenuation studies were conducted which could be due to sampling difficulties or minor importance of this process.

Sorption of organic micropollutants leads to a decrease of the compound concentration in the aqueous phase while desorption from polluted particles increases the aqueous compound concentration. In river systems, the sorbent can be either biofilms, sediment, or suspended particles (Ramil et al. 2010; Rügner et al. 2013). Sorption is not equivalent to an elimination of compounds but only a redistribution in the system river. The compound-specific octanol-water partition coefficient ($K_{ow}$) is a regularly used parameter describing the partition between polar and non-polar (liquid) media, while the distribution coefficient ($K_d$) describes the distribution between water and the (solid) sorbate (Schwarzenbach et al. 2003). Similarly, $K_{om}$ describes the soil organic matter-water partition coefficient (Chiou et al. 1983). Sorption processes depend on the physicochemical properties of the sorbate (water solubility, hydrophobicity, charge of the single compound, ability to bind with molecules of the liquid or solid phase) and of the sorbent (content of organic matter, ion exchange capacity, pH, temperature) (Radović et al. 2016; Svahn and Björklund 2015). For selected organic compounds, sorption was the dominating attenuation process in the sediment compared with biodegradation (Kickham et al. 2012). An increased concentration of suspended particles in rivers facilitates the transport of particle-bound pollutants. If the distribution coefficient $K_d$ is larger than the reciprocal particle concentration, particle bound transport is dominating over transport in solution (Rügner et al.

2019). Transport of phosphorous, PAHs, or heavy metals may be largely governed by suspended sediment transport (Haygarth et al. 2006; Liu et al. 2018; Peraza-Castro et al. 2016; Rügner et al. 2013). Experiments with selected hormones and pharmaceuticals showed a higher sorbing efficiency of the biofilms of a river bed compared with the sediment due to the higher organic matter content in the biofilms and a high partition coefficient ($K_{om}$) of the investigated compounds followed by an accumulation of these substances instream biofilms (Writer et al. 2011a). Substances occurring in the river water are being absorbed in biofilms (especially the extracellular polymeric substances (EPS), explanation below) to protect the microbial community from toxicants. Thus, biofilm compositions are indicators for pollution (Flemming and Wingender 2010; Sabater et al. 2007). Laboratory experiments elucidate the sorption ability of many pharmaceuticals and pesticides to river sediment (Radke and Maier 2014; Radović et al. 2016; Writer et al. 2013a). However, sorption behaviour of selected pharmaceuticals and pesticides cannot be derived from their $K_{ow}$ and water solubility alone, but can be explained by considering the pH-dependent sorption capacity for dissociating compounds. A case study identified sorption besides photolysis as a major attenuation process for a pharmaceutical in the river water (Lin et al. 2006). Therefore, the sorption effect has to be excluded for the investigation of other processes (Kunkel and Radke 2011; Radke et al. 2010). Sorption also impedes or influences other attenuation processes like photolysis, chemical reactions, or bioavailability for organisms (Acuña et al. 2015; Schwarzenbach et al. 2003). Especially resuspended particles might increase the bioavailability of chemical compounds sorbed to the particles (Dong et al. 2016). Sorption is a fast process compared with biological degradation (Joss et al. 2006).

#### *3.3.2.2 Transformation processes*

Photodegradation is a combination of direct and indirect photolysis. Direct photolysis is the chemical or physical reaction of chemical compounds due to direct light absorption, whereas indirect photolysis describes the transformation of organic compounds due to the interaction with other compounds emerging from the light absorption or the energy transfer from these substances (Schwarzenbach et al. 2003; Zafiriou et al. 1984). In many studies, photochemical degradation was shown to be the major degradation mechanism for pesticides and pharmaceuticals (Andreozzi et al. 2003; Barceló and Hennion 1997; Doll and Frimmel 2003; Lin et al. 2006; Pérez and

Barceló 2007). The top level of surface waters is commonly the place where photolysis occurs. Turbulences in rivers allow a mixing of whole water body and the transport of river water to the photoactive upper layer (Klöpffer 2012). The presence of suspended material in the aquatic phase (e.g., suspended particles) influences photodegradation due to light absorption and light scattering (Bodhipaksha et al. 2017; Doll and Frimmel 2003; Kunkel and Radke 2012; Schwarzenbach et al. 2003; Zepp et al. 1998). For direct photolysis, the degradation of a compound depends on its physico-chemical properties (absorption spectrum) and the wavelength (quantum yield). To describe and quantify photodegradation rate constants, the whole absorption spectrum of a chemical compound must be known since several absorption maxima exist for many pollutants (Schwarzenbach et al. 2003). The composition of the organic material providing radicals plays a major role and influences indirect photodegradation rates of pharmaceutical compounds. Faster rates were shown for samples of treated effluents compared with samples of natural waters whereby in both approaches, a defined amount of spiked compounds was added (Bahnmüller et al. 2014). Besides organic substances (e.g., DOC), also nitrate and iron complexes may lead to possible reactants in river systems (Andreozzi et al. 2003; Klöpffer 2012).

Chemical transformations can be relevant for specific compounds (Jekel et al. 2015; Kümmerer 2009). Examples for reactions of organic micropollutants are hydrolysis, nucleophilic substitution, or redox reactions (Schwarzenbach et al. 2003). With these processes, the chemical structure is altered with first a structural alteration of the molecular structure followed by mineralization processes. The specific compound properties and environmental factors are crucial for the specific process (Jekel et al. 2015). For antibiotics, hydrolysis is an important elimination pathway in the environment. Half-lives for selected antibiotics differed depending on pH, temperature, light intensity, and flow rates in laboratory experiments (Kümmerer 2009). To the knowledge of the authors, direct field-based measurements of chemical transformation processes were never conducted so far except for indirect quantification of these processes via non-target screening (e.g., Bletsou et al. 2015; Holcapek et al. 2008; Schollée et al. 2015). A more detailed description of all chemical transformation processes is beyond the scope of this article, but the general process has to be kept in mind while conducting attenuation investigations.

Biodegradation occurs mainly in biofilms of the river bed and the HZ. The microbial community composition of both differs significantly due to light limitation and, consequently, the lack of phototrophy in the subsurface. Even if hyporheic exchange does not play a role for the investigated river system, substances with a high affinity to bed sediments interact just with the upper thin microbial layer of the river bed (Zaramella et al. 2006). Microbial degradation in the HZ may play a major role for attenuation of organic micropollutants (Kunkel and Radke 2012; Peralta-Maraver et al. 2018). Biodegradation governed by the microbial communities within this compartment is often efficient due to the longer contact time in the HZ compared with surface sediments or WWTPs (Lewandowski et al. 2011). Besides the biodegradation, the growth of biofilms can alter hydrological processes by a decrease in permeability (Battin et al. 2003; Schmidt et al. 2017). This aspect of subsurface biofilms is hardly understood so far (Lapworth et al. 2012). Microbial community composition depends on environmental factors. The formation of the redox zonation was shown to be temperature dependent and the connection of the latter to the fate of organic micropollutants within the HZ was pointed repeatedly (e.g., Burke et al. 2014). Biofilms consist of bacteria, algae, and fungi surrounded by a matrix of EPS and can be defined as a biological layer at the solid-liquid interface (Flemming and Wingender 2010). This composition is ubiquitous in the environment (Headley et al. 1998). The wide range of different communities within biofilms leads to different metabolism paths. Biofilms play an important role in instream metabolism and biogeochemical cycling and an increasing number of studies highlight the role of stream bed biofilms for the fate of organic compounds (Matamoros and Rodríguez 2017; Writer et al. 2011a). Biodegradation leads to a breakdown of the parent compound and formation of transformation products or persistent products (Pérez and Barceló 2007 and references therein). Sorption and biodegradation are strongly interacting in biofilms (Writer et al. 2011a).

### 3.3.3 ENVIRONMENTAL BOUNDARY CONDITIONS

Environmental boundary conditions play a significant role for the selection and design of the sampling procedure and for the comparability of degradation rate constants from different field-based investigations. Changing parameters are (additional) emissions of chemical compounds, the characteristics of the river itself (flow conditions, instream chemical composition), and climatic circumstances (solar radiation, temperature). Several different interactions and correlations between these aspects exist, as well as temporal variabilities. Even during one attenuation investigation, boundary conditions can vary significantly. River flow characteristics and the chemical input signal alter due to dynamic variations of the WWTP, as described in the previous chapter. Climatic conditions like solar radiation, temperature, cloud coverage, wind velocity, and wind direction change significantly during the day. Solar radiation, water turbidity, and cloud coverage can directly change the photodegradation rate (Andreozzi et al. 2003; Buser et al. 1998), whereby sorption capacity (sediment, suspended sediment, biofilm) can be altered by temperature. Temperature, light, oxygen, or carbon substrates influence biodegradation in stream biofilms, as well as pH, nutrient availability, or the composition of the biofilm (Writer et al. 2011a). Henry's law constant is temperature dependent as well (Staudinger and Roberts 2001). On a longer time scale, external controls changing especially the volume of the water vary with season (mainly caused by temperature changes and rain/snow). A changed volume of the water due to changed discharge conditions (e.g., initiated by rain or snowmelt) influences residence time of the water, water depth, the ratios of water volume, and surface areas of the river bed or water table, sedimentation and mobilization of particles, turbidity, flow paths in the HZ, and biofilm structure. Residence time of the water influences reactivity of chemical compounds. An increased water depth may reduce penetration depth of sunlight, and an increase of the volume/water surface ratio would further reduce the potential of photodegradation. Moreover, erosion and the subsequent input of particles into rivers during increased flows can mobilize bed sediments and thus increase turbidity. River water flow conditions alter the extent and location of the HZ, flow paths therein, and thus residence times and the exchange of water between river water and HZ (Bräunig et al. 2016; Peralta-Maraver et al. 2018; Wondzell and Swanson 1996). Flow velocity influences the structure of biofilms (Ryder et al. 2006), the half-lives of volatile organic compounds decrease with increasing water velocity (Rathbun 1998). An increase of discharge due to rain can cause dilution or, on the contrary, mobilize pollutants, e.g., from urban surfaces, or trigger additional wastewater inputs via combined sewer overflows. The chemical load of rain and washing out phenomena of the atmosphere lead to a potential chemical input pathway into the river and should not be neglected (Díaz-Cruz and Barceló 2008). On a longer time scale, increased temperatures can lead to more instream vegetation. This in turn affects not only the transport characteristics and water residence times of rivers but also sediment accumulation (Cotton et al. 2006). The complexity and interaction of the environmental boundary conditions on different temporal scales highlight the difficulty in comparing different process-based investigations, even for the same river. Future climatic scenarios and thus implications on river hydrology remain a recent research question (Trenberth 2011).

## 3.4 MEASUREMENT APPROACHES FOR FIELD-APPLICATIONS

The (semi-)quantitative assessment of compound-specific degradation half-lives in the field is challenging due to overlying effects arising from environmental boundary conditions, hydrological processes, and reactive processes. Thus, disentangling the processes that explain the observed substance attenuation only can be obtained by trying to isolate and identify specific processes with a combination of aim oriented field measurements and model-based data analysis. To distinguish these underlying processes, a theoretical step-by-step guideline to design and plan field-based investigations mainly targeting to describe the fate of organic micropollutants is presented in **Fig. 3**. Few attenuation studies on chemical pollutants in rivers aim at measuring the individual processes in an integrated way. Thus, promising approaches of different disciplines showing several possibilities to consider, measure, and disentangle hydrological, distribution, and transformation processes are summarized in this chapter. Even if integrated investigations do not necessarily lead to a comprehensive measurement of all processes consideration of all presented processes is expedient for data interpretation.

### 3.4.1 THEORETICAL BASIS FOR RELIABLE DATA

#### *3.4.1.1 Research question and underlying assumptions*

The superordinate research question together with the underlying assumptions regarding environmental conditions and system dynamics frames the selection of the sampling strategy. In general, two contrasting research approaches exist with regard to organic micropollutants in rivers: occurrence of organic micropollutants and long-term concentration trends on the one hand (**Fig. 3(b)**) and fate of these substances on the other hand (**Fig. 3(a)**). The first one is only briefly touched here, whereby the main focus is on the latter aiming at a quantification of field-based compound-specific parameters such as half-lives, attenuation rate, or attenuation rate constants. Both approaches mainly differ in underlying assumptions for the environmental boundary conditions: dynamic chemical inflow and discharge have to be assumed describing the fate of compounds, whereby a steady state assumption may be sufficient describing the general occurrence and trend of organic micropollutants. For both aspects, temporal and spatial investigations are possible and narrow the respective research question (**Fig. 3(1)**). For the steady state approach (**Fig. 3(b)**), it is assumed that temporal dynamics within the river system, including the dynamics of the WWTP, are of minor relevance in relation to the investigated spatial (e.g., whole river basin) and temporal scale (several months or years). This approach is easier to handle in field campaigns and mathematical fate models since grab samples are sufficient, but it reflects a very simplified environment. Flow dynamics, dispersion processes, interactions with groundwater, or hyporheic exchange (**Fig. 3(2)**) are considered negligible; consequently, no preliminary investigations are necessary (Müller et al. 2018). This sampling approach is only reliable to document the occurrence and concentration of a chemical compound; the non-occurrence or distinct processes influencing the fate cannot be quantified with this method besides lumped parameters, e.g., for substance dissipation in general (Ort et al. 2010b; Ort et al. 2010a; Prasse et al. 2015). Studies in environmental chemistry and toxicology chose this sampling scheme to gain information about the inventory of chemistry or toxicity in a river. For risk assessments and routine monitoring programs, this approach is a suitable tool due to a possible higher spatial resolution on the catchment scale and the determination of potential long term trends if grab sampling is repeated regularly (under consideration of catchment dynamics and emission patterns) and temporal trends are not masked by strong short-term fluctuations. The dynamic approach (**Fig. 3(a)**) is a more elaborated sampling strategy (Ort et al. 2010b; Prasse et al. 2015), but required if more detailed (scientific) processes-based questions regarding the fate of organic micropollutants shall be answered. Sampling of the same water parcel (so-called Lagrangian sampling) moving along rivers considering dynamic input conditions of the chemical compounds was applied for describing the fate of organic micropollutants in rivers of different sizes ranging from about 0.5 to 16,800 $m^3 s^{-1}$ in discharge (e.g., Antweiler et al. 2014; Barber et al. 2011; Brown et al. 2009; Writer et al. 2011a). Depending on the research question, either one or several water parcels (time series) can be tracked. Time series result in the inclusion of environmental dynamics (Radke et al. 2010; Schwientek et al. 2016). For WWTPs as a prominent example of a chemical input into rivers, preliminary investigations measuring conservative organic or inorganic markers of WWTPs can be used to assess the impact of the WWTP dynamics in relation to the receiving river (Dickenson et al. 2011).

### *3.4.1.2 Practical implications*

After confining the superordinate research question and the general temporal/spatial focus of the study, boundary conditions (environmental dynamics) have to be clarified and considered in advance of the actual fate investigation. Environmental boundary conditions may be both controlling and explanatory for the interpretation of fate studies in river systems, though a distinction of both aspects is not trivial. We suggest starting with the idea of a simplified concept (in line with a box model approach) of the tested river segment to clarify these aspects for the respective study. A first on-site inspection of the selected river (**Fig. 3(c)**) should aim at characterising the river itself (e.g., hydromorphological features, artificial structures, and impoundments) and identifying controlling environmental parameters, such as the (additional) input of chemical compounds (**Fig. 2**). Consideration of the river characteristics as environmental boundary parameters constitutes a first estimation of hydrological processes (**Fig. 3(2)**). We suggest the determination of a discharge profile along the river segment to quantify the significance of each, tributaries and groundwater inflows, on a sub-segment basis. Additional longitudinal profile measurements of environmental tracers (e.g., EC) or the performance of dye tracer tests provides information on the general flow conditions, the locations of inputs and mixing of different waters, and hyporheic exchange. Based on the hydrology and accessibility of the river, sampling sites along the river and, if needed, at tributaries and other inputs will be selected (**Fig. 3(i)**). Attenuation rate constants of selected chemical compounds affect locations and distances of the sampling sites, since a significant concentration decline from one site to the other should be aimed at if attenuation is to be quantified and requires reliable and meaningful data (**Fig. 3(e)**). This can be achieved by reviewing the respective literature or taking grab samples for chemical analysis at some of the preselected sampling sites at similar weather and hydrological conditions as expected during the main sampling procedure. After the identification of sampling sites, a determination of the sampling date depending on desired weather conditions is necessary (**Fig. 3(f)**).We recommend referring to weather forecasts and measuring weather parameters, e.g., air temperature, solar radiation, or cloud coverage during the sampling period to be able to correlate measured rate constants with these independent variables. Stable weather conditions during the period of sampling might be expedient depending on the research question. With these hitherto described steps, environmental boundary conditions may be controlled at the best possible rate. By the final sampling campaign, a cumulative signal integrating hydrological (**Fig. 3(2)**), distribution, and transformation processes (**Fig. 3(ii)**) is captured. The individual processes may be separated from each other by the correlation of spatial and temporal patterns of reaction rates with appropriate environmental parameters (e.g., pH, nutrients, water temperature, solar radiation). Distribution and transformation processes, as well as explanatory environmental parameters, are compound-specific and strongly depend on the expected processes of the selected compounds and the temporal and spatial scale that goes along with the research aim. Therefore, the reactive processes (**Fig. 3(3)**) have to be thought through prior to the measurement of weather parameters (**Fig. 3(f)**) in the wake of the expected attenuation rate constants of the selected compounds (**Fig. 3(e)**). Even if a single process seems of minor relevance for selected compounds of interest, we recommend to consider not only “leftover” processes at least for the planning phase, but also for the interpretation of data.

### 3.4.2 SAMPLING STRATEGIES TO ASSESS HYDROLOGICAL PROCESSES

#### *3.4.2.1 Transport processes along the river*

Consideration of advection and dispersion requires sampling of the same water parcel (Lagrangian parcel) in rivers (**Fig. 3(1)**). Therefore, the determination of the river water’s travel time is necessary. Travel time investigations can be conducted in the field with the injection of artificial tracers like salt or dye tracers (Barber et al. 2011; Brown et al. 2009). Sodium chloride is a prominent example of a conservative salt tracer. The electrical conductivity may be measured downstream as a proxy for concentration due to the correlation between dissolved ion concentration and conductivity. Common fluorescent dye tracers are rhodamine or a combination of several dye tracers that can be recorded with portable fluorometers (Antweiler et al. 2014; Barber et al. 2011; Kunkel and Radke 2011; Lemke et al. 2013; Writer et al. 2013a). Besides tracer approaches, measurements of flow velocity or discharge together with information on the average stream depth, width, and travel distance aim at the calculation of the travel time (Acuña et al. 2015; Li et al. 2016). To account for dispersion and thus the mixing of adjacent water parcels, a "verified Lagrangian sampling" was introduced by Antweiler et al. (2014). This approach is based on sampling of conservative compounds along the river reach whereby the correction of substance concentrations for the Lagrangian parcel is possible. Calculations of the load of the Lagrangian parcel were also conducted by Writer et al. (2013a). Schwientek et al. (2016) assumed a large, repeatedly sampled, water volume for the investigated Lagrangian parcel which allows to neglect the effect of dispersion.

#### *3.4.2.2 Tributary inflow*

Dilution caused by tributaries (**Fig. 3(2)**) is indicated by a decrease in concentration of conservative compounds in the main stem downstream of the confluence (Palmer et al. 2011; Yu and Heo 2001). Some previous attenuation studies included transverse mixing of point sources (Alexander et al. 2007; Barber et al. 2011; Barber et al. 2013; Kunkel and Radke 2012; Li et al. 2016). Naturally present tracers are used for the characterization of mixing which requires a difference in concentration between main stem and tributary or the point source. Conservative compounds like sodium, chloride, or isotopic ratios of selected elements often fulfil this claim (Bouchez et al. 2010). Hydrogen and oxygen were used for that in previous studies (Jiang et al. 2018). For the point source WWTP, Schwientek et al. (2016) used the electrical conductivity (EC) since there was a significant difference between river water and sewage water. Sampling of a transversal section of the river with no change in EC indicates complete transverse mixing. A USGS guideline based on artificial tracers to calculate mixing distances was established by Kilpatrick and Wilson (1989). In larger systems, satellite images provide a first estimate of complete mixing between waters with different composition (Bouchez et al. 2010; Du et al. 2001).

#### *3.4.2.3 Groundwater inflow*

To the knowledge of the authors, the measurement of groundwater inflow (**Fig. 3(2)**) did not play a role in any field-based attenuation investigation in rivers. In general, incremental streamflow determination without any surface inflow (velocity gauging method, current meter method, gauging flume method, dilution gauging method) indicates groundwater inflow (Covino et al. 2011; Kalbus et al. 2006; Payn et al. 2009).

This inflow into river systems can be estimated with a range of different methods like direct measurements of the differential total water flux, heat tracer methods, methods based on Darcy's law and mass balance approaches, reviewed by Kalbus et al. (2006). For a higher spatial resolution, tracer approaches are often used for the characterization of groundwater-surface water interactions. Artificial tracer tests allow dilution calculations (Kunkel and Radke 2011). The advantages of artificial tracer tests are, first, controlled conditions for tracer input and, second, the opportunity of a precise mathematical evaluation. Examples of artificial tracers are the same as those usable for the investigation of transport behavior of rivers. Naturally occurring tracers coupled with mass balances allow calculations of dilution, the groundwater flux, or the inflow of compounds from the groundwater into the river (Cook 2013). The measurement of different parameters such as discharge at several locations along the tested river segment and endmember concentrations is indispensable. This is the case not only for the quantification of groundwater flux but also for the identification of a potential chemical contamination of the river via the aquifer. Properties of the inflowing groundwater are displayed and measurable in changes of the surface water properties (Boano et al. 2014; Kalbus et al. 2006). Examples of natural tracers are chloride, electrical conductivity, and isotopes of radon, radium, and other elements (Atkinson et al. 2015; Cook 2013; Frei and Gilfedder 2015; Kalbus et al. 2006; McCallum et al. 2012; Stewart et al. 2010). Persistent compounds emitted via the WWTP can be applied as environmental tracers in river systems to calculate dilution (Dickenson et al. 2011). Prominent examples are carbamazepine or clofibric acid (Antweiler et al. 2014; Barber et al. 2011; Barber et al. 2013; Kunkel and Radke 2012; Radke et al. 2010). Multi tracer approaches improve the spatial and temporal resolution for analysing the processes in river systems (Atkinson et al. 2015; Cook 2013; Kimball et al. 2002).

#### *3.4.2.4 Hyporheic exchange*

Sampling of water of the HZ (**Fig. 3(2)**) for chemical analysis is challenging, though piezometers may help to solve that (Kunkel and Radke 2012; Lewandowski et al. 2011; Manamsa et al. 2016; Piktin et al. 1999; Pittroff et al. 2017; Roy and Bickerton 2010). Piezometers are tubes or pipes, which are inserted into the sediment/river bed (Kalbus et al. 2006). They can be used for the temporal and spatial characterization of the HZ since pore water sampling in several locations/depths is possible (Bridge 2005; Hoehn et al. 1992; Lewandowski et al. 2011; Schaper et al. 2018).

Quantification and profile determination of chemical composition have been carried out in former investigations for selected pharmaceuticals, but also for environmental tracers (electrical conductivity, radon activities or oxygen) to asses hydrological parameters like for instance the residence time (Cranswick et al. 2014; Hoehn et al. 1992; Kunkel and Radke 2012; Lewandowski et al. 2011; Massmann et al. 2006; Pittroff et al. 2017). Together with a persistent compound, e.g., carbamazepine or chloride, dilution and thus, the groundwater proportion in the HZ can be quantified (Kunkel and Radke 2011; Lewandowski et al. 2011; Pittroff et al. 2017). A broad range of different additional measurements exists in the HZ, e.g., in situ recording of the temperature (Bencala et al. 2011; Boano et al. 2014; Knapp et al. 2015; Lewandowski et al. 2011; Ward et al. 2010). Conservative salt tracer tests lead to information about the general magnitude of transient storage (Bencala et al. 2011; Schaper et al. 2018). Reactive tracer tests with resazurin provide, furthermore, information about the microbial activity, especially aerobic respiration due to the irreversible transformation of the tracer in metabolically active zones (transient storage) (Haggerty et al. 2008; Knapp and Cirpka 2017; Lemke et al. 2013).

### 3.4.3 SAMPLING STRATEGIES TO ASSESS REACTIVE PROCESSES

In former studies, chemical processes have, in most cases, either been interpreted by applying knowledge from laboratory experiments or the single process has directly been investigated by calculation of dissipation rates (e.g., Lin et al. 2006). In the following section, methods aiming to quantify processes with examples for the interpretation and the direct measurement, as far as possible, are presented.

#### *3.4.3.1 Distribution processes*

Distribution of organic compounds (**Fig. 3(4)**) into the gas phase by volatilization is well described in literature and is important especially for compounds with high vapour pressure. Nevertheless, the measurement of this process has, to the knowledge of the authors, not been directly investigated by any attenuation study in rivers so far. Indirect information was supplied by a few studies. Quednow and Püttmann (2008) investigated the fate of synthetic musk fragrances and organophosphate in a small German stream. They sampled stream water, but a differentiation between photodegradation and a water-air exchange of compounds as major attenuation processes for musk fragrances was not possible. The occurrence of organic micropollutants in rain and air was shown for pesticides in the Mississippi Delta, even though no processes between the water air interface were derived (Foreman et al. 2000; Majewski et al. 2014). Schwientek et al. (2016) explained the HHCB (galaxolide, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-g-2-benzopyran) loss in a river by volatilization due to a correlation between the maximum loss and the maximum water temperature. Approaches from other disciplines, mainly atmospheric chemistry, could help to define a base for future investigations (Farmer and Jimenez 2010; Wang and Austin 2006). The detection of organic micropollutants in the air phase usually needs the application of sorbent materials (passive samplers). The variety of sorbents is very high and depends on the sorption capacity of the investigated substance (Wang and Austin 2006). In case of passive samplers, the sampler has to remain in the investigation area for several weeks (Wombacher and Hornbuckle 2009). High-volume samplers, e.g., for the sampling of pesticides in the air phase also exists and also the collection of air in a canister is a common approach, at least in North America (Foreman et al. 2000; Majewski et al. 2014; Wang and Austin 2006). Several methods for the sampling of volatile organic compounds have been reviewed by Wang and Austin (2006). Since reactions with atmospheric radicals occur very fast, the gas chromatography itself has to be performed directly in the field after the sample is ready for the direct measurement (Murschell et al. 2017). New measurement methods are developed constantly for different substances like pesticides. The greatest possible problems in the field can be the small limit of detection, changes in relative humidity which is negatively correlated with measurement sensitivity, and potentially interfering peaks in the mass spectrometry (Murschell et al. 2017).

The overall sorbing capacity of river channels and the distribution of the organic compound into the solid phase are commonly evaluated using rhodamine, a strongly sorbing tracer (weakly photosensitive, biologically stable) (Lin et al. 2006; Radke et al. 2010). For a differentiation between the single sorption processes, the sorbents (biofilm, sediment and suspended particles) have to be considered individually. In biofilms, sorption saturation occurs fast after establishing the biofilm (Headley et al. 1998). Sorption to biofilm was investigated in laboratory-based experiments with natural biofilms, though field-based approaches are still a knowledge gap. Sampling of biofilms is described in section “biodegradation” below. Sediment samples can be taken randomly by grab samples but have to be homogenized (Ramil et al. 2010; Shelton and Capel 1994). Results derived from the chemical loading of sediment material have to be evaluated carefully due to the heterogeneity of the sorbents. A proxy for suspended particles in rivers is turbidity (Davies-Colley and Smith 2001; Rügner et al. 2013; Schwientek et al. 2013b). In south western Germany, Rügner et al. (2013) showed a correlation between turbidity and the total suspended solids, as well as a correlation between turbidity and the total concentration of 15 polycyclic aromatic hydrocarbons (PAHs) for several catchments. Turbidity is easy to measure with backscatter sensors or nephelometers (mainly for laboratory use) (Rügner et al. 2013). Field-based measurements of the loading of organic micropollutants on suspended particles remain an open research question. New devices aiming the separation of suspended particulate material from the water phase could close this knowledge gap (Schulze et al. 2017). Based on that, dynamics (mobilization and sedimentation) of suspended particles and particle-bound pollutants along rivers is crucial for attenuation processes in two ways, as a direct "removal" from the aqueous phase, but also as a potential retardation of degradation processes that take place in the aqueous phase of the river. Duration, magnitude, and frequency of sediment resuspension were investigated experimentally using flumes, incubation experiments, and turbulence simulation devices (Dong et al. 2016; Qian et al. 2011; Ståhlberg et al. 2006). Approaches for quantifying sorption kinetics are often laboratory-based batch experiments (Joss et al. 2006; Lin et al. 2006; Löffler et al. 2005; Radović et al. 2016; Ramil et al. 2010).

#### *3.4.3.2 Transformation processes*

Field-based experiments are often conducted to describe the fate of photodegradablemicropollutants, a transformation process (**Fig. 3(5)**). Measurements are based on the difference between exposure and non-exposure of photosensitive compounds to light. Lin et al. (2006) compared water parcels of different times of day (morning, afternoon, night) including travel time of the water. Based on this method, degradation rates can directly be deduced. Thus, it is an easy way to quantify photodegradation as long as other environmental conditions are comparable between night and day. Another approach is the choice of the sampling location depending on the shading grade. Kunkel and Radke (2012) transferred river water taken from different sampling locations with no shading, partial, and complete shading to glass containers and compared the influence of the shading, though water was not moving. Radke et al. (2010) compared quartz glass tubes with ultrapure water (Milli-Q water) and unfiltered river water both spiked with the target pharmaceutical. The tubes were exposed to the sun at the sampling side below the water surface directly in the river. With that approach, the contribution of photolysis of the overall attenuation can be quantified assuming constant solar radiation and no effect of the tubes for the photodegradation. The use of tubes with sunlight-exposed river water and comparison with river water, which was exposed to dark conditions, is also quite common (Buser et al. 1998; Fono et al. 2006). This measurement allows the determination of a direct photodegradation rate constant comparing concentrations at several time steps. The characterization of the transformation product is possible with this investigation. Nevertheless, specific flow conditions of rivers and locally changing exposure of moving water parcels to sunlight are neglected parameters in such approaches. By comparison of day- and night-time degradation rates along a 1.5-km-long river segment, measured using a Lagrangian sampling scheme, and the subsequent fitting of a non-parametric transfer function incorporating rate constants for photo-dependent and photo-independent processes, Guillet et al. (2019) succeeded in determining compound-specific photodegradation rate constants. In the field, a differentiation between direct and indirect photolysis is not trivial and results comprise in most cases a combination of both processes. Direct measurements of indirect photolysis can be approached by chemical actinometry (Andreozzi et al. 2003). Therefore, a reference compound in natural water with known concentrations and measurement of the degradation is conducted. Kunkel and Radke (2012) used phenylglyoxylic acid as chemical actinometer in a field experiment. Under field conditions, the water depth might be the main influencing factor and has to be considered carefully (Guillet et al. 2019). A compensation of the degradation rate for the whole river depth was introduced (Fono et al. 2006; Radke et al. 2010; Schwarzenbach et al. 2003) and applied for a field study at the river Roter Main (Germany) (Radke et al. 2010).

Gaining an understanding and quantification of biodegradation requires sampling of and experiments with microbes. Field-based in situ measurements remain challenging. Investigations of the hyporheic microbial degradation potential are based on sampling either cores or the upper sediment layer. Sediment analysis leads to insights into, e.g., microbial composition that could give hints on microbial functions related to pollutant degradation. Microbiological investigations (community, composition) coupled with profiles of organic micropollutants comprise the freeze coring at different depths (Nogaro et al. 2013). Both field and laboratory experiments showed that antibiotics and other contaminants of the river water sorb to biofilms (Headley et al. 1998; Wunder et al. 2011). Biofilm composition and density can alter due to organic micropollutants and should not be ignored in that context (Díaz-Cruz and Barceló 2008). Previously conducted attenuation investigations showed the dip of concentrations within the stream as the result of biofilms (Writer et al. 2013b). In general, not many studies exist targeting to define attenuation rates of organic micropollutants in biofilms. It is nearly impossible to grow biofilms under the same environmental conditions in the laboratory as observed in the field (Hellal et al. 2016). Thus, the investigation of biodegradation in biofilms includes sampling of biofilms on a carrier medium or investigations with standardized introduced artificial substrata (Sabater et al. 2007; Tien et al. 2009). Sampling of natural biofilm material can be done by representative sampling of existing biofilms from rocks at different locations in the stream by scraping, standardized swab collection, or by ultrasonic treatments (Flemming et al. 2000; Huerta et al. 2016; Writer et al. 2011a; Writer et al. 2013a). The thickness and age of the biofilm are significant if used as proxies for water quality. Water quality can be represented best by one month old biofilms (Tien et al. 2009). General analytical methods to evaluate the chemical load of biofilms have been described elsewhere (Headley et al. 1998; Writer et al. 2011a; Writer et al. 2013a). For field investigations, it is only possible to sample biofilm grab samples.

## 3.5 CONCLUSIONS

Field-based investigations are indispensable for the characterization of chemicals' behavior in rivers. Processes occurring under controlled laboratory conditions are often not observable under field conditions and vice versa. This review presents an overview of relevant in-stream attenuation processes and associated sampling approaches in the field that take complexity and temporal and spatial scale according to the underlying research question into account. Negligence of the complex and mostly transient interactions in environmental systems may lead to oversimplistic sampling strategies and thus to unreliable data. Especially hydrological processes are easily overlooked or awarded minor relevance, even though they constitute the basis of reactive contaminant transport. On the other hand, the complexity and the large number of non-controllable environmental influences exacerbate study designs and often result in data that is ambiguous and too sparse to disentangle several overlapping processes. Field-based attenuation studies at the current state of research can only constitute the best possible approximation for representative river-specific attenuation rate constants, but other approaches are equally important to attain a holistic picture. Supplementary laboratory and modelling approaches are required to describe and quantify reactive processes, e.g., detailed chemical reactions or the chemical potential of a certain compound to undergo a reactive process. Consequently, attenuation studies necessitate merging different research disciplines and thus inevitably require interdisciplinary appreciation and background knowledge from beyond single researchers' expertise. Thus, the collaboration of interdisciplinary consortia is needed to tackle the complexity of environmental systems that are and will be increasingly impacted by humans.

# 4 COMPARISON OF ENVIRONMENTAL TRACERS INCLUDING ORGANIC MICROPOLLUTANTS AS GROUNDWATER EXFILTRATION INDICATORS INTO A SMALL RIVER OF A KARSTIC CATCHMENT

## 4.1 ABSTRACT

Understanding of groundwater-surface water (GW-SW) interactions is vital for water management in karstic catchments due to its impact on water quality. The objective of this study was to evaluate and compare the applicability of seven environmental tracers to quantify and localize groundwater exfiltration into a small, human impacted karstic river system. Tracers were selected based on their emission source to the surface water either as (1) dissolved, predominantly geogenic compounds (radon-222, sulfate and electrical conductivity) or (2) anthropogenic compounds (predominantly) originating from wastewater treatment plant (WWTP) effluents (carbamazepine, tramadol, sodium, chloride). Two contrasting sampling approaches were compared (1) assuming steady state flow conditions and (2) considering the travel time of the water parcels (Lagrangian sampling) through the catchment to account for diurnal changes in inflow from the WWTP. Spatial variability of the concentrations of all tracers indicated sections of preferential groundwater inflow. Lagrangian sampling techniques seem highly relevant for capturing dynamical concentration patterns of WWTP-derived compounds. Contrary to other applied natural or anthropogenic environmental tracers, quantification of GW inflow with the finite element model FINIFLUX, based on observed in-stream Rn activities, led to plausible fluxes along the investigated river reaches (0.265 m$^3$ s$^{-1}$) while observations of other natural or anthropogenic environmental tracers produced less plausible water fluxes. Important point sources of groundwater exfiltration can be ascribed to locations where the river crosses geological fault lines. This indicates that commonly applied concepts describing groundwater-surface water interactions assuming diffuse flow in porous media are difficult to transfer to karstic river systems whereas concepts from fractured aquifers may be more applicable. In general, this study helps selecting the best suited hydrological tracer for GW exfiltration and leads to a better understanding of processes controlling groundwater inflow into karstic river systems.

## 4.2 INTRODUCTION

Groundwater (GW) and surface water (SW) are coupled reservoirs with complex exchange processes that influence both systems (Atkinson et al. 2015; Cook 2013; Gilfedder et al. 2015). In rivers, water and matter fluxes between these compartments play an important role for the water availability, water quality and ecology and are thus relevant processes to be considered for sustainable water management (Brunke and Gonser 1997). Existing methods that aim to characterize and quantify interactions between GW and SW are diverse and were reviewed in detail by Kalbus et al. (2006). Water flux measurements include, among others, e.g. seepage meters (Fryar et al. 2000; Lee 1977) and incremental streamflow discharge measurements (Payn et al. 2009).

During the past decades, environmental tracers have been used for quantification of local groundwater inflows to rivers and streams. GW inflows can be observed at a high spatial resolution and instrumentation costs are, depending on the tracer, often low (Cook 2013). Measurements of environmental isotopic tracers such as the isotopes of hydrogen and oxygen in water (Oxtobee and Novakowski 2002), radon (Frei and Gilfedder 2015; Unland et al. 2013) and strontium (Harrington et al. 2014) are applied for this purpose, as well as measurements of ions (Smith et al. 2010) or electrical conductivity (Oxtobee and Novakowski 2002). For the successful application of these environmental tracers, two main underlying conditions must be met: (1) GW and river water must be significantly and measurably different in their concentrations (so-called endmember concentrations due to their ‘endpoint character’ in a two component mixing concept), and (2) endmember concentrations must be homogeneously distributed within the investigated region or the variability of endmember concentration must be known. Ions and electrical conductivity (EC) were used for the characterization of GW inflows where geological settings lead to a prominent difference in concentrations between GW and SW (Atkinson et al. 2015). EC mass balances describing GW inflows were applied for ~~a~~ different ecosystems all over the world (Gilfedder et al. 2015; Oxtobee and Novakowski 2002; Smith et al. 2010). Also sodium and chloride were used extensively for the characterization of GW-SW interactions (Atkinson et al. 2015; Cartwright et al. 2011; Cartwright and Gilfedder 2015; Kumar et al. 2009; Yang et al. 2012; Yu et al. 2013). In recent investigations, radon ($^{222}$Rn) has been increasingly applied due to the large concentration difference between groundwater and river water as well as its chemical properties (Avery et al.

2018; Cook 2013; Cook et al. 2018; Zhao et al. 2018). Radon-222 is an inert noble gas of the $^{238}$Uran decay chain and characterized by an accumulation in the aquifer depending on chemical composition, mineralogy and lithology. Higher activities in GW, but a fast radioactive decay (half-life of 3.8 days) and loss to the atmosphere in SW maintain the large activity difference between these compartments (1-3 orders of magnitude). In general, multiple tracer approaches and a combination of different techniques reduce uncertainties in the quantification and perhaps more importantly allow uncertainty to be quantified (Avery et al. 2018; Zhao et al. 2018).

Globally, rivers and streams are affected by anthropogenic inputs of organic (micro)pollutants (Malaj et al. 2014; Schwarzenbach et al. 2006). The main emission pathway of majority of organic micropollutants into SWs are wastewater treatment plants (WWTP) (Gros et al. 2007). Continuous improvements in analytical methods have allowed the detection of organic micropollutants even at low concentrations (Clara et al. 2004). Despite the known negative influence of these compounds on freshwater ecosystems such as toxicological effects on biological systems, they also can be used for a scientific purposes: Persistent organic micropollutants may be suitable tracers to better understand and characterize hydrological processes (Clara et al. 2004). Organic micropollutant concentrations (sulfamethoxazole, carbamazepine, ibuprofen) were used as anthropogenic indicators in the hyporheic zone (Banzhaf et al. 2012) and to understand GW-SW interactions in a lowland Chalk catchment (Manamsa et al. 2016). A prominent example is carbamazepine which is often considered conservative due to its long half-life compared to the travel time of river water (Guillet et al. 2019; Kunkel and Radke 2012; Pal et al. 2010; Schwientek et al. 2016). The persistent behaviour of a selected compound is indispensable for its successful application as a tracer, but the persistence may be river specific. The analgesic tramadol for example was described to undergo attenuation processes at the Gründlach River (Li et al. 2016), whereas other studies demonstrate a conservative character (e.g. Glaser et al. 2020e). Concentrations of WWTP-derived compounds in small rivers often show a diurnal signal due to changing discharge from the WWTP (Schwientek et al. 2016). To distinguish advection of the transient concentration signal from actual loss processes, Lagrangian sampling, is necessary for the quantification of processes affecting pollutant concentrations. This sampling technique aims at the repeated sampling of the same water parcel as it moves downstream to follow the advective (and dispersive) transport of the pollutant within this water parcel and thus allow for comparison of pollutant concentrations with regard to loss processes.

Despite the general suitability of specific organic micropollutants for studying water exchange between groundwater and rivers, localisation and quantification of GW inflow has not been conducted so far with these compounds. In addition, tracer based quantification of the GW inflow has, so far, focussed on river systems with little anthropogenic influence and predominantly in rivers embedded in geologically porous media. This is due to the complexity of karstic aquifers (Bittner et al. 2018), that leads to hardly comparable subsurface water flow, transport and storage mechanisms in comparison to porous aquifers (Dvory et al. 2018; Hartmann and Baker 2017). Previous field-based studies have focused on the interaction between karstic rock aquifers and rivers by applying hydraulic head measurements (Bailly-Comte et al. 2009) or artificial tracers (Barberá and Andreo 2017). To date, it is still not fully understood how the connection between catchment and receiving river works hydrologically, i.e. via which flow paths and processes the runoff from the catchment area drains into the river network. This is of particular interest also in the special case of karst landscapes. We hypothesize that in human impacted catchments substances that are emitted via the WWTP might be a suitable tool to close this research gap. Therefore, the aim of this study was 1) to investigate the applicability of environmental tracers in a river (Ammer River, Southwest Germany) that is embedded in a karstic geology by a spatially high resolution approach and 2) to validate the reliability of eight different environmental tracers including selected conservative organic micropollutants for the quantification of GW inflow. To this end, a river segment which is generally assumed to drain the karst system, i.e. with a groundwater flux towards the river and without known water losses to the underground, was selected.

## 4.3 MATERIALS AND METHODS

### 4.3.1 SAMPLING SITE

The Ammer catchment is located in Southwestern Germany and has an area of 238 km² (**Fig. 4(a)**). The catchment is characterized by agricultural land use (50%), urban areas (12%) and managed forest (38%). The average discharge (Q) from the gauged catchment in Pfäffingen (134 km²) is 0.87 $m^3 s^{-1}$. It is a tributary (5th order stream) of the Neckar River with a total length of 22 km. The WWTP Gäu-Ammer (WWTP (1); 80,000 person equivalent (PE)) releases its treated sewage at the left river bank (flow direction) into the Ammer River. The mean dry weather effluent flow rate from the WWTP is 0.10-0.12 $m^3 s^{-1}$. Further details on WWTP flow during the sampling period can be found in Glaser et al. (2020e).

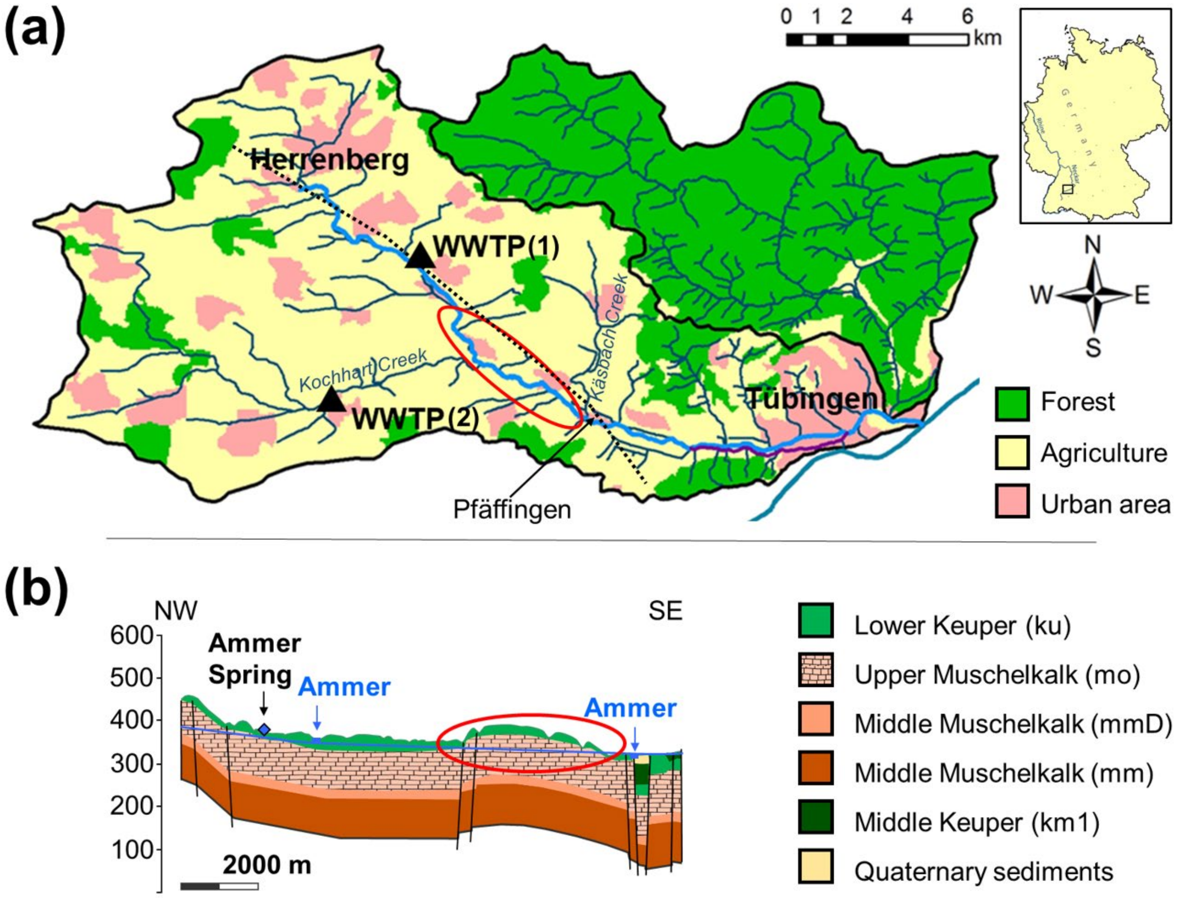

***Fig. 4:*** *Graphical overview of the Ammer catchment (a) with locations of the wastewater treatment plants at the main stem (WWTP 1) and at the tributary Kochhart Creek (WWTP 2), as well as the investigation area (red circle; (a) and (b)). The dotted line of (a) highlights the location of the geological profile (b) that is mostly captured in a parallel line to the course of the Ammer River.*

A 5880 m river reach downstream of the WWTP was selected for our investigations (**Fig. 5**) where a distance of 0 m denotes the most upstream sampling location. In this section, the riverbed consists of larger cobbles with gravel and mainly silty material in the interstitial spaces. The average slope of the streambed for this reach is ~ 4 ‰. The two main tributaries are the Kochhart and the Käsbach creeks. A second WWTP is located at the Kochhart (WWTP (2); Hailfingen, 9,000 PE). The selected river reach has an altered character due to its straightened channel (**Fig. A21**), two constructed diversions in Reusten (length diversion 320 m) and Poltringen (length diversion 200 m), respectively, and two weirs for former mills. Many tributaries are tile drains that carry small amounts of water (0.005-0.015 $m^3\ s^{-1}$) and discharge into the Ammer in pipes. A drinking water treatment plant processing groundwater (Carix method; ion exchange procedure water softening) discharges a pulsed water flow into the Ammer River (6 times per day, in total 83 $m^3$, on June 18, 2018; transferable to other days during the sampling campaign).

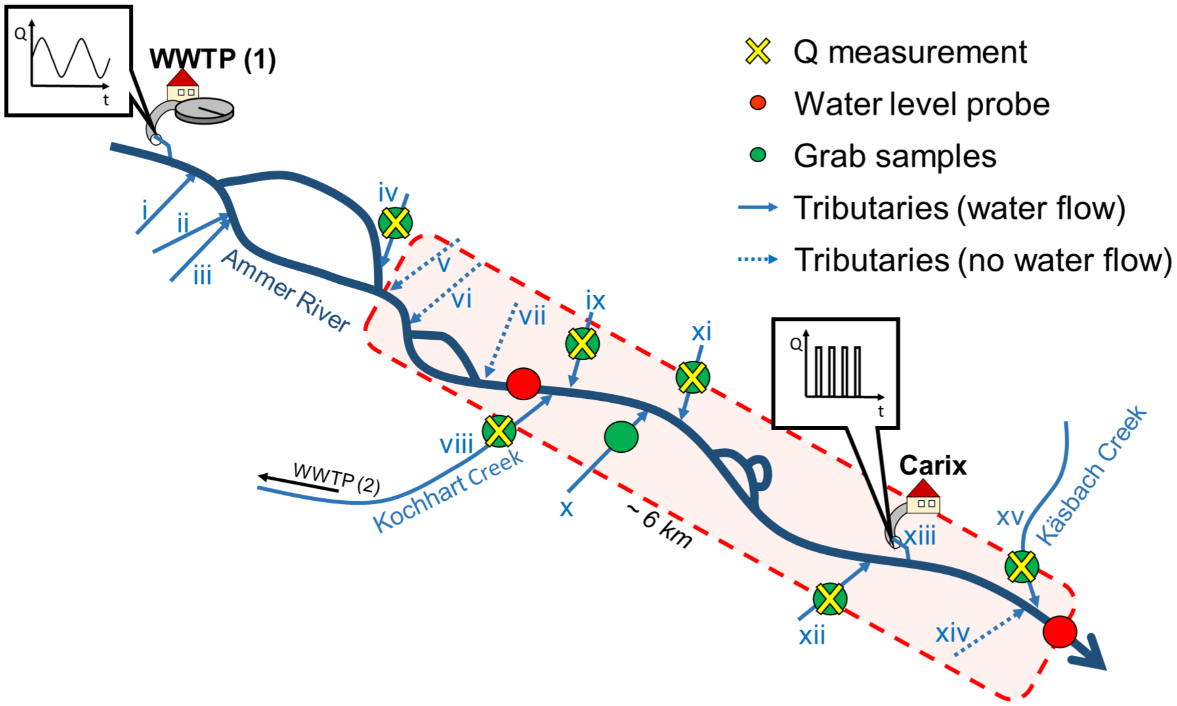

*Fig. 5*: *Conceptual design of the investigation area downstream of the WWTP 1 with the two main tributaries Kochhart (WWTP 2-influenced) and Käsbach.*
*In addition to samples and discharge measurements (ADCP) obtained in the Ammer River (not shown in this graph) long-term rating curve data received from water level probes (red circles) were used for discharge determination. In all tributaries, grab samples for chemical analysis (green circle) and discharge measurements (yellow cross) were conducted. Temporally varying discharge patterns of the wastewater treatment plant (WWTP) and a drinking water treatment plant (Carix) are presented conceptually (text box).*

The geology is dominated by karstic limestones of the Middle Triassic ("Muschelkalk") which form an important regional aquifer. The limestone crops out in the northwest and dips at 1 – 2 ° to the southwest. In this direction it is increasingly covered by claystones and evaporites of the Upper Triassic ("Keuper") which are, in the gypsum bearing parts, also karstified ("Gipskeuper"). "Muschelkalk" dominates in the upper ~4.3 km of the investigation reach (Selle et al. 2013; Ufrecht, 2002), including the Kochhart sub-catchment (**Fig. 4(b)**). Downstream of this, gypsum-rich Middle Keuper formations ("Gipskeuper") overlay the limestone (Villinger 1982). The Käsbach sub-catchment is characterized by mudstone of the Lower Keuper and overlain by Middle Keuper gypsum formations (http://maps.lgrb-bw.de/) which leads to high sulphate concentrations in this tributary. From a hydrogeological point of view groundwater flow follows from the recharge areas located west and north of the city of Herrenberg in southeastern direction towards the Neckar River. In this geological context, the studied Ammer segment serves as one main receiving water body with groundwater contours showing a large-scale convergence of groundwater flow towards the Ammer main stem (Ufrecht, 2002; Ufrecht 2006). The Ammer River is therefore unlikely i) to feature important loosing segments or ii) to be vulnerable to extreme droughts due to the large storage capacity of the contributing karst system. This is expressed by a strong baseflow (Schwientek et al. 2013a).

## 4.3.2 SAMPLING PROCEDURE

### *4.3.2.1 General sampling approach and settings*

Sampling took place from June 19 to 21, 2018, during base flow conditions of a, in general, dry summer. Weather conditions were relatively stable (dry and sunny with few clouds). Air temperature according to data provided by the Environmental Agency of the State of Baden-Württemberg ranged from 14.1 to 29.8 °C. Water temperature obtained from conductivity temperature depth (CTD) measuring stations ranged from 11.0 to 17.4 °C. The distances between the sampling points recorded with a GPS were measured using QGis and cross-checked by measurements in GoogleEarth. All tracers were considered conservative and selected based on the following categorical properties: 1) no expected influence from the WWTP ($^{222}Rn$); 2) dominant influence from rock dissolution ($SO_4^{2-}$, EC); 3) affected by geology and land use, but predominantly originating from the WWTP ($Cl^-$, $Na^+$); and 4) originating exclusively from the WWTP and generally considered conservative (carbamazepine - CAR, tramadol - TRA).

Two contrasting sampling strategies in the Ammer River were conducted and compared based on the possible influence of the WWTP. The first approach was based on a steady-state assumption for the Ammer River, whereby grab samples for $^{222}$Rn, $SO_4^{2-}$, $Na^+$, $Cl^-$, and EC measurements were obtained in a **h**igh spatial **r**esolution (HR, 44 samples at 33 sampling locations, distance < 300 m between sampling points). The HR sampling took 3 days in total (June 19 to 21, 2018). The second approach with a focus on the WWTP-associated compounds took the travel time of the water parcels into account ('Lagrangian sampling'; one-day sampling on June 19, 2018). The methodological approach to estimate the travel time of the Ammer River is based on the concept of tracking prominent EC-peaks that originated from the WWTP along the river from EC time series measurements. The EC concentration at a downstream location can be calculated by convoluting the inflowing EC concentration with the transit time distribution function which includes the fitting of the mean travel time and the dispersion parameter. The latter was identified as small and insensitive towards the mean travel time and was therefore not considered for further interpretation, especially with respect to the potentially larger effect of the measurement uncertainty in comparison to the effect of dispersion. More details of this method are described elsewhere (Glaser et al. 2020e). Mean travel time and the respective distance between the sampling sites can be used to compute the arrival time of a certain water parcel at a selected sampling site. This sampling strategy consequently results in a lower number of sampling locations due to logistical reasons (**l**ow spatial **r**esolution, LR). Samples for TRA, CAR, $SO_4^{2-}$, $Cl^-$ and $Na^+$ were taken (in total 11 samples, 11 locations) on June 19, 2018. In both cases, sampling took place in flow direction. For the tributaries, steady state flow conditions were assumed. Lagrangian-sampling was compared to grab samples. The mass balance-based finite element model FINIFLUX (Frei and Gilfedder 2015) was used for calculating GW inflow using all selected tracers.

#### *4.3.2.2 Chemical sampling and measurements*

For the SW samples, all samples were taken at about 5 cm beneath the water surface in the middle of the river assuming well-mixed conditions at each location which was tested beforehand at two different locations along the river (**Fig. A22**). Grab samples were taken in the tributaries. For $^{222}$Rn samples, water was carefully filled into 1 L polyethylene bottles which were closed tightly without any head space in the bottle until the measurement of the sample. The analysis was conducted shortly after sampling using the portable radon-in-air monitor RAD7 (Durridge Company Inc.) with the $H_2O$ accessory (Lee and Kim 2006). After purging, each water sample was degassed for 5 minutes in a closed loop for at least 30 minutes. Up to six replicate counting runs led to relative errors of 5 to 10%. Results were multiplied with an empirical correction factor obtained from the regression between measured activities of 1 L bottles with measured activities of standardized 250 mL reference bottles (previous experiment, data not shown) to account for the lower degassing efficiency of the measured volume (1 L) in comparison to the reference volume of 250 mL. The samples were corrected for radioactive decay between the time of sampling and time of measurement. Ion samples were taken in 100 ml amber glass bottles. EC along with water temperature (WTW ProfiLine Cond 3310, Germany) was measured approximately 5 cm beneath the water surface and temperature-compensated according to DIN EN 27888 (1993).

For organic micropollutant samples, 1 L amber glass bottles were used. Before sampling of ions and organic micropollutants, the bottles were rinsed with sample water. Samples were stored in cool boxes and at 4°C (dark conditions) until analysis (maximum one day storage for organic micropollutants, maximum about one month storage for ions).

For $^{222}$Rn, a distinct difference in concentration between groundwater monitoring wells and spring water was highlighted for rivers in Spain (Barberá and Andreo 2015) and China (Zhao et al. 2018). Thus, the main strategy for obtaining representative GW samples to determine endmember concentrations was taking samples from springs that directly discharge to the Ammer River (13 samples, up to 3 replicate sampling to reduce deviation). Since spring water is assumed to be representative for the chemical composition of the groundwater, it is hereafter called groundwater sample (GW). EC values of these springs were used as the first step to distinguish between different geological settings since ion concentrations from Triassic Limestone (“Muschelkalk”) and Middle Keuper (“Gipskeuper”) groundwater differ significantly. Tracer measurements ($^{222}$Rn, ions, EC, organic micropollutants) of each geological setting were averaged for a representative endmember concentration. The discrete point source “Schwärzenbrunnen” was treated as an independent endmember since previous investigations identified infiltrating Kochhart Creek water (influenced by WWTP (2)) as origin of this inflow (Harreß 1973). 250 mL bottles were used for $^{222}$Rn samples due to the expected higher activities compared to river water. For ion samples, 100 mL amber glass bottles were used and rinsed with spring water before sampling. Processing after sampling, sample preparation and analysis of major ions are described in more detail in Glaser et al. (2020e), organic micropollutant analysis is described in Müller et al. (2018). Ion chromatography (DX 500, DIONEX) was used for the determination of ion concentrations, and organic micropollutants were measured by a tandem mass spectrometry using an *Agilent* 6490 iFunnel Triple Quadrupole (QqQ) instrument (*Agilent Technologies;* see Glaser et al. (2020e), for more details). All samples were measured at the Center for Applied Geoscience of the University of Tübingen.

#### *4.3.2.3 Measurements of hydrological parameters*

In the Ammer River, discharge (Q) was determined in at least eightfold replicates in cross profiles per sampling site to minimize measurement uncertainties using the SonTek Acoustic Doppler Current Profiler (ADCP, RiverSurveyor). In shallow river sections (depth < 0.2 m), for which the ADCP is not appropriate, an Acoustic Digital Current meter (ADC; Ott C2, Kempten, Germany) was used for discharge measurements with velocity measurements in at least 8 depth profiles (3 depths) per cross section. In total, Q was measured at 26 locations using the ADCP and at 6 locations using the ADC along the reach. Additionally, water level time series (time interval 15 min) from two existing measuring stations (OTT CTD, Kempten, Germany) along the river together with appropriate long-term rating curves were used for Q determination. Q of the two main tributaries Kochhart creek and Käsbach creek were similarly measured using water level time series (time interval 15 min) and pre-existing rating curves. For the additional 9 tributaries (**Fig. 5**), discharge was measured using the ADC as described above for the Ammer main stem (tributaries iv, xi, xii) or estimated by visual judgement (tributaries i-iii, iv,xiii) where flow measurements were not possible due to the shallow water depth. Data evaluation of the ADCP measurements were done using the Matlab based Velocity Mapping Toolbox (Tomas et al. 2016).

### 4.3.3 MODEL APPLICATION AND MASS FLUX QUANTIFICATION

To estimate the groundwater discharge into the Ammer surface water using $^{222}$Rn, the finite elements implicit numerical model FINIFLUX was applied (Frei et al. 2019). This model was originally set up for $^{222}$Rn and based on the following equation:

$$Q \cdot \frac{dc}{dx} = I \cdot (c_{gw} - c) - k \cdot w \cdot c - d \cdot w \cdot \lambda \cdot c + \frac{Q_r}{R_L}(c_{trib} - c) + \frac{\gamma \cdot h \cdot w \cdot \theta}{1 + \lambda \cdot t_h} - \frac{\lambda \cdot h \cdot w \cdot \theta}{1 + \lambda \cdot t_h} \cdot c \tag{1}$$

where Q [$L^3$ $T^{-1}$] is the river discharge, c [M $L^{-3}$] is the activity of the tracer and x [L] is the stream length between sampling locations. I [$L^3$ $L^{-1}$ $T^{-1}$] is the groundwater inflow, $c_{gw}$ [M $L^{-3}$] is the concentration in the groundwater, k [L $T^{-1}$] is the degassing coefficient, w [L] is the stream width, d [L] the stream depth and $\lambda$ [$T^{-1}$] is the decay constant. $Q_r$ [$L^3$ $T^{-1}$] is the discharge of the tributaries, $R_L$ [L] the tributary inflow length and $c_{trib}$ [M $L^{-3}$] the activity measured in the tributary. θ [-], h [L], and $t_h$ [T] are the hyporheic exchange parameters, like the porosity of the streambed, the depth of the hyporheic exchange layer, and the mean residence time of water in the hyporheic zone, respectively, and γ [M $L^{-3}$ $T^{-1}$] is the production rate of Rn within the hyporheic zone. For the parameterization of the degassing coefficient, we applied a degassing equation based on Bennett and Rathbun (1972) and Genereux and Hemond (1992). Overall, this mass balance describes the spatial tracer mass flux development along the river ($Q \cdot \frac{dc}{dx}$) as a function of the tracer exchange with the groundwater flux ($I \cdot (c_{gw} - c)$), the sink terms "degassing" ($k \cdot w \cdot c$) and "radioactive decay" ($d \cdot w \cdot \lambda \cdot c$), the additional inflow via tributaries ($\frac{Q_r}{R_L}(c_{trib} - c)$) and the source term "hyporheic exchange" (exponential residence time distribution). The latter may contribute to the tracer mass flux in the river due to the additional production of the tracer ($\frac{\gamma \cdot h \cdot w \cdot \theta}{1+\lambda \cdot t_h}$), or decrease the tracer mass flux ($\frac{\lambda \cdot h \cdot w \cdot \theta}{1+\lambda \cdot t_h}$) in the river due to (radioactive) decay in this zone. For conservative compounds not undergoing decay, degassing or hyporheic enrichment, the mass balance can be simplified as follows:

$$Q \cdot \frac{dc}{dx} = I \cdot (c_{gw} - c) + \frac{Q_r}{R_L}(c_{trib} - c)$$

*(2)*

with the compound concentrations c and $c_{gw}$ [M $L^{-3}$; mg $L^{-1}$ for ions, µS $cm^{-1}$ for EC and ng $L^{-1}$ for micropollutants] in the river water, groundwater and tributary, respectively. The model was adapted for conservative compounds in the open source MATLAB code of FINIFLUX (http://www.hydro.uni-bayreuth.de/hydro/en/software/software/software_dl.php?id_obj=129191). Rainfall, evaporation and mixing with stream tributaries were assumed to be negligible for the mass balances during the time of sampling. All concentration measurements are used as model input. Since the number of concentration measurements is higher compared to the measurement points of Q, the latter was linearly interpolated between measurements for missing values for all model setups. Additionally, erroneous values obviously influenced by the discharge pattern of the WWTP or arising from estimations of Q that were uncertain due to the locally large amount of macrophytes in the river channel were removed from the dataset.

## 4.4 RESULTS

### 4.4.1 ENVIRONMENTAL BOUNDARY CONDITIONS AND IN-STREAM CONCENTRATIONS OF SELECTED COMPOUNDS

In the Ammer River, measured discharge increased from 0.53 (± 0.05) to 0.78 (± 0.06) $m^3$ $s^{-1}$ between the upper and lower ends of the investigation reach. $^{222}$Rn activities ranged from 500 to 3300 Bq $m^{-3}$ (**Fig. 6(a)**). Similar activities (3000 – 3300 Bq $m^{-3}$) were observed at the first sampling points and between x=2340 and 2620 m downstream of the start of the reach following sharp increases. Three minor, but still significant peaks were observed between 830 m - 1070 m, at 1650 m and at 3200 m along the reach. $SO_4^{2-}$ concentrations ranged from 224 to 291 mg $L^{-1}$ (**Fig. 6(c)**, **(h)**). No significant peaks were detectable. Concentrations were relatively constant along the upper part of the reach at ~ 280 mg $L^{-1}$, but decreased rapidly and flattened out to a value of 240 mg $L^{-1}$ at x=2500 m. EC ranged from 1198 to 1277 µS $cm^{-1}$ (**Fig. 6(b)**). The spatial development of EC was comparable to $SO_4^{2-}$ concentrations, except for a sharp increase only occurring for the EC at x=4310 m. $Cl^-$ and $Na^+$ ranged from 62 to 72 mg $L^{-1}$ and from 32 to 39 mg $L^{-1}$, respectively (**Fig. 6(d)**, **(e)**,

**(i)**, **(j)**). Both ion concentrations were similar in their spatial development and strongly correlate ($R^2 = 0.71$ for HR, $R^2 = 0.76$ for LR). For the HR sampling approach, higher $Cl^-$ and $Na^+$ concentrations occurred between x = 1360 m and 2050 m of the reach followed by a decrease in concentrations and afterwards a slight increase down to the section of geological transition (x = 4840 m). In the segment dominated by Middle Keuper, concentrations decreased again. For the LR sampling approach, the highest concentrations were observed between x = 2050 m and 2620 m. This pattern partly overlaps with the HR sampling approach. Further downstream (x > 4200 m), the profiles did not show any other dominating higher concentrations. CAR concentrations ranged from 106 to 161 ng $L^{-1}$, TRA concentrations ranged from 48 to 73 ng $L^{-1}$ (**Fig. 6(f)**, **(g)**). Two minor peaks were observed at x = 2250 m and at 4600 m. A strong correlation ($R^2 = 0.91$) between CAR and TRA exists (**Fig. A23**).

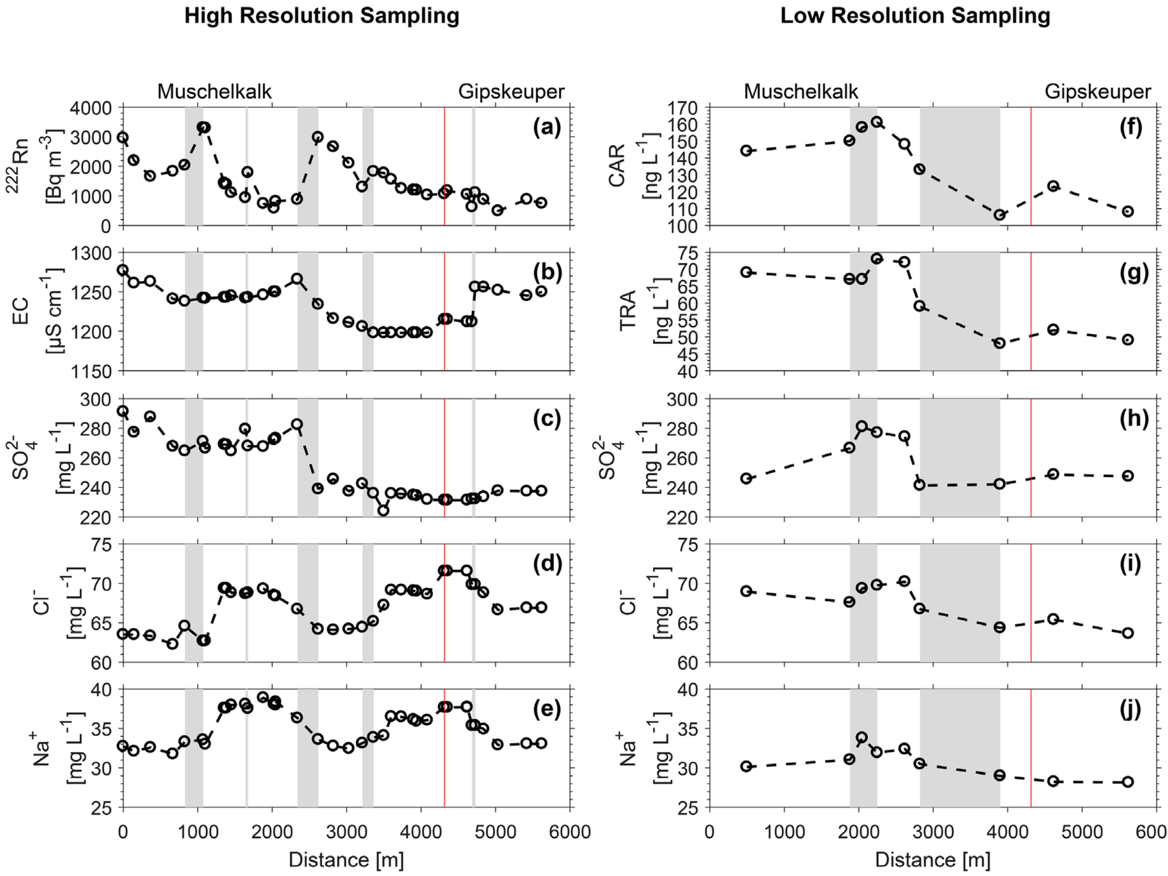

*Fig. 6: Concentrations along the investigation reach starting from the upstream sampling point (0 m). Two different sampling strategies led to different spatial resolutions.*
*Steady-state (3 days of sampling) was assumed for $^{222}Rn$ (a), EC (b), $SO_4^{2-}$ (c), $Cl^-$ (d), $Na^+$ (e) and a Lagrangian Sampling approach (1 day of sampling) was applied for carbamazepine (CAR) (f), tramadol (TRA) (g), $SO_4^{2-}$ (h), $Cl^-$ (i), $Na^+$ (j) leading to less samples along the reach. Grey areas highlight notable changes of $^{222}Rn$ activities for the high resolution sampling approach and changes of CAR for the low resolution, respectively. The red line indicates the shift from Triasic Limestone ("Muschelkalk") to Middle Keuper ("Gipskeuper") geology.*

Groundwater $^{222}$Rn endmember activities derived from the spring water samples differ significantly ($p<0.05$, t-test) between different geological settings with 19,694 ± 1,998 Bq m$^{-3}$ for Triassic Limestone (n = 6) and 11,500 ± 2916 Bq m$^{-3}$ for Middle Keuper formations (n = 5). This was also the case for the Triassic Limestone ion concentrations with 91 ± 1 mg L$^{-1}$ for $SO_4^{2-}$, 33 ± 8 mg L$^{-1}$ for $Na^+$ and 75 ± 12 mg L$^{-1}$ for $Cl^-$ and EC of 915 ± 82 µS cm$^{-1}$. For the Middle Keuper formations, $SO_4^{2-}$ and the EC are significantly higher with 1160 ± 11.6 mg L$^{-1}$ and 2130 ± 371 µS cm$^{-1}$, while $Na^+$ and $Cl^-$ show lower concentrations with 14 ± 1 and 54 ± 4 mg L$^{-1}$, respectively.

In GW, concentrations of CAR and TRA were below the limit of detection, except for one sample from the tributary ix (**Fig. 5**), which is spring water contributing to the river. For this tributary, CAR was detected with 54 ng L$^{-1}$ and also the other measured environmental tracer concentrations of 10,108 ± Bq m$^{-3}$ for $^{222}$Rn which is similar to the Schwärzenbrunnen (tributary x) activity (10,307 Bq m$^{-3}$), 116 mg L$^{-1}$ for $SO_4^{2-}$, 23 mg L$^{-1}$ for $Na^+$ and 58 mg L$^{-1}$ for $Cl^-$ and EC of 975 µS cm$^{-1}$.differed compared to the expected geological signal. Replicate samples of all measurements to test the temporal variability and thus reliability of the GW samples demonstrate a low standard deviation between samples of the same sampling site (Glaser et al. 2020d). In the main tributaries Kochhart and Käsbach, $^{222}$Rn activities were relatively low (102 - 197 Bq m$^{-3}$). Ion concentrations differed between tributaries (**Tab. 1**). CAR and TRA were detectable in the Kochhart creek only.

***Tab. 1:*** *Concentrations of investigated compounds (single measurements) in the two main tributaries Kochhart (WWTP 2-influenced) and Käsbach (LOD = limit of detection).*

| | Kochhart | Käsbach |
|---|---|---|
| $^{222}$Rn [Bq m$^{-3}$] | 102 | 197 |
| $SO_4^{2-}$ [mg L$^{-1}$] | 66 | 247 |
| $Cl^-$ [mg L$^{-1}$] | 116 | 116 |
| $Na^+$ [mg L$^{-1}$] | 58 | 28 |
| EC [µS cm$^{-1}$] | 782 | 1250 |
| CAR [ng L$^{-1}$] | 127 | < LOD |
| TRA [ng L$^{-1}$] | 43 | < LOD |

### 4.4.2 ESTIMATED GROUNDWATER INFLOW

For all environmental tracers, except for $Na^+$ and $Cl^-$, and $SO_4^{2-}$ in the low resolution sampling ($R^2 \leq 0.28$; **Tab. 2**) the coefficient of determination ($R^2 > 0.88$) showed a good linear fit between modelled values and the measured data. Comparing the normalized standard deviation of the residuals (normalized root mean square error) showed the smallest values for $^{222}Rn$ (NRMSE = 0.10; **Tab. 2**) and thus the smallest deviation from the 1:1 regression between modelled and measured data. This indicates that FINIFLUX applied for $^{222}Rn$ fits the data well (**Fig. 7(a)**, **(b)**), contrasting to e.g. CAR (**Fig. 7(c)**, **(d)**).

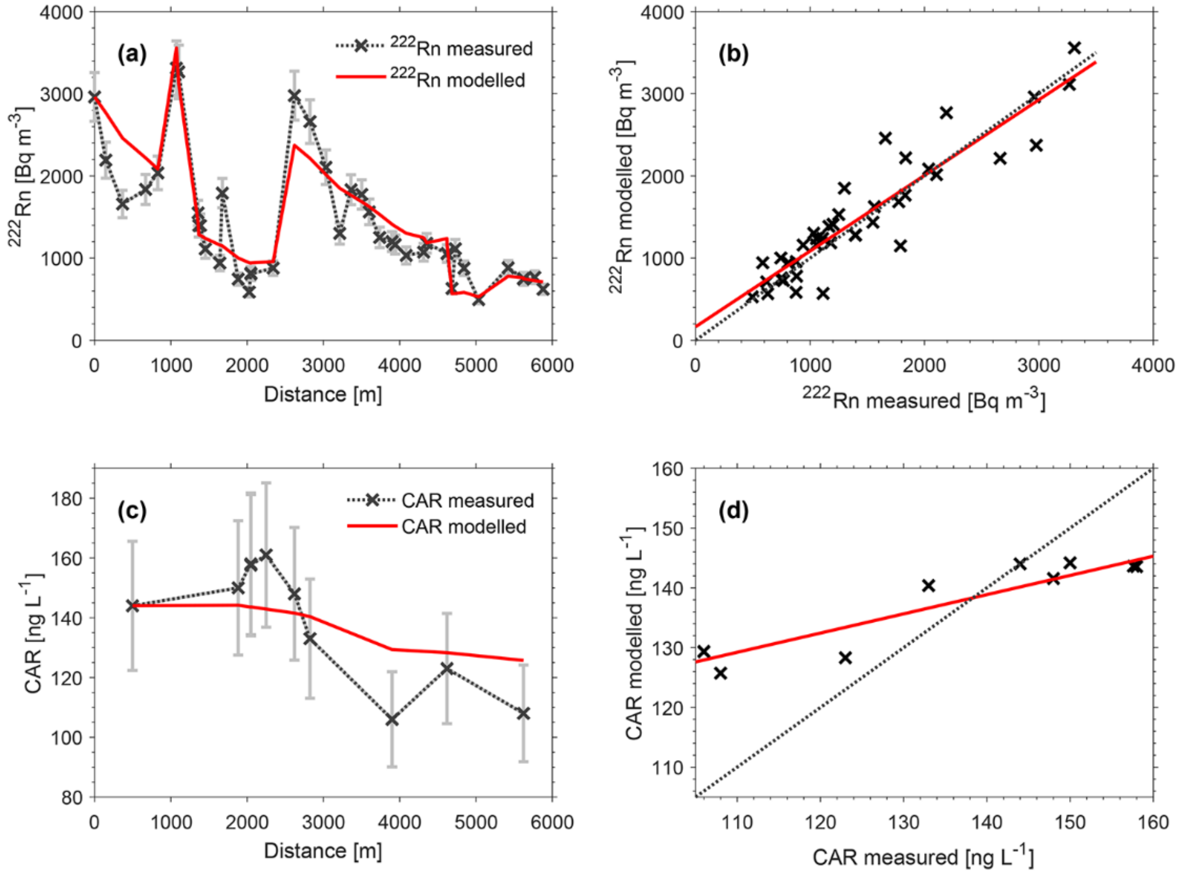

*Fig. 7:* *Measured and modelled (a) $^{222}Rn$ activity with measurement uncertainty (grey errorbars, 10%) and (c) carbamazepine (CAR) concentrations with measurement uncertainty (grey errorbars, 15%) of the investigation reach starting from the upstream sampling point (0 m) and corresponding agreement of measured and modelled (b) activity and (d) concentrations, respectively.*
*The dotted lines in (b) and (d) indicate a 1:1 agreement, the red lines in (b) and (d) result from linear regressions of modelled versus measured activities / concentrations.*

***Tab. 2**: Regression coefficients ($R^2$) and NRMSE (normalized root mean square error, normalized to the difference between the maximum and minimum value of the dataset) between measured and modelled activity, electrical conductivity and concentrations, respectively, and cumulative GW inflow along the tested river reach, based on modelling results with FINIFLUX for the high resolution (HR) and low resolution (LR) sampling approach.*

| | | $R^2$ | NRMSE | cumulative GW inflow [m³ $s^{-1}$] |
|---|---|---|---|---|
| **HR** | $^{222}$Rn [Bq $m^{-3}$] | 0.92 | 0.10 | 0.277 |
| | EC [µS $cm^{-1}$] | 0.88 | 0.41 | 0.082 |
| | $SO_4^{2-}$ [mg $L^{-1}$] | 0.88 | 0.49 | 0.059 |
| | $Cl^-$ [mg $L^{-1}$] | 0.04 | 0.49 | 0.043 |
| | $Na^+$ [mg $L^{-1}$] | 0.11 | 0.54 | 0.050 |
| **LR** | CAR [ng $L^{-1}$] | 0.93 | 0.26 | 0.091 |
| | TRA [ng $L^{-1}$] | 0.88 | 0.27 | 0.112 |
| | $SO_4^{2-}$ [mg $L^{-1}$] | 0.28 | 0.41 | 0.059 |
| | $Cl^-$ [mg $L^{-1}$] | < 0.01 | 0.44 | 0.026 |
| | $Na^+$ [mg $L^{-1}$] | 0.02 | 0.37 | 0.022 |

The modelled $^{222}$Rn-based groundwater inflow indicates some high inflow rates up to $4 \cdot 10^{-4}$ m³ $m^{-1}$ $s^{-1}$ that dominate the overall pattern (**Fig. 8**). EC modelling results agreed with $^{222}$Rn based modelling results in the pattern of GW inflow, but not in the absolute flux of GW volume (maximum $1.3 \cdot 10^{-4}$ m³ $m^{-1}$ $s^{-1}$). CAR and TRA inflows follow a similar spatial pattern, and $SO_4^{2-}$ LR shows similar locations of GW exfiltration like $^{222}$Rn and EC. Modelled cumulative groundwater inflow using FINIFLUX ranged from 0.022 m³ $s^{-1}$ (based on $Na^+$) to 0.265 m³ $s^{-1}$ (based on $^{222}$Rn) (**Tab. 2**).

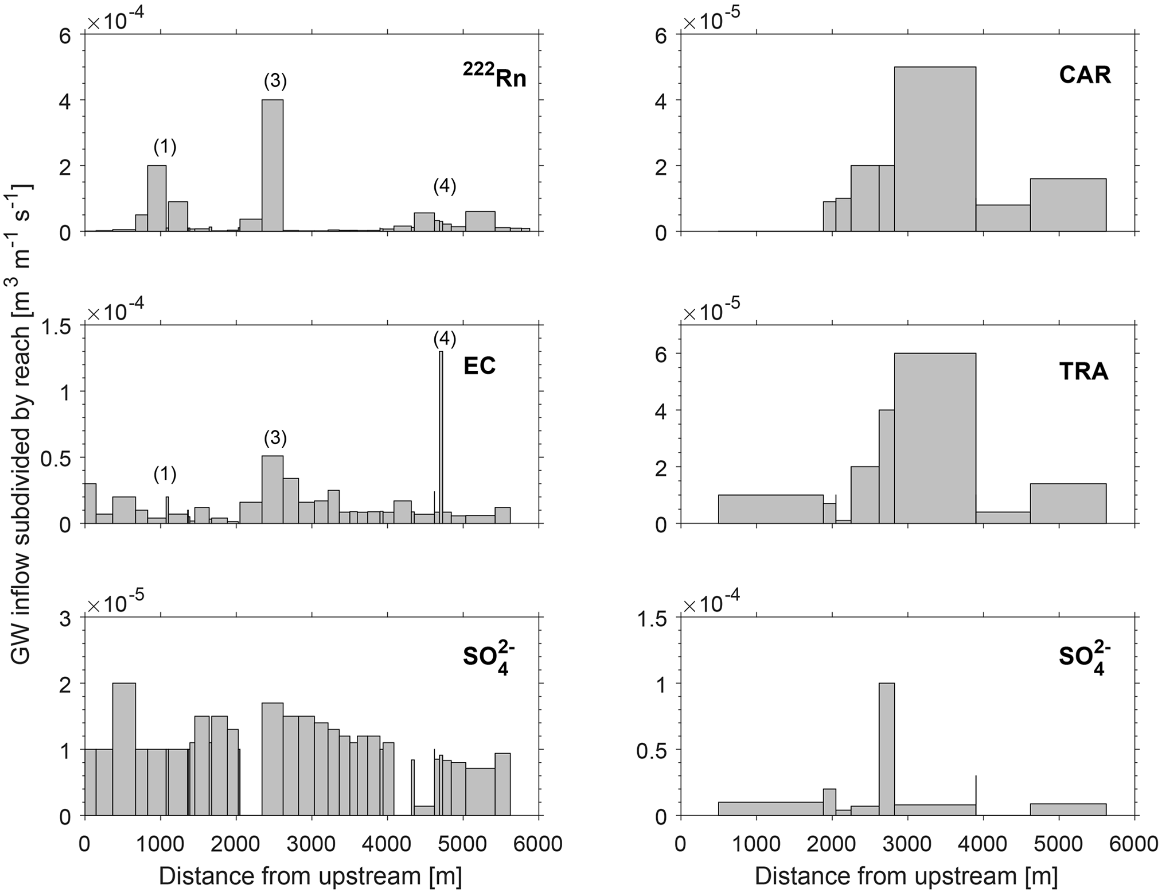

***Fig. 8**: Modelled groundwater inflow using the model FINIFLUX based on the tracers radon ($^{222}$Rn), carbamazepine (CAR), electrical conductivity (EC), tramadol (TRA) and sulphate ($SO_4^{2-}$) with two different sampling settings (left: spatially high resolution (HR), right: spatially low resolution (LR)).*

## 4.5 DISCUSSION

### 4.5.1 COMPARISON OF SELECTED TRACERS

#### *4.5.1.1 General interpretability of concentration patterns*

The dynamics of WWTP effluents significantly influence the selection of an appropriate sampling strategy and thus the general interpretability of selected tracers. For $^{222}$Rn activity measurements, no influence of the WWTP can be determined. Reliable replicate measurements at the same location further downstream in the investigation area but at different times of the day under the prevailing conditions during the sampling period are similar (Glaser et al. 2020d). These arguments demonstrate that grab samples along the river are representative and thus high $^{222}$Rn activities in the river are indicative for GW inflows. The high $^{222}$Rn activities in the Ammer River indicate a strong GW-influence, supported by exceptional sharp increases in $^{222}$Rn activities along certain reaches of the river (**Fig. 6(a)**). Classical first order decreases in $^{222}$Rn activities such as for the first and third prominent $^{222}$Rn peak (grey areas, **Fig. 6(a)**) mainly arise from radioactive decay and degassing (Cartwright et al. 2011). In general, the observed range of $^{222}$Rn activities in the Ammer River is higher compared to previous investigations at different river systems, which were generally between 50 to 1400 Bq m$^{-3}$ (Atkinson et al. 2015; Mullinger et al. 2007; Unland et al. 2013) and can be explained by groundwater that contributes significantly to (perennial) karstic rivers (Bailly-Comte et al. 2012) compared to river systems connected to porous aquifers.

The choice of an appropriate sampling strategy could be more relevant for tracers originating from the WWTP. A diurnal cycle of WWTP-derived ions and organic compounds has been described by previous investigations (e.g., Majewsky et al. 2013; Salgado et al. 2011; Schwientek et al. 2016).Comparing Cl$^-$ and Na$^+$ concentrations of the sampling approach by i) assuming steady state (HR) and ii) taking travel time of the water parcels into account (LR) demonstrates a significant difference in ion concentrations along the selected river segment (**Fig. 6(d)**, **(e)**, **(i)**, **(j)**). Even if the first peak of high concentrations at a distance of ~ 2000 m downstream of the most upstream sampling point is detectable for both sampling strategies, a second very broad peak (between ~3500 – 4500 m) can only be seen for the HR sampling approach for both ions (**Fig. 6(d)**, **(e)**). Previous research demonstrated that an appropriate sampling approach (Lagrangain sampling) that considers the dynamics of the WWTP is required for comparisons of water samples taken along a river profile when aiming to describe the fate of organic micropollutants (e.g., Antweiler et al. 2014; Kunkel and Radke 2012; Writer et al. 2013a). Therefore, we suggest that concentration patterns of Na$^+$ and Cl$^-$ (HR) reflect 'wastewater waves' in the river water during the time of the sampling (3 days). High ion concentrations of HR can, therefore, indicate high WWTP discharge conditions rather than locations of GW inflow. Neglecting the influence of dynamic WWTP releases of these tracers, which in our case corresponds to the HR scenario, leads to a wrong interpretation of the groundwater inflow using Na$^+$ and Cl$^-$ as tracers.

Comparing $SO_4^{2-}$ concentrations of the HR sampling strategy with Na$^+$ and Cl$^-$ (HR) does not show the 'wastewater waves' as described for Na$^+$ and Cl$^-$. However, $SO_4^{2-}$ HR results differ strongly from the LR sampling approach, especially in the upstream segment. High $SO_4^{2-}$ concentrations (HR) occur at the same time as low concentrations of $Na^+$ and $Cl^-$ (HR) in the river (**Fig. 6**), which is obviously due to low WWTP discharge conditions. Low WWTP effluent discharge might lead to a high $SO_4^{2-}$ signal, arising from the gypsum-bearing geology located between the WWTP and the most upstream sampling location. This indicates that $SO_4^{2-}$ is in general a more suitable tracer compared to $Cl^-$ and $Na^+$ though still influenced by the WWTP. EC (HR) as a sum parameter representing the ion concentration of the river is similar to the $SO_4^{2-}$-concentrations along the reach (**Fig. 6**), except for the very prominent EC increase at 4700 m from the most upstream sampling point. This very steep increase can most likely be attributed to wrong measurement settings of the device, since none of the ion concentrations follows this pattern.

#### *4.5.1.2 Applicability of tracers for GW quantification*

A quantitative interpretation of tracer concentrations with regards to GW exfiltration is uncertain due to different GW endmember concentrations arising from different geological settings (**Fig. 6**). Thus, applying FINIFLUX for better comparability between tracers may be a suitable evaluation method for the quantification of GW inflows. ‘Traditional’ approaches linearize the first-order derivative in the ordinary differential equation, followed by solving the mass balances for groundwater inflows into rivers (e.g., Mullinger et al. 2007; Unland et al. 2013). This may lead to physically implausible negative fluxes or instabilities hidden within positive results that look realistic, especially for large spatial scale data. FINIFLUX accounts for these numerical instabilities by discretizing the ODE under application of small discretization steps (Frei and Gilfedder 2015). However, modelling results of FINIFLUX based on different tracers strongly differ in the estimated amounts of water and in the GW exfiltration locations despite partly acceptable coefficient of determination (>0.88). The normalized root mean square error (NRMSE) is a complementary parameter to evaluate the goodness of the model fit to measured data and to interpret the modelling results. A high coefficient of determination coupled with a low NRMSE shows the best agreement of modelled and measured data (**Fig. 7 (a)**, **(b)**, **Tab. 2**). Among the selected tracers, only $^{222}Rn$-based modelling leads to realistic results in this modelling case, indicated by the lowest NRMSE (0.10) combined with a high coefficient of determination (0.92) and a plausible water balance. Therefore, FINFILUX seems most applicable for $^{222}Rn$ in the Ammer catchment and may be reliable for GW inflow localization. This is supported by the fact that the amount of cumulative GW flux (0.265

$m^3$ $s^{-1}$, **Tab. 2**) is similar compared to the discharge difference between upstream (0.55 ± 0.06 m³ $s^{-1}$) and downstream (0.78 ± 0.03 m³ $s^{-1}$) location minus the tributary inflow (0.03 ± 0.008 m³ $s^{-1}$) and to previous assessments of groundwater inflows ranging between 0.2 – 0-3 m³ $s^{-1}$ (Harreß 1973). This outcome is different compared to all the other environmental tracers, where the modelled groundwater inflow significantly underestimates the discharge difference. However, this amount must be interpreted carefully and should not be the only argument in terms of transferability of this method to other river settings. Underlying assumptions for the determination of $^{222}$Rn activity in groundwater is that springs, where samples for the determination of GW endmember activity were obtained from, are representative for the entire reach. In karst environment where degassing in the underground may be relevant, a constantly wrong endmember determination would not necessarily affect the calculated pattern of GW exfiltration, but the absolute contribution. Additionally, a potentially smaller "real" degassing in the river as assumed for this setting could also entail higher GW endmember activities. In rivers embedded in porous media, an appropriate applicability of FINIFLUX for $^{222}$Rn was already shown in two former investigations at the rivers Roter Main and Salzach and gives plausible groundwater fluxes (Frei and Gilfedder 2015; Pittroff et al. 2017). In contrast to the previous applications, which covered scales of 32 km and 52 km, respectively, the spatial resolution of the study at the Ammer River is higher and thus provides a more detailed insight into the specific localization of the GW inflow. This higher resolution enables detection of steep increases and decreases of $^{222}$Rn activities in the Ammer River as described above. This may be the reason of poorer regression coefficients compared to the study results on Roter Main and Salzach (regression coefficients of 0.99 and 0.97, respectively) and thus for the slight overestimation of the cumulative GW inflow considering Q increase with associated measurement errors in the investigation area (Glaser et al. 2020d).

Only LR-ion modelling results are presented due to the ion HR-setup clearly influenced by the transient ion concentrations, except for $SO_4^{2-}$ which showed acceptable results based on the concentration pattern. Even if measured concentrations from the Lagrangian sampling approach seem more reasonable than from grab sampling, modelling of the ion concentrations (LR) did not show GW inflows in a range similar to $^{222}$Rn modelling results or the water mass balance. This may be due to a smaller difference between concentrations in GW and SW for the selected ions, since a difference with a magnitude smaller than a factor of 2 makes ions less sensitive for changes due to GW inflow compared to $^{222}$Rn (Gilfedder et al. 2015). Only concentrations of TRA, CAR and $SO_4^{2-}$ differ by a factor of 5 between GW and SW, in case of $SO_4^{2-}$ only for GW from Gypsum Karst. Thus, insensitive modelling may arise from an insufficient end-member determination. This is also the case for EC measurements (HR). For EC, an oversaturation with respect to calcite could occur if saturated groundwater enters (warmer) surface water leading to a degassing of $CO_2$. This can influence the conservativeness of these tracers and thus restrict their applicability regarding the modelling of GW inflows in karstic environments. Even if the modelled fluxes for $^{222}$Rn and EC results are not similar in regard of the absolute volume flux of groundwater, the spatial pattern of GW inflow is similar. This shows that the general geological shift and the resulting difference in endmember EC is appropriate but not sufficient to quantify reliable GW fluxes based on EC measurements.

The influence of an inappropriate GW endmember concentration determination is also illustrated by comparing measured and modelled data of $^{222}$Rn with CAR (**Fig. 7**). For conservative compounds such as CAR, high measured concentrations are underestimated by the modelled values and reverse for small measured values (**Fig. 7(c)**, **(d)**). The first aspect might be explained by an underestimated GW endmember concentration or due to unexpected contaminated GW inflow into the river (further discussed below). Overestimated modelled values for low concentrations may be ascribed to potentially implausible model assumptions for this compound such as the absence of a degradation term for CAR. Although a small attenuation potential is typically ascribed to this compound (half-life of 50 h for the Ammer River (Glaser et al. 2020e), even a slow degradation might be still relevant in terms of GW exfiltration modelling similar to the comparably small radioactive decay in case of $^{222}$Rn ($t_{0.5}$ = 3.8 days). Additionally, the concentration range of CAR is considerably smaller compared to the range of $^{222}$Rn activity impeding interpretation, and the analytical measurement error (~15%) comes more into effect for the overall small CAR concentrations. This uncertainty propagates through the modelling results. Nevertheless, NRMSE of organic micropollutants are second lowest following $^{222}$Rn results indicating that these compounds might be applicable for river systems with no prevailing concentrations in groundwater and by including a compound specific sink term. Further investigations and a larger data set of CAR in the respective investigation are necessary for validation under different hydrological conditions.

### 4.5.2 LOCALIZATION OF GW INFLOW – CONCEPTUAL MODEL FOR THE INVESTIGATION AREA

Based on a combination of the tracer results as described in the following, a conceptual model was developed for groundwater inflow including stream network patterns and proposed groundwater flow (**Fig. 9**). This conceptual model can reasonably explain the observations along the reach. The most remarkable concentration change for nearly all tracers in SW is between 2340 – 2620 m and leads to the highest GW inflow based on the $^{222}$Rn-modelling results. This GW inflow may be attributed to the Schwärzenbrunnen, a known and extended groundwater exfiltration zone on the right bank of the Ammer River extending over a distance of about 10 m and dominating the GW inflow of the whole investigation area (~50% of overall GW inflow). Besides this important inflow, further sharp $^{222}$Rn increases indicate that discrete GW inflows prevail along the study segment. Bailly-Comte et al. (2009) suggest that concepts for porous media aquifers may be applicable for karst aquifer-surface water interaction, even though they also identified a SW-GW interaction controlled by prevailing fractures and conduits (Coulazou River, Southern France). In contrary, our results are in accordance with other karst rivers, where GW discharge occurs primarily at discrete point sources because of open fractures (Oxtobee and Novakowski 2002).

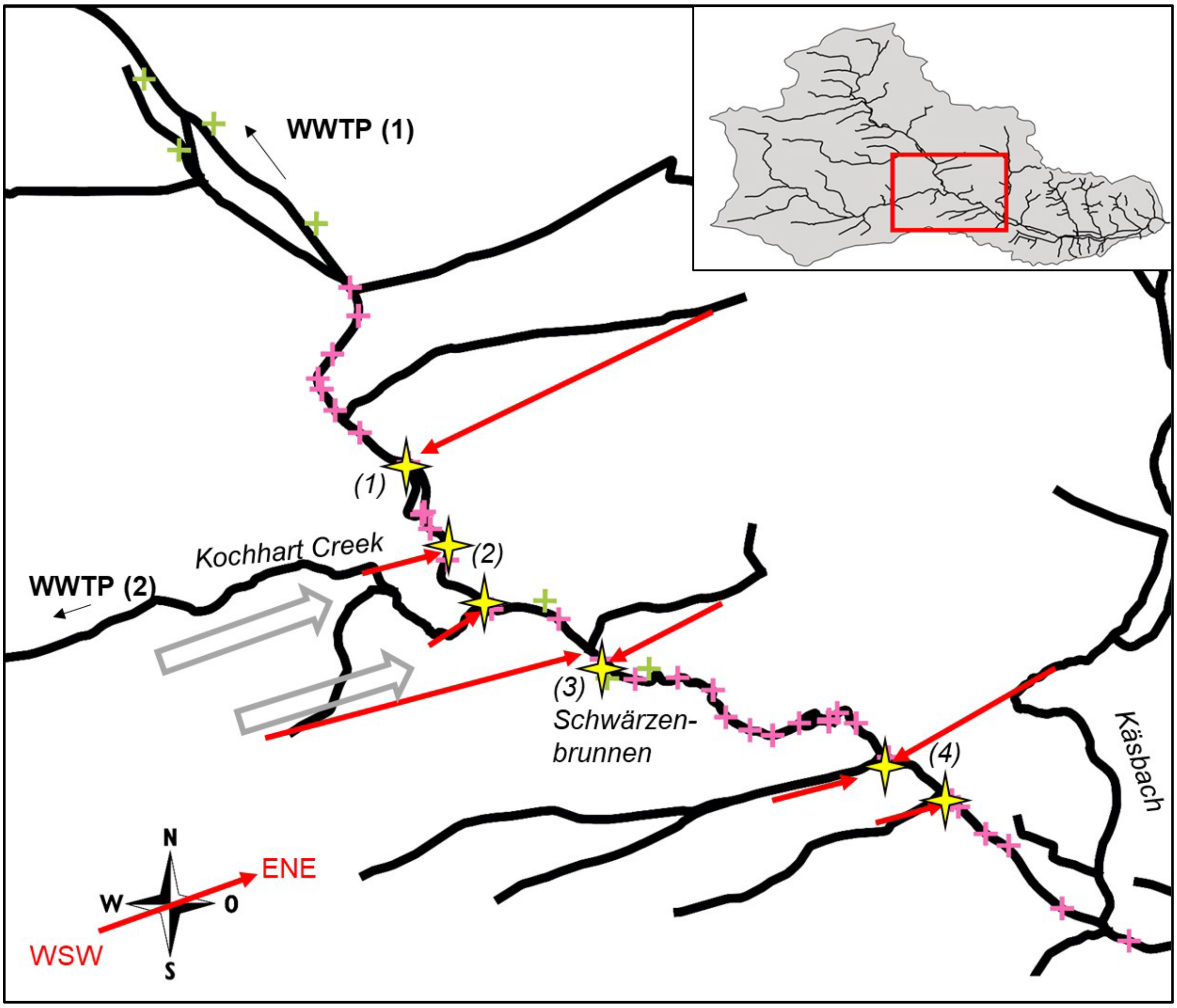

*Fig. 9*: *Conceptual model of groundwater flow into the investigation reach.*
*Straight stream segments were extended in WSW-ENE direction (red arrows) according to the orientation of the dominating faults in the catchments. Extensions meet sampling locations ((1),(2),(3),(4)) with changes in concentrations of environmental tracers ($^{222}$Rn, $SO_4^{2-}$). Grey arrows indicate proposed origins of the GW from infiltrated Kochhart water (that contains organic micropollutants from the WWTP). The pinkish crosses indicate the sampling sites in the surface water, while the green crosses highlight the groundwater sampling sites.*

The locations of $^{222}$Rn activitiy increases and modelled GW inflow can be attributed to the geological setting of the study area. Previous studies in the Ammer catchment attribute a favoured karstification by the degassing of $CO_2$ along faults (Harreß 1973) which may arise from lithological deeper layers. Further investigations confirmed faults by soil $CO_2$ mapping profiles and postulate faults in a pronounced orientation in WSW-ENE direction within the catchment from an implicit geological modelling approach (D'Affonseca et al. 2020). The stream network in the Ammer catchment largely follows this orientation. If straight segments of tributary valleys are extended, they intersect the Ammer River at locations with changes in selected measured environmental tracers in the river water and resulting calculated GW inflows (**Fig. 9**).

The attribution of GW inflow to small-scale, so far unmapped faults in the catchment is in accordance with previous interpretations of the geological settings in southwestern Germany. Ufrecht (2006) already claimed that small-scale geological fractures may exist that are not captured by geological maps, but may though be relevant for the groundwater flow. Former investigations hypothesized that the general pattern and structure of a river network can indicate underlying structures, and the chronology of geological events, which could influence GW-SW connection (Raj 2007; Twidale 2004). A case study in a karstified catchment (Spain) demonstrated a correspondence between the fault direction and orientation of stream channels (Gelabert et al. 2005). In karstic systems, geological faults may lead to a self-reinforcing process by which enhanced GW flow along faults accelerates the karstification and, in turn, further increases the water flow. Thus, in the development of karst conduits and exfiltration into rivers may be largely governed by the orientation and location of faults and fissures. For the areas with a large number of faults, a change in ion concentrations can be seen for LR samples, even if a comparison is restricted due to the lower resolution.

Increased concentrations of CAR are in accordance with some of the earlier described locations of preferential GW inflow due to geological settings which are located, in detail, where straight segments of the Kochhart creek and the Schwärzenbrunnen are extended to the Ammer River (**Fig. 9(2)** and **(3)**). This indicates that the assumption of no prevailing organic micropollutant concentrations in the GW may not be valid for the Ammer catchment. In addition, the measurement uncertainty of the organic compounds can highly impact the wrong assumption of no prevailing micropollutants. It thus explains the unreliable modelled GW fluxes based on CAR data due to an underestimation of CAR endmember concentrations (**Fig. 7(d)**). For a karstic catchment in the UK, organic micropollutants have been described to occur in groundwater and enter SW where the gradient is from the aquifer to the SW (Manamsa et al. 2016). Increased concentrations in the river water may point out the origin of the GW. It has been established in previous studies that water of the Kochhart creek downstream of the WWTP (2) (**Fig. 4**) infiltrates into the GW (Harreß 1973). At the same time, other organic micropollutants, apart from TRA and CAR, have been detected in T9 and in the Schwärzenbrunnen (Glaser et al. 2020e). These organic micropollutants could originate from WWTP (2) and support the previously described hydraulic connection between the Kochhart creek and the

Schwärzenbrunnen (Harreß 1973). Lower concentrations in the Schwärzenbrunnen may be explained by the dilution effect of the Kochhart water infiltrating into the GW. The fact that the Schwärzenbrunnen is bearing Kochhart water is supported by the interpreted subsurface water flow direction obtained from previous tracer experiments and water level measurements in the Ammer catchment. These previous findings indicated an easterly subsurface water flow direction in the area based on previous tracer tests (D'Affonseca et al. 2020, and references therein). Thus, the GW entering the Ammer segment between Kochhart and Schwärzenbrunnen may, at least partly, originate from the Kochhart creek which may also influence other tracer concentrations.

## 4.6 CONCLUSIONS

This study demonstrates that $^{222}$Rn can be used for quantification and localization of GW and is deemed to perform in a more reliable way in comparison to the other environmental tracers. Concepts describing GW-SW interactions for porous media are hardly transferable to karstic rivers, although, in the studied case, the karstic environment turned out to be a smaller challenge than the transient artificial inputs. Modelled GW inflow based on $^{222}$Rn reflects the water budget in the catchment, while other tracers' modelling results significantly underestimate the inflowing GW volume. This is mainly due to a very high concentration difference between GW and SW and the insensitivity of $^{222}$Rn towards the influence of the WWTP. However, various (tracer-specific) uncertainties may lead to limited applicability of tracers for groundwater inflow determination. Heterogeneity of (geogenic) GW endmember concentrations restricts GW quantification. For $^{222}$Rn, degassing constitutes a source of uncertainty in its application as a groundwater tracer. This is especially relevant if degassing is not captured by e.g. gas tracer tests in parallel to the $^{222}$Rn measurements. Thus, it is necessary to rely on established degassing equations, which might not represent the particular conditions of the selected system to its full extent. In addition, uncontrollable degassing in the karstified underground before determining a representative endmember activity can cause uncertainties in the application as a groundwater tracer in karstic catchments. For all tracers that (partly) originate from the WWTP, unsteady concentrations caused by the WWTP dynamics lead to uncertainties which is unlikely to be compensated with a higher resolution sampling approach.

A steady-state assumption is therefore not appropriate for tracers clearly influenced by the WWTP. Additionally, an erroneous estimation of GW endmember concentrations/ activity, not completely mixed water from different origins (e.g. GW-SW, tributary-river) and additional unknown inputs of tracers are important sources of uncertainty. This seems particularly relevant for organic micropollutants in the prevailing karstic river system with partly unexpected contaminated groundwater, but may be of minor importance for other geological settings. Dispersion is a parameter not discussed in detail in this study as well as the accuracy of tracking the same water parcels, but which could be crucial for the mixing between adjoining water parcels for WWTP compounds with comparably small concentrations. Additionally, hydrological turnover measurements (ascertained by artificial tracer tests) that describes the simultaneously occurring water loss and gain at rivers are beyond the scope of this article and was not considered for the data interpretation. However, this aspect might play a role and cannot be excluded from the discharge increase along a river stretch. Despite the fact that many organic micropollutants raise considerable toxicological concern, they are globally omnipresent in aquatic systems and should therefore be considered as ‘emerging hydrological tracers’ in future studies of hydrological systems various in size and flow.

# 5 TEMPORAL AND SPATIAL VARIABLE IN-STREAM ATTENUATION OF SELECTED PHARMACEUTICALS

## 5.1 ABSTRACT

Organic micropollutants enter rivers mainly with discharges of wastewater treatment plants (WWTP) and pose a risk to aquatic ecosystems and water quality. A considerable knowledge gap exists for disentangling overlapping processes and driving conditions that control the fate of these pollutants. Thus, the aim of this study was to identify the driving parameters for attenuation of selected pharmaceuticals (carbamazepine, diclofenac, tramadol and venlafaxine) under field conditions. The presented study was performed at a small river (Ammer River, mean discharge 0.87 $m^3$ $s^{-1}$) which is hydrologically complex due to karstification, numerous artificial discharges, and engineered modifications of the channel. We applied a Lagrangian sampling scheme at two sequential river reaches. In general, for the investigated compounds and over the length of the tested reaches, the absolute net attenuation representative for 24 h was low (≤ 23% net attenuation), yet calculated half-lives were comparable to literature. Photodegradation is specifically relevant for the first river reach characterized by a higher net attenuation of the photosensitive compound diclofenac (14.5% ±11.3%) compared to the second section (9.8% ± 13.7%). This is likely due to a spatial difference in canopy shading, which is supported by significant correlations ($R^2 \geq 0.8$) of the temporally changing 'temperature' and 'solar radiation' with time-specific degradation rate constants of photosensitive compounds for consecutive hourly water parcels. In general, the presented spatially and temporally resolved approach is a suitable tool to determine the attenuation of organic micropollutants and to narrow down the interpretation of net attenuation to a few reasonable processes.

## 5.2 INTRODUCTION

Organic micropollutants are frequently detected in aquatic ecosystems. They enter river systems mainly via wastewater treatment plants (WWTP), and especially small rivers are regularly affected by the chemical burden of sewages due to their low dilution effect (Hassan and Egozi 2001; Mandaric et al. 2018). Micropollutants comprise anthropogenic and natural substances such as industrial chemicals, pharmaceuticals or pesticides. Concentrations of these compounds are per definition very low (nano- to microgram per liter) but still may cause environmental and human health problems (Schwarzenbach et al. 2006). Thus, risk assessment of micropollutants in rivers requires understanding of the environmental fate of these compounds including dissipation in the aqueous and sediment phase (Barth et al. 2007; Barth et al. 2009). Reported compound specific in-stream attenuation rate constants such as for photodegradation, biodegradation, sorption to sediment or suspended particles or volatilization are often deduced from laboratory experiments under controlled conditions (Writer et al. 2011a). The transferability of these process rates to field conditions remains challenging due to the diversity of individual river systems, temporally changing pollutant inputs from WWTP, the large number of transient environmental influences, and the interaction of several attenuation processes. The latter are particularly affected by hydrological variability (Glaser et al. 2019). This comprises dilution or mixing of the compounds by tributaries or groundwater inflow, hyporheic exchange and the spreading of the compounds caused by advection and dispersion. These hydrological processes have to be considered, which makes field-based measurements indispensable for a reliable understanding of attenuation processes.

Even if the number of investigations including hydrological aspects is increasing, there is still a lack of knowledge that could explain the difference in attenuation rate constants from different rivers (Acuña et al. 2015; Barber et al. 2013; Writer et al. 2013a). Application of the same sampling method and measurement of the same parameters enhances comparability of river-specific attenuation processes (Jaeger et al. 2019; Li et al. 2016). Claim of a transferable methodological sampling approach is to capture significant dynamic boundary conditions such as diurnal concentration and discharge patterns of WWTP effluents (Majewsky et al. 2013), and environmental changing parameters, e.g. altering solar radiation or water temperature (Jaeger et al. 2019). The so-called “Lagrangian sampling” is based on tracking defined water parcels along river sections, which allows investigating compound specific reactivity by considering the effect of advective transport. Following the same water parcel over time makes sampling independent of chemistry and discharge patterns of the WWTP and makes it possible to identify transport parameters of the river simultaneously (Antweiler et al. 2014; Barber et al. 2011; Writer et al. 2011b). Recently, investigations aimed on combining both, the daily cycle of the WWTP and environmental dynamic boundary conditions like temperature or solar radiation, with a Lagrangian sampling approach (Guillet et al. 2019; Schwientek et al. 2016). However, it is still hardly possible to identify the driving factors that lead to different attenuation rate constants of a pollutant in different rivers by “only” applying Lagrangian sampling. Investigating river segments that contrast in certain properties is promising to test the effect of these properties. The claim on these spatial differences is to be prominent in certain characteristics such as a significantly different hydraulic regime or other environmental boundary conditions (e.g. direct shading) to identify the process drivers, but not to be too complex and thus less controllable like given by two completely different rivers. Jaeger et al. (2019) thus focused on two sequential river sections which differed in canopy shading and macrophyte abundance. In this way, river-specific attenuation rate constants could be related to spatially different conditions as driving factors. This approach allowed to investigate process-relevant parameters that differ between both reaches and is easily transferable to other investigations. Coupled with a Lagrangian sampling approach, temporally and spatially resolved investigations are possible.

In this study, we test the applicability of this sampling approach to contribute to knowledge on potentially spatially and temporally relevant attenuation process indicators applicable for further field-based studies. In detail, the aims of this study are (1) to quantify the reactivity potential of the Ammer River, a tributary of the Neckar River in southwest Germany, by determining net attenuation of compounds emitted via a WWTP, (2) to identify plausible driving factors relevant for attenuation processes by comparing two sequential reaches, and (3) to assess temporal dynamics of attenuation rate constants and environmental boundary conditions. In this way, the results of our study contribute to disentangling overlapping attenuation processes such as dilution, photodegradation or biodegradation relevant in field-based investigations by merging hydrological and chemical expertise.

## 5.3 CONCEPTUAL APROACH

To achieve the objectives of this study, i) the spatial pattern of daily net attenuation and ii) temporal variable water parcel-specific degradation rate constants of hourly composite samples were investigated both under consideration of the prevailing hydrological settings. For the first objective, two sequential reaches were compared following an approach recently introduced by Jaeger et al. (2019).They were able to identify spatially driving factors such as the canopy shading which significantly controlled the net attenuation within one river. For the determination of compound-specific daily net attenuation, the approach introduced by Schwientek et al. (2016) was applied. This approach accounts for uncertainties that typically arise during Lagrangian sampling due to the inaccurate determination of transit times, the influence of adjacent water parcels through the action of longitudinal dispersion, and mixing by additional water inputs along the tested river segment (**Fig. B24**). To minimize such effects the Lagrangian parcel is enlarged and a mass balance is set up. Additionally, dynamic environmental boundary conditions such as solar radiation and, ideally, the diurnal cycle of the WWTP are integrated by the enlargement, thus representing "mean conditions" and not only a snapshot in time. One water parcel covering 24 h, with high-frequency sampling of discharge and pollutant concentrations at the upstream and downstream ends of each reach, fulfils these conditions since one whole cycle of the WWTP and solar radiation is covered. The cumulative mass flux entering a study reach via n inflows during the sampling period $t_0$ to $t_1$ was compared with the mass flux leaving the same reach through the downstream cross-section during the sampling period shifted by the mean transit time Δt of the water:

$$\int_{t_0}^{t_1} \sum_{i=1}^{n} (C_i \cdot Q_i)_{in} = \int_{t_0+\Delta t}^{t_i+\Delta t} (C \cdot Q)_{out} + \Delta S \tag{3}$$

For a given organic micropollutant, the mass influx comprises the discharge Qi [L $s^{-1}$] and concentration $C_i$ [ng $L^{-1}$] of the pollutant at any inflow i into the river reach. The multiplication of the discharge Q and pollutant concentration C at the outlet denotes the mass outflux of the selected reach. Concentrations and discharges were determined at hourly intervals (see below for details). The gain and loss term ΔS describes all in-stream processes that change the compound flux across this reach. The relation of ΔS and the total mass inflow (left side of the equation) is a measure for the relative reactivity of a specific compound and is, in the following, reported as net attenuation. As a base for applying the presented mass balance approach, the mean transit time Δt was determined by the application of a deconvolution technique that can be described as follows: Generally, the concentration $C_{out}$ of a conservative constituent at a downstream location can be computed from the upstream concentration $C_{in}$ by convoluting the inflowing concentration time series with the transit time distribution function g(τ) (McGuire and McDonnell 2006) under consideration of additional inflows:

$$C_{out}(t) = \int_0^t C_{in}(t-\tau) \cdot g(\tau) \cdot d\tau + \Delta C_{inflows}$$

*(4)*

where τ describes the transit time of a single tracer particle along the river stretch. As transit time distribution function, representing both, advection and dispersion in a river, we chose the following dispersion model (Maloszewski and Zuber 1982, 1993):

$$g(\tau) = \frac{1}{\tau \cdot \sqrt{\frac{4P_D\tau}{\Delta t}}} \cdot exp\left[-\frac{\left(1-\frac{\tau}{\Delta t}\right)^2}{\frac{4P_D\tau}{\Delta t}}\right]$$

*(5)*

with the mean transit time Δt and the dispersion parameter $P_D$. Time series of conservative compounds at the upper cross-section can be used as input function $C_{in}(t)$ in Eq. (4). If $C_{out}(t)$ is also known, the transport parameters Δt and the dispersion parameter $P_D$ are obtained through deconvolution of Eq. (4), i.e. by fitting the modelled output function $C_{out}(t)$ to the measured concentration time series at the lower cross-section. For this purpose, the electrical conductivity (measured at 15-min intervals) was adopted under the assumption to behave conservatively. Temporally varying inputs can in general lead to dispersive effects for neighbouring water parcels, which is why the dispersion model is assumed to be more representative for determining the mean transit time then e.g. a simple piston flow approach. For very small dispersion parameters, the dispersion model is similar to a piston flow transport approach. It is necessary to determine the mean transit time Δt in advance of collecting pollutants' samples for the correct timing in order to sample the same water parcels at different locations. During the actual sampling procedure, Δt has to be re-measured to account for potential hydrological differences between the preliminary experiment and the sampling and thus to (ideally) verify the previously identified Δt. Discharge conditions have to be comparable between the preliminary experiment and the day of the actual sampling procedure.

In parallel to the measurement of the net attenuation over 24 h, diel cycles of reactivity were computed for hourly composite samples to identify the temporal dynamics of the attenuation rate constant. Water parcel-specific degradation rate constants k [$h^{-1}$] for reactive compounds were determined for Lagrangian parcels when entering and leaving the respective reach, based on mass flows and the respective mean transit time Δt assuming first order decay:

$$C(t_0 + \Delta t) = C(t_0) \cdot e^{-k\Delta t}$$

*(6)*

To account for several inputs along the tested river reach such as tributaries or groundwater inflow, mass fluxes are considered through multiplication of concentrations with Q and summed up:

$$(C \cdot Q)_{out,t_0+\Delta t} = \left( \sum_{i=1}^{n} (C_i \cdot Q_i)_{in,t_0} \right) \cdot e^{-k\Delta t}$$

*(7)*

Solving for k yields:

$$k = \frac{\ln\left( \frac{\sum_{i=1}^{n} (C_i \cdot Q_i)_{in,t_0}}{(C \cdot Q)_{out,t_0+\Delta t}} \right)}{\Delta t}$$

*(8)*

The obtained values for k of this equation are temporally highly resolved over 24 h and thus allow a differentiation between water parcels exposed to sunlight and those with no sunlight by assessing the presence of the solar radiation for the time the selected water parcel passed through a selected river section. It must be noted that this approach is likely more affected by potentially inaccurately determined mean transit times and dispersion parameters (Eqs. (4) and (5)) compared to the daily net attenuation since the influence of adjacent water parcels through the action of longitudinal dispersion is more relevant for smaller water parcels. The presented approach thus allows simultaneous determination of hydrological parameters (Eqs. (2) and (3)), and observed net attenuation (Eq. (3)) to disentangle temporal dynamics of degradation rate constants (Eq. (8)) by linking hydrological and chemical transformation processes. Adopting mass fluxes for calculations (Eqs.(3) and (8)) requires a precise determination of potential inflows. Especially diffuse groundwater inflows are crucial in the strongly karst-influenced Ammer River (Schwientek et al. 2013a; Selle et al. 2013). A multitracer approach for the quantification and localisation of these inflows was successfully applied in parallel to this study (explained in more detail in (Glaser et al. 2020b). However, assessments regarding groundwater quality flowing into the selected river system are hardly possible. No significant river water loss along the investigation segment was assumed due to increasing net discharge along the reach. However, increasing discharge does not simply imply the absence of any exchange as illustrated by Mallard et al. (2014) and Payn et al. (2009). They measured the so-called "hydrological turnover" which describes the simultaneously occurring spatially variable stream gain and loss. This aspect was described to be relevant on a reach-scale for rivers despite a net increase in discharge. This aspect has never been investigated within the scope of describing the fate of micropollutants and has not been considered for this study, neither, thus constituting an open research question for future studies.

## 5.4 MATERIALS AND METHODS

### 5.4.1 SAMPLING SITE

Located in Southwestern Germany, the Ammer River (4th order stream) is a tributary of the Neckar River and flows from Herrenberg to Tübingen over a distance of 22 km with a mean discharge (Q) of 0.87 m$^3$ s$^{-1}$ at the gauge Pfäffingen (https://www.hvz.badenwuerttemberg.de/) which is located about 10 km upstream of the Ammer mouth. The gauged Ammer catchment has an area of 134 km$^2$. The annual areal precipitation is 750 mm yr$^{-1}$ (maximum precipitation in summer), the mean annual air temperature is approximately 8 °C for the city of Tübingen. The river is fed by the karstic aquifers of the Upper Triassic Limestone and Middle Keuper gypsum formations (Villinger 1982). Land use is dominated by agriculture (71%) and urban areas (17%) (Schwientek et al. 2013a). The riverbed of the Ammer River consists of larger cobbles with gravel and especially sandy material in the interspaces that are underlain by loamy Holocene deposits. A river segment of 7.7 km length was selected that ranges from the WWTP Gültstein (1) to the village of Pfäffingen and was subdivided into two investigation reaches at the village of Reusten (**Fig. 10**). The river has a heavily altered character with three constructed diversions and three weirs for former mills within the investigated segment.

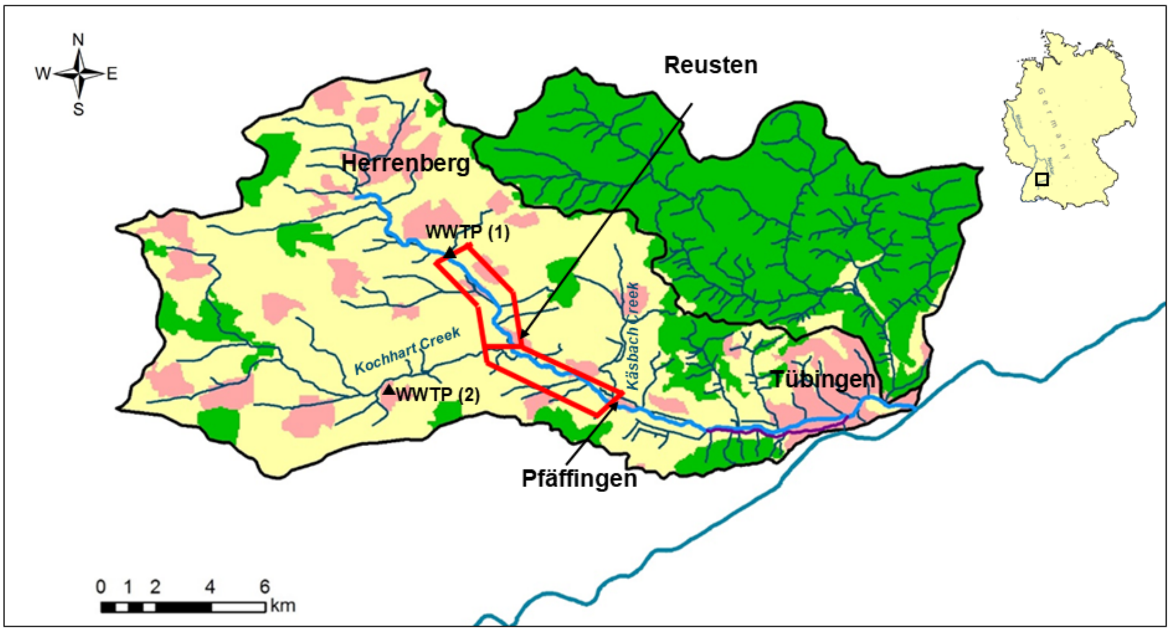

***Fig. 10:*** *Ammer catchment, the investigation area of this study close to Tübingen. The red frame denotes the selected river section conceptually subdivided into two reaches for the sampling campaign.*

The catchment's largest wastewater treatment plant (WWTP (1), 80,000 person equivalents) is located at the upper end of the selected river segment, and releases water at the left bank of the river with a mean dry weather effluent flow rate of 0.10–0.12 m$^3$ s$^{-1}$. A drinking water treatment plant (Carix method; **Fig. 11**) close to Pfäffingen regularly discharges water with a high ion content into the Ammer River (up to 6 times a day, in total approximately 83 $m^3$ per day). Fifteen tributaries to the studied reach were identified which may partly fall dry during very dry weather conditions. The two main natural tributaries are the Kochhart Creek and the Käsbach Creek. The Kochhart receives water from an additional WWTP (2) (Hailfingen, 9000 PE) with flow rates of 0.012–0.015 $m^3\ s^{-1}$. Most of the remaining tributaries are tile drains (**Tab. 3**). Due to the karstification of the catchment, diffuse groundwater inflows and especially discrete groundwater point sources play a crucial role for the selected catchment. Therefore, tributaries often correspond to discrete groundwater inflows (**Tab. 3**), whereas statements regarding water origin, travel time and chemical load of this groundwater are limited. Special emphasis should be placed to the discrete point source "Schwärzenbrunnen" (**Fig. 11**, tributary 10) since previous investigations identified that the water emerging from this karst spring contains infiltrating Kochhart Creek Water (influenced by WWTP (2)) (Harreß 1973).

***Tab. 3**: Environmental parameters (Q, pH, EC, water temperature), concentrations ofmajor ions and of selected organicmicropollutants carbamazepine (CAR), diclofenac (DIC), tramadol (TRA) and venlafaxine (VEN) within the sampling period. LOQ=Limit of quantification; CAR 20 ng $L^{-1}$, DIC 100 ng $L^{-1}$, TRA 15 ng $L^{-1}$, VEN 10 ng $L^{-1}$. For the autosamplers (in bold), a mean value for the parameters (±standard deviation based on the value range over the course of the 24 h water parcel) is given.*

| | | | | | | Ions [mg $L^{-1}$] | | | | | Pharmaceuticals [ng $L^{-1}$] | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Location[3] | Characterization/ name of tributary | Q [$m^3\ s^{-1}$] | pH | EC (temperature compensated) [µS $cm^{-1}$] | water temperature [°C] | $Cl^-$ | $NO_3^-$ | $K^+$ | $Na^+$ | $SO_4^{2-}$ | CAR | DIC | TRA | VEN |
| upstream WWTP | | 0.27<br>(± 0.02) | 8.0 | 916 | 12.7 | 41.1 | 29.9 | 2.4 | 16.0 | 97.8 | 27 | <LOQ | <LOQ | <LOQ |
| **AS 1** | | **0.52**<br>**(± 0.06)** | **7.8** | **1115**<br>**(±17)** | **14.7**<br>**(± 1.1)** | **78**<br>**(±3)** | **34**<br>**(±1)** | **7**<br>**(±1)** | **36**<br>**(±3)** | **126**<br>**(±3)** | **142**<br>**(±14)** | **387**<br>**(±91)** | **72**<br>**(±7)** | **55**<br>**(±6)** |
| 1 | artificial tube | 0.002 | 7.4 | 924 | 12 | 39.3 | 1.2 | 2.7 | 14.6 | 97.2 | <LOQ | <LOQ | <LOQ | <LOQ |
| 2 | groundwater[2] | 0.016 | 7.4 | 997 | 12.4 | 61.5 | 29.9 | 4.0 | 12.6 | 534.0 | <LOQ | <LOQ | <LOQ | <LOQ |
| 3 | groundwater[2] | 0.006 | 7.3 | 936 | 14 | 57.7 | 31.1 | 2.0 | 4.7 | 38.7 | <LOQ | <LOQ | <LOQ | <LOQ |
| 4 | artificial tube | 0.035 | 7.2 | 2549 | 12.4 | 49.3 | 29.6 | 5.0 | 15.7 | 1216.3 | <LOQ | <LOQ | <LOQ | <LOQ |
| **AS 2** | | **0.58**<br>**(±0.03)** | **8.1** | **1438**<br>**(±15)** | **15.3**<br>**(±1.3)** | **55**<br>**(±2)** | **29**<br>**(±1)** | **7.3**<br>**(±1)** | **31**<br>**(±1)** | **266**<br>**(±8)** | **128**<br>**(±12)** | **308**<br>**(±111)** | **64**<br>**(±8)** | **46**<br>**(±5)** |
| 8 | Kochhart | 0.008 | 8.5 | 934 | 19 | 115.6 | 25.1 | 15 | 57.8 | 66.5 | 127 | 560 | 43 | 78 |
| 9 | artificial tube[2] | 0.002 | 7.3 | 954 | 11.1 | 83.4 | 15.4 | 4.7 | 40.3 | 56.5 | 54 | <LOQ | <LOQ | <LOQ |
| 10 | Schwärzenbrunnen | 0.120[1] | 7.1 | 1413 | 11.4 | 57.6 | 38.2 | 3.1 | 22.7 | 100.9 | <LOQ | <LOQ | <LOQ | <LOQ |
| 11 | | 0.001 | 7.7 | 794 | 11.9 | 75.2 | 9.0 | 6.1 | 33.1 | 55.9 | <LOQ | <LOQ | <LOQ | <LOQ |
| 12 | | 0.001 | 8.1 | 964 | 17.4 | 22.4 | 19.1 | 3.6 | 8.1 | 147.4 | <LOQ | <LOQ | <LOQ | <LOQ |
| 15 | Käsbach | 0.012 | 8.1 | 1909 | 20.2 | 30.7 | 25.5 | 4.5 | 14.6 | 880.2 | <LOQ | <LOQ | <LOQ | <LOQ |
| **AS 3** | | **0.75**<br>**(±0.03)** | **8.1** | **1374**<br>**(±84)** | **15.2**<br>**(±0.8)** | **67**<br>**(±1)** | **31**<br>**(±1)** | **5.7**<br>**(±0.2)** | **30**<br>**(±1)** | **287**<br>**(±23)** | **97**<br>**(±8)** | **224**<br>**(±75)** | **49**<br>**(±5)** | **35**<br>**(±5)** |

*[1] (Glaser et al. 2020b). [2]Aboveground inflow, due to very short distance to the spring representative for the groundwater composition. [3]numbers referring to **Fig. 11***

### 5.4.2 SAMPLING PROCEDURE AND FIELD INSTRUMENTATION

Sampling was performed on June 19 and 20, 2018 at the selected segment of the Ammer River (**Fig. 11**). To consider potential groundwater inflows due to the karstification of the catchment, a multi-tracer approach was conducted in parallel to this study. Briefly summarized, different environmental tracers (selected ions, selected organic micropollutants, radon) were measured in the river and the groundwater. Amass balance analysis allowed the quantification and localisation of (diffuse) groundwater inflow along the selected river stretch (see Glaser et al. 2020b for more details). Even if groundwater samples had been measured, it would not be possible to make statements regarding the water quality of the inflowing groundwater due to a hardly predictable spatial origin of the groundwater from the karstic aquifer. We therefore have to assume that no organic micropollutants are transported via the diffuse groundwater inflows into the river. Restrictions and consequences of this assumption are discussed in a later chapter. The study presented here was conducted under approximately mean discharge conditions, which were also used for determination of mean transit times (Eqs.(4) and (5),**Tab. 3**). The sampling distance to the WWTP was chosen as short as possible to ensure high concentrations of WWTP-originated compounds and thus to calculate reliable attenuation rates. Two sequential reaches were selected based on the differences in river morphology between both reaches with sampling sites at the upstream and downstream ends of each reach (**Tab. 3**). Reach length, river slope and general reach characteristics were identified using Google Earth and on-site inspection according to Glaser et al. (2019). Shading of the river was determined using Google Earth satellite images comparing maximum foliage with the river area according to Jaeger et al. (2019). In both reaches, macrophytes (mainly Ranunculus hederaceus) dominated over long sections during the sampling time. The non-invasive determination of the (reactive) macrophytes' leaf area is difficult; possible approaches would e.g. result in a removal of the plants to determine the biomass. This aspect was not included in this study.

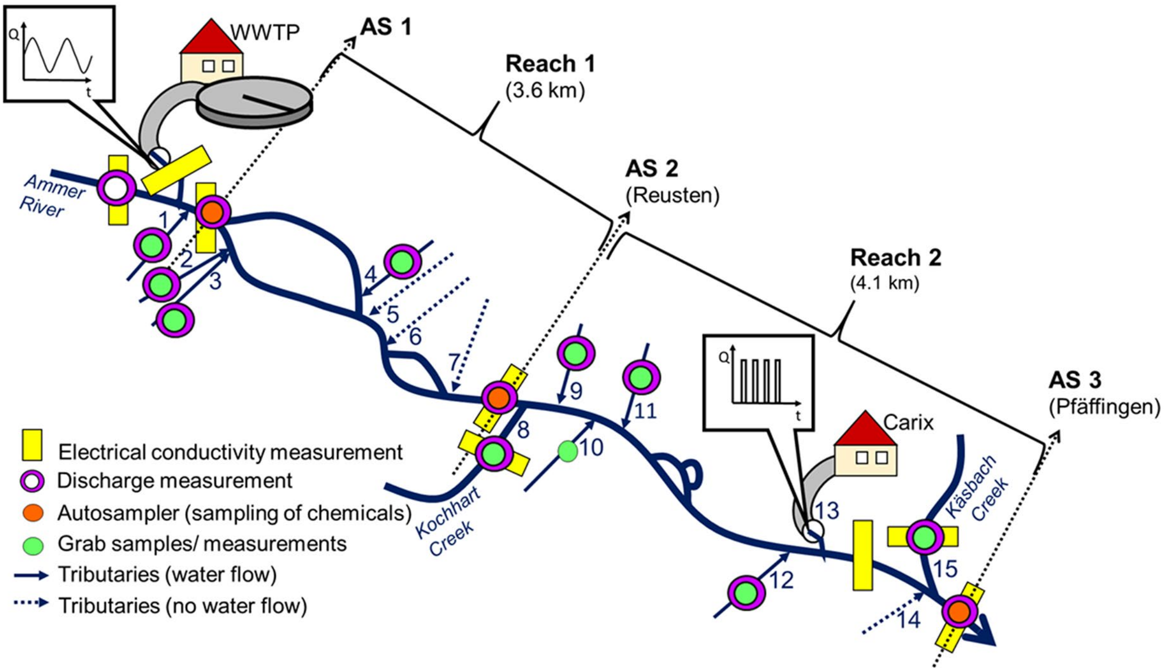

***Fig. 11:*** *Conceptual diagram of the investigation area including all tributaries (labelled 1–15) with and without water flow during the sampling campaign along the two selected reaches.*
*Autosamplers for continuous sampling of chemical compounds (orange circles) were set up at the upper and lower edge of each reach. Electrical conductivity (yellow rectangles) and discharge measurements (purple circles), as well as grab samples for chemical analysis (green circles) were obtained in the tributaries and selected sampling sites along the Ammer River. Theoretical temporally varying discharge pattern of the wastewater treatment plant (WWTP) and a drinking water treatment plant sewage (Carix) are presented conceptually (text box).*

According to **Fig. 11**, discharge and time series of electrical conductivity (EC), major ion concentrations and organic micropollutants were measured at each upper and lower cross section of each reach by installing autosamplers (ISCO 3700, Teledyne Isco, Inc., USA) and probes at the three sampling sites (hereafter called AS 1, AS 2, AS 3 according to the sampling sites). Probes to determine EC, water temperature and water level were installed about 200 m upstream of the WWTP (UIT GmbH, Dresden, Germany; 15 min interval), in the WWTP effluent (Schlumberger Water Sciences Technology, Canada; 5 min interval), about 250 m downstream of the WWTP (AS 1) (Schlumberger Water Sciences Technology, Canada; 5 min interval), in Reusten (AS 2) (OTT CTD, Kempten, Germany; 15 min interval), at the gauge in Pfäffingen (AS 3) (UIT GmbH, Dresden, Germany; 15 min interval) and in the Kochhart and Käsbach Creeks (OTT CTD, Kempten, Germany; 15min interval). Discharge (Q) was obtained from the water level measurements applying pre-established rating curves. Probes in the effluent of the WWTP and at AS 1 only determined EC and water temperature and thus did not directly provide information about Q.

Therefore, the respective flow rates were calculated with a two-component mixing equation based on Q determined upstream of the WWTP and EC time series measured at the same location, in the WWTP effluent, and in the Ammer River at AS 1. The proceeding is described in more detail by Schwientek et al. (2016). For the tributaries not equipped with probes, discharge was either measured using an acoustic current meter (Ott, Kempten, Germany) or estimated for those locations where flow measurements were not possible due to the small water depth. In the latter cases, the flow rates were usually clearly below 1% of Q in the Ammer main stem. Assuming steady-state conditions in the tributaries, grab samples for chemical analysis were taken close to their mouth into the Ammer River.

#### *5.4.2.1 Sampling of chemical compounds and target substances*

Autosamplers allow high-frequency determination of organic micropollutant and ion concentrations. Sampling was possible close to the bank of the river since lateral EC profiles showed complete transverse mixing of the respective upstream wastewater (WWTP) or the water of the tributaries with the Ammer water. The autosamplers were programmed to sample hourly composite samples (250 mL every 15 min) over a total period of one day. The upstream autosamplers started earlier compared to the downstream ones to account for the mean transit time of the river. The sampling program at AS 1 started at 09:00 AM and ended at 01:45 PM the next day. AS 2 started at 11:15 AMand ended at 03:45 PM the following day. AS 3 started at 05:00 PM and ended at 06:45 PM the next day. The samplers were equipped with Teflon tubes and 1 L glass bottles. Crushed ice was placed in the middle of the device in contact to the water bottles to ensure a constantly low temperature over the sampling period. Samples were transferred to 1 L amber glass bottles rinsed with river water in advance. These bottles were stored in cooling boxes containing crushed ice for the transport to the Center for Applied Geoscience of the University of Tübingen. Subsequently, the samples were stored in the dark 4 °C cooling room until analysis. Procedural blank samples were generated by pumping 2.5 L distilled water through each autosampler. The water went through the same sampling and analytical procedure as the river water samples. An additional 1 L grab sample was taken with an amber glass bottle upstream of the WWTP to determine background concentrations of chemical compounds. Grab samples in the tributaries were taken accordingly. All amber glass bottles were rinsed with river water before taking the sample. Three grab samples for the analysis of organic micropollutants and ion concentrations were taken simultaneously at the riverbanks and the middle of the river at AS 2 for quality control.

Four compounds representative as process indicators were selected based on physico-chemical properties, literature review and previous investigations in the Ammer River. The selection comprises the conservative anticonvulsant carbamazepine (Clara et al. 2004; Dickenson et al. 2011; Kunkel and Radke 2012; Li et al. 2016; Schwientek et al. 2016), the anti-inflammatory drug diclofenac as indicator substance for photodegradation (Acuña et al. 2015; Zhang et al. 2008), the opioid tramadol which is only slowly photodegradable (indirect photodegradation) (Bergheim et al. 2012; Müller et al. 2018; Rúa-Gómez and Püttmann 2013), and the analgesic venlafaxine for biodegradation and partly photodegradation (Guillet et al. 2019). Even if these compounds are assigned to a certain turnover process, we are aware of the fact that also other elimination mechanisms such as biodegradation for the photosensitive compound diclofenac might contribute to a certain, but minor, extent to the compound's degradation.

#### *5.4.2.2 Additional measurements*

Data of global solar radiation and air temperature were obtained from the State Institute for the Environment Baden-Württemberg (LUBW). EC of the tributaries was directly measured in the field using hand-held EC meters (Cond 3310, WTW GmbH, Germany). Turbidity was continuously recorded by the probes upstream of the WWTP and in Pfäffingen (both UIT GmbH, Dresden, Germany).

### 5.4.3 LABORATORY PROCEDURE

All lab analyses were performed at the Center for Applied Geoscience of the University of Tübingen. pH of the raw samples of the autosampler was measured using a Multical ® pH 540GLP pH meter (WTW GmbH, Germany). After filtration (0.45 µm, cellulose-acetate filters), major ions in the samples were measured using an ion chromatograph (DX 500, DIONEX). An aliquot of every second filtered sample was prepared for DOC measurement by acidification to pH 2. Measurement was conducted using a TOC analyzer (Elementar HighTOC; thermal oxidation). Sample preparation for wastewater contaminants was performed according to Müller et al. (2018). Compounds were detected by tandem mass spectrometry using an Agilent

6490 iFunnel Triple Quadrupole (QqQ) instrument from Agilent Technologies. Full analytical details are provided in (Glaser et al. 2020b).

### 5.4.4 COMPUTATIONAL ANALYSIS AND MODEL APPLICATION

Two months prior to the sampling campaign, measurements of EC were used for the determination of hydrological parameters. The EC time series of the WWTP effluent was constant in time, while the discharge varied over the day. After complete mixing of treated wastewater and river water, a diurnal pattern of the EC time series downstream of the WWTP reflects the discharge inflow pattern of the sewage effluent as long as the EC is constant upstream of the WWTP. This is only the case if the ECs of river and effluent are distinctly differing (upstream WWTP 916 µS $cm^{-1}$, WWTP effluent 1347 µS $cm^{-1}$; mean values for June 19, 2018). EC serves as a tracer for the WWTP discharge only for smaller rivers like the Ammer River since a high WWTP effluent discharge (mean discharge during sampling campaign 0.258 $m^3\ s^{-1}$, standard deviation of ±0.054 $m^3\ s^{-1}$) compared to the river's discharge (mean discharge upstream of WWTP 0.268 $m^3\ s^{-1}$, ± 0.015 $m^3\ s^{-1}$) is required to produce detectable signals (ideal are similar discharges). The EC pattern is advectively transported downstream. For an adequate timing of the one-hour composite samples, the conservative EC time series were used to fit the mean transit time $\Delta t$ and the dispersion parameter $P_D$ using a lumped parameter model based on Eqs. (4) and (5) and considering additional inflow of EC from tributaries and groundwater inflow as described in an earlier section. With that, the downstream EC is computed from the upstream EC time series by convoluting the inflowing EC with the transit time distribution function $g(\tau)$. Data and modelled EC time-series used for determining $\Delta t$ for the correct timing of the autosamplers are presented in **Fig. 12**.

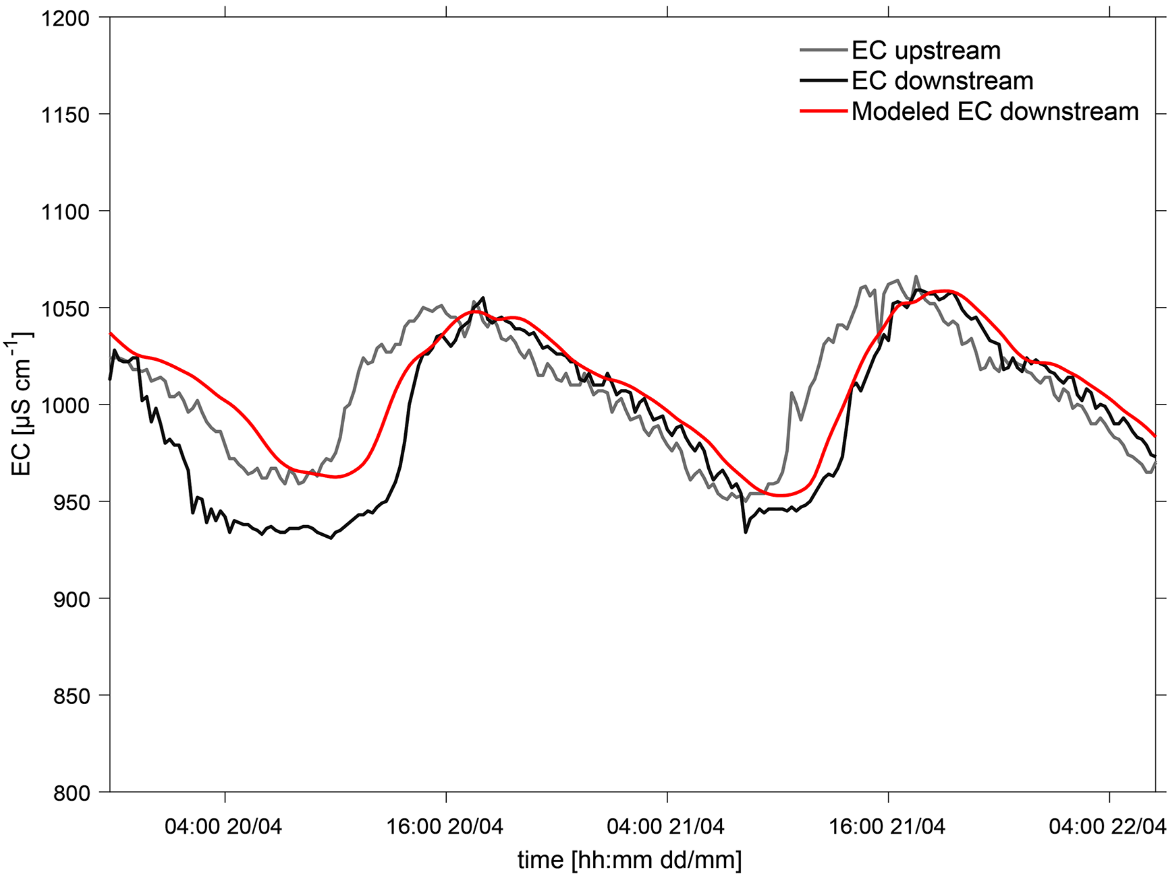

***Fig. 12:*** *Measured electrical conductivity (EC [µS cm$^{-1}$]) upstream (grey) and downstream (black) of reach 1. The upstream time series was used as input parameter to compute the downstream concentration (modelled EC downstream, red) by fitting the mean transit time and the dispersion parameter (Eqs.(4) and (5)). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)*

A mean transit time of 2 h 15 min and a reasonable correlation between modelled and measured EC at the downstream location (Spearman; correlation coefficient of 0.92) were obtained from the fitting routine. Discrepancies between inflowing and outflowing EC pattern in the beginning could be assigned to unsteady tributary inflow, even if these small deviations do not significantly influence the correct determination of Δt. Steady state conditions at each sampling site (**Tab. 3**) were assumed as prerequisite for the model application. Pre-processing of the EC time series was necessary. Artefacts arising from the devices were removed and the time series was Savitzky-Golay filtered for noise reduction. All EC values were corrected by an offset determined by comparing values to an additional EC measurement device, which was applied at all sampling sites for direct comparison with the permanently installed probes. EC values were temperature compensated for 25 °C. For reach 2, the offset of EC arising from the additional inflow of the Carix system was removed before applying the model.

For the net attenuation of compound concentrations in the 24 h water parcel, the uncertainty of the bulk sink flux (Eq. (3)) was estimated by a Monte Carlo simulation with 10,000 realizations for each compound and reach assuming normal distributed errors of discharge and pollutant concentration measurements of inflow and outflow (Glaser et al. 2020c). Water parcel-specific dilution due to the Carix water treatment system was taken into account.

## 5.5 RESULTS

### 5.5.1 CONCENTRATIONS AND ENVIRONMENTAL BOUNDARY CONDITIONS

In the Ammer River, average concentrations of the selected organic micropollutants covered one order of magnitude in the ng $L^{-1}$ range in dependence of the compound (**Tab. 3**). Venlafaxine concentrations were lowest while highest concentrations were found for diclofenac. Concentrations of organic micropollutants were below the limit of quantification (LOQ) for most tributaries, except for the Kochhart (8) and the artificial tube (9). Ion concentrations ranged from a few mg $L^{-1}$ for potassium ($K^+$) up to >1000 mg $L^{-1}$ for sulphate ($SO_4^{2-}$). Downstream of the WWTP, ion concentrations (AS 1) increased compared to upstream (ordered by descending relative change: potassium ($K^+$) > sodium ($Na^+$) > chloride ($Cl^-$) > sulphate ($SO_4^{2-}$) > nitrate ($NO_3^-$)). For the selected organic micropollutant concentrations and the ions, the coefficient of variation of the cross-sectional concentration profile at AS 2 (n = 3) was between 1.3 and 7.7% and between 2.1 and 2.7%, respectively, except for $SO_4^{2-}$ (10.1%) (Glaser et al. 2020c). Deviations of organic micropollutant concentrations in the cross sectional concentration profile may be due to measurement uncertainty, whereas reasonable ion standard deviation confirms a well-mixed cross-sectional profile. Pollutant concentrations in the procedural blank sample were below the LOQ.

An overview on measured concentrations of organic micropollutants, ions and environmental parameters of the three sampling sites and the tributaries is given in **Tab. 3**. Water temperature ranged from 14.7 to 15.3 °C (dependent on sampling location, mean temperature), air temperatures from 14.1 to 29.8 °C and solar radiation from 0 to 1151 $Wm^{-2}$. The mean DOC concentration was 2.7mg $L^{-1}$ (± 0.38 mg $L^{-1}$). Turbidity had a mean value of 12 NTU.

Fitting modelled to measure EC time series led to a correlation coefficient (Spearman) of 0.62 for reach 1 and yielded a dispersion parameter of 0.002 whereby this parameter was very insensitive to the mean transit time. A transit time of 2 h 10 min corresponding to a mean flow velocity of 0.39 m $s^{-1}$ was determined for reach 1. The correlation for reach 2 was not significant and the determination of the mean flow velocity from the model fit was not possible. Previous, unpublished investigations yielded relatively stable flow velocities along the Ammer River, also for the segment with increased slope. A larger profile roughness, associated with the rudimentary riffle – pool morphology in that segment, may provide an explanation. Based on these considerations, the mean flow velocity of reach 1 was transferred to reach 2 and a transit time of 2 h 45 min was determined.

### 5.5.2 NET ATTENUATION

Net attenuation of selected compounds calculated based on Eq. (3) is shown in **Fig. 13**. In reaches 1 (3.65 km length, mean transit time 2 h 10 min) and 2 (4.06 km length, mean transit time 2 h 45min), net attenuations were 2.2% (standard deviation from the Monte Carlo simulation: ±12.9%) and 3.5% (±14.6%) for carbamazepine, 14.5% (±11.3%) and 9.8% (±13.7) for diclofenac, 4.5% (±12.5) and 0.4% (±14.9) for tramadol, and 9.8% (±11.8) and 2.0% (±15.0) for venlafaxine. This led to an integral net attenuation for both reaches of 6.5% (±14.2) for carbamazepine, 23.3% (±11.3) for diclofenac, 6.2% (±14.1) for tramadol and 12.4% (±13.3) for venlafaxine.

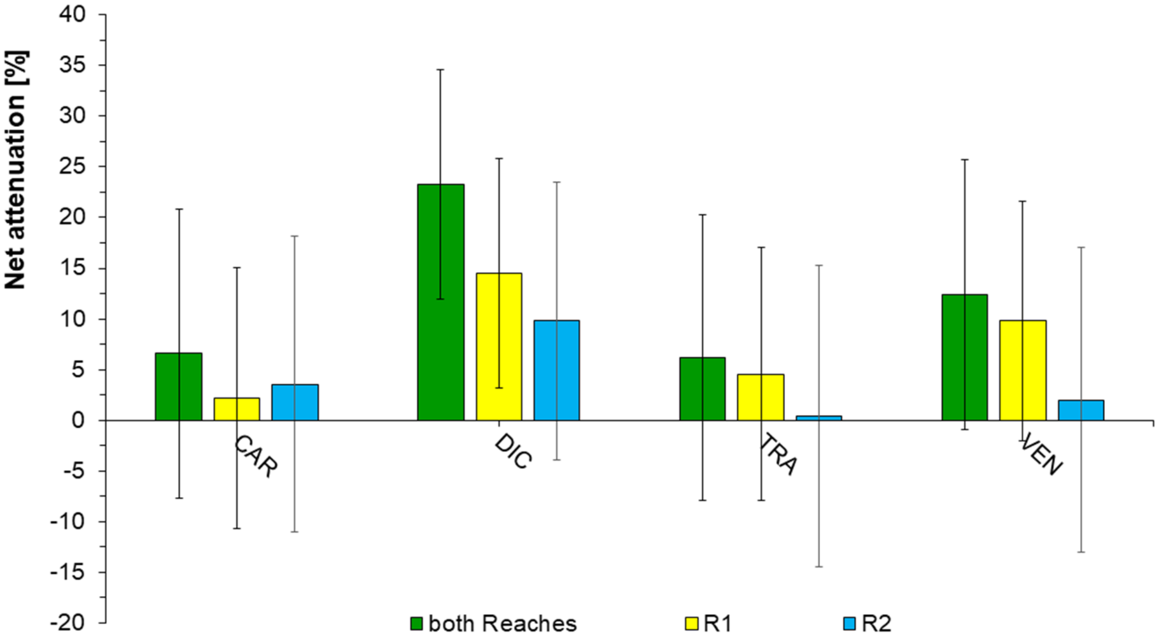

***Fig. 13:*** *Calculated net attenuation of selected compounds in reaches 1 (R1) and 2 (R2) for the selected compounds carbamazepine (CAR), diclofenac (DIC), tramadol (TRA) and venlafaxine (VEN). Deviations result from applying a Monte-Carlo-Simulation with 10,000 realizations altering the error of measurement of discharge and pollutant concentration (normally distributed).*

### 5.5.3 DEGRADATION RATE CONSTANTS

Median degradation rate constants k for both reaches with appropriate minimum and maximum values were calculated based on the hourly k values (**Fig. 14**). Results are displayed in **Tab. 4**, as well as k values representative for water parcels with and without exposure to sunlight. For the first reach, the k value of the water parcels not exposed to sunlight comprises all water parcels entering between 19:30 and 05:30 (leaving between 21:30 and 07:30). Water parcels of the second reach not exposed to sunlight entered the reach between 18:30 and 04:30 (leaving between 21:30 and 07:30).

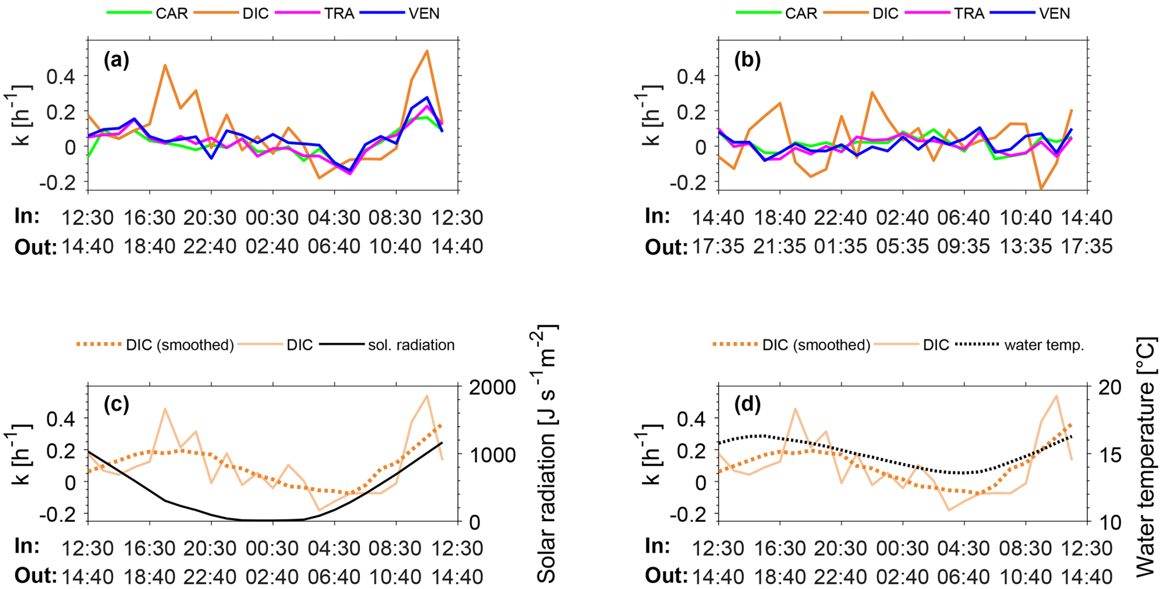

***Fig. 14:*** *Fluctuation of attenuation rate constants k [h$^{-1}$] for all compounds in reach 1 (a) and reach 2 (b) for the 24 water parcels (1 h composite samples).*
*Correlation between solar radiation and k for diclofenac (DIC) in reach 1 (c) is high ($R^2 = 0.80$, $p < 0.05$), same as for the correlation between water temperature and k of diclofenac in reach 1 (d) ($R^2 = 0.89$, $p < 0.05$). DIC (smoothed) represents values with Savitzky-Golay filtering ((c) and (d)).*

For the one-hour water parcels, calculated k values showed a daily variation in reach 1 (**Fig. 14(a)**), especially for diclofenac. The correlation (Spearman correlation coefficient) between k for diclofenac and the solar radiation is strong (0.80) (**Fig. 14(c)**). The coefficient obtained by correlating the water temperature of reach 1 (mean of temperature time series of AS 1 and AS 2) and diclofenac (0.89) (**Fig. 14(d)**) was similarly high. Savitzky-Golay filtering was applied to the correlation to reduce noise arising from measurement uncertainties (concentration and discharge). Values of reach 2 did not depict a similarly clear pattern (**Fig. 14(b)**).

***Tab. 4:*** *Median degradation rate constant k (minimum andmaximum values) [$h^{-1}$] for the selected compounds carbamazepine (CAR), diclofenac (DIC), tramadol (TRA) and venlafaxine (VEN) in all water parcels, the ones exposed to sunlight and those exposed to nearly no solar radiation for reach 1 (R1) and reach 2 (R2).*

| **k [$h^{-1}$]** | **R 1** | | | **R 2** | | |
|---|---|---|---|---|---|---|
| (min - max) | | *sunlight* | *no sunlight* | | *sunlight* | *no sunlight* |
| **CAR** | 0.004 (-0.14 – 0.16) | 0.04 | -0.02 | 0.02 (-0.07 – 0.09) | 0.02 | 0.02 |
| **DIC** | 0.06 (-0.18 – 0.54) | 0.12 | -0.009 | 0.04 (-0.24 – 0.30) | 0.05 | 0.03 |
| **TRA** | 0.03 (-0.16 – 0.26) | 0.06 | -0.01 | 0.004 (-0.08 – 0.10) | -0.003 | 0.03 |
| **VEN** | 0.05 (-0.14 – 0.28) | 0.06 | 0.02 | 0.008 (-0.08 – 0.10) | 0.02 | -0.02 |

## 5.6 DISCUSSION

### 5.6.1 NET ATTENUATION AND HALF-LIFE

The presented study demonstrates in-stream reactivity of four carefully selected compounds (**Fig. 13**). Comparison of the net attenuation for the whole river segment (total mean transit time 4 h 55 min) shows the highest concentration decrease in the selected river segment for diclofenac, followed by venlafaxine, tramadol and carbamazepine. Net attenuation in the Ammer River seems to be small compared to reported literature values. However, only transferring net attenuation representative for the enlarged Lagrangian parcel to half-lives assuming a first-order decay allows the comparison of rivers with different transit times of the water. Half-lives are parameters specific for individual compounds and environmental conditions, but independent of transit times. A calculated half-life of 50.0 h for carbamazepine is comparable to previous investigations ranging from 21 h (Acuña et al. 2015; Writer et al. 2013a) to 102.6 h (Schwientek et al. 2016). For diclofenac, a half-life of 13.0 h (~ 23% net attenuation) is obtained. Li et al. (2016) calculated half-lives of 143.1 h and 40.3 h for diclofenac in a Swedish river (Viskan, ΔT = 26.4 h, attenuation 12%) and a German river (Gründlach, ΔT = 50.4 h, attenuation 58%). In another investigation at the Gründlach River but for the same compound, Kunkel and Radke (2012) derived a half-life of 7.1 h ($\Delta T$ = 12 h, relative attenuation of 69%). (Schwientek et al. 2016) determined a half-life of 14.0 h for diclofenac (attenuation of 17%) in the Steinlach River (Germany) associated with amean transit time of 3.75 h, and a half-life of 4.1 h (45% removal) was observed for diclofenac in another experiment but at the same river, the Steinlach River (Guillet et al. 2019). A calculated half-life for tramadol of 55.1 h (~6% net attenuation) indicates an increased reactivity compared to literature: In field studies, half-lives ranged from 238 h to 134 h (7.4 to 23% attenuation) for the Viskan and Gründlach River, respectively (Li et al. 2016). The calculated half-life of 26.7 h (~12% attenuation) for venlafaxine is higher compared to results from Guillet et al. (2019) who reported a half-life of 5.3 h (mean $\Delta T$ = 3.5 h, ~37% attenuation), whereas no reactivity at all was observed by Aymerich et al. (2016) and Writer et al. (2013a). Results of all compounds indicate that river specific net attenuations are small; though compounds' reactivity represented by calculated half-lives are similar to literature values (e.g., Li et al. 2016). Due to the higher net attenuation of diclofenac and venlafaxine (≥ 10%) compared to the other compounds, river-specific assignment of these measurements to the degradation processes photodegradation and biodegradation, respectively, might thus be more reliable. Measurement uncertainties have more impact for small net attenuations. Thus, distinguishing between low reactivity and a conservative character of a compound or a clear allocation to attenuation processes such as photodegradation might be limited for carbamazepine and tramadol with smallest net attenuations. However, this is not only the case for the Ammer River, but relevant for the interpretation of all studies with calculated small net attenuations. For the Ammer River, calculated net attenuations are in general surprisingly small since previous investigations already indicated the potential of reactivity close to the WWTP (Müller et al. 2018), even though Lagrangian sampling of the same water parcel was not taken into account in that study.

### 5.6.2 DRIVING FACTORS FOR ATTENUATION PROCESSES

Comparison of net attenuation of the two sequential reaches allows statements of spatially changing conditions influencing attenuation processes. The compound behaviour of carbamazepine could be described as conservative due to the small net attenuation (**Fig. 13**). This matches many previous field studies where persistence of carbamazepine was already demonstrated (e.g., Kunkel and Radke 2012; Li et al.

2016; Schwientek et al. 2016). However, a slightly increased net attenuation for reach 2 is obtained. This could be due to measurement uncertainties (error bar, **Fig. 13**) and thus indicative for the limit of this method arising from the short transit time in the selected Ammer section. As discussed above, statements about attenuation from this small value are thus ambiguous and clear assignment to the slightly increased net attenuation of reach 2 for carbamazepine compared to the first reach might be an over-interpretation. Reactivity was interpreted for selected studies with comparable or even higher degradation rate constants for carbamazepine (Acuña et al. 2015; Writer et al. 2013a).

Diclofenac was described to be photosensitive in previous field-based investigations (Acuña et al., 2015; Kunkel and Radke, 2012; Zhang et al., 2008). Indirect photodegradation was reported as dominant degradation process for tramadol in a laboratory test and in a field experiment (Rúa-Gómez and Püttmann 2013). In this investigation, diclofenac and tramadol have higher net attenuations (one order of magnitude) in reach 1. In general, environmental factors such as clouds, turbid water (Kunkel and Radke 2012; Zepp et al. 1998), submerged macrophytes (Jaeger et al. 2019), the day-night cycle (Guillet et al. 2019; Kunkel and Radke 2012; Lin et al. 2006; Radke et al. 2010), or a difference in canopy shading could lead to low net attenuations of photosensitive compounds. The first two aspects can be excluded for the two sampling days. The influence of submerged macrophytes was not captured systematically and thus no clear assignment of their role for the attenuation is possible. This narrows the influence down to shading and the different solar radiation between day and night for the different net attenuations of diclofenac and tramadol of both reaches. Canopy shading is known to exert a high influence on photosensitive compounds (Jaeger et al. 2019; Kunkel and Radke 2012). A lower canopy shading (60%) is observed in reach 1 compared to reach 2 (70%). However, a difference often percentage points between both reaches seems small if interpreted as only driving attenuation factor for photosensitive compounds. Jaeger et al. (2019) identified ~50% difference in canopy shading between two reaches which consequently led to a more distinct interpretation regarding the role for photodegradation. The influence of day and night solar radiation is displayed in significantly different median attenuation rate constants for water parcels exposed and not exposed to sunlight for diclofenac in reach 1 (**Tab. 4**). Also, the median k of tramadol is higher for reach 1 which might be ascribed to photodegradation considering the interpretability of small net attenuations. Overall, photodegradation seems primarily relevant for diclofenac and could be of importance for tramadol.

In field-investigations, venlafaxine was shown to undergo biodegradation in the hyporheic zone (Li et al. 2013), but also photodegradation (Guillet et al. 2019) and sorption (Acuña et al. 2015; Jaeger et al. 2019) were attributed to the attenuation of this compound. Venlafaxine is protonated under environmental conditions and therefore may interact with natural particles which are generally negatively charged, despite the low solid/water distribution coefficient logD of 1.43 at pH 7.4. Schaper et al. (2018) focus on venlafaxine and its transformation product O-desmethylvenlafaxine and explain the in-stream decrease of venlafaxine (half-life between 14.0 and 38.9 h) to the high magnitude of hyporheic exchange in their investigation, with microbial degradation being a crucial attenuation process in this zone (Glaser et al. 2019).With the approach of Schaper et al. (2018), they were able to explain a minor attenuation of venlafaxine in Boulder Creek due to the missing hyporheic exchange of (Writer et al. 2013a). At the Steinlach River, venlafaxine was shown to undergo a higher attenuation during day-time than night-time and thus be photosensitive to a certain extent, even though hyporheic exchange could potentially be prominent due to bed structures of this river (Guillet et al. 2019). Calculated venlafaxine net attenuation of the Ammer River is higher in reach 1 compared to reach 2 (**Fig. 13**). Hyporheic exchange seems of minor relevance on the time scale of this investigation due to largely missing riverbed structures along both investigation reaches coupled with dominating fine-grained riverbed sediment and filling of the interstitial space. Net attenuation in reach 1, where this material dominates compared to reach 2, is higher where cobbles and further downstream silty materials can be found (**Tab. 5**). The dominating streambed material may though be relevant for sorption as potential attenuation process. Unfortunately, we did not estimate the compound masses sorbed to the sediment, which thus limits statements on sorption ability of the Ammer River for these compounds. Sorption capacity of epiphytic biofilms as speculated for the Erpe River (Jaeger et al. 2019) may be a relevant factor for the decrease in venlafaxine concentrations in the Ammer River due to the large amount of Ranunculus hederaceus. Thus, biodegradation arising from biofilms located on hydrophytes could potentially play a role.

*Tab. 5: Characteristics of the sequential reaches. Determination of the mean transit time is explained in more detail in the following section.*

| Reach no. | Length [km] | Slope [‰] | Mean water travel time | Shading | River bed substrate | Further reach characteristics |
|---|---|---|---|---|---|---|
| **I** | 3.65 | ~3 | 2h 10 min | ~60% | Sandy sediment, few cobbles or gravels | Straight course of river dominates in upper section |
| **II** | 4.06 | ~5 | 2h 45 min | ~70% | Cobbles dominate at the upper section, further downstream share in silty material increases | Partially winding course. Additional inflow from Kochhart creek, Käsbach creek and water treatment system (Carix) |

### 5.6.3 VARIABILITY OF ATTENUATION RATE CONSTANTS

Water parcel-specific attenuation rate constants indicate a compound-specific variability over the course of one day for the first reach (**Fig. 14**). Especially solar radiation and water temperature are suspected as relevant driving parameters of this pattern, since these environmental boundary conditions fluctuate over the course of one day at one single sampling site (Hanamoto et al. 2013). Strong positive correlations between solar radiation and the photosensitive compound diclofenac ($\rho=0.80$, $p < 0.05$) and the slightly photodegradable tramadol ($\rho = 0.72$, $p < 0.05$) exist compared to the moderate correlation of the two other selected compounds with solar radiation. Tramadol results show a positive parcel-specific attenuation rate constant for the first reach, whereas no correlation for neither compound with solar radiation was observed for reach 2. These results support photolysis as driving factor of net attenuation, which was higher for diclofenac and tramadol in reach 1, concurrently to less shaded areas and thus these observations fit to literature data (Aymerich et al. 2016; Li et al. 2013; Santoke et al. 2012). The small net attenuation of tramadol does not allow a differentiation between low reactivity or a conservative character of this compound (previous chapter), though the temporal resolution of the attenuation rate may be a hint to photolysis occurring during intense solar radiations. Venlafaxine correlates only moderately with solar radiation ($\rho=0.46$, $p < 0.05$) which could lead to the conclusion that biodegradation might be more relevant for this compound in reach

1. However, photolysis cannot clearly be excluded as attenuation process for venlafaxine from this correlation.

Besides the compound-specific relation to the solar radiation, a correlation between the substances and water temperature is observable. This was already shown in investigations conducted by Jaeger et al. (2019). For photolysis, they explained this pattern by the fact that the photolytic rate increases with water temperature whereas biodegradation is in general also depending on temperature. Even though we think that this explanation seems quite reasonable for explaining the significant correlation of water temperature with diclofenac (**Fig. 14**; $\rho = 0.89$, $p < 0.05$), the given general measurement settings have to be considered for the interpretation as well. Temperature is directly measured in the water phase whereas solar radiation is commonly obtained from stationary meteorological stations. Compounds moving over a defined distance are exposed to a specific water temperature along their path, while the irregular shading pattern along river sections interrupts permanent exposure to solar radiation of the water parcels and may thus lead to restricted correlations. Thus, radiation-dependent attenuation rate constants are integrative for the spatial distribution of nonshaded areas and the amount of solar radiation within the selected stretch. In contrast, water temperature may be a better suited proxy for the net effect of solar radiation since it integrates actual radiation inputs along the flow path for each water parcel. Further studies are needed to include this aspect. Nevertheless, the results presented here show that compound-specific attenuation rate constants are variable in time. Therefore, selective calculations from grab samples are hardly justifiable if this fact is not taken into account for interpretation. The determination of compound- and water parcel-specific attenuation rate constants thus leads to potentially relevant temporally variable process drivers supporting attenuation processes derived from reach-specific net attenuations.

### 5.6.4 IMPLICATIONS FOR DESIGNING UPCOMING STUDIES

Even if the presented results are similar to the ones available in literature and give indications regarding driving turnover processes, the complexity of the Ammer River regarding a representative sampling strategy to catch all potentially relevant boundary conditions and the overall small net attenuations of selected compounds of this study raise further questions. The most eminent ones are i) how to design field-investigations for hydrological challenging rivers to ii) obtain net attenuations at the best larger than 50% for reliable interpretation. Especially for small net attenuations, measurement uncertainties play a larger role, which could thus restrict the informative value of the derived attenuation results. A longer distance and thus a longer transit time are helpful to minimize the impact of uncertainties. This is not only the case for our study, but a well-known concern when interpreting low concentration data. Scaling up the obtained results shows that 50% removal of initial diclofenac concentrations are reached after a distance of ~16 km. For the compound tramadol, even a distance of ~32 km would be necessary under the assumption of a constant flow velocity of 0.39 m $s^{-1}$ and neglecting downstream dilution effects. This is not feasible in practice at the Ammer River due to the shorter total length of this river, but supports the fact that longer reaches for the Ammer River would have been necessary for high (river specific) net attenuations.

Major challenges in the Ammer River arise from the missing daily cycle of the WWTP regarding organic contaminants, ions and EC for the day of sampling, whereas previous, unpublished investigations yielded a clear daily pattern. The missing daily cycle impedes the general interpretation of the data and applicability of the hydrological model. Additionally, the backwash water of the ion exchanger emitted by a Carix process shows a high ion burden with a specific temporal pattern. That also limits the determination of the transit time and dispersion parameter for the second reach when applying EC for the model parameterisation (Eqs.(4) and (5)). However, the influence of the Carix plant is of minor relevance for organic compounds except for the water parcel specific dilution factors which were included in this approach. Additional inflows via tributaries are easily included since obtained net attenuations are based on mass flow calculations of the main stem and the tributaries. Weighting of tributaries with a low discharge but high concentrations like the Kochhart creek can be put into perspective. Groundwater inflow plays a crucial role due to the karstic character of this catchment (Schwientek et al. 2013a; Selle et al. 2013). Comparing the mean discharge upstream and downstream of reach 2 (**Tab. 3**) demonstrates additional, not measured water inflows. Various (diffuse) inflows impede fate investigations since “unknown” gains have to be negligible for the selected approach (Eq. (3)) (Schwientek et al. 2016). Unfortunately, the influence of diffuse groundwater inflows for the organic micropollutant concentration, ions and EC in rivers (dilution or enrichment of concentrations) are in general hardly detectable and entails simplifying assumptions, including only gaining river water conditions in a karstic system. As mentioned above no concentrations of organic micropollutants were assumed in the groundwater. If this was not the case, the chemical inflow via the groundwater could only lead to a mass flux increase, which would be equal to a current overestimation of the dilution potential of the groundwater. Therefore, calculated attenuation rates represent the lowest attenuation assessment in the Ammer River. Manamsa et al. (2016) discussed that organic micropollutants originating from karstic groundwater may enter the river system, and modelling results of Glaser et al. (2020b) show that contaminated groundwater inflow could play a role for the Ammer River. The present study at the Ammer River is representative for a broad range of other catchments and displays a base for further fate studies. The selected sampling scheme is a suitable tool for field experiments to describe the fate of substances in rivers and seems beneficial for this purpose since temporal, but also spatial variabilities are considered and can be analysed.

## 5.7 CONCLUSIONS

In the Ammer River, photodegradation seems to play a major role and is probably governed by differences in canopy shading. Highest uncertainties may arise from various (diffuse) inflows and dynamic wastewater discharges into the river, which are in general difficult to capture. The specific river settings can be controlled with the applied method, but generally hinder the differentiation of overlapping processes. Nevertheless, this study demonstrates that the combination of a temporally resolved Lagrangian scheme in contrasting river reaches and the simultaneous correlation of compound specific degradation rate constants with potentially driving boundary conditions such as solar radiation and water temperature is promising. This approach provides a good opportunity to identify potentially driving elimination mechanisms due to spatially differing factors governing the attenuation of compounds. It remains in general challenging to attribute observed field-based attenuations rates explicitly to one degradation process or driving parameter despite the selected promising sampling scheme. Even sequential reaches of the same river will never differ by nature in just one pronounced process driver. For future studies, (hydro-)morphological features have to be determined systematically and included for the interpretation of turnover processes. Based on that, scaling up the results might thus help to identify driving mechanisms for pollutant attenuation in different rivers.

# 6 ANALYSING PARTICLE-ASSOCIATED POLLUTANT TRANSPORT TO IDENTIFY IN-STREAM PROCESSES DURING A HIGH FLOW EVENT

## 6.1 ABSTRACT

Urban areas are a leading source of polycyclic aromatic hydrocarbons (PAHs) that result from combustion processes and are emitted into rivers, especially during rain events and with particle wash-off from urban surfaces. In-stream transport of suspended particles and attached PAHs is linked strongly to sediment turnover processes. This study aimed to identify particle exchange processes that contribute to the transport of suspended particles during flood events. An urban high-flow signal was tracked in high temporal resolution at two sampling sites in the Ammer River (South-western Germany). Samples were analysed for turbidity, total suspended solids concentrations (TSS), particle-size distribution, organic carbon, and PAH. Maximum discharge and the highest TSS occurred nearly simultaneously at the upstream sampling site, whereas a temporally shifted course was observed for downstream. The total load of particles was similar, yet a decrease of PAH mass (~28%) and an increase of the particulate organic carbon (POC) content (~3.5%-points) occurred. Coarser particles (≥26 µm) dominated at the beginning of the event at both sampling sites. The signal of remobilized riverbed sediment increases downstream and leads to well-established, robust linear correlations between TSS and PAHs. This study highlights that riverbed sediment acts as intermediate storage for contaminated particles from upstream sources that shape, together with the fresh urban input, the "particle signature" of suspensions moving through catchments during high discharge conditions.

## 6.2 INTRODUCTION

Urban areas constitute a significant source of contaminants, such as polycyclic aromatic hydrocarbons (PAHs). Given their strongly hydrophobic and low soluble character, PAHs are associated with particles rather than transported freely dissolved (DiBlasi et al. 2009; Patrolecco et al. 2010). By surface runoff, highly PAH contaminated urban particles are introduced into rivers via, e.g., combined sewer overflows and significantly impact riverine ecosystems (Wang et al. 2011; Zgheib et al. 2012). In the fluvial system, erosion and deposition are the two main processes regulating particle transport (Marttila et al. 2013). Thus, a strong interaction between suspended particles and riverbed sediment exists, and suspension load consequently represents a mixture of particles from different locations, sources, and mobilization history within catchments (Walling 2005). The intermittent and periodic interplay between suspended particles and the riverbed sediment hampers the understanding of processes controlling the storage and export of sediment and associated pollutants. A deeper knowledge of this interplay is highly relevant, especially regarding the residence time and fate of hydrophobic contaminants in stream networks.

Total PAH (concentrations) in bulk water samples and total suspended solids concentrations (TSS) typically correlate linearly (Liu et al. 2013; Nasrabadi et al. 2018; Rügner et al. 2019; Schwientek et al. 2013b). These correlations are catchment-specific and robust over many years. They likely reflect the urban imprint in conjunction with the sediment yield of the respective catchment (Rügner et al. 2019). A large mass of contaminated particles is transported downstream, especially during heavy rain events (Owens et al. 2001; Sicre et al. 2008), when high TSS and discharges occur (Rügner et al. 2013; Rügner et al. 2014). Rain events have the potential to play an important role in the annual flux of strongly sorbing pollutants (solid-water distribution coefficient; log $K_d \geq 4$), despite the short duration of single rain events and their low frequency in comparison to base flow conditions.

There is still a knowledge gap regarding the underlying short-term mechanisms that contribute to the robustness of the correlation between PAH and TSS, despite the temporally and spatially non-uniform inputs. Transport of suspended particles and also the attached pollutants' concentration are linked strongly to dynamic sediment turnover processes such as deposition or (re-) mobilization (Ciszewski and Grygar 2016; Schwientek et al. 2017). Deposition of suspended particles may lead to an accumulation of contaminants on flood plains in, e.g., lowlands (Herrero et al. 2013) or river sections with a mild channel slope (Liu et al. 2018). Riverbed mobilization, on the contrary, initiates the transport of contaminated suspended sediments when the frictional force of the water acting on the riverbed (shear stress) is strong enough to entrain surface river bed particles (Tengberg et al. 2003).

This study aimed to identify instream particle exchange processes that contribute to the transport of suspended particles and associated pollutants within the river. The purpose was to disentangle these local processes and their contribution to the overall correlation between PAHs and TSS during flood events. To this end, a tailored sampling approach was conducted during a pronounced flood event in a small river (Ammer River) in southwestern Germany that is heavily impacted by urban inputs.

## 6.3 MATERIALS AND METHODS

### 6.3.1 GENERAL APPROACH

Direct measurement of relevant local processes that potentially lead to the described correlations between total PAHs in bulk water samples and TSS is complicated since the mass flux, quality, and characteristics of suspended particles integrate processes occurring in the entire upstream river network. Thus, a differential approach was proposed that identified changes to a pulse of urban sediment as it moved along a defined river segment. Given its extraordinarily high, yet stable loading of suspended particles with PAHs, the Ammer River (Baden-Württemberg, southwestern Germany) was selected for the investigations. A sharp, high flood event originating from urban areas located in the upper catchment was sampled in high temporal resolution close to its origin in the vicinity of the city of Herrenberg and further downstream at a location integrative for the gauged catchment. The differential analysis of the temporally resolved data on the quantity and quality of the suspended sediment flux at the beginning and end of the 7.7 km long river segment was performed with a special focus on factors shaping and changing the urban signal, e.g., the exchange between suspended and riverbed sediment particles.

### 6.3.2 SAMPLING SITE

The Ammer River (5th order stream, 22 km length) is a tributary of the Neckar River (Southwestern Germany) with an average discharge (Q) of 0.87 $m^3 s^{-1}$

(https://www.hvz.baden-wuerttemberg.de/) measured at the gauge Pfäffingen (134 km$^3$ catchment size), located about 10 km upstream of the Ammer mouth. Annual areal precipitation is 750 mm, with maximum precipitation peaks in summer. Karstic aquifers of the Upper Triassic Limestone and Middle Keuper gypsum formations contribute groundwater to the Ammer River (Villinger 1982). Land use in the gauged catchment is dominated by agriculture (71%) and urban areas (17%) (Schwientek et al. 2013a). Two wastewater treatment plants (WWTP) are located in the catchment and release water to the Ammer River (WWTP (1), 80,000 person equivalents (PE), mean flow of 0.10–0.12 $m^3\ s^{-1}$) as well as the Kochhart Creek (WWTP (2), 9,000 PE, mean flow of 0.012–0.015 $m^3\ s^{-1}$;**Fig. 15**).

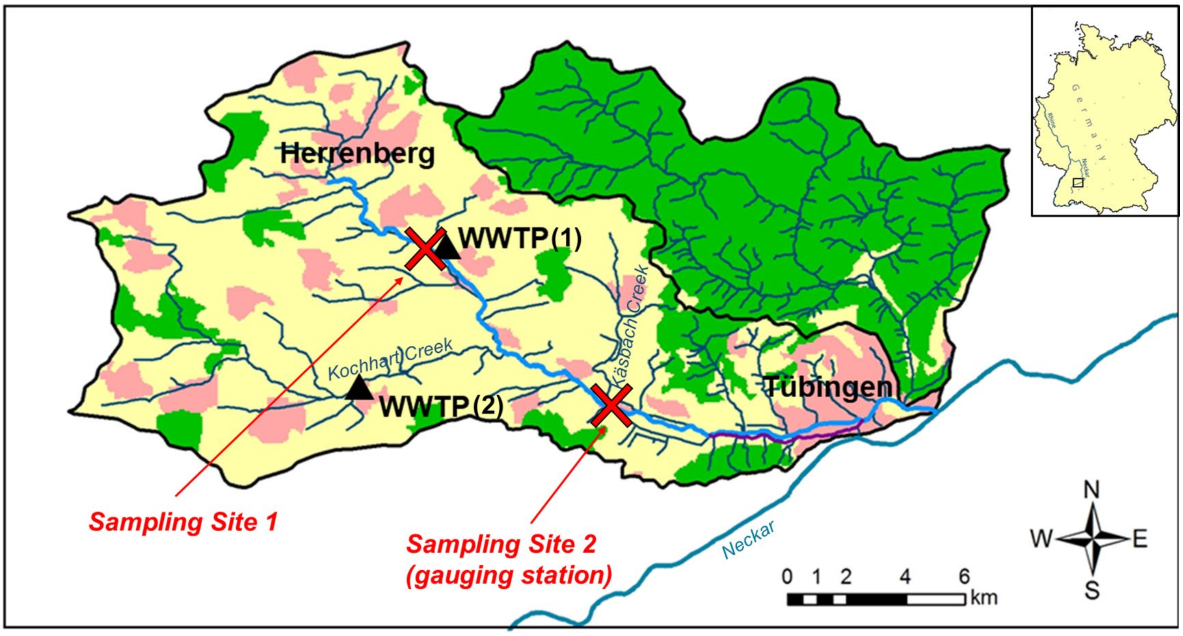

***Fig. 15:*** *The Ammer catchment, its land use (red—urban, yellow—agriculture, green—forest), and sampling locations (red crosses) in the Ammer main stem.*
*The upstream sampling site 1 is located about 200 m upstream of the WWTP, whereas the downstream sampling site 2 is located at the gauging station (Pfäffingen).*

Larger cobbles dominate the riverbed with gravel and sandy material in the interspaces that are underlain by loamy Holocene deposits. Two sampling locations were selected for the investigation in the Ammer River main stem. The upper location is about 200 m upstream of the WWTP effluent directly under a motorway bridge (**Fig. 15**, sampling site 1) and drains a topographic catchment of approximately 45 km$^2$. This sampling site is usually dominated by baseflow arising from several karst springs in the upper catchment, and during rain events, it is characterized by a significant water inflow from the urban areas leading to remarkable discharge peaks.

The downstream sampling site (**Fig. 15**, sampling site 2) is located at the gauging station and integrates hydrological processes of a 134 km² catchment. During baseflow conditions, this location is also fed by water as mentioned above from the karstic springs, (diffuse) groundwater inflows (Schwientek et al. 2013a), and additionally water from many small tributaries and artificial inflows (WWTPs, drinking water treatment plant), leading to a general increase of discharge between the sampling locations. The lower site was already shown to be a suitable location to study particle-transport processes since it integrates significant contributions from riverbed erosion occurring in the upstream river sections during summer months (e.g., Liu et al. 2018). This denotes that high discharge and turbidity peaks occurring right after a sudden precipitation event in this region were already observed for this sampling site leading, e.g., to well established, robust linear correlations between total PAHs in bulk water samples and the total suspended particles (TSS) over several years (Schwientek et al. 2013b; Schwientek et al. 2017). The sampling locations were selected based on these conditions and especially differences in underlying hydrological conditions between both sampling sites. The precipitation forecast was observed during the summer months to catch the discharge increase of the Ammer River directly after a rain event that took place in the city of Herrenberg. Sampling was performed on July 27 and 28, 2019, at the selected sampling sites (**Fig. 15**).

### 6.3.3 FIELD INSTRUMENTATION

Data on precipitation was obtained from the German Meteorological Service (DWD; ftp://ftp-cdc.dwd.de/pub/). At both sampling sites, continuous data from online-probes (UIT GmbH, Dresden, Germany; 15 min interval) measuring the EC, turbidity, water temperature, and water level were derived. The probes were installed at concrete linings of the bank, approximately 20 cm above the riverbed level, i.e., that corresponds to mean discharge conditions. During flood peaks, the water level may rise by >1 m above the sensors. The application of pre-established rating curves on the water level measurements allowed the determination of discharge (Q). Turbidity was measured on-line by optical backscatter sensors at a wavelength of 880 nm. Since the time series of the turbidity probe at the gauging station (Pfäffingen) lacked a reliable calibration for turbidity larger than 10 NTU, the data above this threshold was multiplied by a correction factor (f = 4.932) derived from the correlation of field turbidity with turbidity obtained from laboratory measurements ($R^2 = 0.92$). In the lab, turbidity was quantified by a nephelometer (Hach 2100N Turbidimeter, Loveland, CO, USA). Samples used for laboratory turbidity measurements were sampled automatically using autosamplers (ISCO 3700, Teledyne Isco, Inc., Lincoln, NE, USA). The autosamplers had already been installed in early summer at each sampling site to obtain samples covering a discharge peak at short notice in case of an event. Tubing inlets for sampling were placed next to the online-probes to ensure comparability between the samples and the parameters. The autosamplers were started on July 27, 2019, quickly after the initiation of an intense precipitation event in the upper Ammer catchment. The autosampler at the upstream sampling site was started at 07:09 PM, the downstream autosampler at 08:03 PM, due to the river water travel time, and thus, we expected a later maximum discharge peak. The samplers were equipped with Teflon tubes and clean 1 L glass bottles and programmed to sample 1 L composite samples of 30 minutes (~330 mL every 10 minutes; 11 samples in total per sampling site). On the next day, July 28, samples were transferred to 1 L amber glass bottles after rinsing these bottles with river water. Additionally, two grab samples were taken with 1 L amber glass bottles on the day of transferring the samples from the autosamplers to the amber glass bottles (09:00 AM at sampling site 1, 10:00 AM at sampling site 2) to cover the tailing of the recession curve. In the laboratory, homogenized samples were split up immediately after sampling according to the required volume of the respective analysis (0.5 L for PAHs, 50 mL for dissolved organic carbon, 50 mL for total organic carbon, 250 mL for total suspended solids, 2 mL for turbidity, 50 mL for analysis of the particle size distribution) and stored in a dark 4 °C cooling room until analysis.

## 6.3.4 LABORATORY TREATMENT

### 6.3.4.1 PAH$_{15}$ concentrations in bulk water samples

A mixture of isotope-labeled standards was added to the bulk water samples according to a standardized procedure from the “Deutsche Institut für Normung e.V.” entitled DIN 38407–39 (10 µL, 5 perdeuterated PAH in toluene; each perdeuterated PAH 20 ng $\mu L^{-1}$) before liquid/liquid extraction with cyclohexane to detect PAH and musk fragrance concentrations. Extracts were dried with anhydrous sodium sulfate, concentrated to 100 µL, and analyzed by gas chromatography with a mass spectrometer

(GC/MS; (HP GC 6890 directly coupled with a mass selective detector Hewlett Packard MSD 5973), Santa Clara, CA, USA). Isotope dilution was used for quantification (Boden and Reiner 2004). The detection limit of each compound equaled 1 ng $L^{-1}$. The sum of PAH15, including the 16 US EPA (United States Environmental Protection Agency) without naphthalene, were reported throughout this article.

#### 6.3.4.2 Dissolved Organic Carbon (DOC) and Total Organic Carbon (TOC)

Samples were filtered through 0.45 µm cellulose acetate filters before measurement. The aliquot for DOC (dissolved organic carbon) determination was acidified to pH 2 and purged with nitrogen gas using a TOC analyzer (Elementar HighTOC, Langenselbold, Germany), where thermal oxidation at 680 °C allows $CO_2$ quantification using an IR detector. TOC concentrations were determined in the same way (Elementar vario TOC cube) without preceding filtration of the sample, but with a homogenization of the suspension (Ultra Turrax T18, IKA, Staufen, Germany) for at least 2 minutes (~6000 rpm).

#### 6.3.4.3 TSS, turbidity and particle size distribution

TSS were quantified according to DIN 38409-2 by weighing the dried residues after membrane filtration (1.5 µm cellulose membrane). Turbidity was measured by a nephelometer (Hach 2100N Turbidmeter, Loveland, Colorado, USA) reported in NTU. The particle size distribution of the suspensions was determined using a laser-based device (Mastersizer 2000 linked with a Hydro 200 S pump, Malvern Panalytical, Kassel, Germany) trying to achieve optimal obscurity of 10–20% depending on the turbidity of the respective sample.

### 6.3.5 DATA EVALUATION

#### *6.3.5.1 Particle-associated pollutant transport*

Application of liquid/liquid extraction for sample preparation of measuring PAH concentrations allows the determination of the total PAH concentration of the bulk (=turbid) water sample, which comprises the dissolved and the particle-associated fraction of the selected compound. Thus, the total concentration Cw,tot [M $L^{-3}$] can be described as follows:

$$C_{w,tot} = C_w + C_{sus} \cdot TSS \tag{9}$$

where $C_w$ [M $L^{-3}$] denotes the dissolved concentrations of the contaminant, $C_{sus}$ (M $M^{-1}$) the contaminant concentration on suspended particles, and TSS the total suspended solid concentration in the river water [M $L^{-3}$] (Nasrabadi et al. 2018; Rügner et al. 2019; Schwientek et al. 2013b). Assuming $C_w$ and $C_{sus}$ are time-invariant during the period of sampling and keeping TSS as a sole variable, plotting the total concentration of selected compounds ($C_{w,tot}$) against TSS allows a direct determination of the particle loading ($C_{sus}$) and the dissolved concentration ($C_w$) as the slope and the intercept, respectively, of a linear regression line. The ratio of $C_{sus}/C_w$ may be interpreted as the distribution coefficient between solids and dissolved phase ($K_d$) [$L^3$ $M^{-1}$]:

$$K_d = \frac{C_{sus}}{C_w} \tag{10}$$

Combining Eqs. (9) and (10) allows the determination of the fraction of pollutants ($f_p$) associated to particles:

$$f_P = \frac{TSS}{TSS + \frac{1}{K_d}} \tag{11}$$

From this relation, it may be derived that, if the distribution coefficient $K_d$ equals the reciprocal of TSS (i.e., the water-to-solid concentration ratio), the fraction of particle-facilitated pollutant transport is 50%. However, during pronounced discharge events, uncertainties regarding the representative determination of $C_w$ arise if the intercept is set to zero for these cases. Thus, the determination of a representative $K_d$ value is not possible anymore, and a literature $K_d$ value in the range of $10^5$ L kg$^{-1}$, as reported by Schwientek et al. (2013b) for the Ammer catchment, was assumed.

### 6.3.5.2 Particle and particle-associated pollutant flux

The particle load transported in suspension during the event ($m_{particles}$ (M)) was derived from the integrated particle mass flux from the start of the event (meaning 'mass flux baseflow conditions', t = 0) until the end of the event (return to mass flux baseflow conditions, t = 1), consisting of the discharge ($Q_i$ [$L^3$ $T^{-1}$]) at each time step i multiplied by the respective TSS concentration (M $L^{-3}$):

$$m_{particles} = \int_{t=0}^{t=1} Q_i \cdot TSS_i \, dt \tag{12}$$

A sampling-site specific linear regression between high-resolution turbidity measurements and TSS measurements exists. Thus, missing TSS values can be easily obtained from the turbidity data series to complete the overall time span of the event with:

$$TSS_i = turbidity_i \cdot slope_{turbidity-TSS} \tag{13}$$

This allows a comparison of the mass of transported particles between both sampling sites.

The PAH load attached to particles ($m_{PAH}$) per sampling site was derived from the integration of the PAH flux from the start of the event (meaning 'mass flux baseflow conditions', t = 0) until the end of the event (return to mass flux baseflow conditions, t=1). This consisted of the discharge (Q ($L^3$ $T^{-1}$]) at each time step i multiplied by the respective particle-associated PAH concentration (bulk PAH concentration $C(PAH)_{w,tot,i}$ [M $L^{-3}$] corrected for the particle-associated PAH fraction ($f_{p,i}$) (–) (Eq. (11)):

$$m_{PAH} = \int_{t=0}^{t=1} Q_i \cdot C(PAH)_{w,tot,i} \cdot f_{p,i} \, dt \tag{14}$$

For missing $C(PAH)_{w,tot,i}$ values, TSS values obtained from Eq. (13) were converted into concentrations using the sampling site-specific regression line slope ($C_{sus}$, Eq. (9)).

## 6.4 RESULTS

### 6.4.1 TOTAL MASS FLUXES

Throughout the event, the discharge increase at the upstream sampling site was very steep, with a pronounced maximum of 7.2 $m^3 s^{-1}$. The discharge wave propagated to the downstream location with a maximum discharge of 8.8 $m^3 s^{-1}$ (**Fig. 16(a)**). The total amount of particles transported during the event was 37.6 t at the upstream sampling site with an associated PAH mass of 211 g. At the downstream sampling site, 32.8 t particles were transported for the duration of the event, and the total PAH mass transported at this sampling site was 152 g. Comparing the transported amounts of particles between both sampling sites led to a particle mass loss of ~13%, which was negligible due to possible measurement errors arising, among others, from converting turbidity into TSS measurements for missing data points (Eq. (13)). PAH mass decreased by ~28% along with the longitudinal profile. Downstream, POC content on average increased by 3.5%-points (downstream average of 9.6 ± 3.5 %).

Turbidity, as a proxy for particle concentration ($R^2 \geq 0.82$, **Fig. 16(b)**), peaked slightly before the discharge peak (**Fig. 16(a)**) that led to a clockwise, but generally steep hysteresis relation (**Fig. 16(d)**) for the upstream sampling site. A linear PAH–TSS relation ($R^2 = 0.87$, **Fig. 16(c)**) led to a mean PAH suspended particle loading of ~6.8 $\mu g\ g^{-1}$. A temporal delay of the turbidity peak in relation to the discharge maximum was observed for the downstream sampling site, which led to a counter-clockwise hysteresis with a milder relation between TSS and Q (**Fig. 16(d)**). The linear PAH–

TSS relation ($R^2 = 0.88$, **Fig. 16(c)**) at the downstream sampling site indicated a mean PAH suspended particle loading of ~5.7 µg $g^{-1}$.

### *6.4.2* PARTICLE DYNAMICS

Upstream, larger median particle sizes of 25.5 ± 3.6 µm dominated at the beginning of the event followed by consistently smaller particles (14.0 ± 1.7 µm; **Fig. 16(e)**). In comparison, for the downstream sampling site, a clearly larger median particle diameter dominated at the beginning (36.0 ± 4.8 µm) and was followed by smaller, relatively constant median particle sizes (19.2 ± 5.9 µm), which were similar to the smaller particles at a later time of the upstream sampling site. For all described relations and both sampling sites, the shift in the respective characteristics co-occurred with the shift from increasing to decreasing discharge conditions.

Assessment of the PAH – TSS relation with respect to a differentiation between increasing and decreasing discharge conditions showed that two groups of correlations existed (**Fig. 17(a),(b)**). A reduced PAH loading could be observed for samples obtained during the increasing discharge limb for both the upstream (~5.0 µg $g^{-1}$) and the downstream (~4.4 µg $g^{-1}$) location compared to decreasing discharge conditions (upstream: ~8.3 µg $g^{-1}$; downstream: ~6.4 µg $g^{-1}$).

POC content of particles (POC per TSS; $f_{OC}$) remained constant over the course of the event with 6.1 (± 0.9) % at the upstream sampling site. Downstream, the POC content was significantly higher at the beginning of the event (up to ~17 %) and decreased to 8.5 (± 2.7) % at a later time of the event (**Fig. 18**).

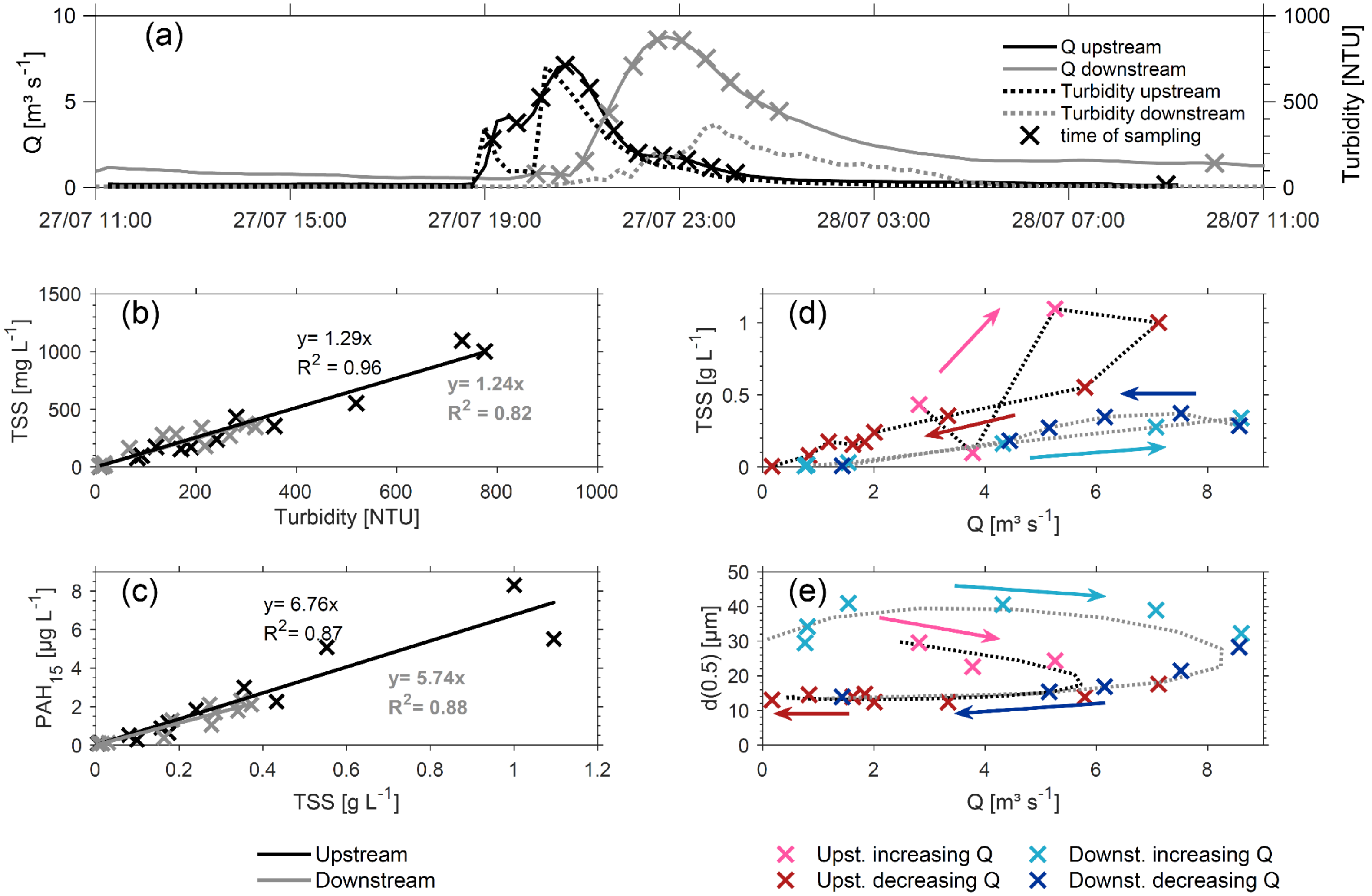

***Fig. 16:*** *(a) Discharge (Q) ($m^3 s^{-1}$) and turbidity [NTU] during the time of the event with samples obtained during the rain event (crosses), (b) total suspended solids (TSS) ($g L^{-1}$) – turbidity [NTU] for upstream (black) and downstream (grey) sampling sites, (c) polycyclic aromatic hydrocarbon ($PAH_{15}$) concentration ($\mu g L^{-1}$) – TSS ($g L^{-1}$) relation for the upstream (black) and downstream (grey) sampling sites, (d) total suspended solids (TSS) ($g L^{-1}$) – discharge (Q) ($m^3 s^{-1}$) relation, and (e) median particle size (d(0.5)) – discharge (Q) ($m^3 s^{-1}$) relation. Arrows in (d) and (e) indicate the direction of the hysteresis.*

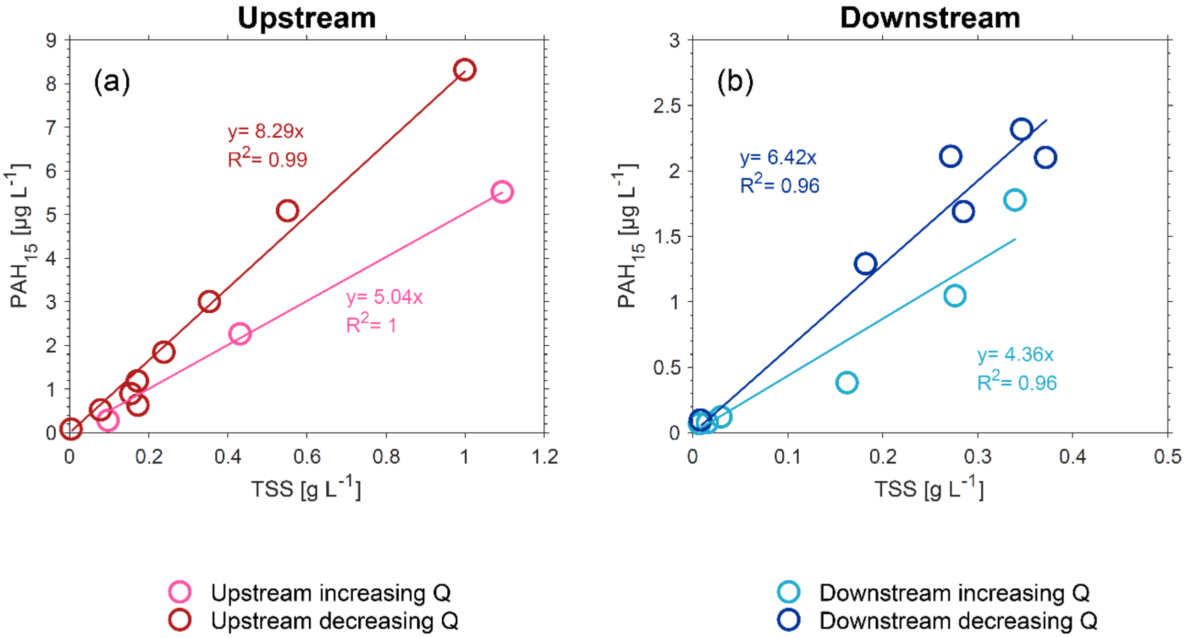

***Fig. 17:*** *PAH$_{15}$–TSS relations for the upstream (a) and downstream (b) location split up into samples under increasing and decreasing discharge conditions.*

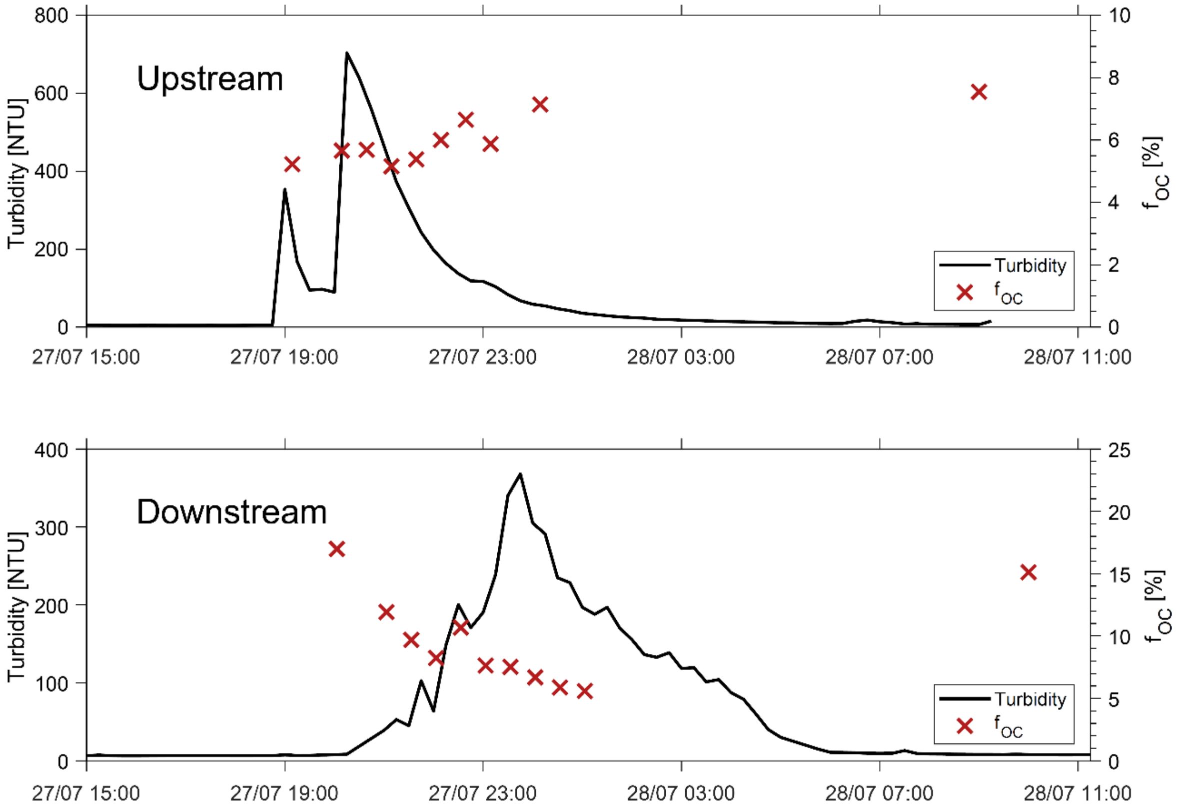

***Fig. 18:*** *Time course of turbidity [NTU] and f$_{oc}$ (%) for the upstream and downstream sampling sites.*

## 6.5 DISCUSSION

### 6.5.1 URBAN IMPRINT

The pulse-like discharge pattern observed at the upstream sampling site (**Fig. 16(a)**) is similar to flushing flows formerly known from controlled flood flows of dams (Batalla and Vericat 2009). As already identified in previous investigations (Schwientek et al. 2013a), the combined sewer system in the upstream catchment introduces stormwater into the Ammer River in case of heavy precipitation at the city of Herrenberg that often leads to prominent discharge peaks. Surface runoff from agricultural areas, on the contrary, does not contribute significantly to the discharge in the Ammer catchment due to a flat topography (Liu et al. 2018) and the lacking connection between soils and streams (Schwientek et al. 2013a). Overbank flows and inundation of the floodplain usually do not occur due to the modified, deeply incised river channel. The loading of particles (**Fig. 16(c)**) with the hydrophobic PAHs being an indicator of urban activities (traffic, combustion/heating) (Schwientek et al. 2013b) was very high. Untreated surface runoff and stormwater release were described as the main source of PAHs in rivers (Blanchard 2001; Zgheib et al. 2012). PAH loading of suspended Ammer particles (**Fig. 17**) up to 8.3 mg $kg^{-1}$ are similar to literature values of urban sediment PAH loadings ranging between 7.6 mg $kg^{-1}$ for Bergen, Norway (Jartun et al. 2008), up to 10 mg $kg^{-1}$ in Luleå, Sweden (Karlsson and Viklander 2008), which shows that the urban areas constitute a major inflow pathway for contaminated particles into the Ammer River during high discharge conditions.

The general discharge pattern downstream is similar to the one at the upstream sampling site, except for a more dampened peak and recession and a larger total Q due to the additional inputs in between both sampling sites. The temporal offset between turbidity and discharge was explained by a distant source of particles in previous investigations (Batalla and Vericat 2009). Suspended particles travel at velocities close to the mean flow velocity (Williams 1989), while the wave velocity is 5/3 times the mean water flow velocity according to the kinematic wave approach under idealized conditions (Dingman 1984). The particle size at a later time of the event is similar to particles upstream already described to originate from the urban inflow in the upper catchment (**Fig. 16(e)**).

### 6.5.2 PARTICLE EXCHANGE ALONG THE LONGITUDINAL PROFILE

The nearly constant load of particles at both sampling sites demonstrates that no significant net gain or loss of particles occurs along the stretch. In contrast, the PAH mass decreases along the longitudinal profile. Only a minor PAH release is expected from the main tributaries due to the mainly agriculturally dominated land use in these sub-catchments. Since the overall particle mass remains constant, less contaminated particles contribute more to the particle load further downstream, which could be indicative of particle exchange that occurred along the stretch. Underlying processes responsible for the exchange can be deduced from temporally changing particle characteristics. At the upstream location, the absence of a significant temporal offset, and thus, similar relative travel time between Q and the turbidity or TSS, respectively, points to a close particle source (Williams 1989) and a clockwise hysteresis for the TSS–Q relation may, besides a generally close particle source, denote a rapid initial delivery of sediment from the channel (Smith and Dragovich 2009). The riverbed mobilization during that time might occur due to a higher discharge energy gradient with the rising limb for a given flow depth compared to decreasing discharge conditions that lead to higher shear stress and enhance the erosion competence of the flow (Julien 2002) or due to a source depletion of to be mobilized sediment particles in the course of the event. The former argument would explain why the turning point of the particle size–Q relation is identical to the change in discharge. The significantly larger median particle size supports the interpretation of initial sediment delivery from river bed mobilization during the rising discharge limb (**Fig. 16(e)**) since coarser particles are expected to dominate in the bed sediment compared to the particle composition in suspension (Wu and Wang 2006). Thus, we suggest that the source of particles at the upstream location that dominates at the beginning of the event until the maximum Q has been reached is mobilized riverbed sediment, followed by the dominant urban inflow contributing with freshly introduced urban particles.

The POC content of suspended particles is higher at the downstream location, which supports the hypothesis that particle exchange bringing more organic particles in suspension occurred along the longitudinal profile. The generally increased POC content is likely due to the influence of the WWTP that introduces nutrients into the river, thus, enhancing inter alia primary production (Gücker et al. 2006). At the beginning of the event, the POC content is increased (**Fig. 18**), which could indicate that an organic-rich layer that covers the riverbed sediment is mobilized first. Previous investigations claim that the breaking-up of biofilms leads to a delaying release of sediment into urban rivers (Lawler et al. 2006), and thus, causes an anti-clockwise hysteresis between TSS and Q. This may also explain the anti-clockwise hysteresis between both parameters for the downstream sampling site (**Fig. 16(d)**) that apparently contradicts the interpretation of an initial bed sediment delivery for this location. Breaking up of biofilm was discussed to be followed by an increased material release in the latter part of the event (Lawler et al. 2006). This seems plausible for the Ammer River since coarser median particle sizes dominate at the beginning compared to upstream mobilized particles (**Fig. 16(e)**). Thus, it supports the interpretation of river bed mobilization as an important first process relevant at this sampling site, as well. Consequently, the source of mobilized particles may be close to the respective sampling site despite the delayed arrival. Since the POC proportion does not reach a constant 'background proportion' of the upstream sampling site at any time, river bed mobilization of POC-rich particles is likely to contribute significantly to an exchange of particles downstream even at a later time of the event despite the dominant urban imprint during that time.

### 6.5.3 PAHS: MEMORY EFFECT FROM PREVIOUS BASEFLOW CONDITIONS?

The total particle-attached PAH mass transported during the event is higher at the upstream location and can be attributed to the urban inputs located in the upper catchment, as discussed in the previous sections. The proportion of particles exchanged through cycling between suspension and bed sediment increases along the longitudinal profile with increasing distance to the main particle source. Particle exchange leads to a mixed-signal of freshly introduced urban particles and particles arising from the intermediate storage compartment integrating the net sedimentation from previous events (**Fig. 19**). Exchanged particles from the sediment storage smoothen the PAH burden of episodic, short-term urban inflows. Exchange with the sediment storage contributes to the robustness of correlations between PAHs and TSS, which was observed over many years, also for other rivers (Rügner et al. 2019; Schwientek et al. 2013b; Schwientek et al. 2017).

Interestingly, the PAH loading of firstly mobilized particles from river bed sediment is lower compared to particles arriving at a later time from the urban inflow for both sampling sites (**Fig. 17**). This could point to a different origin of particles with different sizes, though the high PAH loading demonstrates that also the firstly mobilized particle originally arose from the urban areas. The reduced PAH particle loading could be a particle size-specific mass transfer effect due to the smaller surface area of firstly mobilized large particles (Wang and Austin 2006). A correlation between particle size and PAH particle loading exists for the downstream sampling site ($R^2$ = 0.7), whereas only a trend between particle size and PAH loading can be obtained from the data upstream either due to an insufficient amount of samples or the dominance of the urban inflow (**Fig. 20**). An alternative explanation is the leaching of PAH during prolonged base flow periods without fresh inputs, continuously decreasing the loading of bed sediment particles. Liu et al. (2019) interpret diffusion of PAH from the bed to the river water during low-flow conditions (especially for mild river reaches) as a driving factor for a shorter turnover time (=the renewal of sediments and/or attached PAHs) of the attached PAH in comparison to the bed sediment. Moreover, laboratory column experiments identified that leaching is an important process for PAHs attached to soils (Zand et al. 2010). Under field-conditions, particles may be stored for long times in the riverbed sediment, which is in permanent contact with the river water. During dry weather conditions, contaminated sediments may become the only source of PAH to river water. The result of the leaching process might, therefore, be visible during high discharges in addition to the consequences of the transient interplay between the riverbed and suspended particles. Both processes may form the chemical signature of suspended particles during high discharge conditions. This would imply that leaching is an additional, important exchange process between riverbed sediment and flowing river water occurring during preceding baseflow conditions. According to the assumptions above, the strictly episodic inputs of urban particles via storm sewers and combined sewer overflows are smoothed in a downstream direction by a dual-effect. First, intermediate storage in the bed sediment, the re-mobilization during flood events, and the associated mixing with the freshly introduced suspended particles increasingly homogenize particle-loadings in a downstream direction (**Fig. 19**). Second, the leaching of sediments during low flows results in a redistribution of PAHs from the particle-bound phase towards the dissolved phase, equally increasing downstream. The bulk transfer of PAHs is thereby rendered from purely episodic towards more continuous with increasing distance from the urban inputs. This may be interpreted as a positive self-purification effect, mitigating peak concentrations. However, it may also complicate river basin management since the relationships between the occurrence of contaminants and the input pathways and events are being masked. In essence, urban water management should focus more on retaining urban particles, e.g., by providing larger volumes for stormwater retention. A reduced frequency of overflow events will result in reduced peak concentrations during flood events, as well as in lower dissolved concentrations during baseflow conditions. How quickly mitigation measures become visible in improved sediment and water quality depends, among others, on the sediment residence times of individual river systems.

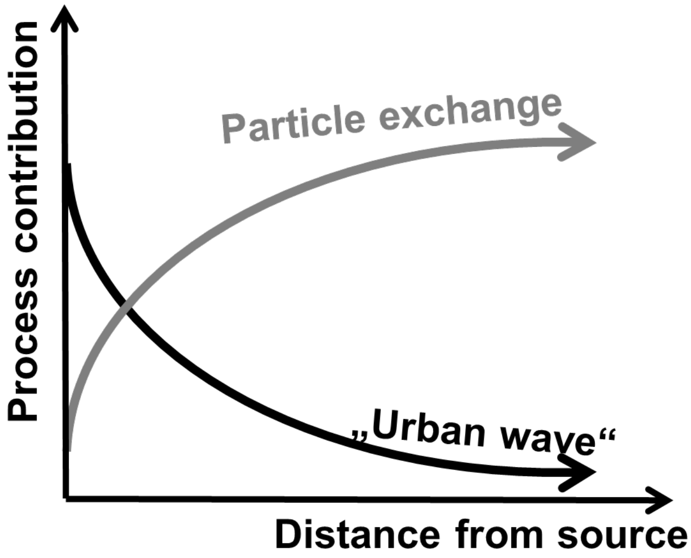

***Fig. 19:*** *Development of suspended particle signature along the longitudinal profile. Exchanged particles are expected to increase with increasing distance from the sewer system, whereas the impact from the urban areas ("urban wave") is expected to decrease along the longitudinal profile.*

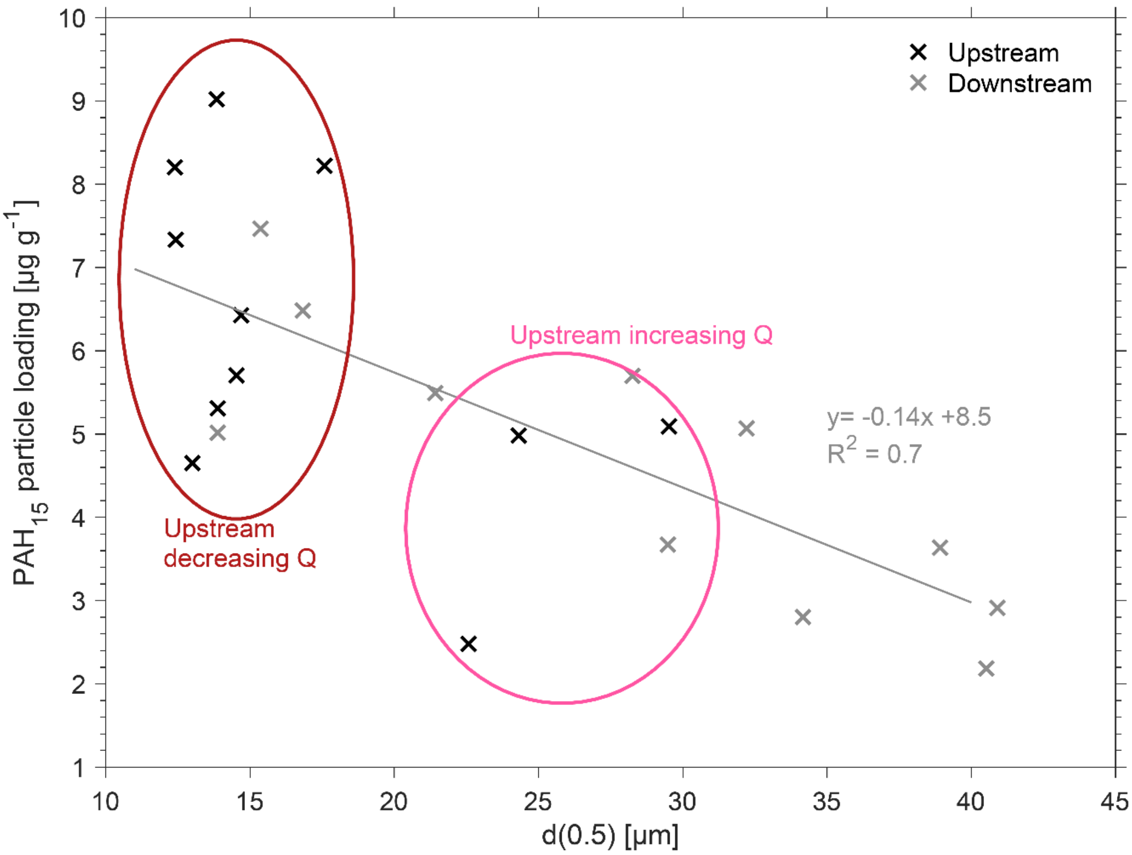

***Fig. 20:*** *Relationship between $PAH_{15}$ particle loading (µg $g^{-1}$) and median particle size (µm).*

## 6.6 CONCLUSIONS

The findings of this study demonstrate that a transient interaction of suspended particles with the riverbed sediment can be deduced from the measurements on PAHs deriving from urban inputs. Spatially and temporally variable particle mobilization mechanisms contribute to the overall particle load, particle composition, and size distribution, as well as particle-associated contaminant load and shape the “particle signature” of suspensions as it moves through the catchment. Therefore, riverbed sediments work as intermediate storage for contaminated particles from upstream sources as the particles are transported downstream during high discharge events. Gradual releases from this intermediate storage, in turn, lead to the well-established robust linear correlations between PAHs and total suspended particles, despite the different particle sources and turnover processes occurring along the river profile. The Ammer River constitutes a vivid example since the input of “clean” background particles from the catchment is limited, and the urban imprint is, therefore, clearly visible. It also emphasizes that the vulnerability of rivers to urban inputs has to be assessed individually and that in such cases, measures to reduce urban sediment inputs further should be considered.

Although, in general, loadings on suspended particles are dominated mainly by the proportion of introduced urban to background particles, particle-attached contaminant turnover processes are relevant on a short timescale (sediment mobilization) and, in addition, face processes relevant on a long timescale (chemical leaching). Hence, processes such as leaching during the preceding baseflow period have to be considered for the interpretation of data obtained during rain events. As a consequence, the comparability of data attained during different flood events will, on the one hand, strongly depend on the hydro-meteorological characteristics of the respective rain event, and, on the other hand, on the duration and general conditions of the previous baseflow situation. Open research questions remain with respect to the identification of the sediment as a source of (dissolved) pollutants. However, reliable field-based measurements are complicated by the expected small mass fluxes between sediment and water column, the potentially long time scale of this process, and the need to overcome heterogeneities in contaminated sediments. Additional tracers to track the “sedimentation age” of particles and compounds could be helpful for this purpose.

# 7 GENERAL DISCUSSIONS AND CONCLUSIONS

The overall aim of this thesis was the assessment of in-stream contaminant fate from a field-based perspective. To put the individual papers into a broader context, I will merge the main outcome of the individual papers and thus present the methodological novelties (experimentally and conceptually) from the papers that are transferable to other studies (chapter 7.1), discuss the general relevance of hydrology for the water quality of rivers (chapter 7.2) and give a future perspective on research in the field of river water quality on the base of this thesis (chapter 7.3).

## 7.1 METHODOLOGICAL APPROACH

### 7.1.1 CONCEPTUAL DESIGN: DISENTANGLING OVERLAPPING PROCESSES

Even if a profound knowledge exists with respect to the allocation of reactive processes to selected compounds and the fact that many studies already quantified attenuation processes for selected rivers (e.g., Guillet et al. 2019; Kunkel and Radke 2012; Li et al. 2016; Writer et al. 2011b), it remains unclear if obtained results are transferable to other river settings. Field-based studies are in contrast to laboratory studies characterized by an increased complexity because of the needed consideration of hydrological processes and a broad range of different environmental boundary conditions that differ significantly between different rivers. In **paper I**, I present a method that attempts to consider all environmental boundary conditions such as the temporal dynamics of the WWTP inflow that is methodologically transferable to other studies. Despite the presented thoughtful concept of how to tackle field-based investigations, it remains challenging to apply an appropriate sampling-strategy with which attenuation processes can be disentangled from each other and, based on that, to explain which transformation process plays the most important role for which environmental settings (e.g., winter in comparison to summer). The clear disentangling of transformation processes is hardly possible due to the facts that I) all potential processes occur simultaneously and overlap, II) the systematic assessment and influence of potential relevant environmental conditions and features relevant for the turnover of pollutants is not trivial, and III) that the chemical structure of most organic pollutants can be altered by different processes (Schwarzenbach et al. 2003). As an example, hydrological processes potentially influencing the fate of pollutants, as well as the environmental boundary conditions were considered in **paper III** and I could show that photodegradation and biodegradation are important reactive processes that influence selected organic compound concentrations in the Ammer River. Nevertheless, a clear explanation by one of both presented transformation process was not possible due to the lack of additional parameters (e.g., potential for microbial degradation) that would have been necessary. Also the results of **paper IV** demonstrate that not only sorption of hydrophobic micropollutants determines their fate along the river, but the inverse process ‘leaching’ that occurred during previous baseflow conditions is important as well, despite the strongly hydrophobic character of selected compounds. This highlights that even previous environmental conditions are relevant for a holistic interpretation of in-stream reactive processes. Distinguishing overlapping environmental conditions is not only relevant for the results presented in this thesis, but also for all other field-based investigations and was taken up in previous publications for dissolved (Guillet et al. 2019) and particle-bound compounds (Liu et al. 2019) in rivers. A deeper insight into the process-specific change of chemical structure by e.g. focussing on the production of specific transformation products along the river (Li et al. 2016) or applying a non-target screening approach (Schymanski et al. 2015), both for dissolved compounds, could help to close this research gap. Additionally, the systematic assessment of spatially and temporally varying (hydro)morphological features as discussed and presented in **paper II** and **III** are crucial for this purpose. Transferring the presented outcome on how to investigate transformation processes to other river settings shows the need for measurements of process-specific parameters such as the solar radiation as proxy for photodegradation or process-specific model substances such as the photosensitive tracer fluorescein. Future research should focus on representative compounds, especially for substances with the same origin like the reactive target compound.

### 7.1.2 EXPERIMENTAL DESIGN

Despite the general difficulty to disentangle overlapping attenuation processes, I successfully applied different sampling techniques to investigate the contaminant fate in rivers that are helpful to design upcoming field-studies at other rivers. In **paper**

**II**, I tested selected environmental tracers for their applicability as groundwater exfiltration indicators in rivers and showed that mainly radon is, in comparison to selected ions and conservative organic micropollutants, applicable for the quantification of the groundwater fluxes. Radon should therefore be taken into account in studies that aim to identify groundwater exfiltration locations and fluxes contributing to the discharge of the river, especially due to the simple handling at rivers of different scales (Frei and Gilfedder 2015). However, results of **paper II** are surprising with respect to the non-applicability of selected conservative ions for this purpose, which might though not necessarily transferable to other river systems. As mentioned in **paper II and III**, a temporal dynamics exists for the Ammer River due to various (artificial) inflows with different ion concentrations which is a special characteristics for this river and most likely causes the restricted applicability of ions. Therefore, further research is necessary to validate the applicability of ions for the quantification of groundwater inflow in rivers of karstic catchments that are not characterized by anthropogenic modifications, especially since ion measurements are comparably easy to conduct. Also the potentially wrong determination of groundwater concentrations might lead to the mismatch with respect to the applicability of ions as groundwater tracers. This is not only a weakness for ions, but also for organic micropollutants and, as discussed in **paper II**, entails assumptions for the groundwater endmember concentration such as the assumed absence of pollutant concentrations in groundwater. Additional measurements on the groundwater inflow's concentration by e.g. seepage meter to catch the direct groundwater flux would be helpful to handle that problem and might be helpful to close this research gap.

In **paper III**, the electrical conductivity was used as a conservative tracer to obtain transport parameters in the Ammer River. Even if this method was already successfully applied in previous investigations (Schwientek et al. 2016), the presented approach was shown to be prone to error for the Ammer River due to inflowing tributaries and groundwater with different electrical conductivities that lead to a mixture of different signals like already discussed in the previous section. Dye tracer tests might be more applicable with respect to an explicit determination of transport processes, mainly the dispersion in rivers, but would entail a non-parametric deconvolution of the dye tracer signal (Guillet et al. 2019) due to the expected multi-peak tailing of the breakthrough curve caused by e.g. mill channels. Nevertheless, electrical conductivity is still a robust and easy to measure parameter that can be used in other river systems at different scales that are influenced by comparably large amount of WWTP inflow in comparison to the river discharge, and I interpret the difficult applicability of this study more as the exception than the rule.

For representative samples of compounds’ concentration, time-series were chosen for baseflow conditions. For dissolved compounds (**paper III**), this helped to catch the daily fluctuation of the solar radiation and the dynamic WWTP inflow as already discussed in previous investigations (Guillet et al. 2019; Schwientek et al. 2016) and is most likely applicable to all investigations on different scales that only require a small amount of water (1 L) and aim to investigate degradation rate constants of pollutants. Also for the identification of particles and associated pollutant turnover processes, I used a time-series approach of suspended solids with attached pollutants that was obtained during a high discharge event (**paper IV**). Experimentally, the focus on suspended solids in comparison to investigating the particle phase separately to the water phase has the advantage of I) a comparably easy sampling approach that can be controlled automatically and II) a method that is less error-prone, since an additional and especially fast separation step between the water and the particle phase is not necessary after obtaining the sample. However, this approach might only be applicable for strongly hydrophobic compounds and future research will most probably have to deal with the question of how to investigate the fate of only slightly hydrophobic compounds in field-based approaches. With a profound base on how to conduct field-based experiments for these compounds, it might be possible to disentangle reactive processes (mainly sorption).

## 7.2 INTERACTION BETWEEN HYDROLOGY AND WATER QUALITY

### 7.2.1 CATCHMENT SETTINGS AND IN-STREAM CONCENTRATIONS

In **paper II** I showed that a strong connection exists between in-stream concentrations of selected compounds and the hydrogeological settings of the catchment. The river is connected to the catchment by the considerable amount of groundwater that contributes to the water flux during baseflow conditions to the selected karstic river system (Ammer River). I demonstrated that the location of groundwater inflow in karstic environments might be controlled by the geological features, in detail by the intersections between fault lines with the river course. In karstic geology, development of preferential flow paths is not surprising since conduits, caves and open fractures can be created (Hartmann et al. 2014). These preferential flow paths may favour groundwater flow and are a general characteristics of karstic catchments Therefore, these mechanisms can play a role for other catchments with comparable karstic geological settings which is why obtained results are generally transferable to other river settings. Due to the higher order of the Ammer River in combination with the comparable high contribution of groundwater to the river discharge, this system would be outstanding if the river was not located in a karstic catchment. This is due to the fact that the groundwater flux per river flow sections in comparison to the overall discharge is in general assumed to decrease with increasing river-order for non-karstic systems and, on the contrary, mainly lower-order streams are influenced by a high proportion of groundwater inflow (Alexander et al. 2007; Ranalli and Macalady 2010). For the Ammer River, the large amount of groundwater leads to the fact that the chemical status of the exfiltrating groundwater into the river contributes to the overall water quality in the river. Results of **paper II** present that this is especially relevant for ions, but could also be the case for selected organic micropollutants. Thus, the results of **paper II** clearly evidence that rivers, especially those located in karstic catchments cannot be seen as aboveground channels slicing through the landscape, but are systems that are connected to the hydrogeology of catchments with a considerable influence on the water quality of the river.

### 7.2.2 RIVER SETTINGS AND REACTIVE PROCESSES

Scaling down from the water-fluxes on catchment-scale to reactive in-stream processes, I showed in **paper III** that a small reactivity dominates for selected photosensitive, as well as biodegradable organic compounds which was mainly attributed to a short travel time in the Ammer River. Physically, photo- and biodegradation are time-dependent processes. The travel time depends on the water transport parameters, in detail the transport velocity and the transport pathway lengths between input and output location of pollutants (Darracq et al. 2010). Previous studies already identified that lower velocities maintain the natural retention threshold for pollutants thus leading to a higher self-purification of the river (Glińska-Lewczuk et al. 2016). This raises the question which river-specific settings might cause the short travel time and if general statements regarding the reactivity of compounds can be drawn from this. A potential explanation for this might be the general river settings. The Ammer River is characterized by anthropogenic modifications expressed by the straightened river course and the deeply incised river. Modified rivers are known to have less structures in comparison to natural river systems, also regarding the presence of riffle-pool sequences (Knust and Warwick 2009; Schwartz et al. 2015). Additionally, the karstic geology is known to show a high base flow during the whole year (Harreß 1973), whereas discharge peaks during heavy precipitation events are comparably low due to the buffering capacity of the geology in the catchment (Schwientek et al. 2013a). Discharge peaks with sufficient energy to trigger bed load transport are besides other factors such as e.g. solid matter characteristics/ amount in the river, erodibility or the river bed slope necessary for sediment transport/deposition and may lead to the formation of riffle-pool sequences if river morphodynamics allows the formation (Clifford 1993; Schwartz et al. 2015). Pools lead to an increased cross sectional area of the river profile which in turn decreases the water velocity at constant discharge conditions. A decrease in the velocity can promote the time-dependent photodegradation, and generally low photodegradation rates as presented in **paper III** can thus may be traced back to the lack of pools. Additionally, riffle-pools have a significant influence on surface-subsurface exchange (Harvey and Bencala 1993). One conclusion of **paper III** was that biodegradation in fluvial systems is reduced, which was explained by the lack of riffle-pool sequences. In summary, these results may indicate that the lack of discharge peaks due to the karstic character, as well as the anthropogenic modification of the river explain the short transit time which entails a low reactivity in the Ammer River.

The influence of the (hydro-) morphological settings on the fate of pollutants is also relevant for hydrophobic pollutants attached to particles as discussed in **paper IV**. One of the main outcomes of **paper IV** is that particles that are most likely already contaminated by associated pollutants enter the Ammer River nearly exclusively from urban areas. The overall sediment load in the river is therefore mainly controlled by the input of contaminated particles which determine the pollutant concentrations during high discharge conditions. Due to the hydrophobic character of the selected pollutants, reactive processes along the river are limited and “turnover” of pollutants are rather controlled by particle turnover processes (Liu et al. 2019). The anthropogenic character of the Ammer River expressed by the deeply incised river allows mainly a particle exchange with riverbed sediment. The water rarely flows over the banks which restricts an exchange with floodplain particles and narrows down relevant particle processes to the interaction between transported suspensions and the riverbed. Additionally, as discussed in the previous section, the discharge peaks in the river is not very high due to the karstic hydrogeology and the anthropogenic character, even after heavy precipitation events which also restricts the flooding of large areas and consequently hampers the catchment surface erosion as particle origin for the river. This shows that the anthropogenic settings of the Ammer River and the hydrogeology of the catchment control also the suspended particle transport and thus the particle-associated pollutant transport during precipitation events. Thus, in summary, **paper II-IV** demonstrate that hydrological and reactive processes are strongly coupled, and in-stream hydrological processes and fluxes are strongly determined by the catchment and river characteristics.

### 7.2.3 POLLUTION PRESSURE ON RIVERS: ARE BASEFLOW CONDITIONS AND HIGH DISCHARGE EVENTS COMPARABLE?

Both dissolved and particle-attached contaminants have to be considered for a holistic understanding of the water quality and pollution pressure on rivers. In **paper III,** turnover processes of dissolved, hydrophilic compounds are presented, whereas **paper IV** focusses on the particle-associated transport of hydrophobic compounds. Driving hydrological processes vary significantly between both settings and trigger different pollutant origins, turnover processes and control the dominating type of transport (either dissolved or particle facilitated). I demonstrate that organic compounds are detected at the gauged catchment outlet for both hydrological settings despite a variety of transformation and distribution processes occurring upstream. In general, origin, underlying pollutant turnover processes that lead to the chemical status of rivers at the catchment outlet are well understood for selected compounds for both discharge conditions and differ significantly between both settings. Additionally, the comparability between both scenarios is restricted with respect to the importance of the respective situation for the total pollutant pressure and disturbance of ecosystems. This might though be important, since high river discharge conditions are expected to occur more frequently in the future due to global climate change (Trenberth 2011) which is why the role of high discharge conditions might be more important for the future pollution pressure on rivers in comparison to baseflow conditions. For the Ammer River, comparability of both discharge settings (**paper III** and **paper IV)** is limited since only few compounds were selected that differ significantly from each other regarding their physicochemical properties. Future research should therefore focus on selected compounds during both discharge scenarios for both the dissolved and the particle-bound phase. However, even if a broader range of target compounds had been investigated, detected target chemicals would not represent the *total* chemical status of water (Brack et al. 2017). The total chemical status would, however, be necessary to focus on when aiming to understand the pollution pressure on rivers. The quantification of cell growth/viability in bioassays as a reaction on a sample added to a bioassay independent of its chemical composition is called cytotoxicity and is representative for (known and unknown) chemical mixtures which are hardly covered by only chemical analysis (Escher and Leusch 2012). If cytotoxicity is only interpreted as a measure for the chemical mixture in water and not as the ultimate biological endpoint for organisms, measurements either for the dissolved or the particle bound phase of environmental samples may represent the overall pollutant pressure on rivers and may allow the holistic comparison between both discharge settings. However, cytotoxicity can also be triggered by specific compounds and not only by unspecific mixtures which is why this aspect has to be taken into consideration for the interpretation and evaluation. Under consideration of this aspect and potential matrix effects, the comparison of the dissolved phase with the particle-bound chemicals may close the research gap of identifying the relevance of prevailing hydrological conditions for the pollutant pressure on rivers at the catchment scale.

### 7.2.4 MICROPOLLUTANTS AS PROCESS-INDICATORS?

In **paper II** and **III**, I used conservative organic micropollutants as tracers to identify the processes “dilution” and “particle turnover” in the Ammer River. Previous studies claim that organic pollutants might be helpful as “anthropogenic markers” in hydrological systems to identify e.g. mixing processes between river water and groundwater in the hyporheic zone (Banzhaf et al. 2012; Clara et al. 2004). This is due to their omnipresence in rivers and the recent general achievements in analytical precision and lower detection limits. In **paper II**, I tested the applicability of the conservative compounds carbamazepine and tramadol as process indicators, in detail to quantify and localize groundwater inflow in rivers. Both compounds led to unreliable results for the quantification of the groundwater inflow. Small concentrations, a small concentration range between minimum and maximum values in combination with a relative high measurement uncertainty are the main restrictions for a successful applicability as process indicator. Additionally, the term “conservative” must be questioned carefully. Many studies attribute a conservative character especially to carbamazepine in rivers (e.g., Arlos et al. 2014; Guillet et al. 2019) and use it as conservative comparative substance for the determination of reactive pollutants (Müller et al. 2018). Attenuation rates are low and calculated half-lives are high, especially in comparison to the respective travel time of the river water as discussed in **paper III**. On the contrary, many hydrological studies that focus on reactive processes address nitrate (e.g., Pittroff et al. 2017; Schwientek et al. 2013a; Schwientek and Selle 2016). This nutrient is classified as highly reactive with comparable degradation rate constants obtained from literature (between 0.02 – 0.005 $h^{-1}$ for the Steinlach River; Schwientek and Selle 2016) to the rates of carbamazepine presented in **paper III**. This demonstrates that different definitions exist among adjoining disciplines and challenges the applicability of hydrophilic pollutants as exclusive process indicator.

In **paper IV**, polycyclic aromatic hydrocarbon (PAH) concentrations were used to deepen knowledge on particle transport in rivers. In contrast to the results of **paper II**, results of this study show that PAH concentrations are applicable for determining turnover processes when combining the persistent character of PAHs with particle characteristics. The decisive factor for the applicability is not only the very large half-lives (Shuttleworth and Cerniglia 1995), but in particular the strongly hydrophobic character of these substances (Patrolecco et al. 2010) which narrows down the options on attenuation processes in the dissolved phase to the distribution process “sorption”. The combination of the large half-life and the ability to undergo nearly exclusively one distribution process allows the application as tracers to understand sediment transport processes in rivers. However, the reverse process (desorption; leaching) is also a relevant aspect as discussed in the previous chapter and has to be considered carefully. This outcome of potentially applicable organic micropollutants as tracers might be transferable to other compounds and other environmental scientific research questions and leave room for future research.

## 7.3 FUTURE PERSPECTIVE: FROM A SMALL SCALE TO A BROADER CONTEXT

Based on the results of the present study (papers I – IV), the following recommendations can be derived for future investigations that **aim to understand transformation processes and degradation rate constants of pollutants in rivers**: Since mainly the environmental conditions such as the morphology of the river or the shading area of the river restrict the comparability between studies at different rivers, investigations at the same river or catchment are indispensable to **narrow down the number of potential influencing factors** for attenuation processes. The interpretation of underlying processes is more profound when results of investigations at the same river are repeatable. Therefore, studies could mainly focus on the **repetition of the conducted experiments** I) to verify the outcome of the presented studies that were only conducted once (e.g., quantification of groundwater inflows or analysing particle turnover processes) and II) to investigate the individual contributions of the environmental conditions (e.g., during winter to investigate solar radiation dependent photodegradation). The experiments at the Ammer River clearly show that rivers with a WWTP inflow are affected by a dynamic discharge and pollutant pattern, which is why specific characteristics such as the anthropogenic influence expressed by the daily discharge dynamics could be caught by **time-series studies instead of grab samples** at the same location as applied in the case of paper III, though neglected in the case of paper II for each sampling site. Scaling up these process-related field studies to different rivers/streams within the same catchment gives insight into the **contribution of individual (hydrological and reactive) attenuation processes at different scales** for the catchment outlet whereas the number of varying environmental conditions might still be manageable within the same catchment unlike the comparison between different rivers. In a next step, investigations that focus on **catchment characteristics** (e.g., the fluvial morphology as controlling factor for the travel time that may be caused by the karstic character of the catchment) has to be taken into consideration for a holistic understanding of in-stream turnover processes of pollutants. In a broader context, I expect that future research may focus more on small-scale processes such as e.g. **the role of macrophytes** for the river water quality, but also on “adjoining river compartments” of the river such as the **contamination of groundwater** after contaminated water from rivers or soil recharges the groundwater. The reason why the latter aspect might come more to the fore in future research is that the response in the groundwater on the chemical pollution might not be visible now due to the long groundwater recharge rates. On a **long-term perspective** of water quality and associated river-in processes, it is questioned if the topic of organic micropollutants in rivers will be relevant with **continuously improving water treatment in Europe** that might potentially entail a decrease of pollutants in rivers. As an example, research in Europe focuses on understanding turnover processes of compounds to improve understanding of the water quality at present low concentrations, whereas a look at other continents shows that **untreated and especially uncontrolled wastewater inflow leads to very high concentrations** (e.g. 20,000 higher maximum concentrations of pharmaceuticals in African environments in comparison to Europe) which is a major concern in developing countries (Fekadu et al. 2019). Thus, the **identification and quantification of contaminations' input** is highly relevant to identify the main causes for a reduced water quality for these countries. For a holistic assessment of water quality, **monitoring** programs are thus crucial as a first step and future research might focus on these highly contaminated regions to deepen knowledge on turnover processes in rivers, which in turn might help to improve process understanding in European systems.

## 7.4 FINAL CONCLUSIONS

The rising recognition of organic micropollutants in rivers within the last decades led to a great effort in better understanding the behaviour of these compounds in the environment to evaluate the risk for humans and fluvial aquatic systems. This yields the necessity of a field-based assessment of in-stream contaminant fate. The results of this thesis present a holistic picture of hydrological and reactive mechanisms controlling the water quality in rivers under consideration of different hydrological conditions, as well as factors that determine these mechanisms. This thesis demonstrates that hydrological and reactive processes are equally important to describe the in-stream fate of pollutants and that both aspects influence each other. A profound knowledge on the water origin and connection to catchment processes is necessary to get a deeper insights into the ‘occurrence’ of water and particles for dissolved and particle-associated compounds, respectively, since this may influence the pollutant flux in rivers and thus the in-stream compounds’ reactivity. In addition, this thesis provides initial insights into the usability of selected organic pollutants as (hydrological) process indicators, as well as the cytotoxicity as tool to compare the overall pollution pressure on rivers at different discharge conditions. With that, this work provides not only many starting points for future research on in-stream fate of pollutants, but also constitutes a profound basis on the assessment of river water quality.

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# APPENDIX

# LIST OF PAPERS

I. **Glaser, C.,** Schwientek M., Zarfl C.; 2019. Designing field-based investigations of organic micropollutant fate in rivers. Environ. Sci. Pollut. Res. 28, 28633-28649, doi: https://doi.org/10.1007/s11356-019-06058-1.

> *Individual contributions: **Clarissa Glaser**, Marc Schwientek and Christiane Zarfl designed the concept of this study. **Clarissa Glaser** reviewed literature and wrote the manuscript with the support of Marc Schwientek and Christiane Zarfl.*

II. **Glaser, C**., , Schwientek M., Junginger T., Gilfedder B. S., Frei S., Werneburg M., Zwiener C., Zarfl C. (2020): Comparison of environmental tracers including organic micropollutants as groundwater exfiltration indicators into a small river of a karstic catchment. Hydrological Processes 34(24), 4712-4726. Doi: https://doi.org/10.1002/hyp.13909

> *Individual contributions: **Clarissa Glaser**, Tobias Junginger, Christiane Zarfl and Marc Schwientek designed this study. **Clarissa Glaser** and Tobias Junginger analysed the data with the support of Ben Gilfedder and Sven Frei. Analytical measurements were supported by Martina Werneburg and Christian Zwiener. **Clarissa Glaser** wrote the manuscript with the support of Marc Schwientek and Christiane Zarfl.*

III. **Glaser, C.,** Zarfl C., Werneburg M., Böckmann M., Zwiener C., Schwientek M. (2020): Temporal and spatial variable in-stream attenuation of selected pharmaceuticals. Sci. Total Environ. 741, 139514, doi: https://doi.org/10.1016/j.scitotenv.2020.139514.

> *Individual contributions: **Clarissa Glaser**, Christiane Zarfl and Marc Schwientek designed this study. **Clarissa Glaser** and Matthias Böckmann analysed the data. Analytical measurements were supported by Martina Werneburg and Christian Zwiener. **Clarissa Glaser** wrote the manuscript with the support of Marc Schwientek and Christiane Zarfl.*

IV. **Glaser C**., Zarfl C., Rügner H., Lewis A., Schwientek M. (2020): Analysing particle-associated pollutant transport to identify in-stream sediment processes during a high flow event. Water 12(1794), 1-16, doi: https://doi.org/10.3390/w12061794.

> *Individual contributions: **Clarissa Glaser**, Christiane Zarfl and Marc Schwientek designed this study with the support of Hermann Rügner. Amelia Lewis performed laboratory analysis. **Clarissa Glaser** analysed the data. **Clarissa Glaser** wrote the manuscript with the support of Marc Schwientek and Christiane Zarfl.*

# A. SUPPORTING INFORMATION: COMPARISON OF ENVIRONMENTAL TRACERS INCLUDING ORGANIC MICROPOLLUTANTS AS GROUNDWATER EXFILTRATION INDICATORS INTO A SMALL RIVER OF A KARSTIC CATCHMENT

***Fig. A21***: *Ammer River upstream directly upstream of the selected reach (photo: Marc Schwientek, June 2018).*

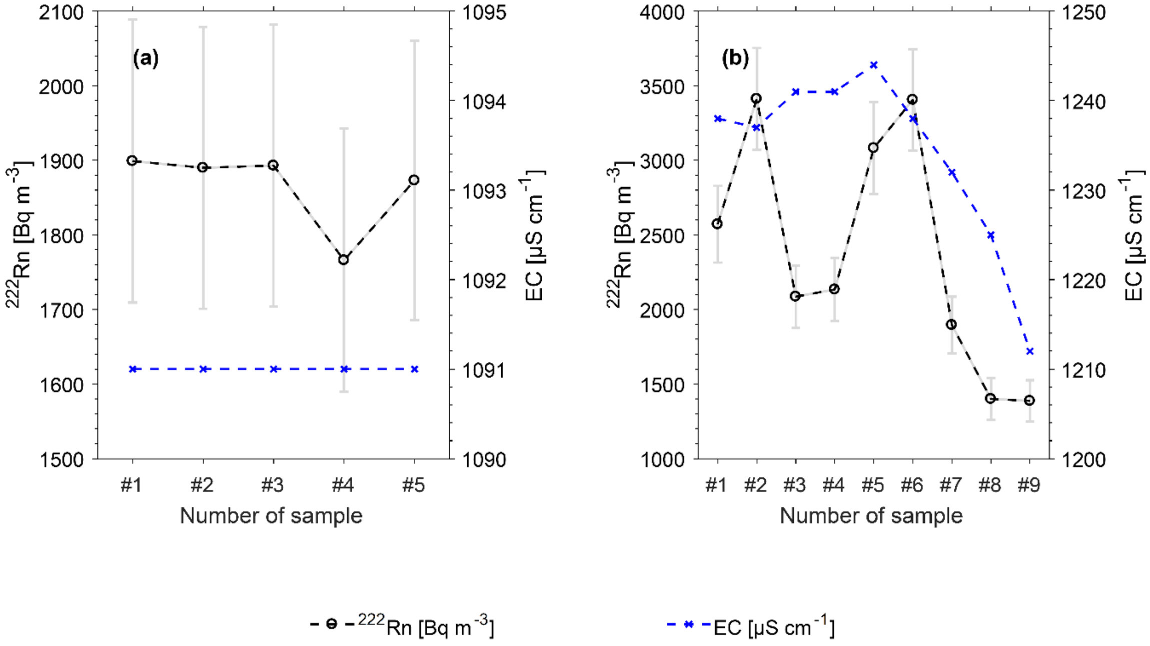

***Fig. A22**:* *Transverse profile of $^{222}$Rn [Bq m$^{-3}$] and EC [µS cm$^{-1}$] at two different sampling locations. No. 1 (number of sample) represents ta sample taken about 10 cm from the left bank side, the highest number of sample (5 and 9, respectively) was taken about 10 cm from the right bank side. Sampling locations between these samples were homogenously distributed across the transverse profile. Sampling site (a) represents a mixed transverse profile in Reusten (~100m upstream of the Kochhart confluence), sampling site (b) represents an inhomogenously mixed sampling site located about 15 m downstream of the Schwärzenbrunnen.*

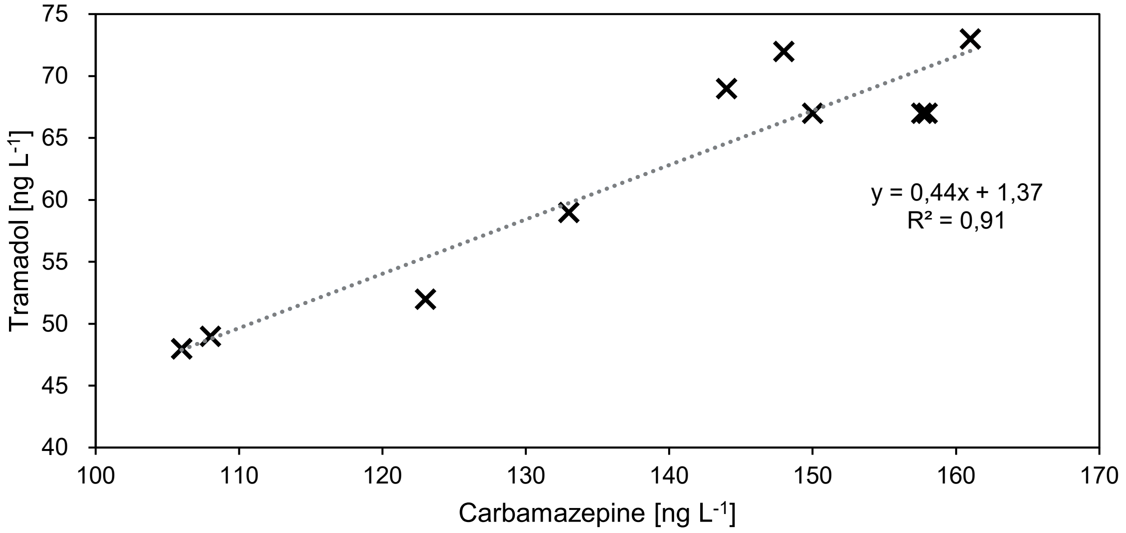

***Fig. A23**:* *Correlation between tramadol and carbamazepine concentrations [both ng L$^{-1}$].*

# B. SUPPORTING INFORMATION: TEMPORAL AND SPATIAL VARIABLE IN-STREAM ATTENUATION OF SELECTED PHARMACEUTICALS

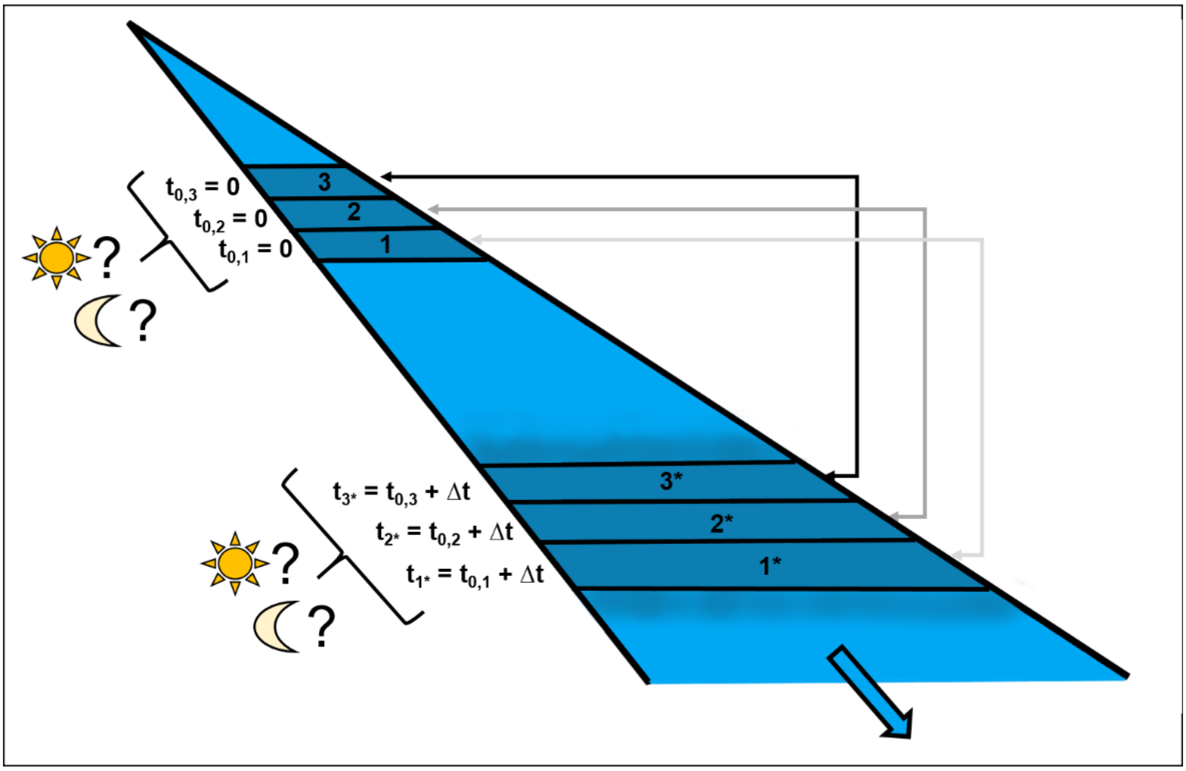

***Fig. B24****:* *General concept of the Lagrangian approach*

The general concept of the Lagrangian approach is based on tracking individual water parcels along a defined river stretch. For this purpose, water parcels of a defined temporal length are repeatedly sampled at an upstream location at a start time $t = t_0$ and at a downstream location after the mean transit time of the water. All water parcels are exposed to the biological, (hydro-) morphological, and sedimentological features of the river stretch they pass. Depending on $t = t_0$ and $t = t_0 + \Delta t$, the environmental conditions such as the exposure to sunlight (indicated by sun and moon) or the water temperature differ between the individual parcels. The water parcels downstream are affected by dispersion compared to the upstream water parcels, but mixing due to dispersion at the boundary of the water parcels becomes negligible if the temporal length of the water parcels is large.