

Interaction of surface water and groundwater in the hyporheic zone – application of pharmaceuticals and temperature as indicators

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Abstract

The hyporheic zone is the area below and adjacent to a water body where surface water and groundwater mix and exchange. For this study the stream Mess at a field site in the Grand Duchy of Luxembourg was investigated. Along the streambed alluvial sediments occur, which are underlain by Liassic marls and marly sands. Changes of effluent and influent aquifer conditions result in an input of pharmaceuticals, which were frequently detected in the stream, and the propagation of temperature changes into the riverine groundwater. Furthermore, a sensitivity of these organic compounds, which are detected in surface water and groundwater, to different redox conditions was expected to influence their transport in the fine-grained riverbank sediments. To validate the application of pharmaceuticals and temperature as indicators for hyporheic exchange, results of field data and a laboratory experiment were combined in this work.

In the field studies the applicability of selected pharmaceuticals (e.g. sulfamethoxazole) as anthropogenic indicators for the interaction of surface water and groundwater was evaluated. During the observed period of one year effluent aquifer conditions dominated. However, during flood events also influent aquifer conditions were observed. To prove the assumed interaction, water samples from the stream as well as from single-screen and multilevel observation wells in the riverbank were analysed for selected pharmaceuticals. Nearly all compounds that were detected in the stream were also found in the riverine groundwater, even though concentrations were significantly lower. Considering these first results, seven pharmaceuticals were selected based on their transport relevant properties (mobile and sorbing/degradable) and verified by field data. The analyses supported the assumption that these compounds enter the riverbank via the stream only. Even gradients with depth for some of the pharmaceuticals were observed. A balance of exchanged masses, however, was not possible. Altogether, it was demonstrated that selected pharmaceuticals are suitable anthropogenic indicators in the hyporheic zone. The mobile compounds (e.g. carbamazepine, sulfamethoxazole) turned out to be more suitable for this application. In addition, the field data proved that water exchange also takes place in riverbanks which have a low hydraulic conductivity. However, not all compounds seemed to be suitable indicators as their transport behaviour is not fully understood.

To enhance the knowledge on the fate of the pharmaceuticals detected in the field, a laboratory column experiment under water saturated conditions was conducted. The transport behaviour of sulfamethoxazole, carbamazepine, diclofenac, and ibuprofen (inflowing concentrations 165 – 295 $\mu\text{g L}^{-1}$) were investigated under varying but specific redox concentrations. Sediment and surface water from the field site were used for the experiment. The specific redox conditions were systematically varied throughout the experiment by adding nitrate in the influent water in stepwise decreasing concentrations between 131 and 20 mg L^{-1} . Accordingly, temporarily denitrifying conditions were established in the column during the reduction of nitrate. Sulfamethoxazole was severely influenced by this process and during denitrification the concentrations in the effluent water decreased rapidly. This observed redox-dependency of sulfamethoxazole occurrence and transformation may help to explain the wide ranges of reported degradability. Ibuprofen was more stable under denitrifying redox conditions. For carbamazepine, the apparent retardation was attributed to sorption and also to degradation. In contrast, degradation under nitrate reducing conditions seemed the dominating process for the apparent retardation of diclofenac.

In the last part of the thesis a new approach to derive seepage rates from thermal records is presented. Wavelet analysis was tested for its applicability as a band-pass filter for non-stationary time series of water temperature records. This new processing technique was successfully applied to a virtual data set and to real data from temperature time series that were measured over a two-year period in the streambed sediments at the field site. For the analysed time series the estimated seepage velocities based on the amplitude ratio of the daily temperature oscillation were always negative and ranged from -0.7 to -2.5 m d^{-1} , which indicated permanent effluent aquifer conditions. Hydraulic measurements from the field studies confirmed the dominance of this flow direction. However, the calculated Darcy velocities were about one magnitude lower than the seepage rates based on the thermal records. Altogether, this study confirms the use of the presented method to calculate seepage rates and to detect effluent and influent aquifer conditions.

This thesis demonstrates the applicability of the presented methods – pharmaceuticals and temperature as indicators – for the investigation of surface water and groundwater interaction. Furthermore, a more comprehensive understanding of processes in the hyporheic zone was yielded, a basis for future studies.

Zusammenfassung

Die hyporheische Zone ist der Bereich im Umfeld eines Gewässers in dem Interaktion von Oberflächen- und Grundwasser stattfindet. Standort für die vorliegenden Untersuchungen war der Bach Mess im Großherzogtum Luxemburg, welcher von Liasischen Mergeln und mergeligen Sanden unterlagert wird. Wechsel von effluenten zu influenten Grundwasserverhältnissen führen zu einem Eintrag von im Bach nachgewiesenen Pharmazeutika sowie zu Temperaturänderungen im ufernahen Grundwasser. Auch eine Abhängigkeit dieser Stoffe von den Redoxbedingungen, die sich auf deren Transport in den feinkörnigen Sedimenten der Uferbank auswirkt, wurde vermutet. Zur Überprüfung der Anwendbarkeit von Pharmazeutika und Temperatur als Indikatoren für Wasseraustausch in der hyporheischen Zone wurden Ergebnisse von Feldmessungen sowie eines Laborexperimentes in dieser Arbeit zusammengeführt.

Anfangs wurde in Feldstudien die Eignung von ausgewählten Pharmazeutika (z.B. Sulfamethoxazol) als anthropogene Indikatoren für die Interaktion von Grund- und Oberflächenwasser in der Uferbank überprüft. Während des einjährigen Untersuchungszeitraumes dominierten effluente Grundwasserverhältnisse am Standort. Allerdings wurde während Hochwasserereignissen ein Wechsel zu influenten Grundwasserverhältnissen beobachtet. Um den Austausch von Wasser zu belegen, wurden Proben aus dem Bach sowie aus einfach und mehrfach verfilterten Grundwassermessstellen in der Uferbank auf Pharmazeutika analysiert. Dabei wurden nahezu alle im Bach nachgewiesenen Stoffe auch im ufernahen Grundwasser detektiert, wenn auch in deutlich geringeren Konzentrationen. Aufbauend auf den ersten Ergebnissen wurden sieben Pharmazeutika anhand ihrer transportrelevanten Eigenschaften in mobile und sorbierende/abbaubare Stoffe unterteilt. Die Ergebnisse belegen einen Eintrag der Stoffe nur von Seiten des Baches. Außerdem weisen einige Pharmazeutika Gradienten mit der Tiefe auf. Eine Bilanzierung der ausgetauschten Massen war allerdings nicht möglich. Insgesamt werden die ausgewählten Pharmazeutika als geeignete anthropogene Indikatoren in der hyporheischen Zone bewertet. Wie erwartet scheinen die mobilen Stoffe (u.a. Carbamazepin, Sulfamethoxazol) für diesen Zweck besser geeignet zu sein. Des Weiteren konnten die Studien erstmals zeigen, dass hyporheischer Austausch auch in hydraulisch gering durchlässigen Uferbänken stattfindet. Da das Transportverhalten einiger Pharmazeutika noch nicht ausreichend bekannt ist, sind nicht alle untersuchten Stoffe als Indikatoren geeignet.

Um die Kenntnis über Verhalten und Verbleib der im Feld nachgewiesenen Stoffe zu vertiefen, wurde ein Säulenexperiment unter wassergesättigten Bedingungen durchgeführt. Der gewählte Versuchsaufbau erlaubte die Untersuchung des Transportverhaltens von Sulfamethoxazol, Carbamazepin, Diclofenac und Ibuprofen (Eingangskonzentrationen zwischen 165 und 295 µg/l) unter variierenden spezifischen Redoxbedingungen. Für den Versuch wurden Sediment und Wasser vom Standort verwendet. Die spezifischen Redoxbedingungen in der Säule wurden durch die Zugabe von Nitrat gezielt variiert. Dabei wurden schrittweise abnehmende Konzentrationen von 131 bis 20 mg/l eingestellt. Dies führte zu zeitweise denitrifizierenden Bedingungen in der Säule. Sulfamethoxazol wurde während der Nitratreduktion schnell und deutlich transformiert. Die beobachtete Redoxabhängigkeit der Transformation trägt zum besseren Verständnis der großen Spannweite der bisher beschriebenen Abbaubarkeit von Sulfamethoxazol bei. Ibuprofen war hingegen stabiler unter denitrifizierenden Bedingungen. Die bei Carbamazepin beobachtete Retardation wurde auf Sorption und Abbau zurückgeführt. Im Gegensatz dazu war Abbau unter Nitratreduzierenden Verhältnissen der dominierende Prozess für die Retardation von Diclofenac.

Im letzten Abschnitt der Arbeit wird ein neuer Ansatz für die Berechnung von Sickeraten auf Basis von Wassertemperaturmessungen vorgestellt. Die Wavelet-Analyse wurde für die Anwendung als Bandfilter für instationäre Temperaturzeitreihen getestet. Diese neue Prozesstechnik konnte sowohl auf virtuelle Daten als auch auf Felddaten, die über zwei Jahren gemessen wurden, erfolgreich angewendet werden. Die auf Basis des Amplitudenverhältnisses der täglichen Temperaturosillation berechneten Sickerraten waren negativ und reichten von -0,7 bis -2,5 m/d, was permanent effluente Grundwasserverhältnisse impliziert. Diese Dominanz von effluenten Verhältnissen wurde durch hydraulische Messungen bestätigt. Allerdings waren die berechneten Geschwindigkeiten um eine Größenordnung niedriger als die temperaturbasierten. Insgesamt konnte die Nutzbarkeit der vorgestellten Methode für die Berechnung von Sickerraten sowie die Bestimmung von effluenten und influenten Grundwasserverhältnissen gezeigt werden.

Zusammenfassend belegt die vorliegende Arbeit die Eignung der vorgestellten Methoden – Pharmazeutika und Temperatur als Indikatoren – für die Untersuchung der Interaktion von Oberflächenwasser und Grundwasser. Außerdem wurde ein vertieftes Verständnis der Prozesse in der hyporheischen Zone gewonnen, das die Grundlage für zukünftige Studien darstellt.

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Chapter 1

1 Introduction

1.1 Surface water and groundwater interaction

The interface of surface water and groundwater, where waters from these two compartments mix (Fig. 1-1), is referred to as the *hyporheic zone*. This term was introduced by Orghidan (1959) as a new habitat of subsurface water. In this transition zone – depending on the hydraulic gradient and the shape of the riverbed – surface water can stream in, remain, and stream out again. During the subsurface passage it mixes with the riverine groundwater. This mixing allows distinguishing between surface water, groundwater, and hyporheic water.

Recently, the hyporheic zone has attracted researchers of different disciplines worldwide as it was identified to be of great importance for the character and the rate of material changes of surface water (Sophocleous, 2002). With this, also different definitions of the hyporheic zone were proposed, e.g. using biological, geochemical, and hydrological classifications (Gooseff, 2010). The biological definition refers to the area of the subsurface water where conditions are similar to those in the surface water (e.g. availability of dissolved oxygen). This area therefore provides a suitable habitat for the hyporheic fauna. The geochemical approach describes the mixing of the two end member water types – surface water and groundwater – and builds upon the biological definition. Hydrological definitions describe flow paths that begin and end at different locations in the stream and have a subsurface passage in between. Following this definition, hyporheic exchange has an influence on stream water as it is assumed that hyporheic water always re-enters the stream (Gooseff, 2010).

However, the great variety of research on and in the hyporheic zone and its function offers the opportunity to study, understand, and finally treat surface water and groundwater as a single resource (Winter et al., 1998). This holistic approach is crucial to assure an effective and sustainable present and future use of the resource water.

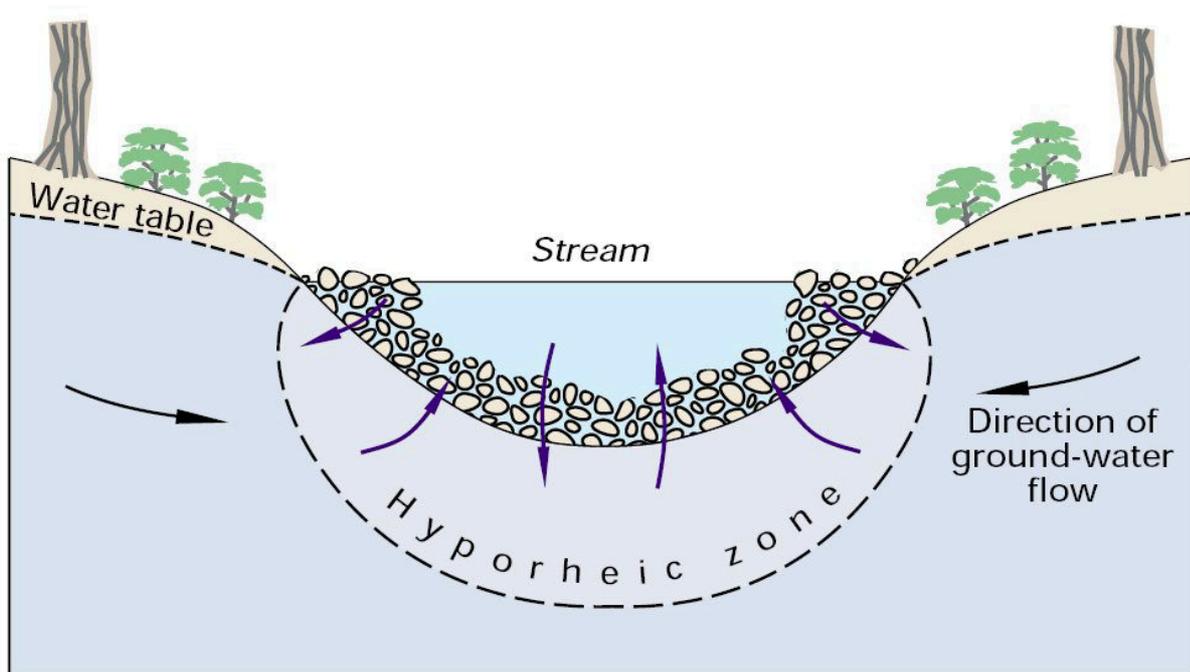


Fig. 1-1 Schematic cross section of the hyporheic zone (Winter et al., 1998)

A sound knowledge of hydraulic conditions, chemistry and biology, and also human impacts in and on the hyporheic zone are prerequisites for the comprehensive understanding of the system surface water/groundwater. The determination of the flow regime (effluent or influent aquifer conditions) is appropriate to obtain a rough image about potential flow directions and mixing of surface water and groundwater. The assumption that – typical for the humid climate zone – effluent aquifer conditions are dominant only applies for regional flow systems. Local flow systems are much more complex (Winter, 1999; Woessner, 2000). One characteristic of the hyporheic zone is its dynamic on temporal and spatial scale. Therefore, its hydraulically controlled shape and extent are often difficult to assess and vary over time (Wondzell and Swanson, 1999).

Triska et al. (1993) studied the hyporheic zone as a hydrological exchange zone and also as an ecotone. They introduced a conceptual model for nitrogen cycling in the hyporheic zone and its influence on surface water habitats. Malcolm et al. (2009) studied the character of the hyporheic zone in salmon spawning gravel. Their main conclusion was that a holistic understanding of hyporheic processes is needed to determine the (potentially negative) impact of degrading hyporheic water quality on salmon spawn. Furthermore, Brunke and Gonser (1997) presented a review on the ecological significance of exchange processes in the hyporheic zone. They con-

cluded that human activities, like reducing the connectivity of surface water and groundwater, altering exchange processes, and supplying toxic or organic contaminations threaten the ecological integrity of this system. Also Hancock (2002) reviewed human impacts on the exchange of stream and groundwater. He stated that many human activities are able to disturb hydrological exchange and biological activity in the hyporheic zone beyond the threshold from which the system can recover.

Numerous methods are available to study the hyporheic zone in the field. However, the selection of the appropriate method depends on the spatial and temporal scale of the respective study (Kalbus et al., 2006) and on the respective research question. An overview of the current state of the art was presented, e.g. by Briddock (2009) and Kalbus et al. (2006). Amongst others seepage meters, measurements of hydraulic gradients, tracer tests, passive samplers, sampling of observation wells, grab samples of surface water, and integral pumping tests were described as appropriate methods for this purpose. Other methods are, e.g. a colonisation corer to monitor abiotic and biotic processes (Fraser et al., 1996), mini drive-point piezometers and multilevel samplers (Rivett et al., 2008), or a heat pulse technique to determinate small-scale flow directions and velocities (Lewandowski et al., 2011a).

Also numerical modelling of the hyporheic zone under different constraints is a common tool in hydro(geo)logical sciences. Wroblicky et al. (1998) modelled the seasonal variation of the lateral hyporheic area of two alluvial streams. They found a significant decrease of this area during high flows in the stream. Lateral hyporheic fluxes through the hyporheic zone were modelled by Cardenas (2009). His model required channel slope and/or sinuosity and hydraulic conductivity to predict horizontal fluxes. Wondzell et al. (2009) tested how increased data availability influences groundwater flow models of the hyporheic zone. They suggested that geomorphic data may be sufficient when predicting water fluxes through the hyporheic zone and approximating travel times.

For this thesis surface water and groundwater samples were analysed, amongst others for pharmaceutical trace compounds, to study lateral interaction between the two compartments and within the hyporheic zone. Also the hydraulic boundary conditions were determined and temperature measurements were used to calculate seepage rates for a comprehensive system understanding. The focus of this work is on the

geochemical interaction at the surface water/groundwater interface in an alluvial riverbank with an emphasis on pharmaceuticals as anthropogenic indicators.

1.2 *Pharmaceutical compounds*

1.2.1 Occurrence in the aquatic environment and environmental impact

Pharmaceutical compounds have been detected in nearly all parts of the aquatic environment worldwide with increasing detection frequency during the last decade. They were found in surface waters and in groundwater (Halling-Sorensen et al., 1998; Tixier et al., 2003), and occasionally even in drinking water (Heberer et al., 2002). To some extent the rising detection frequency of pharmaceuticals is corresponding to the continuously improving analytical methods. Current techniques allow a detection of these compounds even at the low ng L⁻¹-range (Nödler et al., 2010; Pailler et al., 2009). However, also the global consumption rates of pharmaceuticals are rising (Corcoran et al., 2010).

The highest input of (human) pharmaceuticals in the aquatic environment is via the effluent of wastewater treatment plants, as these compounds are present in untreated wastewater and are not completely removed during conventional treatment (Gros et al., 2007; Paxeus, 2004; Reemtsma et al., 2006). Also, a complete removal of pharmaceutical compounds from raw water for drinking water production is not always achieved during conventional treatment (Stackelberg et al., 2007; Vulliet et al., 2011). The input of organic compounds in the environment, which impact is not yet fully understood, should be avoided. Therefore, the efficient removal of these compounds during water treatment is a priority.

Nikolaou (2007) studied occurrence patterns in water and wastewater environments and proposed two important challenges for the future: further development and optimisation of analytical methods and studies on environmental risk assessment. Diaz-Cruz and Barcelo (2008) studied emerging organic micropollutants in different source waters, which are used for artificial aquifer recharge. They stated that the quality of these waters has to be tested and possibly pre-treated before infiltration to protect the groundwater.

Kümmerer (2009) discussed the presence of pharmaceuticals in the environment due to human use of these compounds. His review demonstrated the ongoing relevance of this topic. However, he pointed out that research has moved on from the simple detection of the compounds to different other approaches like risk assessment, technical management measures, including people handling and using the compounds. Accordingly, Schirmer et al. (2011) addressed issues resulting from pollution of urban water systems and water protection in these areas. They concluded that precautionary and preventive approaches should be established to protect urban water. Loos et al. (2009; 2010) presented EU-wide surveys of polar organic persistent pollutants in river waters and in groundwater. They proposed *indicative warning levels* in surface water as only 10% of the river water were classified as *very clean*. However, only 1.7% of the analysed groundwater samples showed concentrations above the European groundwater quality standard for pesticides of $0.1 \mu\text{g L}^{-1}$.

Although doses for pharmaceuticals are significantly higher than those found in the environment, these compounds pose a potential environmental risk that is not yet thoroughly characterised. When entering drinking water, e.g. via bank filtration, pharmaceuticals and their transformation products pose a potential risk to humans (de Jongh et al., 2012; Massmann et al., 2009; Stuart et al., 2012), and therefore their occurrence and transport behaviour is of great concern.

Pal et al. (2010) presented a review of the impact of emerging organic contaminants on freshwater resources. They concluded that the assessment of human and ecotoxicological risk is still difficult, e.g. due to the wide range of properties of the organic compounds and also the multiple environmental surroundings. However, the relevance of pharmaceuticals in the aquatic environment and their impact is discussed controversial. For instance, Webb et al. (2003) stated that the indirect human exposure to pharmaceuticals via drinking water is not a threat. They mainly referred to the fact that the potential indirect daily exposure via drinking water is at least three orders of magnitude lower than the daily therapeutic use. Also Schwab et al. (2005) concluded that no human risk exists from the presence of trace concentrations from the 26 studied pharmaceuticals in surface and drinking water. On the contrary, Jones et al. (2005) claimed that continual life-long exposure to trace levels of pollutants is an unexplored area of toxicology. They suggested keeping *a watchful eye* on the development of the pharmaceuticals' presence in the environment to avoid future problems due to unawareness.

Numerous studies were also carried out to investigate the effect of pharmaceuticals on the aquatic flora and fauna. Henschel et al. (1997) assessed the environmental hazard of pharmaceuticals on algae, *Daphnia*, fish embryos, luminescent bacteria, and ciliates. They found that more sensitive tests are needed, as the standard tests would have underestimated the toxicity of, e.g. the analgesic and antipyretic paracetamol and the blood lipid regulator clofibrilic acid. Furthermore, Dussault et al. (2008) investigated the toxicity of human pharmaceuticals to benthic invertebrates. Considering the low concentrations observed in the environment, e.g. the lipid regulator atorvastatin poses only negligible risk to benthic invertebrates. On the other hand, potential risk does exist from the anticonvulsant carbamazepine and the antimicrobial triclosan even at very low concentrations. Moreover, Thomas and Klaper (2012) found that a mixture of psychoactive pharmaceuticals induces autism-like gene expression in fish – at concentrations that were already observed in the environment. This does, however, not conclusively indicate that this is also a threat to humans. Nevertheless, this study demonstrated the toxicity of these compounds in the aquatic environment even at very low concentrations. Finally, also negative impacts on the wellbeing of *Petrophaga lorioti* cannot be excluded.

Recently, Lapworth et al. (2012) presented a review on sources, fate, and occurrence of emerging organic contaminants, which focussed on groundwater. They concluded that, in the coming decades, drinking water standards, environmental quality standards, and/or groundwater threshold values will likely be defined and therefore spatial and temporal variation of these compounds in the aquatic environment remains a research priority.

The occurrence of pharmaceutical compounds at the interface of surface water and groundwater is also in the focus of research, as the hyporheic zone is assumed to be of great importance for surface water quality (chapter 1.1). Therefore, profound knowledge about the presence and fate of these compounds in the hyporheic zone is needed. Daneshvar et al. (2010) studied seasonal variations in the occurrence and fate of pharmaceuticals in a river-lake system. They observed a clear seasonal pattern with the highest attenuation in summer and the lowest in winter. Furthermore, Lewandowski et al. (2011b) studied the fate of organic micropollutants in the hyporheic zone of a lowland stream. They found some attenuation of the pharmaceuticals in the subsurface. Concentrations of the compounds were high in the surface water, and also in the subsurface water, where river water was infiltrating.

In summary, both occurrence and environmental impact of pharmaceuticals are important areas of current research. However, the presented study, which found pharmaceuticals at the low ng L⁻¹-range, did not focus on the impact of these compounds on the aquatic environment.

Although (human) pharmaceutical compounds were detected even in the hyporheic zone, little is known about their transport and fate in this area. Thus, selected pharmaceuticals that were detected in surface water and groundwater at the studied fieldsite were used as *anthropogenic indicators* in the hyporheic zone in this thesis.

1.2.2 Application as indicators

The continuously improving analytical methods and the resulting decreasing limits of quantification of organic substances like pharmaceuticals have opened new research possibilities (Nödler et al., 2010; Pailler et al., 2009). The detection of, e.g. pharmaceuticals on the ng L⁻¹-scale in the environment enables the use of these compounds as indicators for a variety of applications. As the main input paths into the aquatic environment are generally well known (chapter 1.2.1), the respective source of a compound can be identified. Using this knowledge, the influence of the "contaminated" source on, e.g. surface water or groundwater can be qualified and, depending on the available data, even quantified. A selection of applications is presented in the following.

For example, Strauch et al. (2008) tested indicators for assessing anthropogenic impacts on urban waters. They demonstrated that – amongst others – xenobiotic compounds are suitable to indicate these impacts. However, they raised the issue that different geochemical environments may result in different behaviour of these compounds. Dickenson et al. (2011) evaluated the application of indicator trace organic compounds to assess the contribution of wastewater effluent to overall river flow. Their study identified more than 56 compounds to be well suited as potential indicators. Daneshvar et al. (2012) evaluated caffeine and selected pharmaceuticals as indicators of fecal contamination in drinking water sources. They suggested a high ratio of caffeine/carbamazepine as indicative of a greater proportion of raw sewage versus treated wastewater in surface water. Kiney et al. (2008) studied bioaccumulation of pharmaceuticals and other anthropogenic waste indicators in earthworms from agricultural soil. They documented that these compounds can be transferred to earth-

worms if they are present in the biosolids and swine manure that is applied to the soil.

Seiler et al. (1999) studied if caffeine and pharmaceuticals can be used as indicators of well contamination by wastewater. They found that these compounds are appropriate as indicators for recharge from domestic wastewater at the studied field site. Fenz et al. (2005) used carbamazepine as marker species to identify and quantify sewer exfiltration. Altogether, they could estimate an average sewage loss of 1% with this method. Buerge et al. (2009) studied the occurrence of artificial sweeteners in the aquatic environment. They showed that acesulfame fulfils all criteria of an ideal marker for the detection of domestic wastewater in groundwater. Furthermore, Müller et al. (2012) used a set of human pharmaceuticals to identify groundwater influenced by sewage. Apart from the proof of sewage water influence, which resulted from former sewage farms, they distinguished different times of recharge, as the consumption rates of the investigated pharmaceuticals have changed over time.

Townsend and Young (2000) surveyed the herbicide atrazine and its metabolites in groundwater and surface water. They found atrazine to be a suitable indicator for stream-aquifer interaction as this process contributes to the presence of atrazine in groundwater. Recently, Engelhardt et al. (2011) compared different tracer methods to quantify hydrodynamic exchange in the hyporheic zone. Analysed pharmaceutical compounds in an observed transition zone between surface water and groundwater allowed estimating the amount of river water within the groundwater.

In this thesis, the application of selected (human) pharmaceuticals as anthropogenic indicators for surface water and groundwater interaction in the hyporheic zone is evaluated. The findings presented in this work enhance the understanding of the transport and also degradation behaviour of the selected pharmaceuticals in the aquatic environment. It is demonstrated that these compounds, which are often referred to as *micropollutants*, can also be used as indicators/tracers to study hyporheic interaction.

1.3 Temperature as a tracer

For more than 100 years researchers have used heat as a natural tracer for surface water and groundwater interaction (Slichter, 1905). This method was frequently used to detect exchange between these two compartments, and recent advancements have made temperature an accurate tracer to assess hyporheic exchange in streams (Anderson, 2005).

As the ambient temperature propagates into the aquifer, it is attenuated and shifted in time (Molina-Giraldo et al., 2011; Stallman, 1965). The degree of signal attenuation and its shift are determined by the fluid flow velocity, thermal properties of the sediment (or soil) matrix, and the frequency of the temperature signal (Stallman, 1965). Stream water temperature fluctuates on different time scales, with strong diurnal and seasonal fluctuations (Hoehn and Cirpka, 2006).

Beginning with the simple description of temperature differences, researchers proposed methods for the calculation of water flow velocities and seepage rates based on temperature measurements. Among the best-known mathematical solutions, the one-dimensional heat transport equation by Stallman (1965) is the most popular. The basis for these calculations of water fluxes is the fluctuation of the temperature signal on different time scales (e.g. diurnal, seasonal). Diurnal oscillations of the temperature signal are widely used to assess vertical flow rates of water fluxes in the streambed (Hatch et al., 2006; Keery et al., 2007; Silliman et al., 1995). The propagation of seasonal signals is studied to document exchange of surface water and groundwater on a larger timescale (Anibas et al., 2011; Molina-Giraldo et al., 2011). Conant (2004) used point-derived temperature measurements in the streambed to delineate and quantify groundwater discharge. Lewandowski et al. (2011a) used a heat pulse sensor to detect flow velocities and flow directions in the streambed on a small scale.

Temperature measurements in streams using fibre-optic cables (DTS) were recently introduced to hydrological sciences to detect gaining and losing reaches along the streambed (Briggs et al., 2012; Selker et al., 2006; Vogt et al., 2010). Westhoff et al. (2011) quantified hyporheic exchange using temperatures measured with DTS. Gordon et al. (2012) presented VFLUX, an automated calculation of pore-water flux in the hyporheic zone from high resolution field temperature measurements using a MATLAB code applying Dynamic Harmonic Regression.

However, deriving diurnal temperature fluctuations from non-stationary temperature time series is still challenging. In this thesis an alternative and new approach to the established methods, e.g. Fourier analysis is presented.

1.4 Outline of the thesis

This cumulative thesis comprises four manuscripts. All papers are already published in an issue or online:

1. Banzhaf, S., Krein, A. & Scheytt, T. (2011). Investigative approaches to determine exchange processes in the hyporheic zone of a low permeability riverbank. *Hydrogeology Journal* 19 (3), pp. 591-601 (*Chapter 2*);
2. Banzhaf, S., Krein, A. & Scheytt, T. (2012). Using selected pharmaceutical compounds as indicators for surface water and groundwater interaction in the hyporheic zone of a low permeability riverbank. *Hydrological Processes*. doi: 10.1002/hyp.9435 (*Chapter 3*);
3. Banzhaf, S., Nödler, K., Licha, T., Krein, A. & Scheytt, T. (2012). Redox-sensitivity and mobility of selected pharmaceutical compounds in a low flow column experiment. *Science of the Total Environment* 438, pp. 113-121. (*Chapter 4*);
4. Onderka, M., Banzhaf, S., Scheytt, T. & Krein, A. (2013). Seepage rates derived from thermal records using wavelet analysis. *Journal of Hydrology* 479, pp. 64-74. (*Chapter 5*).

The first two papers present the results of field studies which addressed the potential use of selected pharmaceutical compounds as anthropogenic indicators for surface water and groundwater interaction in the hyporheic zone. The third paper presents the results of a laboratory column experiment, which was designed to study the redox-dependent transport behaviour of selected pharmaceuticals under water saturated conditions. The fourth paper presents a new approach to derive seepage rates from thermal records. All studies used water, sediment, and data which were collected at a field site in the Grand Duchy of Luxembourg. A more detailed outline is presented in the following.

Chapter 2

In this pilot study, the use of selected pharmaceutical compounds as anthropogenic indicators for the interaction of surface water and groundwater in the hyporheic zone was evaluated. The area of investigation was a field site in Luxembourg where single-screen observation wells in the riverbank of an alluvial stream as well as the stream itself were sampled and analysed for pharmaceutical residues. The hydraulic boundary conditions were monitored in surface water and groundwater and frequent changes from effluent to influent aquifer conditions were observed. Previous studies identified a wastewater treatment plant further upstream as the main source of pharmaceuticals in the stream. Pharmaceuticals, which were detected in the riverine groundwater samples, could therefore be related to inflowing surface water. Thus, the selected pharmaceuticals were regarded as characteristic for the field site and suitable as anthropogenic indicators for surface water and groundwater interaction. Furthermore, it was demonstrated for the first time that even for riverbanks with a low hydraulic permeability hyporheic exchange has to be considered as a relevant process.

Chapter 3

This follow-up study focused on pharmaceutical compounds as indicators for surface water and groundwater interaction and their spatial distribution in the riverine groundwater. The investigations were carried out at the same field site as the pilot study. However, additional multilevel observation wells were installed in the riverbank and allowed to compare both vertical and horizontal concentration distributions of the chosen compounds. A classification into mobile and sorbing/degradable pharmaceuticals based on their transport relevant properties was verified by the field data and gradients with depths for some compounds were documented. However, the respective distribution in the riverine groundwater was ambiguous for some of the compounds. This might be caused by unknown heterogeneities in the riverbank or unexpected transport behaviour of the pharmaceuticals, e.g. due to observed varying pH. Altogether, the group of mobile compounds turned out to be more suitable as anthropogenic indicators at the field site as their transport behaviour is more conservative. In addition, some of the studied pharmaceuticals are supposed to be sensitive to the prevailing redox conditions.

Chapter 4

The redox-dependent transport behaviour of selected pharmaceutical compounds was investigated in a laboratory column experiment under water saturated conditions. Selected compounds that were also detected in the two previous studies both in surface water and groundwater at the field site in Luxembourg were studied under controlled boundary conditions using natural water and sediment from the study site. The redox conditions were controlled by adding nitrate to the inflowing process water in stepwise decreasing concentrations. The pharmaceuticals showed a huge variation of retardation during the experiment. Especially for sulfamethoxazole the temporarily established denitrifying conditions had a strong influence on the transformation of this compound. It was demonstrated that changes in nitrate concentrations in the aquifer can have a strong influence on the degradation behaviour of the investigated pharmaceuticals. This study therefore significantly contributed to the understanding of the transport and degradation behaviour of the studied pharmaceuticals.

Chapter 5

A new approach to derive seepage rates from a time series of thermal records is presented in this study. Surface water temperature and groundwater temperatures at different depths and distances from the stream were recorded at the field site in Luxembourg over a period of two years. To obtain daily seepage rates, the diurnal frequency components from these highly non-stationary signals (e.g. due to seasonal variations and influence from flood events in the stream) were extracted. This was done using the continuous wavelet transform. In the next step the one-dimensional analytical solution of the heat-transport equation was used to calculate seepage velocities based on the time lags and the amplitude ratios of two temperature signals. When compared with Darcy velocities that were calculated using hydraulic data of the riverine groundwater level and the stream, the seepage velocities appear to be too high. However, both indicate the dominance of effluent aquifer conditions at the investigated field site. The presented approach of the continuous wavelet transform is quite new for this application in hydrological sciences and seems to be an appropriate method also for other study sites to detect effluent/influent aquifer conditions and to calculate seepage rates.

Chapter 6

In this chapter the results and conclusions of the four manuscripts are summarised and discussed. Furthermore, open questions are addressed and recommendations for future studies are given.

Please note that as a result of the cumulative nature of this thesis, references are provided at the end of every chapter.

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Chapter 2

2 Investigative approaches to determine exchange processes in the hyporheic zone of a low permeability riverbank

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2.1 Abstract

The hydraulic and hydrochemical interactions of surface water and groundwater in the riverbank of an alluvial stream in the Grand Duchy of Luxembourg were investigated. Hydraulic conductivity in the riverbank is low and the aquifer is confined. Gauged surface-water levels and groundwater levels were recorded over several months to observe potential effluent and influent aquifer conditions. Water samples were taken under different hydraulic conditions in the stream and from three observation wells in the riverbank. Samples were analysed for inorganic parameters and selected dissolved pharmaceuticals. The recorded groundwater levels in the riverbank responded almost without delay to changes in stream stage, which is very dynamic. Frequent changes from effluent to influent aquifer conditions were observed. The analyses for selected ions and pharmaceuticals support the assumption that the pharmaceutical compounds enter the riverbank via the stream only. The chosen trace organics are therefore suitable as anthropogenic tracers for groundwater and surface water interactions at this field site. They prove that water exchanges also take place in riverbanks even where the hydraulic conductivity is low and for this reason indicate the existence of a hyporheic zone in the investigated section of the stream.

2.2 Introduction and state of the art

The interaction of surface water and groundwater is a subject of recent research worldwide. The hyporheic zone, the area in the vicinity of streams where groundwater and surface water mix, has been recognised for its importance regarding composition and quality of surface water (Cardenas 2009; Hancock et al. 2005; Sophocleous 2002). To understand the processes on this scale, knowledge of groundwater flow paths and their linkage to streams as well as exchange rates between surface water and groundwater and the mechanisms that generate spatial and temporal variations is required (Wroblicky et al. 1998). In the case of bank filtration, hyporheic processes have to be considered as well (Massmann et al. 2009). The hyporheic zone is a unique habitat for a diverse invertebrate community and therefore understanding the biological processes taking place is also important (Fraser et al. 1996).

Knowledge of the chemical and the hydraulic properties of this zone is necessary since they control these processes.

It has been assumed that in the humid climatic zone, generally, effluent conditions are observed; the groundwater infiltrates to surface water resulting in a gaining stream. However, several studies (Larkin and Sharp 1992; Woessner 2000) show that this assumption may have to be reassessed. A simplified flow from topographically high to topographically low areas can only be assumed for regional flow systems; local flow systems are much more complex (Winter 1999). Within a relatively short section of a river channel there may be regions where the stream gains water or loses water (Woessner 2000). Due to this fact the flow regime of groundwater and surface water changes from effluent to influent and vice versa along the river and over time, resulting in a very dynamic system.

The geology and morphology of the catchment and the streambed are important factors that characterise the hyporheic zone. However, the extent of this zone is often difficult to assess, as its size can vary laterally, vertically, and over time. Wondzell and Swanson (1999) point out that variations in hydraulic heads within the floodplain cause changes in the extent of the hyporheic zone and therefore have great influence on flow paths of groundwater. Furthermore, they describe the impact on the ecosystem in the riparian zone resulting from changes in volume and retention time of water in the hyporheic zone.

It is also important to determine whether groundwater enters the stream both via the streambed and the riverbank or by only one of these two interfaces. Langhoff et al. (2006) distinguished flow directly through the streambed and superficial flow or a combination of these. They observed seepage entering the stream through the streambed, seepage through the stream banks and also overbank flow during field investigations.

The interaction between surface water and groundwater is not only important for the groundwater movement but for the transport of solutes as well. Tremolieres et al. (1994) studied the influence of the river Ill (France) on surrounding groundwater and observed that polluted river water with high contents of ammonium, phosphate, and mercury infiltrated into groundwater. Furthermore, a variety of organic compounds has been detected in surface water and groundwater. Among those are several groups of pharmaceuticals from human medical use (Halling-Sorensen et al. 1998;

Heberer et al. 2002; Kummerer 2009; Loos et al. 2009; Loos et al. 2010; Nikolaou et al. 2007).

Therefore, the fate and transport of mobile trace organics, such as pharmaceuticals, at the surface water/groundwater interface may help to elucidate the processes during water exchange. Strauch et al. (2008) used pharmaceuticals to demonstrate anthropogenic impacts on groundwater and regarded them as suitable for tracing anthropogenic emissions into the urban water cycle.

The aim of this study was the identification of transport processes in the hyporheic zone of a small catchment in the Grand Duchy of Luxembourg. The focus was on the lateral exchange between the stream and its riverbank at a small scale of a few meters. Selected pharmaceuticals which were detected in the surface water and in the local groundwater were used as tracers to document exchange processes at the interface of these two water bodies. Variations of hydraulic head and concentrations of pharmaceutical compounds were evaluated over time.

The stream site in Luxembourg has already been the subject of several studies (Pailler et al. 2009a; Pailler et al. 2009b; Pfister et al. 2002) where variations of pharmaceutical concentrations and fluxes during flood events were analysed in the surface water. The concentrations of the investigated pharmaceuticals were highly variable during these events (Pailler et al. 2009a). However, information on the groundwater adjacent to the stream and its interaction with the surface water is missing. To close this gap, time series of hydraulic and chemical measurements in the surface water were combined with sampling of groundwater in the adjacent riverbank with the aim of identifying appropriate indicators for exchange processes of surface water and groundwater.

2.3 Study site

The investigation area is located around a stream gauge in Pontpierre southwest of Luxembourg City in the Grand Duchy of Luxembourg (Fig. 2-1). The Mess stream has a surface catchment area of 32.5 km². The catchment is underlain by Liassic rocks of the sedimentary Paris Basin comprising marls and marly sands. Alluvial sediments occur along the stream and cover 7% of the surface area. About 9.6% of the area is covered by housing, and the remaining area consists of grassland (58%),

arable land (22.7%), and forests (9.7%). Runoff from roads, effluents from small industries and untreated wastewater from farms influence the river water quality. Additionally, there is a mechanical-biological wastewater treatment plant in the village Reckange (Fig. 2-1). Housing areas are drained by a combined sewage water system with nine storm control reservoirs. This wastewater treatment plant and the storm water draining directly from the sewer system are the main sources for the detected pharmaceuticals (Pailler et al. 2009a).

The streambed at the field site cuts approximately 1.8 m into the gently sloping land surface and has a steep bank slope. The geological cross section of the riverbank (Fig. 2-2) shows mainly three layers that follow more or less the topography. At the bottom is a silty clay and fine sand layer with a thickness between 2.2 and 3.3 m, representing the final depth of the two boreholes close to the river (wells A and B). Above this is a layer of clay with fine sand and medium sand, with an average thickness of 0.8 m. On top is a clayey layer with fine and medium sand, with an average thickness of about 0.4 m. At a distance of 2.5 m from the bank (well C) a silty and gravelly clay and fine sand layer was reached at 4.0 m below ground surface (bgs) up to the final depth of 4.6 m bgs.

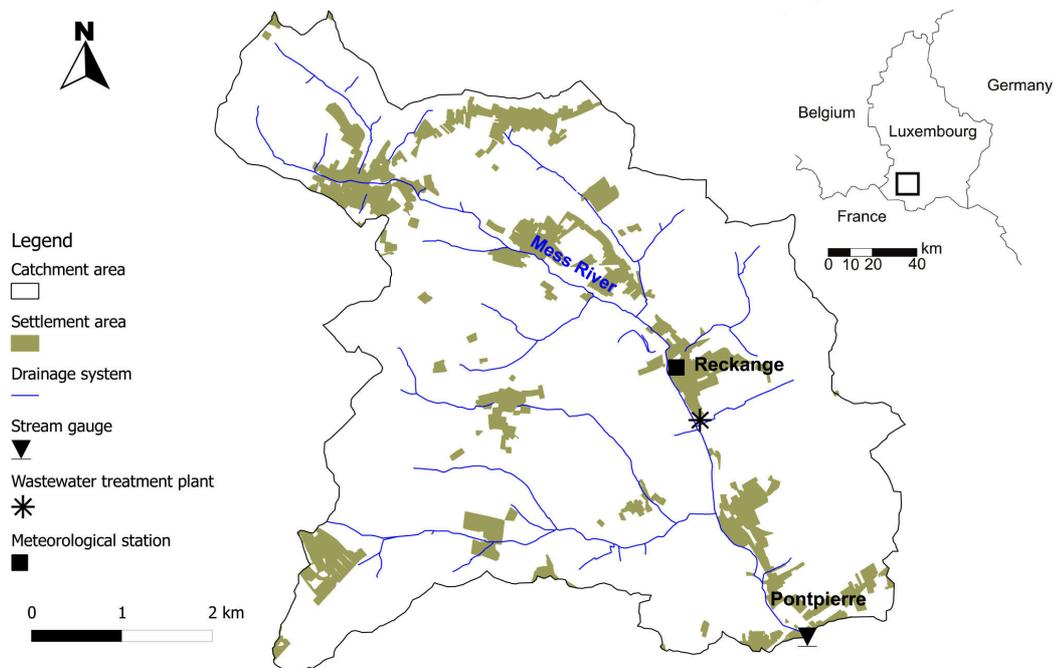


Fig. 2-1 The Mess basin: drainage system, settlement areas, and measurement network.

The morphology on both sides of the river is similar and the streambed in this section is more or less straight. Geological properties and layers can be assumed to be similar for both riverbanks. The chosen profile therefore is assumed to be representative for the stream. Investigations of the streambed at the field site prior to this study revealed a clogged bottom.

The water levels for both the surface water and groundwater are very dynamic: the water level in the stream varied during the investigation period of six months by 1.95 m with a low flow stream stage of 0.15 m in relation to the stream-gauge zero. Groundwater level fluctuations decrease with the distance from the stream from 1.84 m to 1.07 m in well A to C. During high-water peaks the investigated part of the riverbank is temporarily flooded. Under low-water conditions the Mess is a gaining stream and the piezometric surface is located in the middle layer of clay with fine sand and medium sand (Fig. 2-2).

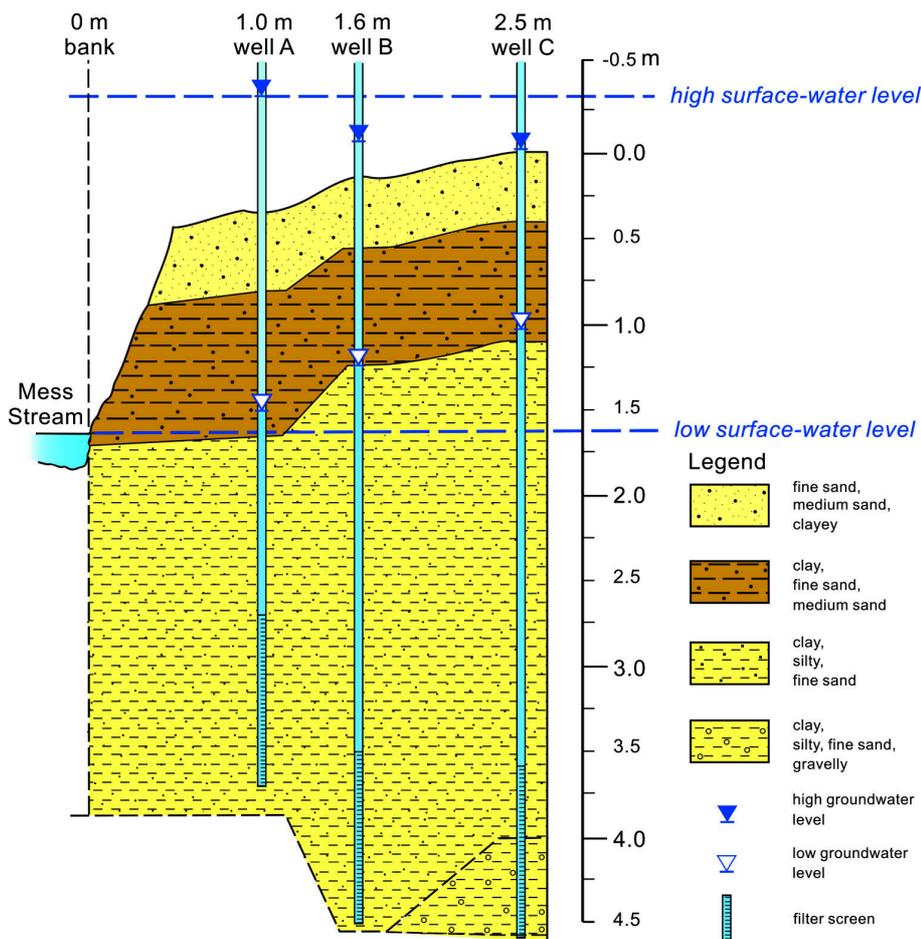


Fig. 2-2 Geological cross section of the field site including the observation wells (A, B and C), and high and low levels of groundwater and surface water.

2.4 Materials and methods

During the investigation period relevant parameters such as surface water level and precipitation at the field site were measured continuously. Groundwater and surface water samples were taken and analysed regularly.

The stream gauge (ISCO 4120 flow logger, pressure probe) in Pontpierre registers 15 min-average water levels. A meteorological station of the Administration des Services Techniques de l'Agriculture (Agriculture Administration) is located in Reckange, about 3 km north of the field site (Fig. 2-1). Relevant parameters such as air temperature and humidity (both 2 m above ground), and rainfall (1 m above ground) are recorded in 10 min intervals. For this study day-values for precipitation were calculated.

Three observation wells (50 mm in diameter) were installed in the riverbank close to the stream gauge at a distance of 1.0 m (well A), 1.6 m (well B) and 2.5 m (well C) from the riverside (Fig. 2-2); they are grouped as a triangle with a distance of 2.5 to 4.0 m between the wells, respectively.

The wells reach a maximum depth of 3.5 (well A) and 4.5 m bgs (wells B and C) and are each equipped with a 1-m filter screen at the bottom and solid pipe above, both PVC tubes. The wells are protected against inflow from the surface during flood events by 2 m long steel casings (75 mm in diameter) which reach at least 0.5 m into the ground and are covered with steel caps. For measurements of hydraulic head all wells were equipped with pressure probes (OTT Orphimedes) which record the water level every 30 min.

Groundwater samples were taken from the observation wells using a peristaltic pump (Eijkelkamp compact). After measuring the static water level in the well with a water level meter, a polyethylene tube was installed above the filter screen. To minimize the impact on the groundwater flow regime low-flow sampling was conducted with a pumping rate of 1 L min⁻¹. The water from the well was pumped through a flow-through cell, where the physicochemical parameters (pH, electrical conductivity, redox potential and dissolved oxygen) were measured using field devices from WTW (Wissenschaftlich Technische Werkstaetten). Pumping was operated until the physicochemical parameters were constant to assure a representative sample. The samples for the inorganic analyses were filtered with 0.45 µm cellulose acetate filters, preserved on-site, and stored in PET-bottles. Samples for the analyses of pharma-

ceuticals were taken using glass bottles, brought to the laboratory immediately and then filtered through 0.45 µm cellulose acetate filters. All samples were stored in a cool box and light-protected directly after sampling.

Surface water samples were taken every two weeks from July 2009 until April 2010, with longer intervals during winter. Groundwater was sampled every two months from October 2009 until April 2010, as slow changes in composition due to the low permeability of the sediments were expected.

Analyses for ions were performed with inductively coupled plasma emission spectroscopy (ICP-AES - Trace Scan Thermo Jarrell (cations)), atomic absorption spectroscopy (AAS - Analytik Jena NovAA 400G (cations)), and Dionex DX 120 (anions). For the analysis of pharmaceutical compounds the water samples were adjusted to a pH-value of 2 and then extracted by solid-phase extraction (SPE) using a non-encapped reversed phase sorbent. Before extraction, the samples were spiked with a surrogate standard for quality control and afterwards analysed using liquid chromatography – mass spectrometry (LC-MS/MS). The analytic methods for the pharmaceutical substances are described in detail by Pailler et al. (2009b). The detection limit for the chosen pharmaceuticals with this method is 0.3 ng L⁻¹.

Four pharmaceutical compounds were analysed in this study: sulfamethoxazole, ibuprofen, diclofenac, and 4'-hydroxy-diclofenac. These compounds are all soluble in water. Sulfamethoxazole is an antibiotic which belongs to the sulfonamides, a group of antibacterials. It is prescribed as a combination product with trimethoprim for treatment of human urinary tract infections but also in veterinary medicine. Ibuprofen is a widely used nonsteroidal anti-inflammatory drug with analgesic and antipyretic properties. Diclofenac also is a nonsteroidal anti-inflammatory drug prescribed as an analgesic and for reduction of inflammation. 4'-hydroxy-diclofenac is a metabolite of diclofenac, which is readily metabolised in the human body.

2.5 Results

2.5.1 Hydraulic measurements

The first step in understanding the surface water/groundwater system and its dynamic as a whole is the acquisition of knowledge of the hydraulic properties. Therefore, water levels in the three wells and in the stream were levelled relative to the zero point of the stream gauge to allow a comparison of the measured values. Fig. 2-3 shows the hydrographs of groundwater and surface water, and the daily precipitation from October 2009 until April 2010. Low water periods are sparse in the stream: from the beginning of the hydrological year in November 2009 onwards, the stream stage is very dynamic due to only short periods without precipitation. Five major flood events, which flood the field site including the observation wells partly or completely, were observed: 1.68 m on 27 November, 1.99 m on 25 December, 1.45 m on 29 December, 2.09 m on 3 February, and 1.82 m on 28 February.

It is obvious that groundwater levels follow the increase and decrease in stream stage almost without delay. However, the amplitude of the hydraulic signal is more and more damped with increasing distance from the bank. This is illustrated by the different ranges of the recorded water levels: the stream stage has a range of 1.95 m, the well A 1.84 m, the well B 1.29 m and the well C only 1.07 m. The highest and lowest groundwater and surface water levels are also plotted in the cross section in Fig. 2-2. In general the piezometric surface has a steep incline in the riverbank, following the topography during low water.

To identify effluent and influent aquifer conditions in the investigated riverbank, hydraulic gradients between each well and the stream stage were calculated on the basis of the hydrographs in Fig. 2-3. The results are shown in Fig. 2-4 and demonstrate changes of the flow regime in the riverbank. In the well A the conditions often change from effluent to influent and vice versa. During 11% of the recorded period of half a year influent conditions (water flows into the aquifer) were observed and during 89% of the time groundwater flows towards the stream. In the wells B and C only short flood peaks lead to influent aquifer conditions resulting in effluent conditions during 99% of the observed period.

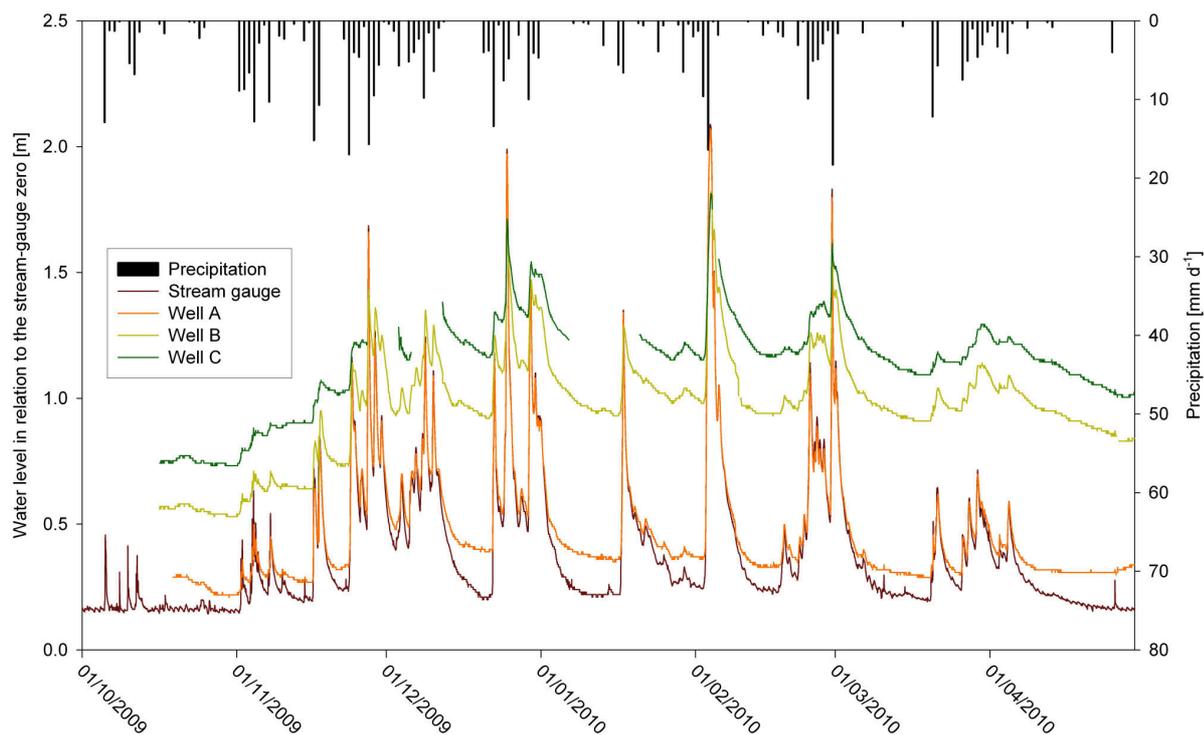


Fig. 2-3 Hydrographs of the observation wells and the surface water, and precipitation data; gaps on the hydrographs are due to temporary breakdowns of the pressure probes. Date format: dd/mm/yyyy.

Hydraulic conductivities were calculated from measurements of well water-level rise after pumping tests. Values are $1.3 \times 10^{-6} \text{ m s}^{-1}$ at well A, $5.0 \times 10^{-6} \text{ m s}^{-1}$ at well B, and $6.4 \times 10^{-7} \text{ m s}^{-1}$ at well C. The hydraulic conductivity of the aquifer has to be classified as poor and the aquifer is confined.

The hydraulic measurements for groundwater and surface water clearly indicate dynamic conditions in the whole system and, therefore, transport of solutes in and out of the bank is assumed. However, a high exchange or mixing of surface water and groundwater is expected only for well A as the influent periods at the other two observation wells are very short. It is assumed that flow of surface water into the river-bank takes place only during high water conditions.

2.5.2 Water analyses

To obtain mean, minimum and maximum concentrations of the pharmaceuticals, surface water samples were taken at the field site from July 2009 until April 2010. Sampling of groundwater began in October 2010 after suitable compounds were chosen with the help of the surface water analyses. Furthermore from October 2009 onwards groundwater and surface water were analysed for major anions and cations. Sam-

ples were taken at different water-level and discharge conditions in the stream. Tab. 2-1 contains the mean values and ranges for the analysed pharmaceuticals and ions, as well as the physicochemical parameters measured on-site.

Fig. 2-5 shows the time series of the surface water level and precipitation data; as the substances sulfamethoxazole, ibuprofen, diclofenac, and 4'-hydroxy-diclofenac were also detected in groundwater samples, the concentrations of these four compounds in the stream water are also plotted in Fig. 2-5. The figure indicates hydraulic conditions. Other pharmaceutical compounds like sulfathiazole, sulfamethazine, tetracycline, and chlortetracycline (Pailler et al. 2009a) were detected in the surface water samples but not included in this study since they are not relevant for the subject of exchange processes in the riverbank. The mean concentrations in the stream water are: 29 ng L⁻¹ sulfamethoxazole, 78 ng L⁻¹ ibuprofen, 95 ng L⁻¹ diclofenac, and 32 ng L⁻¹ 4'-hydroxy-diclofenac.

Rapid changes in concentrations of pharmaceutical compounds both on a seasonal and a daily scale were observed in surface water. The wastewater treatment plant upstream of the study site discharges treated water into the stream with a high degree of volume variability, but at approximately 340,000 m³ per year. In addition to this main source, nine combined sewer overflows and an unknown number of private discharges exist in the catchment. This makes it very challenging to quantify the mass flux of pharmaceuticals in water that enters the stream. Loads for selected flood events were calculated by Pailler et al. (2009a). For ibuprofen, loads range from 0.3 to 24.0 mg for a single event.

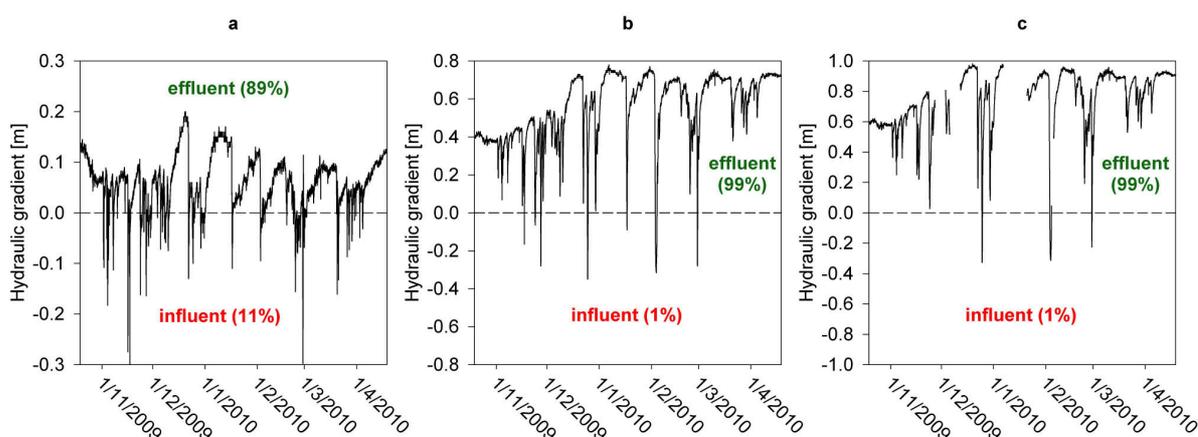


Fig. 2-4 Time series of hydraulic gradients in the riverbank indicating effluent and influent aquifer conditions, also in percentages: a 1.0 m from bank (well A), b 1.6 m from bank (well B), and c 2.5m from bank (well C). Note: different vertical scales.

Fig. 2-6 shows the concentrations for selected ions which were analysed between October 2009 and April 2010 for groundwater and surface water samples. The anthropogenic indicators nitrate and chloride are more concentrated in the stream than in the observation wells. Nitrate had a peak concentration of 32.0 mg L⁻¹ in November 2009 with decreasing concentrations until April 2010 which corresponded with a peak of 27.5 mg L⁻¹ in November 2009 in well A. The other two wells did not exceed 3.5 mg L⁻¹ of nitrate. Chloride had the highest surface water concentrations in October 2009, an intermediate peak in November 2009, lowest concentrations in December 2009, and then increasing concentrations until April 2010. In contrast to nitrate this trend was not observed in well A. Although concentrations varied, a clear trend could not be identified; similarly for the chloride in the distant wells.

Tab. 2-1 Mean values and ranges of all analysed ions, pharmaceuticals, and physicochemical parameters in the surface water and the observation wells.

	Surface water		A – 1.0 m from bank		B – 1.6 m from bank		C – 2.5 m from bank	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range
Chloride [mg L ⁻¹]	43.0	26.2–61.2	19.9	17.2–21.9	22.0	19.8–25.3	23.8	18.0–32.4
Nitrate [mg L ⁻¹]	19.0	2.5–32.0	9.0	1.9–27.5	1.7	bdl–3.5	1.4	bdl–2.5
Sulphate [mg L ⁻¹]	9.0	43.1–87.6	287.9	217.1–327.2	374.4	366.6–396.7	392.4	352.2–435.8
Calcium [mg L ⁻¹]	91.0	73.2–107.7	185.5	156.0–211.4	208.2	187.7–221.6	213.8	190.9–235.1
Sodium [mg L ⁻¹]	32.7	16.9–45.4	40.5	35.0–45.1	44.9	43.5–46.4	44.4	41.8–46.4
Iron [mg L ⁻¹]	bdl	bdl	4.4	1.7–6.8	7.1	bdl–13.0	6.4	3.2–10.1
Sulfamethoxazole [ng L ⁻¹]	29	1–151	bdl	bdl–1	bdl	bdl–1	bdl	bdl
Ibuprofen [ng L ⁻¹]	78	bdl–421	5	bdl–17	4	bdl–17	1	bdl–2
Diclofenac [ng L ⁻¹]	95	bdl–828	4	1–11	3	1–5	2	bdl–5
4'-hydroxy-diclofenac [ng L ⁻¹]	32	bdl–138	2	bdl–9	1	bdl–4	bdl	bdl
pH value	7.3	6.3–7.9	7.3	7.1–7.6	7.4	7.0–8.1	7.0	6.9–7.1
Electrical conductivity [μ S cm ⁻¹]	638	383–874	1,254	1,082–1,358	1,352	1,307–1,406	1,381	1,323–1,455
Redox potential [mV]	nd	nd	166	134–198	179	108–278	154	145–166
Dissolved oxygen [mg L ⁻¹]	nd	nd	2.0	0.7–2.8	1.4	0.9–2.0	0.6	0.2–1.1

bdl = below detection limit; nd = not detected

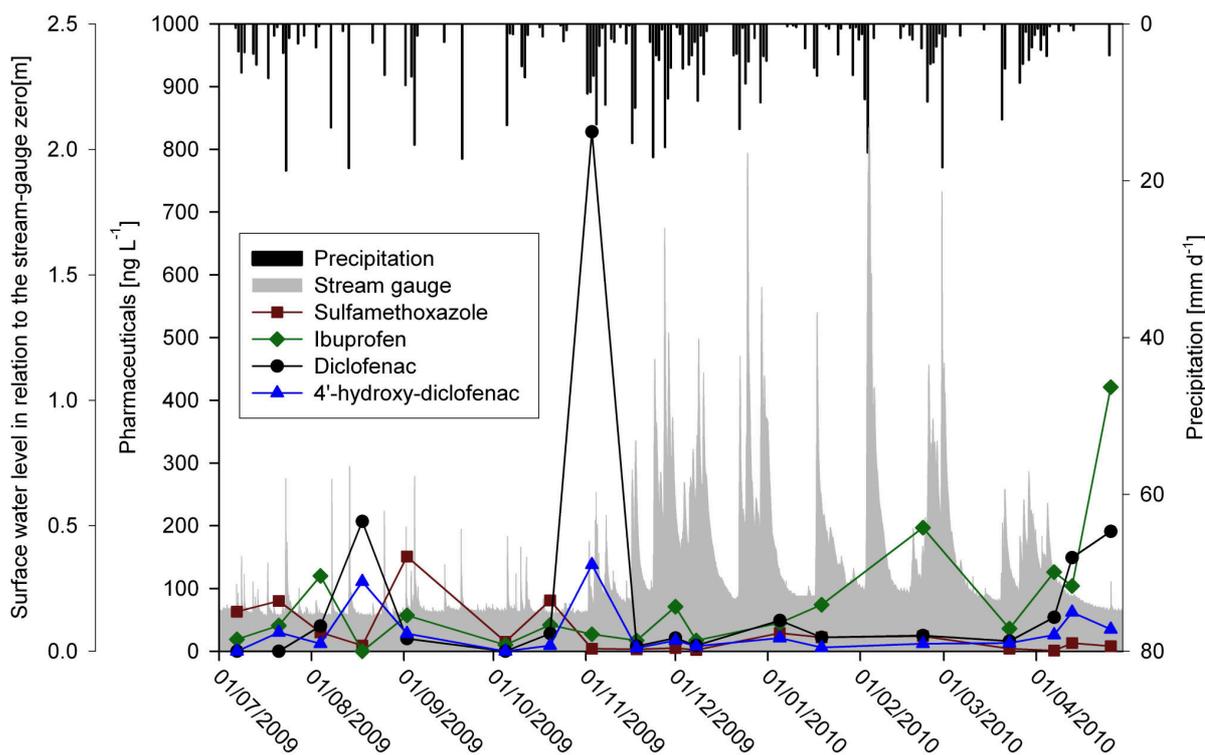


Fig. 2-5 Time series of analysed pharmaceuticals in the surface water, surface water level, and precipitation data.

Other ions indicative of mixing of groundwater and surface water are calcium and sulphate. Concentrations in groundwater are much higher than in surface water due to the higher mineralisation caused by the underlying marls. In addition gypsum lenses occur in the bedrock. This higher mineralisation is also demonstrated by the measured electrical conductivities. The mean value for the stream is $638 \mu\text{S cm}^{-1}$; mean groundwater electrical conductivities increase with distance from the bank from $1,254 \mu\text{S cm}^{-1}$ up to $1,381 \mu\text{S cm}^{-1}$ (for wells A to C). The mean calcium concentration in the surface water is 91.0 mg L^{-1} , while in groundwater mean concentrations increase with distance from the bank from 186 mg L^{-1} to 214 mg L^{-1} . Sulphate concentrations have an even higher gradient between surface water and groundwater. Mean concentrations in the wells range from 288 mg L^{-1} to 392 mg L^{-1} , also showing increasing concentrations with distance. Surface water concentrations reach 66.2 mg L^{-1} on average. Minimum calcium and sulphate concentrations were found in the groundwater sample from well A in November 2009. As concentrations rise again until April 2010 this suggests, together with the nitrate peak, an inflow of surface water to the aquifer at well A in November 2009. The distant wells do not show this behaviour for the mentioned ions. They, in contrast, have the highest concentrations for

calcium and sulphate in November 2009. Iron was always below the detection limit in the stream due to oxidation and precipitation, and reaches maximum concentrations up to 13.0 mg L^{-1} in groundwater.

The inorganic chemistry supports the assumption that significant exchange of surface water and groundwater mostly takes place at well A. This coincides well with the pattern of changes between effluent and influent conditions in the riverbank based on the hydraulic data. The two other wells do not show clear trends for the selected ions over time.

Fig. 2-7 shows the concentrations of the four pharmaceutical compounds (sulfamethoxazole, ibuprofen, diclofenac and 4'-hydroxy-diclofenac) which were detected both in groundwater and surface water for the investigation period from October 2009 until April 2010. The points are shown joined for surface water and separate for groundwater. To indicate the hydraulic conditions the surface water level is also plotted.

As described above, surface water concentrations for the four pharmaceuticals show a wide range from below detection limit up to more than 800 ng L^{-1} . Concentrations in the groundwater samples, apart from diclofenac, show a lower range of values from below detection limit (0.3 ng L^{-1}) up to 17 ng L^{-1} for ibuprofen. Concentrations in groundwater are, as expected (based on the hydraulic gradients), and are much lower than in the stream for all substances. Although concentrations are low and single flood events do not indicate trends in concentration, the more reliable mean values for ibuprofen, diclofenac and 4'-hydroxy-diclofenac show decreasing concentrations with increasing distance from the stream. This tends to justify the theory that there is an input of the pharmaceuticals from the stream into groundwater. Only a few samples do not fit this trend and show higher pharmaceutical concentrations in groundwater than in surface water. The highest values for all four pharmaceuticals in well A were measured in October 2009 which does not correspond with the analysed ion concentrations indicating an inflow of surface water in November 2009 (Fig. 2-6).

However, it is difficult to assess travel times of potentially infiltrating surface water. Although increases of groundwater level occur almost without delay in relation to changes in stream stage, a lag is expected in groundwater quality. Hydraulic conductivities are rather low and therefore stream water can infiltrate only slowly into the riverbank.

As the redox potential is a factor that influences the degradation of the detected pharmaceuticals, this parameter was measured on-site. Mean values in the wells are between 154 mV (at well C) and 179 mV (at well B). This indicates nitrate reducing conditions in groundwater. Mean dissolved oxygen contents drop from 2.0 mg L⁻¹ in well A to 0.6 mg L⁻¹ in well C, with low values between 0.7 mg L⁻¹ and 0.2 mg L⁻¹, respectively. This is also consistent with the high concentrations of iron reported for groundwater. In groundwater pH is neutral to basic with a range between 7.0 and 8.1 which demonstrates the high carbonate content in groundwater due to the marly bed-rock. Surface water pH values are more variable, from 6.3 to 7.9.

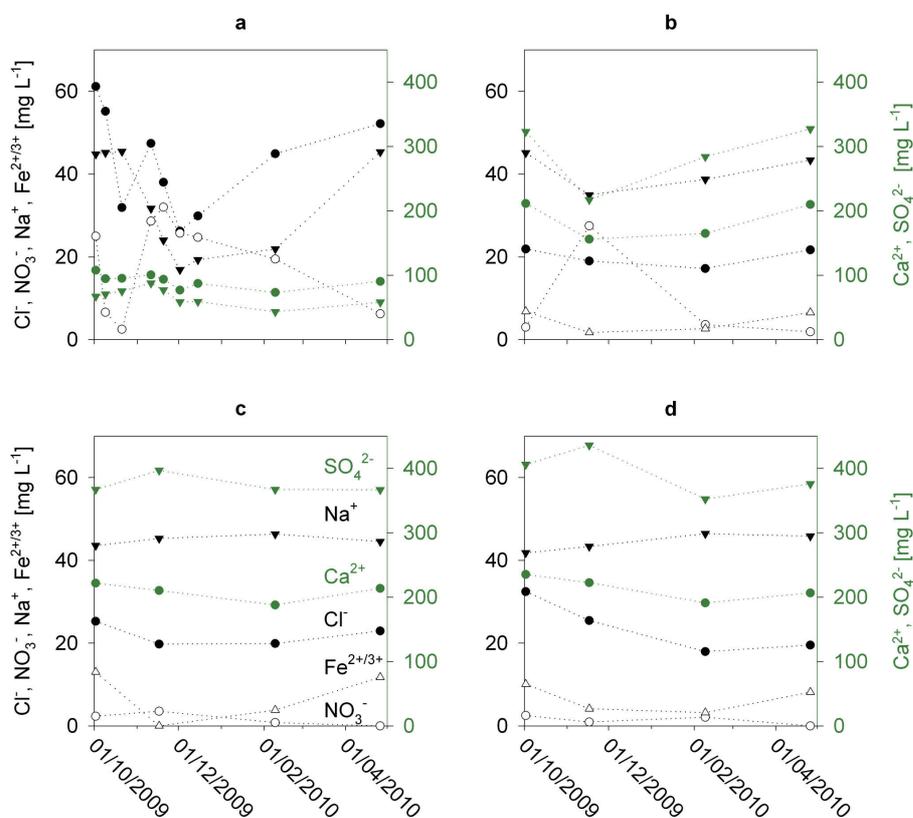


Fig. 2-6 Selected analysed ions: a in the surface water, b 1.0 m from bank (well A), c 1.6 m from bank (well B), and d 2.5 m from bank (well C).

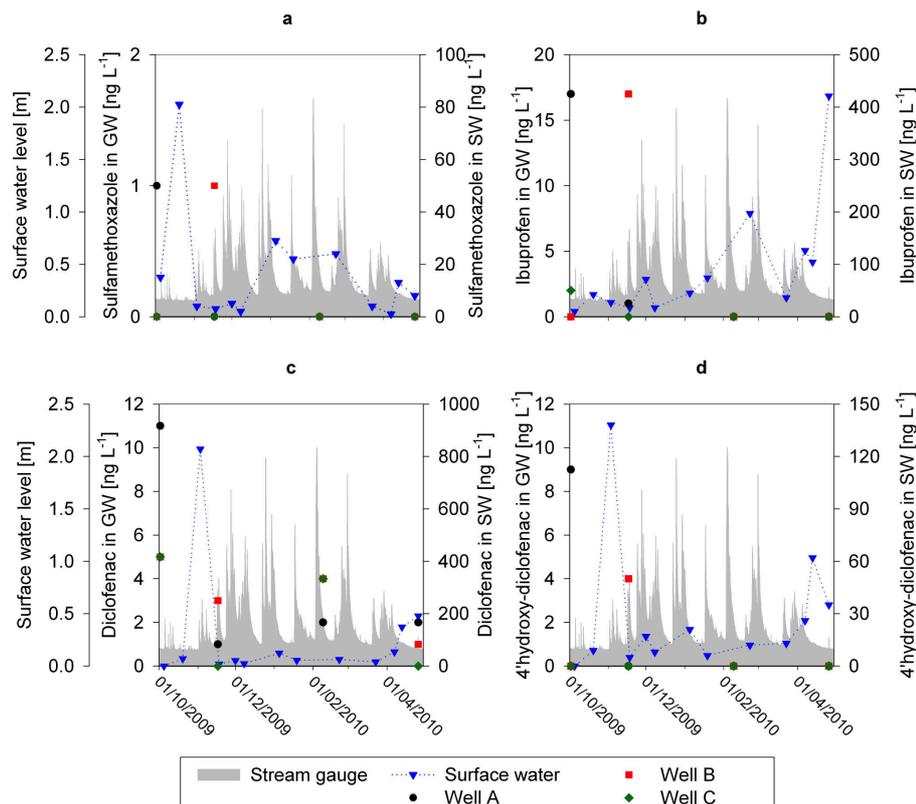


Fig. 2-7 Pharmaceuticals analysed in groundwater (GW) and surface water (SW), and surface water level: a sulfamethoxazole, b ibuprofen, c diclofenac, and d 4'-hydroxy-diclofenac.

2.6 Discussion

The results show that even in a riverbank with low hydraulic conductivity, exchange of surface water and groundwater takes place. Hydraulic measurements clearly demonstrate the reaction of the groundwater level to changes in stream stage. Hydraulic gradients between surface water and groundwater shift from effluent to influent aquifer conditions and vice versa during the investigation period. Frequencies of this shift vary for the different wells. In the well nearest to the stream (well A), flow direction changes once a week on average. For the other two wells the frequencies are much lower. Influent conditions occur every 4 weeks at well B and every 9 weeks at well C on average.

The assumption that surface water enters the riverbank for short periods is underlined by the water analyses for ions and pharmaceutical compounds which display changes in concentrations. These variations are traced back to an inflow of surface water of some kind to the observation wells. Analyses for the pharmaceutical compounds indicate an input from infiltrating stream water only. However, other pathways

may exist. Due to the temporary flooding of the wells a vertical inflow of surface water into the riverbank cannot be excluded. Also groundwater flow parallel to the stream can occur. Leaky sewers may contribute to input of pharmaceuticals in groundwater as well. The bottom of the streambed at the field site is clogged and therefore assumed to be impermeable and not relevant for exchange of groundwater and surface water at the field site.

The rate and mechanisms of degradation of pharmaceuticals are sensitive to redox potential and pH. In contrast to ibuprofen and diclofenac, which are degradable under aerobic conditions (Roembke et al. 1996; Schmidt et al. 2004), sulfamethoxazole is only slightly degradable under these conditions (Grunheid et al. 2005; Heberer et al. 2008; Schmidt et al. 2004). Ibuprofen and diclofenac are also degradable under anaerobic conditions but more slowly than under aerobic conditions (Schmidt et al. 2004) whereas sulfamethoxazole is more rapidly degraded in anaerobic conditions. Heberer et al. (2008), who investigated the redox sensitivity of antimicrobial residues during bank filtration, found an elimination for sulfamethoxazole of 99% under anoxic conditions but only 52% if temporarily under oxic conditions. The prevailing reducing conditions in groundwater at this site could explain the absence of sulfamethoxazole in the wells, although detected in the stream, and the detection of ibuprofen and diclofenac in groundwater.

As each observation well is only equipped with one filter screen at one depth, vertical zones of redox potential could not be detected. However, zoning of redox potential might be important for the degradation of the investigated pharmaceuticals. A clear horizontal trend for the redox potential in the riverbank could not be observed in the field.

The changes in concentration of diclofenac and its metabolite 4'-hydroxy-diclofenac both in surface water and groundwater correspond very well. This may indicate the simultaneous input of both substances into the stream or the degradation of diclofenac both in surface water and groundwater, as peaks and low concentrations occur at the same time (Fig. 2-5 and Fig. 2-7). Since sorption is low for all detected pharmaceuticals (Christian et al. 2003; Loeffler et al. 2005; Roembke et al. 1996; Scheytt et al. 2005) concentrations in groundwater are considered to be uninfluenced by sorption and desorption on the sediment. Especially for diclofenac, a high mobility is reported for sediments at neutral pH values (Roembke et al. 1996).

The concentration ranges of the analysed pharmaceutical compounds are very wide. For ibuprofen, diclofenac and 4'-hydroxy-diclofenac minimum values are below the detection limit and maximum values exceed the mean values by up to a factor of 9. This corresponds with the results of Pailler et al. (2009a) who investigated chemographs of pharmaceuticals in the stream during single flood events at this field site. They identified significant changes in concentrations during the investigated floods: maximum values of ibuprofen, diclofenac and sulfamethoxazole exceeded mean values by up to a factor of 6.

Some analyses of the pharmaceutical compounds plotted in Fig. 2-7 yield higher values for groundwater than for surface water or higher values with increasing distance from the stream. This apparent anomaly may be due to the low sampling frequency and the fact that surface water and groundwater were sometimes sampled on different days.

An understanding of the processes involved during the passage of water from the riverbank to the groundwater is crucial with respect to drinking water supply and bank filtration. Several studies recently investigated the behaviour of pharmaceuticals during bank filtration, demonstrating the relevance of this topic (Heberer et al. 2008; Massmann et al. 2009; Müller et al. 2010; Varga et al. 2010).

2.7 Conclusion

Defining the hyporheic zone as the area where groundwater and surface water mix, the water samples from the wells document the existence of a hyporheic zone in the investigated riverbank. Because hydraulic gradients between the groundwater and surface water change the aquifer conditions from effluent to influent and vice versa, the extent of the hyporheic zone is dynamic.

The chosen pharmaceuticals that are detected in the wells are regarded as characteristic for the field site and suitable as anthropogenic tracers for surface water/groundwater interactions. As all analyses emphasise an entry via the stream only, changes in concentrations of the pharmaceuticals can be interpreted as exchange of groundwater and surface water. This study also revealed that low permeability riverbanks are relevant for hyporheic exchange processes.

2.8 Acknowledgements

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Chapter 3

3 Using selected pharmaceutical compounds as indicators for surface water and groundwater interaction in the hyporheic zone of a low permeability riverbank

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3.1 Abstract

This study investigates the applicability of selected pharmaceutical compounds (e.g., sulfamethoxazole, carbamazepine, ibuprofen) as anthropogenic indicators for the interaction of surface water and groundwater in the hyporheic zone of an alluvial stream. Differences in transport behaviour and the resulting distribution of the pharmaceuticals in the riverine groundwater were evaluated. The investigated field site in the Grand Duchy of Luxembourg, Europe is represented by low permeable sediments and confined aquifer conditions. Water samples from single-screen and multi-level observation wells installed in the riverbank at the field site were taken and analysed for selected pharmaceuticals and major ions for a period of six months. Surface water and groundwater levels were recorded to detect effluent and influent aquifer conditions. Nearly all pharmaceuticals that were detected in the stream were also found in the riverine groundwater. However, concentrations were significantly lower in groundwater than in surface water. A classification into mobile and sorbing/degradable pharmaceuticals based on their transport relevant properties was made and verified by the field data. Gradients with depth for some of these pharmaceuticals were documented and a more detailed understanding of the system stream/riverbank was obtained. It was demonstrated that the selected pharmaceutical compounds can be used as anthropogenic indicators at the investigated field site. However, not all compounds seem to be suitable indicators as their transport behaviour is not fully understood.

3.2 Introduction

Occurrence and behaviour of pharmaceutical compounds in the aquatic environment are more and more discussed by the research community as well as by regulatory authorities and water suppliers. As pharmaceuticals pose a potential risk, e.g. for drinking water supply, knowledge about their fate in the water cycle is crucial. Up to now they have been detected in the effluent of wastewater treatment plants (WTPs), in surface waters, in groundwater (Halling-Sorensen et al., 1998; Loos et al., 2010), and even in drinking water (Heberer et al., 2002).

This ubiquitous presence of pharmaceuticals in the aquatic environment encourages the investigation of the surface water groundwater interface as it connects these two

water bodies and can – depending on its shape and composition – work as a natural reservoir, source, reactor, and also as a barrier for pharmaceuticals and other compounds. The main input path for pharmaceuticals into surface water is via the effluent of WTPs (Gros et al., 2007; Paxeus, 2004). Once in the surface water, the organic compounds can enter the aquifer when surface water and groundwater are hydraulically connected (Müller et al., 2011). In this case the two water bodies and the dissolved solids mix at the interface. This area below and beside a stream or lake where interaction and exchange processes are observed is called the hyporheic zone, a term which was introduced by Orghidan (1959). However, the shape and the extent of this zone is often difficult to assess and variable over time (Woessner, 2000; Wondzell and Swanson, 1999). Heterogeneities of streambed and riverbank also have to be considered as they can have a significant influence on hyporheic exchange (Fleckenstein et al., 2006; Kalbus et al., 2008). There are various approaches to investigate processes in the hyporheic zone like hydraulic modelling (Cardenas, 2009; Wondzell et al., 2009), temperature measurements (Anderson, 2005; Anibas et al., 2011), and the use of indicative compounds like pharmaceuticals or isotopes (Baskaran et al., 2009; Strauch et al., 2008). Reviews and studies that name and compare different methods are provided, e.g., by Briddock (2009), Engelhardt et al. (2011), and Kalbus et al. (2006).

In this study, the interaction of surface water and groundwater in the riverbank of an alluvial stream was investigated at a field site in the Grand Duchy of Luxembourg using selected pharmaceutical compounds as anthropogenic indicators. Ongoing improvements of the analytical methods currently allow a detection of these compounds on the ng L^{-1} -scale (Nödler et al., 2010; Pailler et al., 2009b). This fact has opened new research possibilities using these organic compounds as environmental indicators even at very low concentration (Clara et al., 2004; Müller et al., 2012). For this work the distribution and mobility of selected pharmaceuticals – that were already detected both in surface water and groundwater samples in previous studies carried out at the field site (Banzhaf et al., 2011; Pailler et al., 2009a) – were monitored in the stream and the adjacent groundwater. Furthermore, the hydraulic conditions of the system stream/groundwater were investigated as they are essential for the understanding of surface water and groundwater interaction. The aim was to gain deeper knowledge of spatial and temporal variability of these compounds in the investigated riverbank and to test their potential use as anthropogenic indicators for

surface water groundwater interaction at this field site. Therefore the concentration distribution of the selected pharmaceutical compounds in the riverbank was evaluated regarding their transport-relevant properties like sorption and degradation.

3.3 Study area

The investigated field site is located at a stream gauge in Pontpierre southwest of Luxembourg City in the Grand Duchy of Luxembourg (Fig. 3-1). The catchment of the Mess basin at the stream gauge covers an area of 32.5 km². It is underlain by Liassic rocks of the sedimentary Paris Basin, represented by marls and marly sands. Along the stream alluvial sediments are found, which cover 7% of the surface area. The land use is: grassland (58%), arable land (22.7%), forests (9.7%), and residential area (9.6%). River-water quality is influenced by runoff from roads, effluents from small industries, and untreated wastewater from farms. In addition, there is a mechanical-biological WTP in the village Reckange approximately 2.5 km upstream of the study site (Fig. 3-1). A combined sewage-water system with nine storm control reservoirs drains the housing areas. The WTP and the storm water which is draining directly from the sewers are the main sources for the detected pharmaceutical compounds (Pailler et al., 2009a). Diffuse sources for pharmaceuticals, e.g. from agricultural use, can not be excluded. However, investigations in an adjacent catchment (2 km away) with similar land use, similar geology, and also wastewater influence showed, that there were no pharmaceuticals present in groundwater in larger distances from the stream.

Fig. 3-2 contains a schematic map and a geological cross section of the field site which also shows the steep bank slope of the streambed, cutting approximately 1.8 m into the gently sloping land surface. The cross section displays mainly three layers which follow the topography of the riverbank. The deepest layer consists of silty clay and fine sand and has a thickness of 2.2 to 3.3 m. Above follows a clay layer with fine sand and medium sand and an average thickness of 0.8 m. The uppermost layer consists of clayey fine sand and medium sand and has an average thickness of 0.4 m. At well C (2.5 m from the bank) a silty and gravelly clay and fine sand layer was reached at 4.0 m below ground surface (bgs) up to the final depth of 4.6 m. The investigated section of the stream is supposed to be representative for the study area

as the morphology on both sides of the stream is similar and the streambed in this section is more or less straight.

Water levels of surface water and groundwater are dynamic. The stream stage during the investigation period of six months ranged from 0.12 m to 1.87 m above the stream-gauge zero. Fluctuations of the groundwater level are smaller and decrease with increasing distance from the bank. From 0.28 m/1.84 m at well A to 0.72 m/1.61 m at well C, respectively. During flood peaks, the riverbank is temporarily flooded and the flow direction in the riverbank is reversed to influent aquifer conditions. However, under baseflow conditions the Mess is a gaining stream with the piezometric surface located in the middle layer (Fig. 3-2).

Hydraulic conductivities calculated from measurements of well-water-level after pumping tests were $1.3 \times 10^{-6} \text{ m s}^{-1}$ at well A, $5.0 \times 10^{-6} \text{ m s}^{-1}$ at well B, and $6.4 \times 10^{-7} \text{ m s}^{-1}$ at well C (Banzhaf et al., 2011). Based on these values the hydraulic conductivity of the aquifer was classified as low. The aquifer is confined.

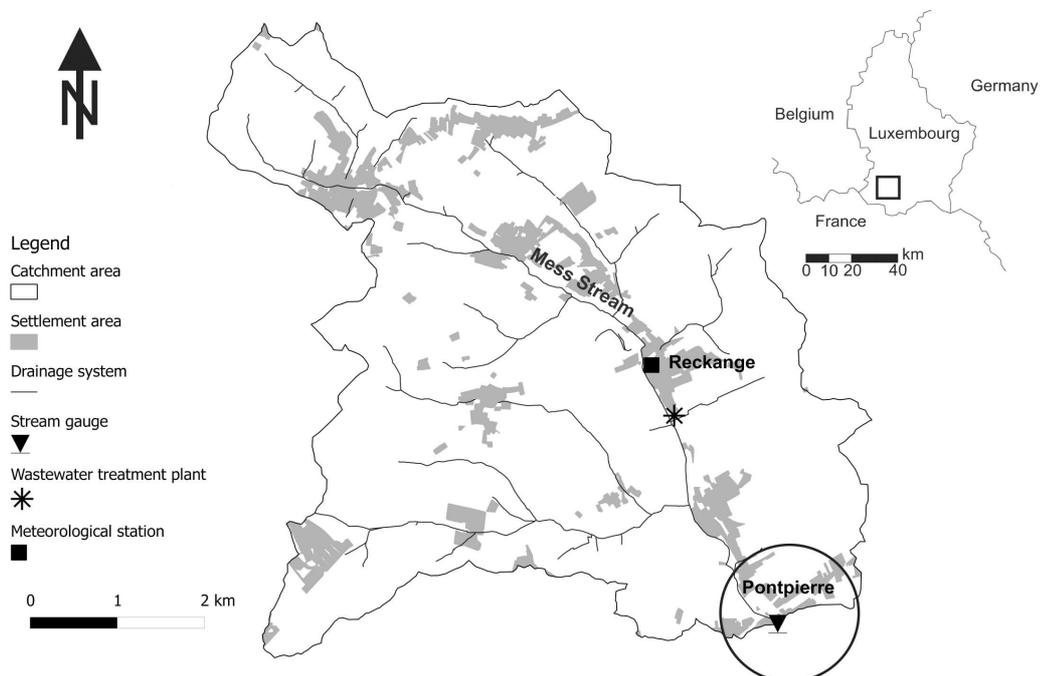


Fig. 3-1 Map of the Mess Stream catchment: settlement area, drainage system, and measurement network; the field site is located at the stream gauge in Pontpierre (circle), modified from Banzhaf et al. (2011).

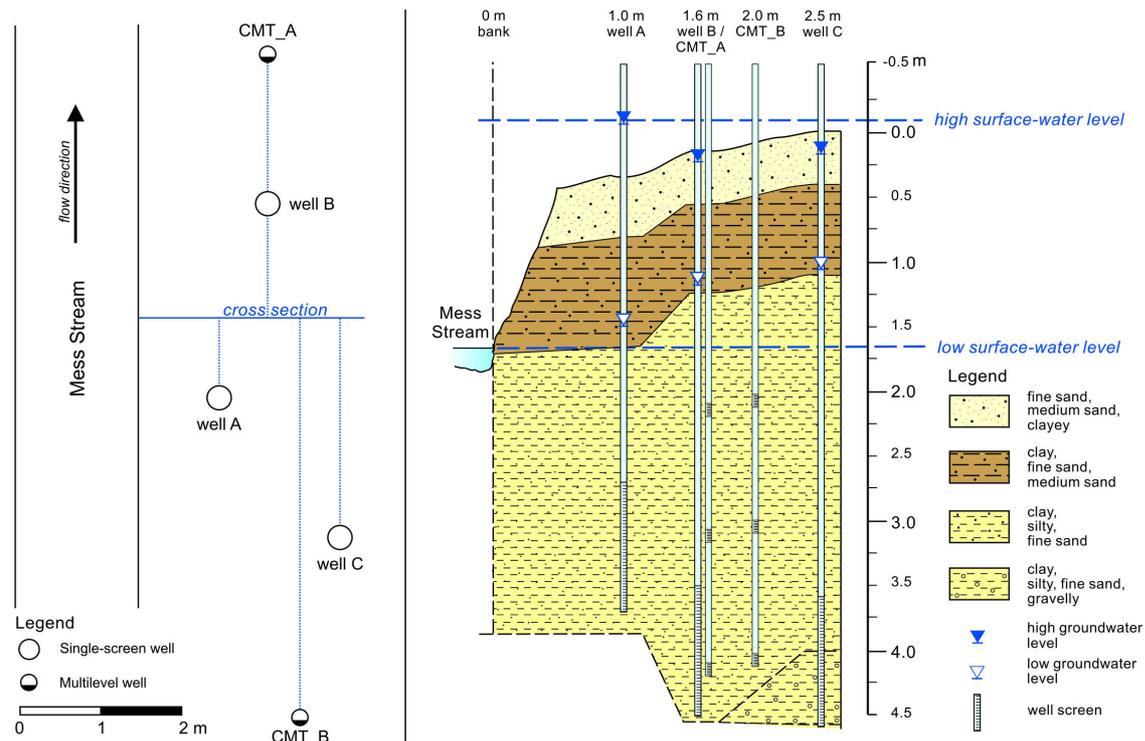


Fig. 3-2 Top view (left) and cross section (right) of the field site including the location of the observation wells, and highest and lowest levels of groundwater and surface water during the observation period, modified from Banzhaf et al. (2011).

3.4 Materials and methods

3.4.1 Field installations

The groundwater in the riverbank was sampled at single-screen and multilevel observation wells. Three single-screen wells were installed at a distance of 1.0 m, 1.6 m, and 2.5 m from the bank. They reach a maximum depth between 3.5 m bgs for well A and 4.5 m bgs for wells B and C. The casing consists of 50 mm PVC pipes and each well is equipped with a 1.0 m long screen at the bottom. Two multilevel-wells were installed at a distance of 1.6 m and 2.0 m from the bank and both reach a depth of 4.0 m bgs. These Continuous Multichannel Tubing (CMT) wells from Solinst Canada Ltd., Georgetown, Ontario, Canada are made of one single tube with a diameter of 28 mm that contains three separate channels with a diameter of 10 mm each. The CMT-wells are equipped with three 10-cm well screens with a spacing of 1.0 m. The deepest sampling port is located at the bottom of each well. These lowermost screens of the CMT-wells (CMT_A_3, CMT_B_3) are installed at the same depth as the screens of wells B and C. The middle screens of the CMT-wells

(CMT_A_2, CMT_B_2) are at the level of the screen of well A and the uppermost screens (CMT_A_1, CMT_B_1) are located above. All wells are protected against inflow of surface water during flood events by a bentonite sealing of several decimetres at the top, 2 m steel casings which reach at least 0.5 m into the ground, and steel caps. For details of the installations refer to Fig. 3-2. This setup of sampling equipment allowed a comparison of horizontal (single-screen wells) and vertical (CMT-wells) gradients of pharmaceutical concentrations in the riverbank.

3.4.2 Hydraulic measurements

To understand the interaction of groundwater and surface water as one dynamic system, the hydraulic conditions have to be known. Hence, water levels of the three single-screen wells and the stream were monitored for the detailed investigation period of six months. All values were levelled relatively to the stream gauge zero to allow a correlation of the measurements.

The hydraulic conditions at the field site were determined by logging of surface water levels with a stream gauge (ISCO 4120 flow logger, Isco Inc., Lincoln, Nebraska, USA) and logging of water levels in the three single-screen wells with pressure probes (OTT Orphimedes, OTT Hydromet GmbH, Kempten, Germany, and UIT CTD, Umwelt- und Ingenieurtechnik GmbH, Dresden, Germany). The logging interval was 15 minutes (average values) for surface water and 30 minutes (individual values) for groundwater. Precipitation values (1 m above ground, 10-min intervals) were obtained from a meteorological station of the Administration des Services Techniques de l'Agriculture (Agriculture Administration) in Reckange about 3 km upstream of the field site (Fig. 3-1).

3.4.3 Sampling

As the two multilevel-wells (CMT_A and CMT_B) were installed later than the three single-screen wells (Wells A – C), this study focused on four sampling campaigns in June, August, October, and November 2010 (Fig. 3-3), comprising 35 groundwater samples in total. However, altogether, 47 groundwater (24 from the single screen wells and 23 from the multilevel-wells) and 21 surface water samples were taken at the field site between October 2009 and November 2010. Groundwater was sampled every seven weeks and surface water was sampled every two weeks over the whole period.

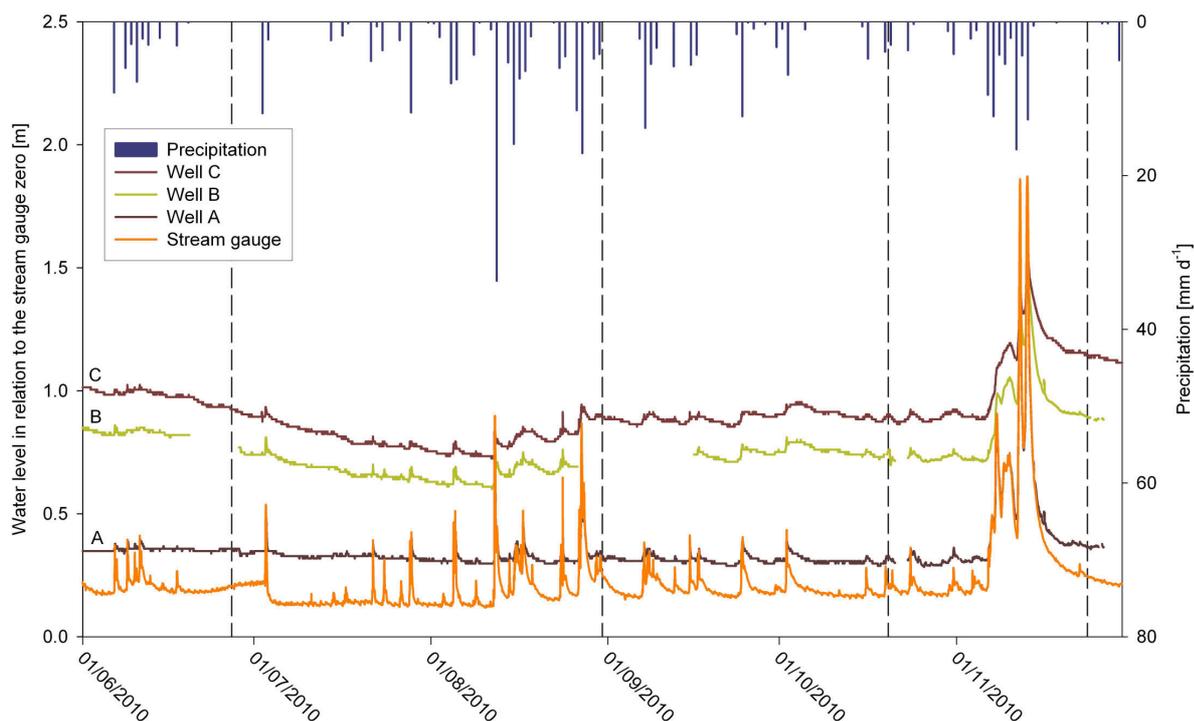


Fig. 3-3 Hydrographs of groundwater and surface water, and precipitation data; gaps on the hydrographs are due to temporary breakdown of the pressure probes. Dashed vertical lines indicate sampling campaigns. Date format: dd/mm/yyyy.

Bailer samples were taken from the stream and groundwater was sampled with a peristaltic pump (Eijkelkamp compact, Eijkelkamp Agrisearch Equipment, Giesbeek, The Netherlands). To minimize the impact on the flow regime, low-flow sampling was performed with a pumping rate of 1 L min^{-1} for the single-screen wells. For the sampling of the CMT-wells a flow-rate can not be given as the flow out of the CMT-wells was unsteady and very low. This is due to the short well screen in combination with the low hydraulic conductivity. The extracted groundwater was pumped through a flow-through-cell, where the physicochemical parameters (pH, electrical conductivity, oxidation reduction potential, and dissolved oxygen) were measured with field devices from Hach (HQ40d, Hach Company, Loveland, Colorado, USA) and WTW (340i, WTW Wissenschaftlich-Technische Werkstätten GmbH, Weilheim, Germany). Samples for the analysis of the pharmaceutical compounds were stored in glass bottles, brought to the lab within hours, and then filtered with $0.45\text{-}\mu\text{m}$ cellulose acetate filters. Samples for ions were filtered on-site with $0.45\text{-}\mu\text{m}$ cellulose acetate filters and stored in PET-bottles. Cation samples were acidified with nitric acid and anion samples were preserved with trichlorotrifluorethan immediately. All samples were stored light-protected in a cool box directly after sampling.

3.4.4 Selection of compounds and analysis

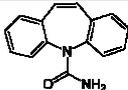
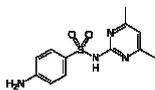
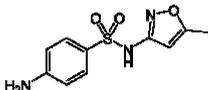
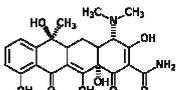
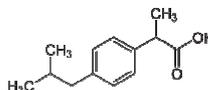
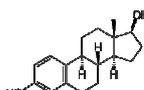
In this study 7 pharmaceutical compounds from four groups and one hormone were analysed: anticonvulsants (carbamazepine), sulfonamides (sulfamethazine and sulfamethoxazole), tetracyclines (tetracycline), analgesics (ibuprofen and diclofenac), and estrogens (17- β -estradiol). Carbamazepine is a widely applied anticonvulsant used to treat epilepsy, bipolar disorder, and trigeminal neuralgia. Sulfamethazine is a bacteriostatic reagent for treatment of humans for inhibition of folic acid synthesis in bacteria. It is also used as growth promoter in animals. Sulfamethoxazole is an antibiotic which is mainly used to treat infections of the urinary tract. It is often prescribed in combination with trimethoprim and is used both in human and veterinary medicine. Tetracycline is a broad spectrum antibiotic which is used to treat bacterial infections and can be used as an alternative to penicillin in case of allergic reactions, it is also used in veterinary medicine. Ibuprofen is a popular nonsteroidal anti-inflammatory drug with analgesic and antipyretic properties. Diclofenac also is a nonsteroidal anti-inflammatory drug. It is prescribed as an analgesic and to reduce inflammation. 17- β -estradiol is a mammalian estrogenic steroid and prescribed for the treatment of urogenital symptoms.

For this study the described pharmaceuticals were divided into mobile and sorbing/degradable compounds (Tab. 3-1). This simplified classification into two groups was based on the different transport relevant properties of the pharmaceuticals. First of all, all compounds are soluble in water in an amount which is magnitudes higher than analysed in all water samples (all analyses were on ng L⁻¹-scale), which is a prerequisite to use them as indicators. If evaluating the mobility of an organic compound the K_{OW} has to be considered as it has a strong influence. The K_{OW} is the octanol/water-partitioning coefficient which describes the proportion of the concentration of a compound in the two phase system octanol and water.

In general, substances with a lower K_{OW} are supposed to be more mobile than those with a higher K_{OW} (Scheytt et al., 2006). Tetracycline, though having a very low K_{OW} , is supposed to be more or less immobile (Pils and Laird, 2007). In addition, it has to be considered that ibuprofen and diclofenac show increasing mobility with increasing pH values as they are carboxylic acids (Scheytt et al., 2005b). When looking at the pH values which were measured in this study (chapter 3.5.2) this means that these two compounds might be more mobile than, e.g., carbamazepine at a pH of 8.2 while

less mobile at a pH of 7.0 although having a higher K_{OW} . The pK_a is an acid dissociation constant: the lower the pK_a the higher the extent of dissociation. Therefore it also influences the mobility of the pharmaceuticals as a higher ionization increases their solubility. Also the degradability of the compounds influences their occurrence in the aquatic environment. Carbamazepine is reported as persistent in the aquatic environment (Clara et al., 2004), the sulfonamides in general are described as degradable compounds with considerable formation of metabolites (Jesus Garcia-Galan et al., 2008), the degradation of sulfamethoxazole, however, is depending on the redox conditions (Nödler et al., 2012). Ibuprofen and diclofenac are classified as degradable (Scheytt et al., 2006), and 17-estradiol is described as rapidly degraded (Patterson et al., 2011).

Tab. 3-1 Properties of the selected pharmaceutical compounds (K_{OW} = octanol/water-partitioning coefficient; pK_a = acid dissociation constant).

Compound	Structure	Solubility [mg L ⁻¹]	log K_{OW}	pK_a	Classification (this paper)
Carbamazepine		112 ^b	2.30 ^a , 1.51 ^c	13.9 ^e	mobile
Sulfamethazine		1,500 ^b	0.28 ^a	7.59 ^a	mobile
Sulfamethoxazole		610 ^b	0.89 ^a	5.81 ^a	mobile
Tetracycline		231 ^b	-1.3 ^b	3.30 ^a	sorbing, degradable
Ibuprofen		21 ^b	3.50 ^a , 2.48 ^c	4.91 ^a	sorbing, degradable
Diclofenac		2.37 ^b	4.40 ^a , 1.90 ^c	4.15 ^a	sorbing, degradable
17-β-estradiol		3.6 ^b	4.01 ^a	10.71 ^d	sorbing, degradable

^a(Sangster Research Laboratories, 2011)

^b(SYRRES, 2011)

^c(Scheytt et al., 2005a)

^d(Lewis and Archer, 1979)

^e(Jones et al., 2002)

Altogether, carbamazepine, sulfamethazine, and sulfamethoxazole were classified as mobile, whereas tetracycline, ibuprofen, diclofenac, and 17- β -estradiol were classified as sorbing/degradable for this study. The selected and classified pharmaceutical compounds are regarded as representative examples for mobile and sorbing/degradable substances for the investigated field site.

For the analysis of the pharmaceutical compounds water samples were adjusted to a pH-value of 4 with diluted sulphuric acid solution (25%) and then extracted by solid-phase extraction (SPE) using a non-encapped reversed phase sorbent. Before extraction, the samples were spiked with a surrogate standard for quality control and afterwards analysed using liquid chromatography – tandem mass spectrometry (LC-MS/MS). The analysis method used for the pharmaceutical compounds is described in detail by Pailler et al. (2009b). With a limit of detection (LOD) of 0.3 ng L^{-1} and a limit of quantification (LOQ) of 1.0 ng L^{-1} all analysed values for the pharmaceutical compounds are interpretable even at the small ng L^{-1} -scale. Only for the hormone 17- β -estradiol both the LOD (1.0 ng L^{-1}) and the LOQ (3.0 ng L^{-1}) are slightly higher. Analyses for cations were performed with inductively coupled plasma emission spectroscopy (ICP-AES - Trace Scan Thermo Jarrell) and atomic absorption spectroscopy (AAS - Analytik Jena NovAA 400G). Analyses for anions were performed with ion chromatography (Dionex DX 120).

3.5 Results and discussion

3.5.1 Hydraulic measurements

Fig. 3-3 shows the obtained hydrographs of surface water and groundwater and also the daily precipitation from beginning of June until end of November 2010. In addition, the four sampling campaigns of groundwater and surface water are indicated by dashed lines.

Reactions in stream-stage to precipitation events were immediate and corresponded to the amount and duration of the rain events. It is apparent that groundwater levels reacted directly to changes in stream stage and that the amplitude was damped with increasing distance from the bank, resulting in smoother hydrographs for wells B and C (1.6 m and 2.5 m from the bank) compared to well A (1.0 m from the bank). This damping was also represented by the different ranges of the recorded water levels: the stream stage had a range of 1.75 m, the water level in well A 1.56 m, the water level in well B 0.95 m, and the water level in well C 0.89 m. An immediate reaction of hydraulic head to changes in stream stage and their significant rise are a proof for confined aquifer conditions (Sophocleous, 1991; Wett et al., 2002), which were therefore confirmed at the field site. Maximum and minimum water levels during the investigation period are also indicated in the cross section in Fig. 3-2. During the summer months only one rain event in August led to a surface water level exceeding all logged groundwater levels, indicating influent hydraulic conditions in the whole riverbank. However, several rain events in this period resulted in surface water levels above the groundwater level in well A, which demonstrated partly influent hydraulic conditions. Altogether, changes in water level during summer were moderate and ranged from 0.2 m (well B and well C), over 0.5 m (well A) to 0.8 m (stream). A different situation was observed in November. Due to strong rain events over several days the surface water level rose to more than 1.8 m relative to stream gauge zero. Although groundwater levels also rose significantly, influent groundwater conditions prevailed during this time and the riverbank was even flooded (Fig. 3-2). These differences in hydraulic conditions between summer and winter were confirmed by a former study at the field site carried out in winter (Banzhaf et al., 2011). Whereas water levels in well A were more or less constant and only rose as a reaction to rain events, wells B and C seemed to follow a trend from the beginning of the measure-

ments until August 12. Their water levels decreased in this period from 1.01 m to 0.73 m and from 0.85 m to 0.61 m, respectively. This reflected the decline of groundwater levels after the winter half year with high precipitation and corresponding increase of groundwater levels (Banzhaf et al., 2011). The hydrographs documented that the part of the riverbank which was mainly influenced by the stream was located between well A and well B, which therefore may be considered the horizontal extent of the hyporheic zone. Wells B and C were more influenced by groundwater than by surface water.

The hydraulic measurements in the riverbank document predominately effluent aquifer conditions and only short-time influent aquifer conditions during the summer months. These periods of infiltrating surface water are supposed to affect only the nearby part of the riverine groundwater up to well A. However, in November strong rain events led to a complete turnaround of the hydraulic gradient and influent aquifer conditions were observed up to the farthest well. Based on the hydraulic gradients between well A and the surface water level, the hydraulic conductivity in well A, and a porosity of 0.3 groundwater flow velocities were calculated using Darcy's law. The velocities range from -0.08 m d^{-1} (effluent aquifer conditions) to $+0.06 \text{ m d}^{-1}$ (influent aquifer conditions). During more than 95% of the investigated period effluent aquifer conditions were observed. These observations of the hydraulic conditions encourage the assumption, that only during strong flood events relevant amounts of surface water and organic trace compounds infiltrate into the riverbank.

3.5.2 Analytical results

To characterise the water chemistry and to describe the surface water groundwater system not only based on the pharmaceuticals, also the analyses of the anthropogenic indicators nitrate and chloride, mean values for pH and electrical conductivity (EC) for groundwater and surface water are shown in Tab. 3-2. The EC of groundwater was always higher than that of surface water, which is due to the higher mineralisation caused by the underlying marls. One multilevel-well (CMT_A) showed an increasing EC with depth. However, the other multilevel-well did not confirm this trend. The three single-screen wells all had more or less the same EC which matched the EC at CMT_A_3, which is located at a similar depth (Fig. 3-2). The mean pH-values ranged from 7.0 to 8.2 for groundwater, for surface water the mean pH-value was 7.7. No trend for pH was observed in the riverbank but the values for the CMT-wells

were in general higher than for the single-screen wells. The anthropogenic indicators chloride and nitrate delivered ambiguous results. Chloride concentrations in surface water were twice as high as in groundwater. The concentrations in groundwater did not show a significant trend for distance or depth which matched the results from a former study (Banzhaf et al., 2011) and might indicate the conservative behaviour of chloride. For nitrate some parts of the multilevel-wells had mean concentrations which are up to five times higher than those in the surface water. Again CMT_A showed a trend: nitrate concentrations were decreasing with depth, which could indicate an inflow of the nitrate from the surface or the stream. The other multilevel-well did not confirm this observation, which, together with the EC-values, is an indicator for heterogeneities of the permeability in the riverbank.

The analyses of the 7 analysed pharmaceutical compounds and 1 hormone which were yielded from all samples taken between October 2009 and November 2010 both for surface water and groundwater are presented as box plots in Fig. 3-4. This shows the high variability of the concentrations of the analysed pharmaceuticals at the field site both in surface water and groundwater. First of all, the large differences of the measured concentrations between surface water (up to 850 ng L⁻¹) and groundwater (all results below 18 ng L⁻¹) are apparent.

Tab. 3-2 Mean values and ranges (in brackets) of nitrate and chloride concentrations, pH-values and electrical conductivities (EC) of surface water and groundwater; sampling campaigns 06/2010 – 11/2010 (n = 4).

	Nitrate [mg L ⁻¹]	Chloride [mg L ⁻¹]	pH	EC [μS cm ⁻¹]
Surface water	11.1 (1.8–23.9)	49.1 (24.4–66.0)	7.7 (7.5–8.0)	752 (660–915)
Well A	1.5 (0.8–2.5)	20.9 (19.4–22.6)	7.1 (6.9–7.3)	1,340 (1,331–1,353)
Well B	3.7 (0.8–10.4)	23.8 (22.2–25.2)	7.1 (6.8–7.2)	1,345 (1,322–1,371)
Well C	1.0 (0.4–1.4)	21.2 (19.7–23.2)	7.0 (6.7–7.1)	1,343 (1,322–1,368)
CMT_A_1	24.8 (0.8–95.8)	18.3 (17.4–19.9)	8.1 (7.9–8.2)	1,213 (1,051–1,277)
CMT_A_2	3.5 (0.4–10.6)	26.7 (21.8–36.5)	8.2 (8.1–8.3)	1,247 (1,099–1,336)
CMT_A_3	1.3 (0.4–2.8)	23.9 (21.2–27.7)	7.8 (7.1–8.2)	1,341 (1,291–1,371)
CMT_B_1	56.3 (1.6–165.7)	19.2 (15.9–24.9)	7.9 (7.4–8.2)	1,029 (824–1,314)
CMT_B_2	6.0 (0.4–22.1)	21.7 (18.7–25.4)	7.1 (7.0–7.3)	1,290 (1,262–1,309)
CMT_B_3	17.6 (1.2–59.3)	20.9 (17.5–25.9)	7.7 (7.3–8.0)	1,169 (908–1,392)

Especially in the surface water there is a great variety of concentrations for the different substances. Carbamazepine, for example, is detected in concentrations of up to 600 ng L⁻¹ and sulfamethazine only of up to 19 ng L⁻¹.

This high variation of pharmaceutical concentrations in the Mess stream was already discussed in former studies which measured maximum pharmaceutical concentrations between 2 and 2,383 ng L⁻¹ during flood events (Meyer et al., 2011; Pailler et al., 2009a).

All analysed compounds detected in the surface water samples are also detected in the groundwater samples. This indicates an interaction of the stream and the adjacent groundwater up to the farthest well, as an input of the pharmaceuticals into groundwater is expected via the stream only. The possibility of leaky sewers or diffuse entries via agriculture, e.g. sulfamethoxazole, which is also used in veterinary medicine, might exist but is not assumed as relevant (see also chapter 3.3). Also the spatial distribution of the compounds in the riverbank does not indicate this (see below in this chapter). The concentrations for nearly all pharmaceuticals detected in the observation wells vary from below detection limit to several ng L⁻¹. For all compounds maximum values are observed, which exceed the 90 percentile significantly (Fig. 3-4) and demonstrate the high variability of the pharmaceuticals found in the riverine groundwater. It has to be mentioned that other studies found much higher concentrations of pharmaceutical compounds in riverine groundwater at other sites which reflects the huge variety of hydraulic and biogeochemical conditions in riverbanks and its influence on the occurrence and transport behaviour of the pharmaceuticals (Lewandowski et al., 2011). Strauch et al. (2008), for example, detected carbamazepine concentrations of up to 100 ng L⁻¹ in groundwater near a riverbank.

The results for the selected mobile pharmaceuticals from the four sampling campaigns for all observation wells are shown in Fig. 3-5 as depth over concentration for the CMT-wells and concentrations over distance for wells A to C. Carbamazepine, sulfamethazine, and sulfamethoxazole are classified as mobile substances which are only slightly degradable. These compounds are detected in all sampled observation wells, different distributions are, however, observed. CMT_A shows a significant decrease of concentrations with depth for all three substances and all sampling campaigns except from June. In contrast, CMT_B does not show a trend for none of the substances over depth for all sampling campaigns. The horizontal distribution represented by wells A to C also does not indicate a significant trend of concentrations

over distance. Carbamazepine concentrations are slightly higher than sulfamethazine and sulfamethoxazole concentrations. The expected mobility of these three substances is proven by the observed occurrence in all wells and especially by the gradients with depths in CMT_A. As the maximum concentrations of the mobile pharmaceuticals were detected at the uppermost sampling port of CMT_A (Fig. 3-5), it seems that the transport of these substances takes place mostly at a shallow depth. This may indicate that infiltration/exchange of/with surface water takes place from "top to bottom" during flood events, which would not be classified as hyporheic exchange. Therefore it has to be considered that the screens of the single-screen observation wells (well A, well B, and well C) are maybe installed too deep to detect the maximum concentrations of the pharmaceutical compounds in the riverine groundwater which are assumed closer to the groundwater table.

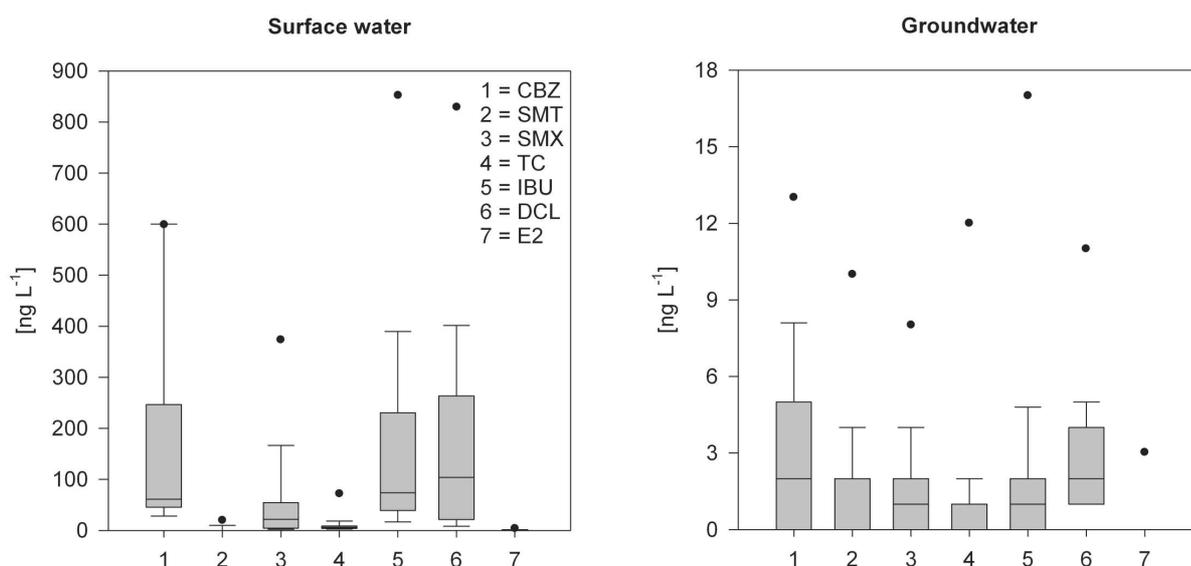


Fig. 3-4 Box plots of pharmaceutical concentrations in surface water and groundwater showing concentrations vs. compound (all sampling campaigns from 10/2009 – 11/2010), grey bars indicating 25/75 percentiles, whiskers indicating 10/90 percentiles, dots indicating maximum values, and horizontal lines indicating median values (CBZ = carbamazepine, SMT = sulfamethazine, SMX = sulfamethoxazole, TC = tetracycline, IBU = ibuprofen, DCL = diclofenac, E2 = 17- β -estradiol).

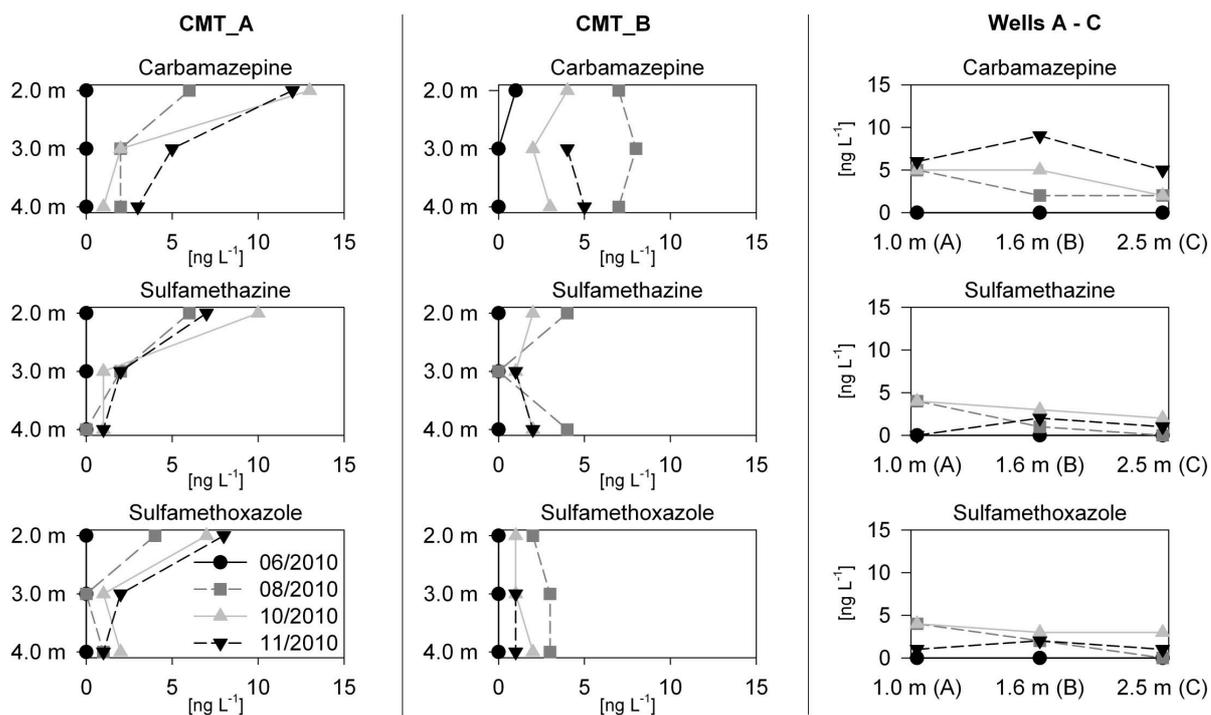


Fig. 3-5 Concentration distribution of selected mobile pharmaceuticals detected in the observation wells, showing depth vs. concentration (CMT_A and CMT_B) and concentration vs. distance (Wells A – C).

Fig. 3-6 shows the concentration distribution of the selected sorbing and degradable pharmaceuticals detected in the observation wells during the four sampling campaigns from June until November 2010. Again, the results are plotted as depth over concentration and concentration over distance, respectively. In contrast to the mobile pharmaceuticals presented in Fig. 3-5 these compounds do not follow a significant trend neither in the multi-level wells nor the single-screen wells. Ibuprofen shows both increasing and decreasing concentrations over depth for different sampling campaigns at CMT_A. Diclofenac even shows significantly higher concentrations for the deepest sampling port of CMT_A for two of the four sampling campaigns. However, the different gradients of diclofenac and ibuprofen in CMT_A for the four sampling campaigns might also be due to the pH-dependent sorption behaviour of these compounds, as the pH in CMT_A varies from 7.1 to 8.3. The hormone 17- β -estradiol is detected only in one sample in well C. This rare occurrence was expected as the substance is not very stable in the aquatic environment and also sorbed. Tetracycline is showing high sorption and is detected only in low concentrations up to 3 ng L⁻¹. However, one sample for well B was analysed with 12 ng L⁻¹.

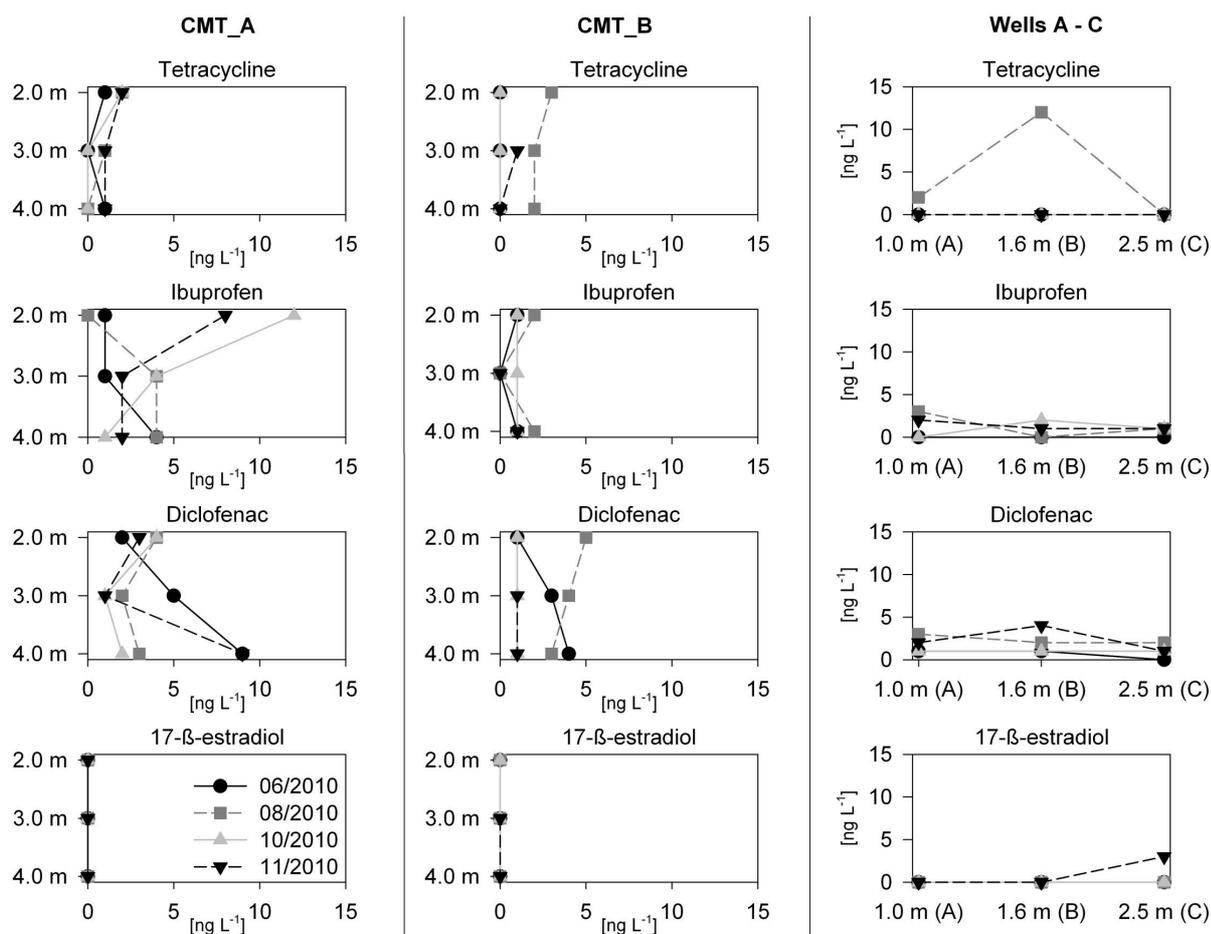


Fig. 3-6 Concentration distribution of selected sorbing and degradable pharmaceuticals detected in the observation wells, showing depth vs. concentration (CMT_A and CMT_B) and concentration vs. distance (Wells A – C).

In general, it was assumed that the selected pharmaceutical compounds present in stream and groundwater would show gradients between surface water and riverbank. Furthermore, it was expected that concentrations in the riverine groundwater would decrease with distance from the stream, both vertical and horizontal. For the substances which were classified as mobile in this study (chapter 3.4.4), higher concentrations in larger distances/greater depths were also expected; if compared to the sorbing and degradable compounds. Summarising the results of the pharmaceutical analyses of the groundwater samples, several compounds fit the expected distribution in the riverbank. The mobile compounds presented in Fig. 3-5 show gradients with depth in one of the multilevel-wells (CMT_A). The other multilevel-well (CMT_B) does not confirm this distribution over depth for the pharmaceuticals. On the other hand, e.g. carbamazepine shows variations over time in this well. These differences in distribution between the two multilevel-wells were not expected and can not ex-

plained properly. However, this might be an indicator for heterogeneities in the riverbank which influence the transport and occurrence of the pharmaceuticals. A hydraulic connection of the three screens of CMT_B can be excluded by the measurements of pH and EC, as both parameters differ significantly between the three sampling ports (Tab. 3-2). The distribution of the sorbing and degradable pharmaceuticals presented in Fig. 3-6 also might indicate the existence of hydraulic heterogeneities as, for example, the well degradable compound ibuprofen was detected in similar concentrations as the persistent compound carbamazepine in some samples. Both groups of pharmaceuticals show differences in concentrations over depth between the two multilevel-wells which demonstrates the heterogeneity of the investigated riverbank. This heterogeneity on small scale can have a significant influence on groundwater discharge (Kalbus et al., 2009) and therefore also on the interaction of water and solutes between surface water and groundwater. However, since the pharmaceutical concentrations in surface water range between values that are below the detection limit up to high ng L^{-1} -values, a constant input of pharmaceuticals from the stream into groundwater is not very likely. As mostly short periods of influent aquifer conditions are observed which are not assumed to have a significant influence on the groundwater chemistry (Banzhaf and Scheytt, 2009) it is difficult to assess what is the dominant process for interaction of surface water and groundwater in the riverbank. The hydraulic conductivity of the riverbank is very low and therefore also diffusion might contribute to the transport of the pharmaceutical compounds in the riverbank. Altogether, this study demonstrates that even for low hydraulic conductivities interaction of surface water and groundwater has to be considered as a relevant process. Therefore studies of groundwater/surface-water interactions should not be reduced to streambeds and riverbanks with a high permeability (Brunke et al., 2003; Massmann et al., 2004; Smith and Lerner, 2008).

3.6 Conclusions

The presented study documents that selected pharmaceutical compounds occur in the riverine groundwater of the investigated low permeable riverbank. Furthermore, gradients with depth for some mobile pharmaceuticals are observed. However, e.g. the distribution of ibuprofen and diclofenac can not be explained properly. Heterogeneities in the riverbank sediments might be an explanation but their existence could not be verified in this study. Although effluent aquifer conditions are dominant during the investigated period and an input of the selected pharmaceuticals is assumed via the stream only, the pharmaceutical compounds are detected in groundwater. Therefore a preferred infiltration of surface water into the riverbank during flood events is concluded.

Altogether, this study demonstrates that the selected pharmaceutical compounds can be used as anthropogenic indicators for the interaction of surface water and groundwater at the investigated field site. However, the group of the mobile substances (carbamazepine, sulfamethazine, and sulfamethoxazole) is regarded as more suitable for this purpose, as their transport behaviour is more conservative than that of the other investigated compounds. Clara et al. (2004) and Müller et al. (2012) also found carbamazepine an appropriate tracer to detect anthropogenic influence on the aquatic environment.

The investigated period of six month and four sampling campaigns maybe was too short to observe the transport of the selected pharmaceuticals properly, especially when looking at the low flow rates which were estimated in the riverbank. For a better understanding of the occurrence and distribution of the selected trace compounds in the low permeable sediment laboratory experiments should be conducted. As some of the compounds are supposed to be sensitive to pH and the redox conditions their transport behaviour under defined pH and redox conditions should be investigated to identify the relevant processes for their mobility in low permeable sediments. With this deeper knowledge also quantitative estimates of surface water and groundwater interaction based on measurements of persistent pharmaceutical compounds should be possible.

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Chapter 4

4 Redox-sensitivity and mobility of selected pharmaceutical compounds in a low flow column experiment

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4.1 Abstract

In this study a laboratory column experiment under water saturated conditions was conducted to investigate the transport behaviour of the pharmaceutical compounds sulfamethoxazole, carbamazepine, diclofenac, and ibuprofen under varying nitrate concentrations. Organic rich sediment ($f_{OC} = 0.01$) and surface water from a formerly investigated field site were used. The water was spiked with the four compounds and the specific redox conditions in the column (0.351 m height) were varied throughout the experiment by adding nitrate in the influent water. Stepwise controlled decreasing influent nitrate concentrations between 131 and 20 mg L⁻¹ were applied in the course of the experiment which lasted 71 days. This established temporarily denitrifying conditions in the column during the reduction of nitrate. Sulfamethoxazole was severely influenced by this process. During denitrification sulfamethoxazole concentrations in the effluent water decreased rapidly and significantly. This experiment demonstrates the strong dependency of sulfamethoxazole transformation specifically on nitrate reducing redox conditions and therefore may help to explain the wide ranges of reported degradability for this compound. Ibuprofen was more stable under denitrifying redox conditions. Both for carbamazepine and diclofenac apparent retardation was observed. For carbamazepine this was attributed to sorption and also to degradation. For diclofenac nitrate controlled degradation seems the dominating process for the apparent retardation of this compound.

4.2 Introduction

Human pharmaceuticals are detected worldwide in all parts of the aquatic environment. They are detected in surface water and groundwater (Lewandowski et al., 2011; Loos et al., 2010; Müller et al., 2012; Nödler et al., 2011; Pal et al., 2010). This ubiquitous presence requires sound knowledge of fate and behaviour of these compounds especially under the chemical variability of their subsurface passage as they pose a potential risk for future drinking water resources.

Column experiments on laboratory scale are appropriate to investigate the transport behaviour of pharmaceuticals and its sensitivity to different hydrochemical environments like the redox conditions (Baumgarten et al., 2011; Mersmann et al., 2003; Nay et al., 1999; Scheytt et al., 2004). Ambient redox conditions and also pH are re-

garded as key parameters, which can influence the transport and transformation of pharmaceutical compounds. Maeng et al. (2010) found that the performance of natural treatment systems for the removal of pharmaceutical compounds is influenced by the redox conditions. Barbieri et al. (2011) claim that, although the predominant redox conditions were identified as one of the controlling factors for removal of organic pollutants from water, sound knowledge in the case of organic micropollutants on this potential redox-dependent behaviour is still limited. One prominent example for this is sulfamethoxazole (SMX): several studies agree that the degradation and the formation of metabolites of this compound are triggered by the redox conditions (Baumgarten et al., 2011; Heberer et al., 2008; Mohatt et al., 2011; Nödler et al., 2012). However, contradictory degradation behaviour for this compound is reported in the literature. For example, Drilia et al. (2005) describe biodegradation of SMX under aerobic conditions in a sequencing batch reactor whereas Heberer et al. (2008) found a more rapid degradation of SMX under mainly anoxic conditions at a bank filtration site. The bulk-parameter oxidation reduction potential, however, may not always be appropriate as key parameter when investigating the fate of pharmaceutical compounds. Nödler et al. (2012) showed that high nitrate concentrations in combination with easily biodegradable organic carbon resulted in a fast transformation of SMX. In contrast, Mohatt et al. (2011), who applied lower nitrate concentrations, did not observe significant reduction in SMX concentrations. This basically emphasizes the sensitivity of this compound to nitrate reducing redox conditions. However, the controlling boundary conditions of the transformation are yet unclear. Nödler et al. (2012) proposed that the initial nitrate concentration influences the transformation of SMX.

For the other pharmaceuticals, which were investigated in this study, different degradation behaviour is described in the literature. Mersmann et al. (2003) reported no significant degradation for carbamazepine (CBZ) and diclofenac (DCL) but observed degradation for ibuprofen (IBU) in a column experiment under aerobic conditions and inflowing nitrate concentrations of 5.2 mg L^{-1} .

When classified by their K_{OW} values (Tab. 4-1), a mobility of the pharmaceutical compounds in increasing order would be proposed as $DCL < IBU < CBZ < SMX$. However, as SMX, DCL, and IBU are anions they are expected to show virtually no retardation. In contrast, e.g. Scheytt et al. (2005b) ranked some of these compounds by their experimentally determined sorption coefficients (in increasing order) as $DCL < IBU < CBZ$, which demonstrates the huge variability in mobility of the pharma-

ceuticals. However, these experiments did not focus on the combined effects of sorption and degradation on the transport of pharmaceuticals. Also the pH (Schaffer et al., 2012; Strauss et al., 2011) and especially the organic content of the sediment and water (Rauch-Williams et al., 2010; Thiele-Bruhn et al., 2004) can have a significant influence on retardation behaviour of some of the investigated pharmaceuticals.

Amongst others, the mobility of, SMX, CBZ, DCL, and IBU was studied by Banzhaf et al. (2011; 2012) in the riverbank of an alluvial stream in a small rural catchment in Luxembourg. They used the pharmaceuticals as indicators for the interaction of surface water and groundwater. All compounds showed a high variation in concentration in the stream (below detection limit up to 850 ng L^{-1}) and were found (in low ng L^{-1} concentrations) also in the riverine groundwater, which demonstrates the interaction of these two compartments and the infiltration of pharmaceuticals into groundwater. However, the key parameter specific redox conditions and also the nitrate concentration varied over the investigated period. As these dynamic parameters can have a significant influence on the transport behaviour of the compounds, a laboratory experiment under controlled and varying boundary conditions was designed using sediment and surface water from this field site. This setup with corresponding natural sediment and water is appropriate to investigate selected specific processes on laboratory scale.

The presented study focuses on the influence of the specific redox conditions on the transport behaviour of the four pharmaceuticals SMX, CBZ, DCL, and IBU in a water saturated laboratory column experiment under a descending nitrate concentration. The compounds were selected as they were expected to show different transport behaviour due to their different properties. By controlling the influent nitrate concentrations during the experiment and changing the nitrate-supply into the column, the influence of this key parameter on the transformation of SMX, DCL, CBZ, and IBU was investigated. By starting with high nitrate concentrations a potential toxic effect of nitrite on the microorganisms in the column during denitrification as earlier observed by Hu et al. (2011) should be avoided.

The design of the column experiment allowed studying the combination of degradation and sorption under varying and controlled boundary conditions. Also the sometimes competing influence of sorption and degradation on the mobility of the selected pharmaceuticals was investigated. By changing the inflowing nitrate concentrations,

a defined variation of boundary conditions was realised within a timeframe of days. The applied concentrations were comparable to natural systems, e.g. Wolter (2002). The influence of fertiliser application and the resulting breakthrough of high nitrate concentrations in the aquifer are an example of the decreasing nitrate concentrations, which were applied in the experiment. This study may therefore help to explain the sometimes contradictory reported degradation and sorption behaviour of the selected pharmaceutical compounds under different and even varying boundary conditions. However, a simple upscaling of the results to field conditions has to be handled carefully as the spatial scale was limited to a few decimetres.

4.3 Material and methods

4.3.1 Properties of the pharmaceutical compounds and environmental relevance

The properties of the investigated pharmaceuticals are shown in Tab. 4-1. SMX belongs to the group of the sulfonamides. It is an antibiotic, which is used to treat bacterial infections. SMX is used both in human and veterinary medicine. CBZ is a widely applied anticonvulsant, which is used to treat epilepsy, bipolar disorder, and trigeminal neuralgia. DCL is a nonsteroidal anti-inflammatory drug. It is widely used as an analgesic and also to reduce inflammation. IBU is a popular nonsteroidal anti-inflammatory drug with analgesic and antipyretic properties.

Although present in all parts of the aquatic environment, the reported concentrations of the pharmaceutical compounds vary strongly in the different compartments. Joss et al. (2005) report SMX concentrations up to $1.0 \mu\text{g L}^{-1}$ in the effluent of a WWTP. Ternes (1998) found the following median concentrations in the effluent of a wastewater treatment plant (WWTP): CBZ $2.1 \mu\text{g L}^{-1}$, DCL $0.81 \mu\text{g L}^{-1}$, and IBU $0.37 \mu\text{g L}^{-1}$. Müller et al. (2012) detected CBZ concentrations of up to $2,280 \text{ ng L}^{-1}$ and DCL concentrations of up to $2,480 \text{ ng L}^{-1}$ in surface water downgradient of a WWTP. A pan-European survey of Loos et al. (2010) found the following maximum groundwater concentrations: SMX 38 ng L^{-1} , CBZ 390 ng L^{-1} , DCL 24 ng L^{-1} , and IBU 395 ng L^{-1} . Heber (2002) found diclofenac concentrations of $<10 \text{ ng L}^{-1}$ in tap water.

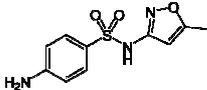
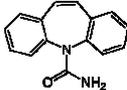
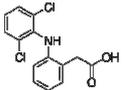
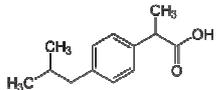
Although effect levels for pharmaceuticals are significantly higher than those found in the environment, these compounds pose a potential environmental risk, e.g. for wild

fish populations, that is not yet thoroughly characterised. Knowledge about this risk for the aquatic environment is of increasing importance as global consumption of pharmaceuticals rises (Corcoran et al., 2010). When entering drinking water, e.g. via bank filtration, pharmaceuticals and their transformation products also pose a potential risk to humans (de Jongh et al., 2012; Stuart et al., 2012) and therefore their occurrence and transport behaviour is of great concern.

4.3.2 Chemicals

Methanol (LC/MS grade) and IBU were purchased from Fisher Scientific (Schwerte, Germany). Formic acid, ethyl acetate, acetonitrile, and ammonium acetate (all analytical grade) were obtained from VWR (Darmstadt, Germany). CBZ, DCL, and SMX were purchased from Sigma-Aldrich (Steinheim, Germany). The transformation products (TP) of SMX desamino-SMX and 4-nitro-SMX were synthesized according to Nödler et al. (2012). The internal standards (IS) SMX-¹³C₆ and CBZ-D₁₀ were purchased from LGC Promochem (Wesel, Germany) and IBU-D₃ was from Sigma-Aldrich. A mix of all IS (20 ng µL⁻¹ of each individual IS) in acetonitrile was prepared for sample spiking. Potassium nitrate and lithium bromide were purchased from VWR (Darmstadt, Germany).

Tab. 4-1 Properties of the studied pharmaceutical compounds.

Compound	Structure	Solubility [mg L ⁻¹]	log K _{OW}	acidic pK _a
Sulfamethoxazole		610 ^b	0.89 ^a	5.81 ^a
Carbamazepine		112 ^b	2.30 ^a , 1.51 ^c	13.9 ^d
Diclofenac		2.37 ^b	4.40 ^a , 1.90 ^c	4.15 ^a
Ibuprofen		21 ^b	3.50 ^a , 2.48 ^c	4.91 ^a

^a(Sangster Research Laboratories, 2011)

^b(SYRRES, 2011)

^c(Scheytt et al., 2005a)

^d(Jones et al., 2002)

4.3.3 Experimental setup

The setup of the column experiment was designed to investigate the combined effect of sorption and fate during controlled descending nitrate concentrations on the breakthrough behaviour of selected pharmaceuticals. This was achieved by a column experiment under saturated flow conditions. Hydraulic conditions, inflowing pharmaceutical substances, and the inflowing nitrate conditions were controlled throughout the experiment. In order to allow an adaptation of the microorganisms to the declining nitrate concentrations, a low flow rate (14.1 mL h^{-1} on average) was applied resulting in an experimental duration of 71 days. The flow rate corresponded to estimated groundwater flow velocities at the field site from which sediment and water were taken.

A scheme of the experimental design is shown in Fig. 4-1. From the respective storage tank the inflowing water was pumped through the column with a peristaltic pump from bottom to top. This should avoid problems from gas accumulation in the column. The pH and dissolved oxygen were monitored at the outlet. At the column outflow automatic sampling in glass test tubes using an automatic sampler with three hours intervals was realised.

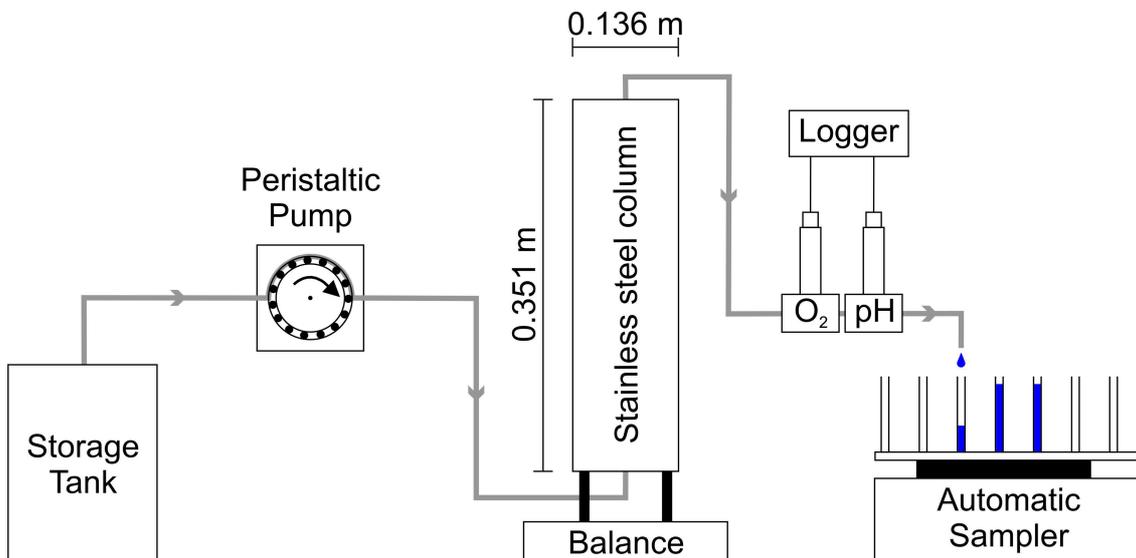


Fig. 4-1 Scheme of the experimental design.

The column was made of stainless steel, had a height of 0.351 m, a diameter of 0.136 m, and a volume of 5.1 L. It was filled with natural organic rich sediment ($f_{oc} = 0.01$) from a field site in Luxembourg, which was stored in the refrigerator until the

experiment started. The sediment mainly consisted of clay and silt with fine sand, and medium sand and had a hydraulic conductivity (K_f) of $2.3 \cdot 10^{-6} \text{ m s}^{-1}$, which were obtained from in-situ field measurements (Banzhaf et al., 2011). Before inserting the sediment into the column it was dried and sieved to remove grain sizes $> 2 \text{ mm}$ and thus allowing an adequate packing of the column. The dry sediment was then filled in small portions into the column and compacted after each addition. This should guarantee a homogeneous distribution of the sediment in the column with no preferential flow paths, e.g. along the inner wall of the column. A layer (0.02 m thick) of coarser sandy sediment was added first at the bottom of the column to avoid the potential issue of transversal dispersion which might result from a point source. After the filling of the column was completed, it was flushed from bottom to top and a total porosity of 0.42 was determined, which corresponds to a volume of 2.14 L (= 1 pore volume). The bulk density of the sediment in the column was 1.4 g cm^{-3} and the effective porosity (n_e) obtained from the tracer experiment was 0.41. The column was placed on a balance during the experiment to detect potential gas accumulations or leaching of sediment.

The inflowing water was natural surface water taken from the Mess Stream at the field site in Luxembourg. It was also stored in the refrigerator until the experiment started. This system of corresponding natural sediment and water – together with the controlled boundary conditions – should assure appropriate conditions to study the selected processes. The pharmaceuticals SMX, CBZ, DCL, and IBU were analysed in concentrations between 175 and 852 ng L^{-1} in this sample. To assure more significant and directly measurable (without the need for preconcentration as a potential further error source) concentrations for the analysis, the water was spiked with the selected pharmaceuticals (SMX, CBZ, DCL, IBU) with concentrations between 165 and 295 $\mu\text{g L}^{-1}$ (Fig. 4-3).

The column experiment consisted of 7 steps (Tab. 4-2). At each step a new storage tank was connected to the column, which was individually spiked with pharmaceuticals, nitrate, and LiBr-tracer. To assure a homogeneous distribution of the spike in the storage tank it was stirred regularly with a magnetic stir bar. The composition of the inflowing water and hydraulic data for each experimental step is shown in Tab. 4-2. To investigate the influence of the initial nitrate concentration on the breakthrough behaviour of the selected pharmaceuticals different nitrate concentrations were established in the influent water within each storage tank, starting with

131 mg L⁻¹ and decreasing stepwise and controlled to 129 mg L⁻¹, 96 mg L⁻¹, 50 mg L⁻¹, 21 mg L⁻¹, and 20 mg L⁻¹, which was the "background" concentration of the stream water. This was done with potassium nitrate. During each step the nitrate concentration remained constant in the respective storage tank. The addition of nitrate to the storage tank was due to technical reasons.

For the detection of the hydraulic conditions in the column, the conservative tracer lithium bromide was added with a concentration of ~50 mg L⁻¹ two times during the experiment. The tracer was added at the beginning and at the end of the flushing with the spiked water (Tab. 4-2, steps 1 and 6). In total, 11.2 pore volumes (PV) were exchanged including a final step of 3.5 PV with non-spiked water (step 7). One PV was exchanged every 6.3 days on average.

Prior to the experiment the column was flushed with non-spiked influent water (in-flowing nitrate concentration was 20 mg L⁻¹) until constant values for the physico-chemical parameters of the effluent water were reached. This adaption phase lasted for ~2.5 months (~11 PV) and should ensure the establishment of equilibrium conditions at the beginning of the experiment and also the growth of biofilms in the column Worch et al. (2002).

Tab. 4-2 Characteristics of experiment steps and corresponding influent water.

Step	Duration [d]	Exchanged PV, stepwise [-]	Exchanged PV, progressive [-]	Flow rate [mL h ⁻¹]	NO ₃ ⁻ [mg L ⁻¹]	Spiked with pharmaceuticals	Spiked with LiBr
1	1.04	0.17	0.17	14.9	131	x	x
2	10.0	1.68	1.85	15.0	129	x	
3	11.9	1.91	3.76	14.3	96	x	
4	13.3	1.78	5.54	12.0	50	x	
5	11.0	1.83	7.37	14.9	21	x	
6	1.92	0.31	7.68	14.5	20	x	x
7	22.0	3.54	11.2	14.4	20		
Total	71.2			14.1			

4.3.4 Chemical analysis of storage tank water and column effluent

To detect potential attenuation or transformation of the pharmaceutical compounds in the storage tank, influent samples were taken and analysed daily for the pharmaceuticals. The analysis of the collected influent samples was stopped during the last step of the experiment when non-spiked water was applied (Tab. 4-2) and therefore 51 samples were analysed altogether. Effluent samples for the pharmaceutical analysis were collected every 3 hours and every 5th sample was analysed throughout the experiment, which corresponds to an interval of 15 hours (=0.098 PV). During the breakthrough of SMX at the outlet of the column the analysis frequency was raised to varying intervals of one, two, or three samples, respectively. Altogether 133 effluent samples were analysed for the selected pharmaceuticals. Water samples for bromide, nitrate, nitrite, and DOC analysis from the storage tank were collected and analysed every 2 days (35 samples altogether). Effluent samples for these compounds were collected every 6 hours and every 5th sample was analysed throughout the experiment, which corresponds to an interval of 30 hours (=0.197 PV). During the breakthrough of the LiBr-tracer at the outlet of the column each sample was analysed. Altogether 110 effluent samples were analysed for these compounds.

Water samples for bromide, nitrate, and nitrite analysis were filtered using 45- μm cellulose acetate filters, preserved, and stored in PET-bottles. The samples for dissolved organic carbon (DOC) were filtered using 45- μm cellulose acetate filters and stored in brown glass bottles. All samples were stored in the refrigerator until analysis. Bromide, nitrate, and nitrite were determined by ion chromatography (Dionex DX 120). Analysis for DOC was performed with a total carbon analyser (Shimadzu TOC-5000/5050).

The samples for the analysis of pharmaceutical compounds were stored in 12-mL glass bottles and frozen directly after sampling. Prior to analysis, aliquots of 980 μL were mixed with 10 μL of the IS mix (200 ng of each IS) and 10 μL of an aqueous ammonium acetate solution (1 M) and centrifuged at 1500 rpm for 30 min. Pharmaceuticals were determined by means of high-performance liquid chromatographic separation, electrospray ionisation with tandem mass spectrometric detection (HPLC/MS–MS). Details regarding the instrumentation and the individual MS-parameters of all analytes (e.g. capillary voltage, collision energy, transition) were published previously (Nödler et al., 2012; 2010). Eluent A was 0.015% formic acid

+ 5% methanol in ultrapure water. Eluent B was methanol. The elution started with 25% B followed by a gradient of 16.5 min to 95% B. This was kept constant for 11 min followed by a gradient of 0.5 min to 25% B. These conditions were maintained for 8 min to equilibrate the system. The injection volume was 100 μL and the separation was operated at 30 $^{\circ}\text{C}$. Seven concentration levels (5-500 $\mu\text{g L}^{-1}$) were used for the calibration and the linear correlation coefficients exceeded 0.99. CBZ-D₁₀ was used as the IS for the quantification of CBZ, IBU-D₃ for IBU and DCL, and SMX-¹³C₆ for SMX and its TPs. An analytical error of < 5% derived from multiple injections was maintained by this procedure.

4.3.5 Chemical analysis of remaining pharmaceuticals in the column

After the column experiment was finished all sediment material was removed from the column and samples from four equivalent sections (0-8.8 cm, 8.8-17.5 cm, 17.5-26.3 cm and 26.3-35.1 cm) were analysed for pharmaceutical compounds and for SMX TPs. For this purpose 5 g (ww) of each homogenised sample was spiked with 10 μL of the IS mix (200 ng of each IS) and suspended with 30 mL methanol/ethyl acetate (15/10; v/v) mixture. After ultrasonic extraction for 30 min at 25 $^{\circ}\text{C}$ the solids were allowed to settle for 12 h at 4 $^{\circ}\text{C}$. The supernatant was carefully transferred into a glass vial and the organic solvents were evaporated by a gentle stream of nitrogen at 40 $^{\circ}\text{C}$. The remaining aqueous extract was mixed with 1 mL of aqueous 10 mM ammonium acetate solution + 4% methanol, transferred to a 2 mL autosampler vial and centrifuged for 30 min. The extract was analysed according to 2.4.

4.3.6 Hydraulic modelling

To obtain the pore velocities and the longitudinal dispersivities for the experiment the measurements of the conservative LiBr-tracer were fitted using the CXTFIT-code (Toride et al., 1995). The solution is based on the convection-dispersion equation:

$$R_f \frac{\partial c_r}{\partial t} = D \frac{\partial^2 c_r}{\partial x^2} - v \frac{\partial c_r}{\partial x} - \mu c_r + \gamma(x) \quad (\text{Eq. 1})$$

where R_f is the retardation factor, c_r [kg m^{-3}] is the resident concentration of the liquid phase, t is the time [d], D is the dispersion coefficient [$\text{m}^2 \text{d}^{-1}$], x is the travel distance

[m], v is the average pore-water velocity [m d^{-1}], and μ and γ are combined first- and zero-order rate coefficients (Toride et al., 1995).

By using the dimensions of the column, porosity, and flow rate the breakthrough curves of the LiBr-tracer were fitted using the deterministic equilibrium model type with resident concentration. The retardation factor was set to 1 and the first order decay coefficient was set to 0. Then the average pore-water velocity and the dispersion coefficient were fitted. The hydraulic data from the column experiment were used as a starting value. The dispersion coefficient was also fitted with 1.0 as a starting value. The longitudinal dispersion D_L was also calculated applying the longitudinal dispersivity α_L and the pore velocity v with the formula:

$$D_L = \alpha_L \cdot v \quad (\text{Eq. 2})$$

where α_L [m] is the longitudinal dispersivity and v is the average pore-water velocity [m d^{-1}]. As a layer of filter sand was added at the inlet of the column – which had a higher hydraulic conductivity than the sediment above – the flow into the studied sediment was assumed to be uniform through the whole cross section. For small-scale studies, like this column experiment, the transversal dispersion is assumed to be negligible.

The effluent bromide concentrations were normalised to the influent concentrations (C/C_0) and modelled as inverse problem with no retardation and no degradation. The input of the tracer was modelled as multiple pulse: 0 for the initial concentration, 1 for the beginning of tracer input and 0 at the end of the tracer input. Input values for flow velocity were estimated from the experimental flow rate and for longitudinal dispersivity taken from the literature Schulze-Makuch (2005). These input values were fitted by CXTFIT using the normalised bromide breakthrough curve.

4.4 Results and discussion

Note that for all figures in this section all concentrations are plotted versus exchanged PV. This normalisation of the time axis to pore volumes corrects for variations of the flow rate (see Tab. 4-2) and therefore is more appropriate than using time. The duration of the experimental steps and the corresponding flow rates are shown in Tab. 4-2.

4.4.1 Hydraulic conditions

The knowledge of the hydraulic conditions in the column is important for assuring a meaningful interpretation of the pharmaceutical compounds transport. LiBr was added to the inflowing water twice during the experiment with different pulse length and the breakthrough curves of bromide (Fig. 4-2) were fitted using CXTFIT (Toride et al., 1995). This allowed deriving the respective pore velocities and longitudinal dispersivities. The tracer was added in two "pulses" (see Tab. 4-2) and the maximum effluent concentrations did not reach the influent concentrations ($C/C_0 < 0.6$). The calculated pore velocities were 6.5 cm d^{-1} (A) and 6.3 cm d^{-1} (B). With the decrease of the pore velocity the longitudinal dispersivity increased from $1.4 \cdot 10^{-3} \text{ cm}$ to $5.9 \cdot 10^{-3} \text{ cm}$. This could be an indicator for a slight reduction of effective pore volume by clogging of the column during the experiment.

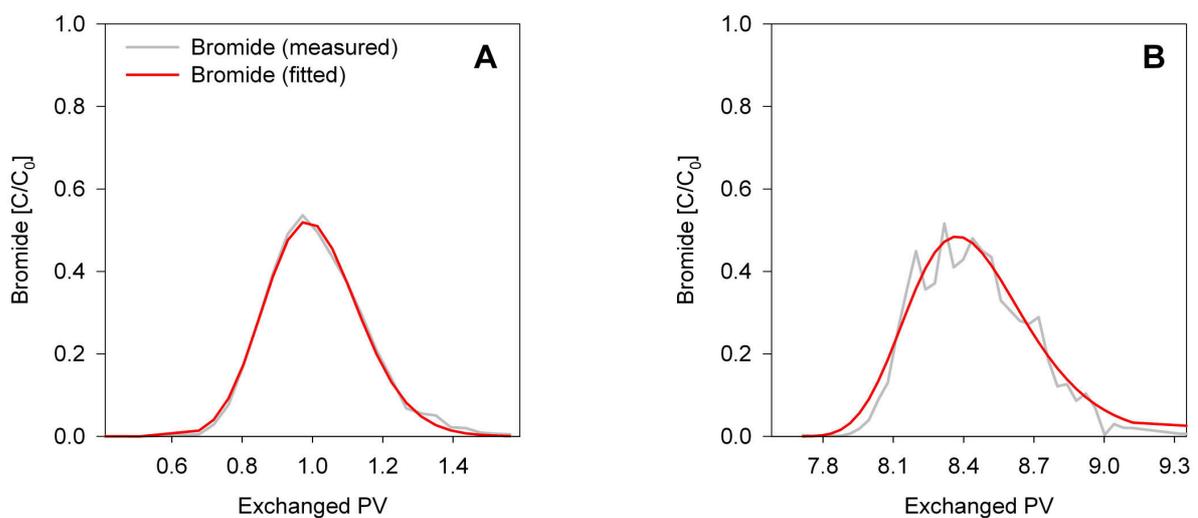


Fig. 4-2 Normalised breakthrough curves (C/C_0) of bromide for LiBr-Tracer 1 (A) and LiBr-Tracer 2 (B); inflow pulse lengths: 1 = 0.17 PV and 2 = 0.31 PV (1 PV = 6.3 d).

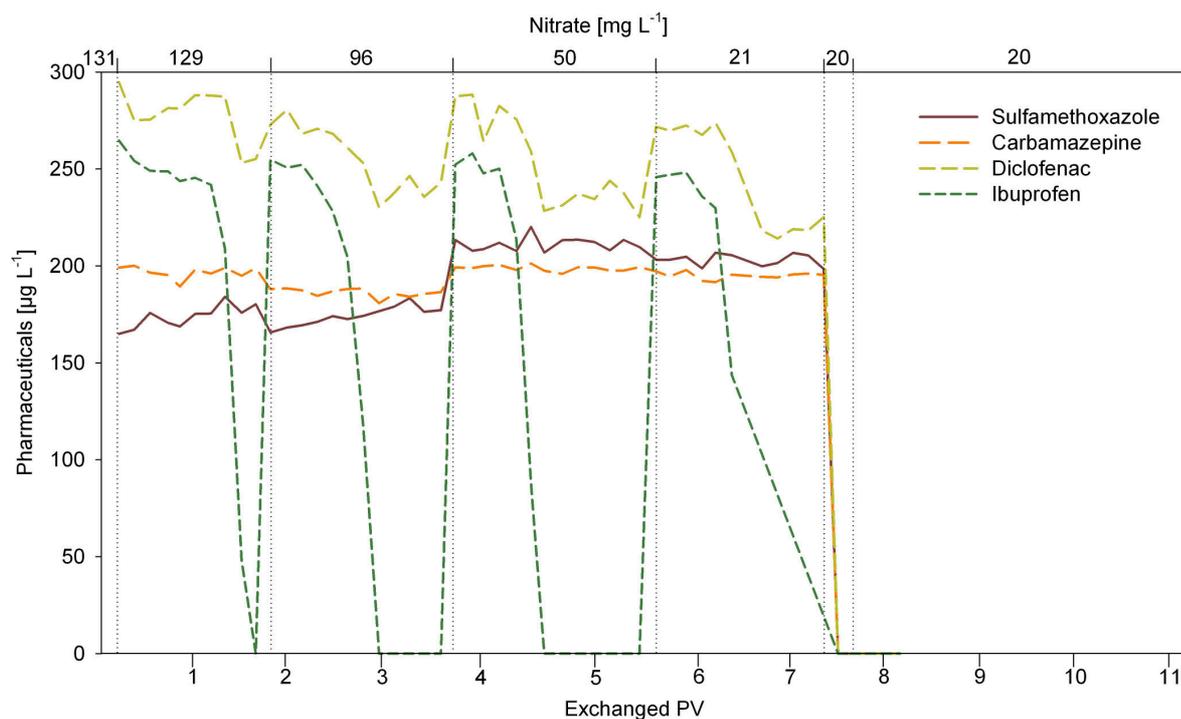


Fig. 4-3 Inflowing concentrations of sulfamethoxazole, carbamazepine, diclofenac, ibuprofen, and nitrate; dashed vertical lines separate experiment steps (1 PV = 6.3 d).

4.4.2 Pharmaceuticals in the inflowing water

No error bars are plotted on the graphs for a better readability of the figures. However, the analytical error was $< 5\%$. The influent concentrations of the four pharmaceutical compounds are shown in Fig. 4-3. SMX concentrations varied between 165 and 213 $\mu\text{g L}^{-1}$ and CBZ concentrations ranged from 188 to 199 $\mu\text{g L}^{-1}$. This variation in influent concentrations was due to the individual spiking processes for the different steps of the experiment (Tab. 4-2). SMX and CBZ did not show significant decline in concentration over time in the storage tank. In contrast, DCL and especially IBU concentrations declined significantly in the storage tanks, although the containers were protected against light. The saw tooth shaped curve of IBU reflects the connection of new storage tanks with "fresh" solution to the column. This additionally indicates the nitrate concentration steps (Fig. 4-3, Tab. 4-2). After 1 to 1.5 PV (which corresponds to approximately 6 to 9 days) IBU concentrations dropped regularly below the detection limit ($1 \mu\text{g L}^{-1}$) in the storage tank. Obviously, IBU was more stable in the presence of high nitrate concentrations: during the step with 129 mg L^{-1} nitrate, IBU concentration decline was significantly slower compared to the subsequent steps with lower but still high nitrate concentrations. Suarez et al. (2010) describe high aerobic

degradation rates of IBU, whereas anoxic degradation only occurs after long adaptation times of 340 days. Also Zwiener et al. (2000) observed removal rates for IBU of more than 90% under oxic and only 15% under anoxic conditions. The respective start concentrations of IBU ranged from 246 to 265 $\mu\text{g L}^{-1}$. DCL inflow concentrations varied from 271 to 295 $\mu\text{g L}^{-1}$. However, some DCL was regularly lost in the storage tanks after several days. After ~ 7.5 exchanged PV the column was flushed with non-spiked water (nitrate concentration 20 mg L^{-1}) and all pharmaceutical concentrations in the influent water dropped below the detection limit of the here applied chemical analytical method without pre-concentration.

4.4.3 Fate and transport of the pharmaceuticals

The pH at the outlet of the column remained constant at 6.9 throughout the experiment. This means that a pH depended transport resulting in a different mobility of the studied pharmaceuticals, e.g. resulting in a higher retardation of CBZ with decreasing pH (Schaffer et al., 2012) can be neglected. Dissolved oxygen at the outlet started at 5.3 mg L^{-1} at the beginning of the experiment (step 1). It decreased rapidly to zero after 0.6 PV and stayed at this level until the end of the experiment.

The breakthrough curves of the pharmaceuticals measured at the outflow of the column are plotted in Fig. 4-4. The first arrivals in the effluent were as follows: SMX after 1.0 PV, IBU after 1.1 PV, DCL after 3.0 PV, and CBZ after 6.0 PV. The first breakthrough of the conservative bromide was detected after 0.7 PV (peak maximum at ~ 1.0 PV). Based on the first arrivals the compounds were separated into two groups: SMX/IBU and CBZ/DCL. The first group was not/negligible retarded and the second group was significantly retarded in the column. In order to describe the transport behaviour of the second group adequately, we introduce the term *apparent retardation*. This was done as due to the stepwise decrease in nitrate supply during the experiment the compound breakthrough is a result of sorption and degradation. Once a critical nitrate concentration is reached at which degradation is no longer possible, the compound can be detected at the column outflow after its sorption influenced retardation.

SMX reached a maximum effluent concentration of 163 $\mu\text{g L}^{-1}$ ($c/c_0 = 0.85$) and the tailing was almost complete at the end of the experiment. The breakthrough curve of SMX is discussed in detail in chapter 4.4.4. IBU was slightly retarded and reached a maximum effluent concentration of 199 $\mu\text{g L}^{-1}$ (c/c_0 cannot be calculated due to the

strong attenuation in the storage tank). However, the interpretation of the IBU breakthrough curve was difficult, as a huge amount of the compound was already attenuated in the storage tank (Fig. 4-3). The fast decrease of IBU concentrations after a short peak in the effluent water emphasizes a fast attenuation of this compound. The higher stability in the presence of higher nitrate concentrations, which was observed in the storage tank, is supported by the effluent concentrations. A small peak after 5 PV and a larger peak after 7 PV reflect the breakthrough of the respective "fresh" influent solutions (Fig. 4-3, Tab. 4-2).

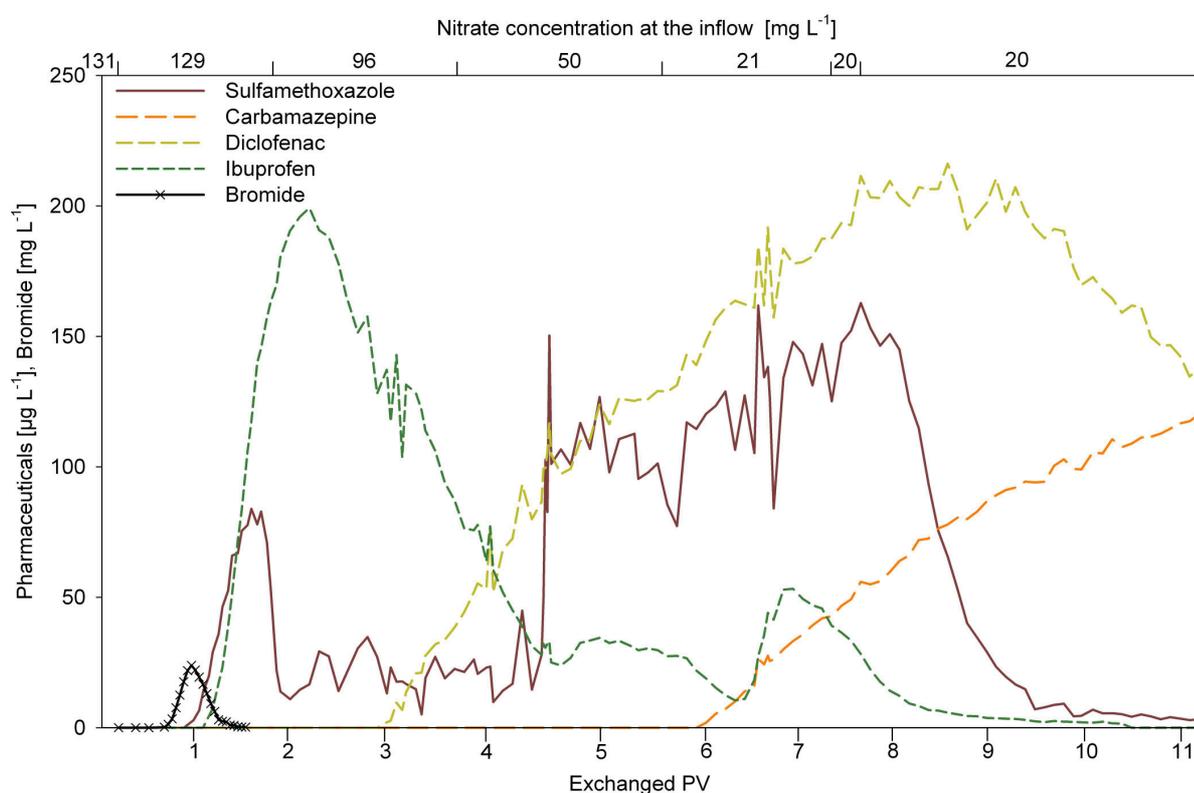


Fig. 4-4 Effluent concentrations of sulfamethoxazole, carbamazepine, diclofenac, ibuprofen, and bromide, and inflowing concentrations of nitrate (1 PV = 6.3 d).

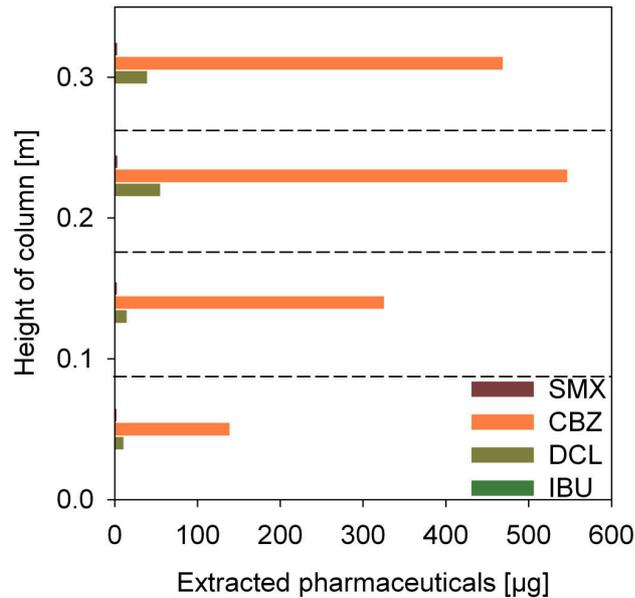


Fig. 4-5 Masses of sulfamethoxazole, carbamazepine, diclofenac, and ibuprofen extracted from the sediment material; dashed horizontal lines separate the four sampled sections.

For CBZ the apparent retardation was strong. Based on the properties of CBZ with a K_{OC} between 1.9 and 2.11 (Stevens-Garmon et al., 2011) and the sediment (bulk density = 1.4 g cm^{-3} , $n_e = 0.41$, $f_{OC} = 0.01$), the first arrival was expected just before 4 PV and full breakthrough at approximately 5 PV. The observed delay therefore indicates that CBZ can be degraded if f_{OC} and nitrate are present at significant concentrations. However, CBZ was also retarded due to sorption, as concentrations were still rising after 8.5 PV (arrival of the non-spiked inflowing water). At the end of the experiment a maximum effluent concentration of 120 µg L^{-1} ($c/c_0 = 0.62$) was reached. The retardation of CBZ was also observed in other column experiments (Schaffer et al., 2012).

For DCL, in contrast to CBZ, the apparent retardation is assumed to be mostly degradation of the compound at the highest applied nitrate concentration. DCL, like SMX and IBU, is an anion and therefore its first arrival was expected simultaneously with these other organic anions. The peak of DCL at 8.5 PV (arrival of non-spiked inflowing water) demonstrates that sorption does not contribute significantly to the apparent retardation of DCL. A maximum effluent concentration of 216 µg L^{-1} ($c/c_0 = 0.84$) was analysed for this compound. CBZ and DCL seem to have their breakthrough only after degradation is no longer dominating. The apparent retardation of these compounds is therefore assumed to be controlled by the nitrate concentrations.

After the experiment was finished the sediment material was removed from the column and samples from four sections of the column were taken and analysed for the pharmaceutical compounds. No IBU and only little SMX were found in the sediment samples (Tab. 4-3). However, for DCL and especially CBZ high concentrations were analysed. The distribution of the pharmaceuticals in the column sediments is plotted in Fig. 4-5. These analyses support the hypotheses regarding the apparent retardation of the compounds, which were based on the effluent pharmaceutical concentrations. No/negligible sorption for SMX and IBU was observed. The low recovered DCL concentration from the wet sediment demonstrates that its observed apparent retardation is degradation dominated. According to Barbieri et al. (2012) TP from DCL formed under denitrifying conditions has the potential to retransform into DCL under a changing redox condition. Thus, the here observed low DCL concentration from the sediment can not unambiguously be assigned to sorption. The high concentrations of CBZ which were extracted from the sediment material demonstrate that the observed apparent retardation for CBZ was sorption dominated.

Together with the water analyses therefore a simple mass balance was calculated (Tab. 4-3) and recovery rates between 45% (SMX) and 74% (CBZ) were obtained. The degradation rates of DCL and IBU matched the results from former column experiments under water unsaturated conditions which found elimination rates of 35% for DCL and 54% for IBU (Scheytt et al., 2006). However, as the apparent retardation of the compounds in this experiment was assumed to be controlled by the nitrate concentrations, a comparison with experiments under constant boundary conditions is difficult. For the conducted experiment the degradability of the pharmaceutical compounds in increasing order can be described as $CBZ < DCL < IBU < SMX$.

Tab. 4-3 Mass balance of the pharmaceuticals.

	SMX	CBZ	DCL	IBU
Influent water [μg]	2995	3057	4040	2027
Effluent water [μg]	1340	799	2553	1067
Extracted from sediment [μg]	7	1476	116	0
Recovery [%]	45	74	66	53

4.4.4 Spotlight on sulfamethoxazole

Especially for SMX, a strong dependency on the initial nitrate concentration was observed. Fig. 4-6 shows the effluent concentrations of SMX, nitrite, and nitrate. A negative correlation of nitrite/nitrate and SMX concentrations was very clear. As a direct reaction to increasing concentrations of nitrite/nitrate SMX concentrations dropped significantly. Immediately after nitrite and nitrate concentrations decreased SMX concentrations rose again.

By adding nitrate to the influent water (chapter 4.3.3) nitrate reducing conditions were supposed to establish in the column approximately between 1.9 and 4.5 PV, and its main indicator for this condition nitrite was detected at the outflow (Fig. 4-6). Nitrate reached its maximum concentration of 47.2 mg L^{-1} after 2.6 PV at the outlet of the column. During the supposed denitrification process nitrite was occasionally formed with concentrations up to 3.9 mg L^{-1} after 1.9 PV. The inflowing ammonium concentration was 0.17 mg L^{-1} on average and did not vary significantly. In the outflow, an average concentration of 1.05 mg L^{-1} was analysed, which was not influenced by the nitrate inflow concentration. Overall, 80% of the nitrogen was attenuated in the column. However, it is not possible to conclude which processes were simultaneously occurring inside the column during all stages of the experiment. Nitrite can also be formed during nitrate ammonification, especially in prolonged saturated condition with soil rich in carbon (Burgin and Hamilton, 2007). The nitrogen pathway is very complex and nitrite is also involved in nitrification, nitrate ammonification, chemical degradation, and nitrifier denitrification. Also, microbial uptake and decomposition may be involved. A limitation of N in the column during the experiment is not assumed, as throughout the whole experiment nitrate, nitrite, and ammonium were detectable at the outlet of the column.

As nitrite formation started, SMX concentrations dropped rapidly from 84 to $11 \text{ } \mu\text{g L}^{-1}$ and then sensitively responded even to slight variations of nitrite concentrations. After nitrate was removed completely (4.5 PV) the SMX concentration recovered as fast as it dropped before and reached $150 \text{ } \mu\text{g L}^{-1}$ within 12 h. This clearly demonstrates the connection of the stability/persistence of SMX to nitrite and the initial nitrate concentration, which was suggested by Nödler et al. (2012). The authors applied a high nitrate concentration (4.1 g L^{-1}) to anoxic water/sediment batch experiments and observed a negative correlation of SMX and nitrite. Effluent and sediment samples were

also analysed for the two transformation products of SMX, 4-nitro-SMX and desamino-SMX, which were observed by Nödler et al. (2012). They found that these two transformation products are formed under denitrifying conditions and that even a re-transformation of 4-nitro-SMX to SMX is possible. However, in the current experiment the metabolites were only detected in low concentrations up to $3.5 \mu\text{g L}^{-1}$ for desamino-SMX and up to $1.4 \mu\text{g L}^{-1}$ for nitro-SMX in the effluent water of the column. It is therefore assumed that denitrification was not the dominating process in the nitrate removal and the reactions of SMX and NO suggested by Nödler et al. (2012) occurred but that the expected metabolites were not formed preferably. This molar imbalance was also observed by Nödler et al. (2012). They discussed sorption of the analysed TPs and also the formation of other compounds. In the presented study TP sorption can be excluded as a significant reason for their low abundance. This is demonstrated by the extraction of sediment material (Tab. 4-3) as none of analysed TPs were found. However, desamino-SMX and nitro-SMX are reported as an unstable transformation product of SMX under denitrifying conditions (Nödler et al., 2012).

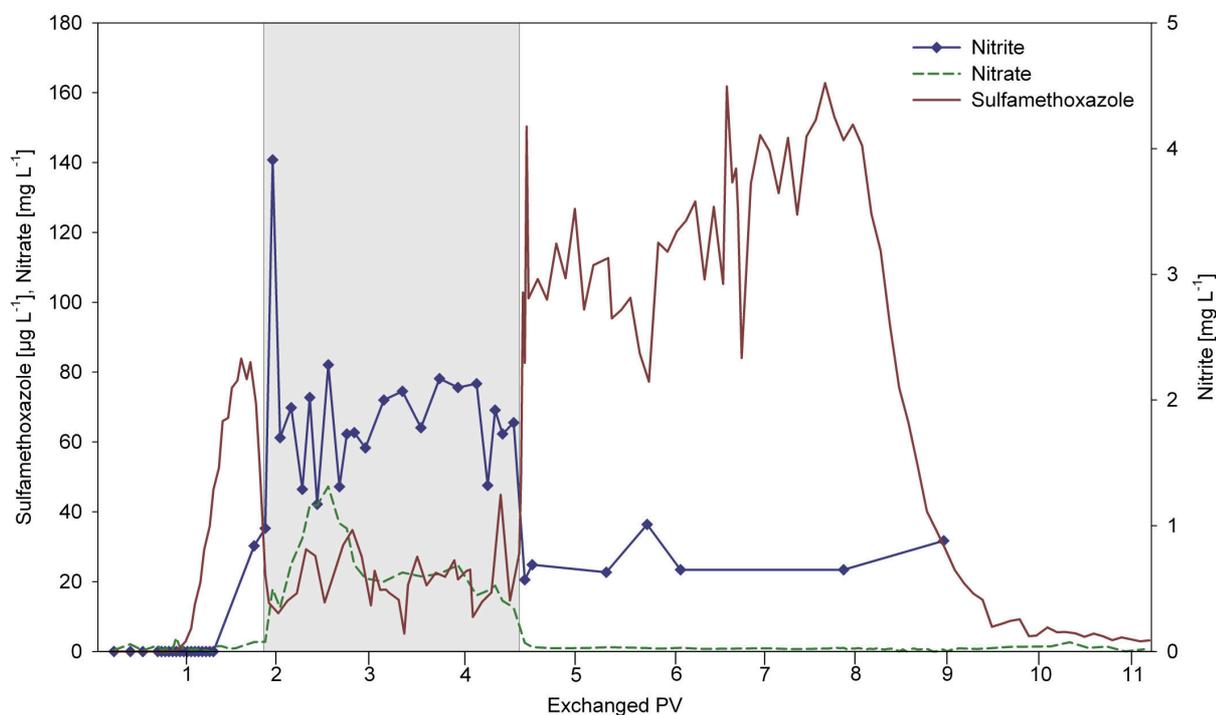


Fig. 4-6 Effluent concentrations of nitrite, nitrate, and sulfamethoxazole (1 PV = 6.3 d).

Apart from nitrate/nitrite and microorganisms (not investigated in this study) the sediment f_{OC} and dissolved organic carbon is also expected to contribute as a relevant parameter to the formation of the metabolites during nitrite/NO formation (Nödler et al., 2012). Dissolved organic carbon (DOC) concentrations in the influent water ranged from 0.9 to 6.8 mg L⁻¹ and decreased during the experiment. Effluent water DOC concentrations varied from 2.3 to 8.6 mg L⁻¹ and did not show a clear trend during the experiment. Baumgarten et al. (2011) investigated the removal of SMX in laboratory column experiments and described that the presence of a few mg L⁻¹ biodegradable DOC supports microbial activity and with that fosters the degradation of SMX. A study of Underwood et al. (2011) found that the presence of SMX significantly reduces bacterial growth rates and lowers the nitrate reduction rate potential. These findings support the strong dependency of SMX transformation on denitrification processes presented in this study. In contrast to studies by Baumgarten et al. (2011) who observed probably specific biological degradation of SMX after long adaption times of months to years, in this study the transformation of SMX was obviously chemically controlled and microbial-assisted by the formation of nitrite and NO, which was also observed by Nödler et al. (2012). However, other studies, which addressed the degradation and formation of SMX-metabolites, emphasize the results of this study (Barbieri et al., 2012; Nödler et al., 2012). Altogether, the described transformation behaviour and the redox-sensitivity of SMX explain why it is crucial to know the redox and specific boundary conditions such as the nitrate concentration when investigating and interpreting the occurrence and transport of SMX in the aquatic environment.

The use of corresponding water and sediment was appropriate to study the selected processes in the column experiment. The reproduction of identical natural conditions and from that a simple upscaling of the results to field scale was not the goal of this study. The presented results therefore are limited to the laboratory scale.

4.5 Conclusions

- Laboratory experiments that address the combination of sorption and degradation are important when studying micropollutants such as pharmaceuticals on field scale. The proposed apparent retardation therefore is more appropriate to characterise the mobility of the compounds in the environment.
- CBZ seems to be degradable when the f_{OC} of the sediment is high.
- IBU is more stable under denitrifying redox conditions.
- SMX is highly sensitive to nitrate reducing redox conditions.

This study demonstrates that changes in nitrate concentrations in the aquifer can have a strong influence on the degradation behaviour of the studied pharmaceuticals. The applied maximum nitrate concentrations of 131 mg L^{-1} were high. However, nitrate concentrations in German groundwater, which is influenced by agricultural use, are in more than 24% above 90 mg L^{-1} (Wolter, 2002). Therefore the results of this study are also relevant for studies in groundwater, especially at bank filtration sites. This study may also help to explain the sometimes contradictory wide ranges of reported degradability of SMX under varying specific redox conditions. As the here studied TPs of SMX were not predominantly formed, further experiments with higher nitrate inflow concentrations might be useful to investigate the transformation yields of the analysed SMX-TPs. Furthermore, the column experiment demonstrated the mobility of the compounds even for very fine-grained sediments.

4.6 Acknowledgements

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4.7 References

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Chapter 5

5 Seepage rates derived from thermal records using wavelet analysis

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5.1 Abstract

The main objective of this study was to determine if wavelet analysis can be used as a band-pass filter for non-stationary time series of temperature records. It was demonstrated that this new processing technique is efficient in calculating seepage velocities by using a virtual experiment and field data measured in the Mess Stream, Grand Duchy of Luxembourg, Europe. Temperature time series were measured continuously over a two-year period in the streambed sediments. The seepage velocity was derived from the one-dimensional analytical solution of Stallman. However, the ubiquitous property of the temperature signal is that it is non-stationary, i.e. the frequency component of the signal becomes a function of time. Instead of applying traditional filtering techniques based on the Fourier transform, we introduce the continuous wavelet transform (CWT) as a band-pass filter to extract the daily component from raw temperature data. For the analysed time series, the estimated seepage velocities based on the amplitude ratio were always negative and within the range of -0.7 to -2.5 m d^{-1} , indicating gaining conditions prevailing in the Mess Stream. The uncertainty associated with the seepage velocities was calculated by the Monte Carlo analysis allowing several physical parameters of the model to vary over pre-defined intervals with normal distribution. Auxiliary hydraulic measurements in the stream and in the riverbank confirm the dominance of gaining stream conditions. However, the seepage rates based on the thermal records were much higher than the calculated Darcy velocities. This study demonstrates the applicability of continuous wavelet transform as an alternative method to Fourier transform for the analysis of non-stationary temperature time series.

5.2 Introduction

For more than 100 years researchers have used heat as a natural tracer for surface water and groundwater interaction (Slichter, 1905). This cost-effective method was frequently used to detect exchange between these two compartments, and recent advancements have made temperature an accurate tracer to assess hyporheic exchange in streams (Anderson, 2005). The term hyporheic zone was introduced by Orghidan (1959) and describes the area below and adjacent to a stream where groundwater and surface water mix. It has been recognised that this zone is of great

importance regarding composition and quality of surface water as well as subsurface fauna (Hancock et al., 2005; Sophocleous, 2002; Triska et al., 1993).

Beginning with the simple description of temperature differences, researchers proposed methods for the calculation of water flow velocities and seepage rates based on temperature measurements. The best-known and hence most popular mathematical solution is the one-dimensional heat transport equation of Stallman (1965). The basis for these calculations of water fluxes is the fluctuation of the temperature signal on different time scales (e.g. diurnal, seasonal). Diurnal oscillations of the temperature signal are widely used to assess vertical flow rates of water fluxes in the streambed (Hatch et al., 2006; Keery et al., 2007; Silliman et al., 1995). The propagation of seasonal signals is studied to document exchange of surface water and groundwater on a larger timescale (Anibas et al., 2011; Molina-Giraldo et al., 2011). One advantage of using temperature as a groundwater tracer is that fluxes can be detected in a temporal and spatial distribution. Temperature measurements in streams using fibre-optic cables were recently introduced to hydrological sciences to detect gaining and losing reaches along the streambed (Briggs et al., 2012; Vogt et al., 2010).

The main issue when calculating seepage fluxes based on fluctuating temperature signals is to extract the daily component from raw temperature time series containing different frequencies (diurnal, seasonal, instrument noise, etc.). Among the various tools in time-frequency analysis, Fourier transform is the most commonly used (Hatch et al., 2006; Keery et al., 2007). The Fourier transform is useful to analyse the frequency signature over the entire time domain (defined by the length of the time series), but it cannot capture the frequency response with respect to time (Salerno and Tartari, 2009). In addition, it requires that the data under investigation are stationary. However, the ubiquitous property of environmental signals is that they are commonly non-stationary, i.e. the magnitude of the signal at a particular frequency varies with time. Wavelet analysis can be seen as a natural extension to spectral and Fourier analysis. While its application to hydrology is relatively recent, the potential for wavelet analysis is quite broad. Pidlisecky and Knight (2011) used wavelet analysis to derive infiltration velocities in a pond based on resistivity measurements. A study by Henderson et al. (2009) applied wavelet transform to analyse fibre-optic temperature data. Wavelet analysis has also been used for hydrograph recession analysis (Sujono et al., 2004), river flow forecasting (Adamowski, 2008), and to analyse the rain-

fall-runoff processes on various temporal scales (Liu et al., 2011). Another new approach to analyse non-stationary temperature time series is the dynamic harmonic regression that was recently introduced by Gordon et al. (2012).

The aim of this study is twofold: i) to introduce the continuous wavelet transform (CWT), cross-wavelet spectra, and wavelet-phase difference as a tool for the extraction of diurnal temperature signals from time series of streambed temperatures measured at two depths; and ii) to use the time lag and amplitude ratios calculated from the wavelet analysis to calculate seepage velocities. The method is demonstrated first on a virtual experiment and then using real temperature measurements conducted in an alluvial stream and its riverbank in the Grand Duchy of Luxembourg, Europe. Previous studies carried out at this field site (Banzhaf et al., 2011) are used to cross-check the results.

5.3 *Materials and methods*

5.3.1 Field site and installations

The practical application of wavelet analysis and seepage flux calculations based on temperature time series – which is described in sections 5.3.2 to 5.3.4 – is demonstrated using field data, which was collected over a period of almost two years in a small brook and its riverbank in the Grand Duchy of Luxembourg. The field site is described in detail by Banzhaf et al. (2011) and investigated by other studies like Banzhaf et al. (2012) Meyer et al. (2011) and Pailler et al. (2009). For this study, data from two temperature sensors and surface water and groundwater levels in the riverbank of the Mess Stream (Fig. 5-1) were used. Surface water levels were measured with a stream gauge (ISCO 4120 flow logger, pressure probe) with a logging interval of 15 minutes (average values), and groundwater levels were measured with pressure probes (OTT Orphimedes and UIT CTD) with a logging interval of 30 minutes (individual values). Temperatures were measured with PT 100 sensors (Model 107 temperature probe, Campbell Scientific) with a logging interval of 30 minutes (individual values) next to the stream gauge with a spacing of 0.13 m. The total error (thermistors interchangeability, bridge resistor and applied linearization) of the probe is $< \pm 0.3^{\circ}\text{C}$ over -25 to $+50^{\circ}\text{C}$.

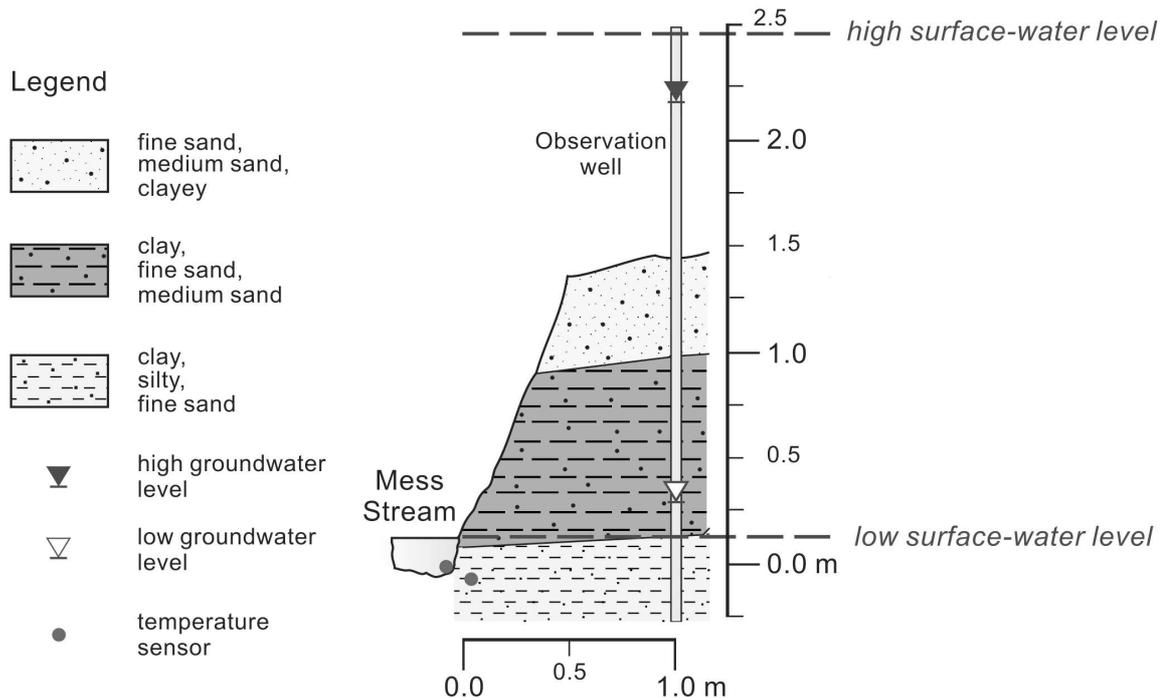


Fig. 5-1 Geological cross section of the field site including measuring equipment, and corresponding high and low levels of groundwater and surface water, modified from Banzhaf et al. (2011).

The cross section of the field site in Fig. 5-1 displays three layers in the riverbank: the uppermost layer has a thickness of 0.4 m and consists of clayey fine sand and medium sand, below follows a layer with a thickness of 0.8 m which consists of clay, fine sand, and medium sand. The deepest layer consists of silty clay and fine sand. During the installation of the observation well a maximum thickness of 3.3 m was measured (not displayed in Fig. 5-1).

Water levels in the stream and the riverbank are dynamic. During the investigated period levels of surface water ranged from 0.13 to 2.44 m and groundwater levels (in a distance of 1.0 m from the bank) from 0.31 to 2.19 m; all values were levelled relative to the stream gauge zero. During high-water peaks, the riverbank is temporarily flooded and losing stream conditions are indicated by the hydraulic measurements (Fig. 5-1). However, under low-water conditions the Mess is a gaining stream with the piezometric surface located in the middle layer of the riverbank.

The mean discharge of the Mess was 261 L s^{-1} in the year 2008. In summer, multi-peaked flood waves are characteristic in the catchment. Especially thunderstorms produce runoff events characteristic of a steep gradient and a relatively short outlet. Precipitation events of very small intensities and amount are indicated by small dis-

charge peaks, which result predominantly from the runoff from impervious surface areas. The long-lasting, low intensity winter precipitation events cause singular broad discharge maxima, which are primarily composed of laterally flowing soil water and groundwater (Meyer et al., 2011).

The hydraulic conductivity in the vicinity of the riverbank, which was calculated from measurements of well-water-level after pumping tests in the observation well, is $1.3 \times 10^{-6} \text{ m s}^{-1}$. The aquifer is confined (Banzhaf et al., 2011).

5.3.2 Calculation of seepage rates

As the ambient temperature signal propagates into the aquifer, it is attenuated and shifted in time (Molina-Giraldo et al., 2011; Stallman, 1965). The degree of signal attenuation and its shift are determined by the fluid flow velocity, thermal properties of the sediment (or soil) matrix, and the frequency of the temperature signal (Stallman, 1965). Stream water temperature fluctuates on different time scales, with strong diurnal and seasonal fluctuations (Hoehn and Cirpka, 2006).

Suzuki (1960) was among the first who applied diurnal fluctuations in the form of a sinusoidal function as the upper boundary condition to the heat transport equation. He presented a method for estimating vertical fluxes of water from the amplitude ratios of temperature oscillations measured between two depths in a streambed sediment layer. Stallman (1965) refined the mathematical solution to the one-dimensional advection-convective problem. For the vertical movement of water in saturated sediments (Hatch et al., 2006), the upper boundary conditions are defined as a sinusoidal forcing:

$$T_w(t) = \sum_i A_i \cos\left(\frac{2\pi t}{P_i} - \varphi_i\right) \quad (\text{Eq. 1})$$

where $T_w(t)$ is water temperature above the streambed ($^{\circ}\text{C}$) as a function of time t in s ; A_i is the amplitude of temperature variation at the water-sediment boundary ($^{\circ}\text{C}$); P_i is the period of temperature variations ($P = 1/f$, where f stands for frequency and P stands for period) and φ is the phase lag. With the upper boundary defined as a periodic fluctuation of temperature (Eq. 1), the analytical solution according to Stallman (1965) and Goto et al. (2005) leads to Eq. 2. Assuming the existence of a vertical

flow with a constant seepage velocity v_f (m d^{-1}) ($v_f > 0$ for a losing stream and $v_f < 0$ for a gaining stream), the thermal response of a sediment layer with depth z (m) to the upper boundary periodic forcing (Eq. 2) is defined as:

$$T(t, z) = A \exp\left(\frac{vz}{2k_e} - \frac{z}{2k_e} \sqrt{\frac{\alpha_i + v^2}{2}}\right) \cos\left(\frac{2\pi t}{P_i} - \varphi_i - \frac{z}{2k_e} \sqrt{\frac{\alpha_i - v^2}{2}}\right) \quad (\text{Eq. 2})$$

where A ($^{\circ}\text{C}$) is the amplitude of temperature variation at the water-sediment boundary; z is depth (m), v is the velocity of the thermal front (m s^{-1}); $k_e = \lambda / \rho c + \beta |v_f|$ ($\text{m}^2 \text{d}^{-1}$) is the effective thermal diffusivity dependent on the baseline thermal conductivity λ ($\text{W m}^{-1} \text{K}^{-1}$) of the sediment layer in the absence of fluid flow, the volumetric heat capacity of the saturated sediment-water matrix $(\rho c)_m$, ($\text{J m}^{-3} \text{K}^{-1}$) and dispersivity β (m) (Hatch et al., 2006). The saturated thermal conductivity λ can be calculated as the geometric mean of thermal conductivity of the sediment grains in the absence of water λ_s and thermal conductivity of water λ_f ($\text{W m}^{-1} \text{K}^{-1}$) as $\lambda = \lambda_s^n \lambda_f^{(n-1)}$, n (-) reflects the streambed sediment porosity. The thermal front velocity v is proportional to the vertical fluid flow velocity v_f through the ratio of the heat capacity of the fluid $(\rho c)_f$ and fluid saturated sediment matrix $(\rho c)_m$ as:

$$v = \frac{(\rho c)_f}{(\rho c)_m} v_f \quad (\text{Eq. 3})$$

where ρ (kg m^{-3}) stands for the specific density and c ($\text{J kg}^{-1} \text{K}^{-1}$) is the specific heat of fluid. The parameter α_i ($\text{m}^2 \text{d}^{-2}$) in Eq. 2 is defined as:

$$\alpha_i = \sqrt{v^4 \left[1 + \left(\frac{8\pi k_e}{P_i v^2} \right)^2 \right]} \quad (\text{Eq. 4})$$

where P_i (s) is the period ($P = 1/f$) of the signal.

Eq. 2 shows that sediment temperature is determined by the combination of thermal conduction, advection and dispersion, which is a nonlinear function of sediment and fluid thermal properties, fluid velocity and the frequency of surface temperature variations (Hatch et al., 2006). Higher-frequency temperature variations penetrate more rapidly into the streambed than do lower frequency variations, but are stronger dampened with depth. As described by Goto et al. (2005), Hatch et al. (2006), and Keery et al. (2007), two approaches can be adopted for calculating the seepage fluxes. For a pair of temperature measurements at depths z_1 (sensor T_s) and z_2 (sensor T_d) (m) beneath the streambed, and assuming that the effective sediment properties between these two depths are homogeneous, the velocity of the thermal front can be expressed as a function of amplitude or phase relations. One can use either the amplitude ratio (Eq. 5) or the phase shift (Eq. 6) to derive the seepage velocity.

$$A_r = \frac{A_d}{A_s} = \exp\left\{\frac{\Delta z}{2k_m}\right\} \left(v - \sqrt{\frac{\alpha_i + v^2}{2}}\right) \quad (\text{Eq. 5})$$

where A_r (-) is the amplitude ratio, k_m ($\text{m}^2 \text{d}^{-1}$) is the thermal diffusivity, and A_d and A_s ($^{\circ}\text{C}$) being amplitudes of the deeper and the shallower temperature series, respectively, Δz (m) is the spacing between two thermometers..

$$\Delta\phi = \frac{P\Delta z}{4\pi k_e} \sqrt{\frac{\alpha - v^2}{2}} \quad (\text{Eq. 6})$$

There are two possibilities to derive the thermal front velocity from Eq. 5 and Eq. 6. We can use either iterative techniques or look-up tables. While other authors suggest using iterations or optimization (Gordon et al., 2012; Goto et al., 2005; Hatch et al., 2006; Keery et al., 2007; Shanafield et al., 2011; Swanson and Cardenas, 2011); their temperature series covered only short periods of record, usually not exceeding a few months. We argue that for longer time series (several years), look-up tables might be a better option in terms of computation simplicity and hence reduce processing time. For example, having a 2-year record of 30-minute measurements of temperature, and running the model 1000 times to assess the uncertainty of input

variables, one would get $1000 \times 24 \times 48 \times 365 \times 2 = 840$ millions of runs. Considering that for each run the thermal velocity would be obtained by iterations, the computation process would become extremely time-consuming. Also, we used look-up tables to reduce the risk of finding a false minima in objective functions and hence incorrectly determined seepage velocities, which is a problem of all optimization techniques. The look-up table is simply a data array that stores a pre-calculated function response (in our case amplitude ratios versus seepage velocities) simulated for an arbitrarily chosen range of input parameters expected for a given stream reach (physical parameters of the sediment-water system). Retrieving an array of values from such a look-up table is much faster than making time consuming iterations, that would be essential to express the thermal front velocity, because it cannot be calculated implicitly (see that in Eq. 5 and Eq. 6 v is embedded also in α).

5.3.3 Sensitivity and Monte Carlo analysis

Thermal properties of the streambed sediments depend on many factors and differ with areas of application. Only few studies have attempted to determine these variables directly or explored the sensitivity of parameter selection on the uncertainty of the calculated seepage rates (Hatch et al., 2006). Since we did not measure the thermal properties of the streambed sediments, we opted to use the Monte Carlo Analysis (Briggs et al., 2012; Gordon et al., 2012) to estimate the seepage velocities for a pre-defined range of thermal properties of the streambed sediments. Assuming that the thermal properties of the streambed sediments are within the range of the considered values (Tab. 5-1), we estimated the mean and standard deviation of seepage velocities running 1000 Monte Carlo realisations. A normal distribution was selected for those variables that have been previously shown to have a great impact on uncertainties in the estimation of seepage velocities from thermal records (Shanafield et al., 2011): i.e. sediment porosity, thermal conductivity of sediment, specific heat capacity of sediment, density of sediment, and the spacing between two sensors (Tab. 5-1). The range of physical properties in Tab. 5-1 was chosen based on values reported in the literature (Hatch et al., 2006; Keery et al., 2007; Shanafield et al., 2011) and adjusted to expected values to be applicable for the silty conditions of the Mess Stream. Physical properties of water were not expected to exert a substantial effect on the seepage estimates, and were treated as constants.

The estimated range of seepage velocities was determined by calculating the real amplitude ratios (i.e. the ratio between amplitudes of diurnal fluctuations of temperature detected for the deeper A_d and the shallower A_s temperature series, see Eq. 5), and finding the corresponding seepage velocities in the look-up table. The same procedure was used in the case of the time lags and their relation to seepage velocity in Eq. 6. In natural systems such as rivers and streams, the only useful oscillation (of frequency) for solving Eq. 5 or Eq. 6 is the daily cycle. The daily cycle is usually obtained by filtering raw thermal signal using methods based on the Fourier analysis, as already presented by other studies (Gordon et al., 2012; Goto et al., 2005; Hatch et al., 2006; Keery et al., 2007; Shanafield et al., 2011).

Tab. 5-1 List of static and varying input parameters.

Name of variable	Abbreviations	Mean, standard deviation (indicated in parenthesis) and units for the Monte Carlo simulation
Varying input parameters		
Sediment porosity	n	0.3 (0.1)
Thermal conductivity of sediments	λ_s	1.4 (0.4) W m ⁻¹ K ⁻¹
Specific heat capacity of sediments	c_s	850 (100) J kg ⁻¹ K ⁻¹
Density of sediments	ρ_s	2700 (300) kg m ⁻³
Sensor spacing	Δz	0.13 (0.01) m
Thermal diffusivity	β	0.01 (0.005) m
Static input parameters		
Thermal conductivity of water	λ_f	0.7 W m ⁻¹ K ⁻¹
Density of water	ρ_f	999 kg m ⁻³
Specific heat capacity of water	c_f	4183 J kg ⁻¹ K ⁻¹

5.3.4 Frequency analysis using wavelets

The ubiquitous property of environmental signals is that they are commonly non-stationary, since the statistical properties of the diurnal signal (mean, maximum, minimum) change in time. While the dominant reason for the non-stationarity of the temperature signal in streambed sediments is the annual variation of solar income, the streambed hydraulic and thermal conductivity may also change over time due to scouring, clogging, growth of macrophytes and biofilms (Genereux et al., 2008). The use of classical Fourier analysis is therefore not suitable for the processing of such environmental signals, because the Fourier transform provides only a global information on the frequency content and hence the time localization of a specific frequency is lost in the analytical process (Salerno and Tartari, 2009). While applications of the continuous wavelet transform in hydrological applications are relatively recent, wavelets were first introduced in the geophysical sciences by Grossmann and Morlet (1984) as a tool for analyzing seismic signals (Bartosch and Wassermann, 2004). Sujono et al. (2004) used wavelet analysis in hydrograph recession analysis, Salerno and Tartari (2009) described the potential of wavelet analysis to define the nature and behaviour of karstic streams and their flow components. Anctil et al. (2008) used continuous wavelet analysis to characterise the temporal patterns of soil temperature profiles.

Since wavelet transform decomposes a signal into a time-frequency space, it can also detect localized intermittent periodicities in the signal (Grinsted et al., 2004).

The continuous wavelet transform (CWT) for a discrete sequence of measurements x_n with equidistant spacing δt is defined as the convolution product of x_n with a scaled (dilated) and translated wavelet $\psi(\eta)$ to balance between the time domain and frequency domain resolution depending on a non-dimensional time parameter η as:

$$W_n^X(s) = \sum_n^{N-1} x_n \psi * \left[\frac{(n'-n)\delta t}{s} \right] \quad (\text{Eq. 7})$$

where W^X is the wavelet power, n is the time index, s is the wavelet scale, δt is the sampling period, N is the number of observations in the time series, and the asterisk indicates the complex conjugate (Torrence and Compo, 1998). Since the above

equation leads to complex wavelet coefficients (containing real and imaginary parts), the wavelet power spectrum $|W_n(s)|^2$ is a convenient way to describe the fluctuations of the variance of a signal at different times and frequencies. A scalogram is the absolute value and square of Eq. 7, i.e. a graphical representation of $|W_n(s)|^2$ over the entire time and frequency domains.

Several mother wavelet functions can be used in the calculation of the CWT. An admissible mother wavelet has to have zero mean and a good localization in both time and scale domains (Farge, 1992). An appropriate mother wavelet should have a similar shape pattern as the investigated time series. We use the Morlet mother wavelet in this paper, as this mother wavelet has already been shown to work well with soil temperature time series due to its shape compared to other mother wavelets (Anctil et al., 2008). The Morlet wavelet is defined as:

$$\psi_0(\eta) = \pi^{-1/4} e^{j\omega_0\eta} e^{-\eta^2/2} \quad (\text{Eq. 8})$$

where ω_0 is the non-dimensional frequency ($\omega_0=6$) see Torrence and Compo (1998). The Morlet wavelet can be viewed as an attenuated Gaussian waveform. Because one is dealing with finite-length time series, a bias occurs at the beginning and at the end of the wavelet power spectrum because the wavelet is not completely localized in time (Grinsted et al., 2004; Torrence and Compo, 1998). A cone of influence (COI) has been proposed to ignore the edge effects. The COI is an area in which the wavelet power caused by the poorly localized wavelet near the beginning and end of a time-series has dropped to e^{-2} of the wavelet power at the edge (Grinsted et al., 2004).

For the calculation of the wavelet transform and its inverse, we used the suite of free-source Matlab codes for CWT written by Erickson (2011).

Since we are interested in quantifying the relationship between two time series of temperature, namely the phase shift and amplitude differences, the concept of cross-wavelet power and wavelet phase-difference are natural generalizations of the fundamental wavelet analysis. They allow us to analyse the time-frequency dependencies between the two time series of temperature.

The cross-wavelet transform (XWT) of two time series x_t and y_t , as described in Aguiar-Conraria and Soares (2010), is defined as

$$W_{xy} = W^X W^{Y*} \quad (\text{Eq. 9})$$

Where W^X and W^Y denote the wavelet transforms of x_t and y_t , respectively. The asterisk indicates the complex conjugate of the series y_t . A cross-scalogram is then a graphical representation showing the measure of the similarity of power at different frequency bands for two separate signals. Since we are using a complex-valued mother wavelet (the Morlet mother), the XWT is also complex-valued with an imaginary part and a real part. Therefore, the phase-difference between $\Delta\phi_{xy}$ the two time series at any point in time is defined as:

$$\Delta\phi_{xy} = \arctan\left(\frac{\Im(W_{xy})}{\Re(W_{xy})}\right) \quad (\text{Eq. 10})$$

Taking the inverse tangent function (Eq. 10) of the ratio of the imaginary and real parts of the XWT we obtain a phase difference between the two series anywhere between $-\pi$ and $+\pi$ (rad). A phase-difference of zero indicates that the two series are in perfect phase, i.e. moving together without any time lag. If $\Delta\phi_{xy}$ is constrained by zero and $\pi/2$, it is said that the time series y_t leads x_t ; and if ϕ_{xy} is constrained by $-\pi/2$ and zero, then the time series x_t leads the time series y_t . Having a space of phase-differences for all time scales (s) and all points in times (t), we can define the instantaneous time-lag $\Delta T_{xy}(s,t)$ between the two series for each scale and point in time as:

$$\Delta T_{xy}(s,t) = \frac{\phi_{xy}(s,t)}{\omega(t)} \quad (\text{Eq. 11})$$

Where $\omega(t)$ is the angular frequency corresponding to the wavelet scale s . We are interested in calculating the time-lag of the diurnal component of the signal, so that we can use it to estimate the seepage velocities. As we are interested in reliable es-

estimates of the phase difference between the components of the two signals, we estimate the seepage velocities only for intervals of cross-power with higher than 95% statistical significance that are outside the COI.

However, the wavelet cross-spectra power does not permit to describe separately the relations of amplitude and phase between two signals (Sello and Bellazzini, 2000). As we are interested also in the amplitude relations between the two signals, the amplitude ratios in particular, we chose to use the cross-wavelet coherence function (CWCF). The CWCF has been defined by Sello & Bellazzini (2000) as:

$$CWCF(s,t) = \frac{2|W_{xy}|^2}{|W_x|^4 + |W_y|^4} \quad (\text{Eq. 12})$$

Note that the values of CWCF range between zero and one. We will calculate the CWCF as a surrogate of the amplitude ratio which has also a range of values between zero and one.

As already mentioned before, the main advantage of wavelet analysis over spectral analysis is the possibility of tracing transitional changes across time.

In addition, to obtain only reliable estimates of seepage velocities, the wavelet spectra were subject to significance tests. We used the null hypothesis that the variability of the temperature signal does not arise from random noise. The wavelet power spectra and the wavelet coherence spectra were tested against white-noise spectrum (Torrence and Compo, 1998). Using a confidence level of 95%, if the diurnal signal was not above this level, we did not use the amplitude ratio and the time lag for the calculation of seepage velocities.

5.4 Results and discussion

5.4.1 Synthetic data set

As described in section 5.3.4 we used the CWT as a tool to extract the time lags and amplitude ratios between a pair of temperature measurements from two thermometers buried in streambed sediments. As the wavelet analysis is a rather new technique, and to familiarize the reader with it, we present an example with synthetic data mimicking a situation when the seepage velocities change from negative values to positive ones (Fig. 5-2). First, we generated two sets of 20 days of synthetic temperature data with 30-minute temporal resolution according to the following data generating process. We used forward-analytical modelling with Eq. 1-6 to derive virtual temperature signals in the hypothetical streambed under a fixed interval of seepage velocities. The range of seepage velocities (Fig. 5-2-C) was allowed to vary from ~ -3 to $+3 \text{ m d}^{-1}$. Fig. 5-2-A shows the synthetic time series. Then we applied the CWT to the synthetic series to derive the amplitude ratios and time lags. The wavelet-derived values of amplitude ratios and time lags are compared to the synthetically generated values in Fig. 5-2-B. Fig. 5-2-A shows that the temperature series measured by the deeper thermometer is lagging the temperature series from the shallower thermometer by a continuously increasing time lag from zero to 15510 seconds and the decreasing to zero time lag again (Fig. 5-2-B). At the same time the amplitude ratios change from 8.3×10^{-5} (virtually zero) to 0.999 (Fig. 5-2-B). Both time series have one periodic component representing the diurnal cycle. The synthetic temperature series have a 30-minute sampling interval, since we attempted to mimic a real-world situation when temperature readings are taken every 30 minutes.

Finally, in Fig. 5-2 D-E we see the calculated seepage velocities from the phase lags and the amplitude ratios approximated by the CWCF. We compared the synthetic velocities to the calculated ones to discover any discrepancies between the two. In the case of the amplitude ratios (Fig. 5-2-D), the wavelet-derived velocities do not substantially deviate from the synthetic series, perhaps except from a short period at the beginning and the end of the series where the edge-effect becomes dominant. On the other hand, the seepage velocities derived from phase lags are overestimated over the entire range of the considered seepage velocities (Fig. 5-2-E). This example

shall serve as an illustration of how precisely the time lags and amplitude ratios can be estimated from the wavelet analysis.

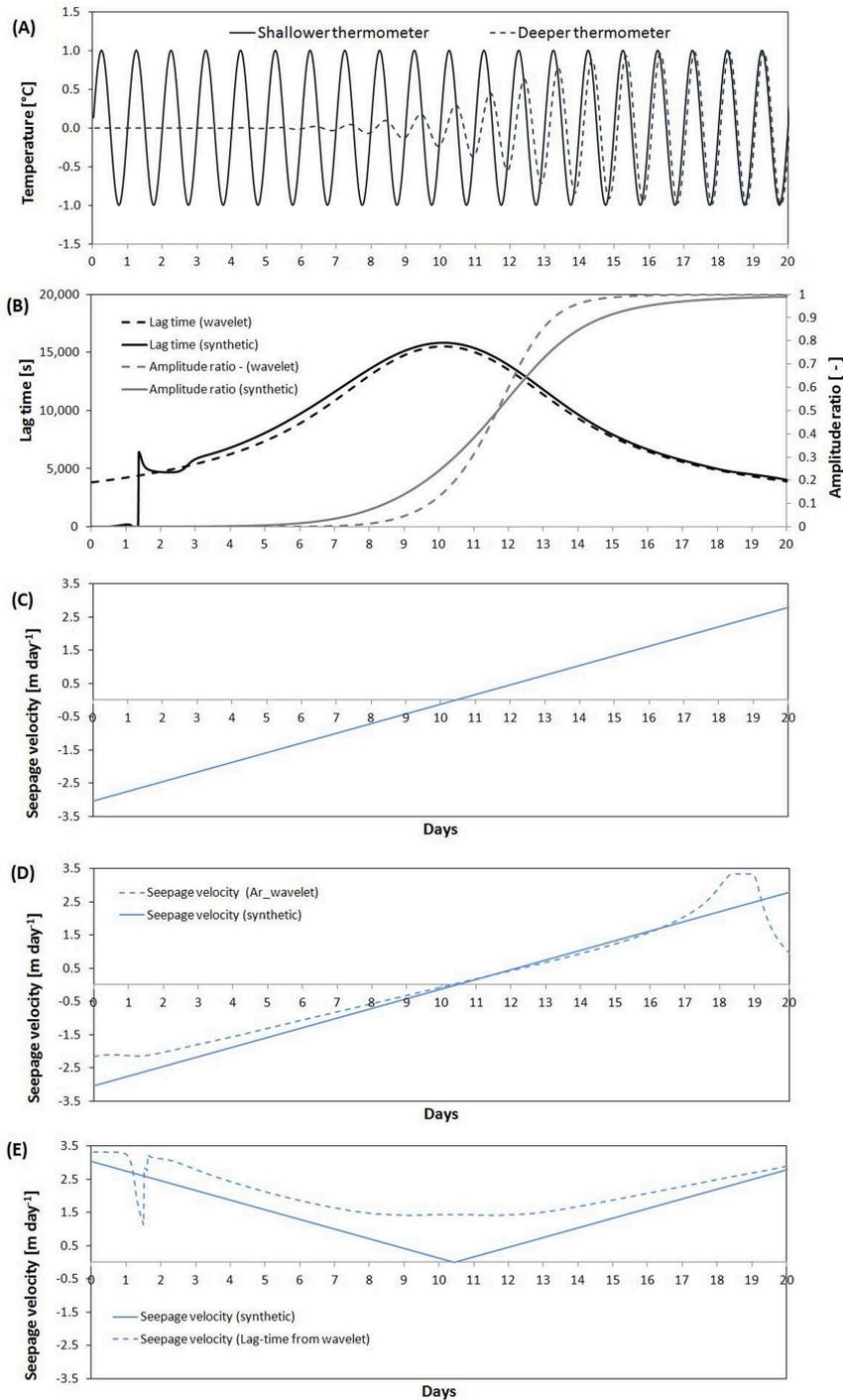


Fig. 5-2 (A) Time series of synthetic temperature series generated for seepage velocities (C) from -3.0 to +3.0 m d⁻¹. The amplitude ratios and the time lags between the two series (deeper and shallower thermometer) were generated by applying Eq. 1 through Eq. 5, with the following sediment properties: porosity $N=0.25$; thermal conductivity of sediments $\lambda_s=1.51 \text{ W m}^{-1} \text{ K}^{-1}$, specific heat capacity of sediments $c_s=911.9 \text{ J kg}^{-1} \text{ K}^{-1}$, density of sediments $\rho_s = 2203 \text{ kg m}^{-3}$, sensor spacing $\Delta z = 0.13 \text{ m}$, thermal conductivity of water $\lambda_f = 0.7 \text{ W m}^{-1} \text{ K}^{-1}$, density of water $\rho_f = 999 \text{ kg m}^{-3}$, specific heat capacity of water $c_f=4183 \text{ J kg}^{-1} \text{ K}^{-1}$. (B) comparison between synthetic amplitude ratios and time lags derived from wavelets; (D-E) comparison between synthetic seepage velocities and seepage velocities derived from amplitude ratio and lag times, respectively.

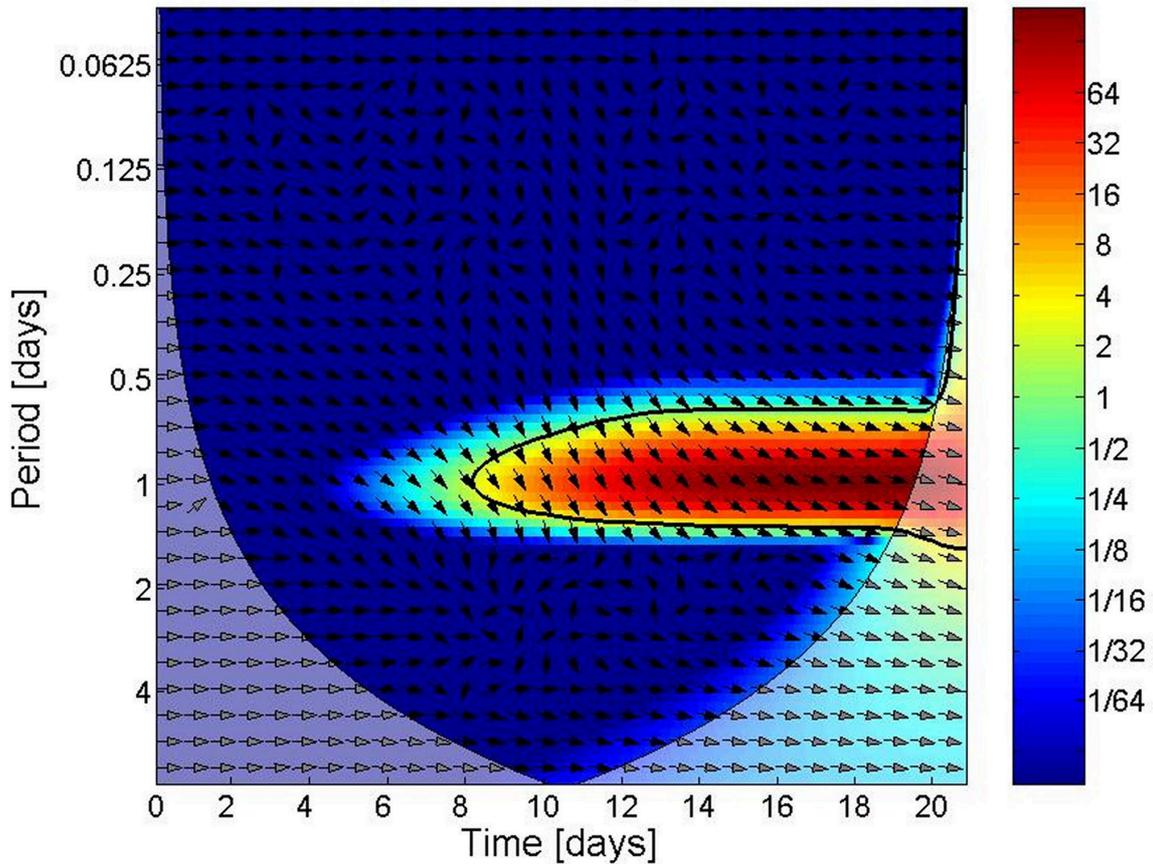


Fig. 5-3 Cross-wavelet spectra of the synthetic time series of temperature (see Fig. 5-2). The arrows indicate the phase relationship between the two temperature series. The colour bar indicates the “strength” of wavelet power. The more “red” it appears in the scalogram, the more power the spectra contains at that particular scale.

The corresponding cross-wavelet spectrum is shown in Fig. 5-3. The thick contour line shows the region of significant cross-wavelet power (95% significance level). The COI is indicated as the lightened areas. The scales corresponding to the diurnal signal lie between ~ 0.8 -1.2 days. Right-pointing arrows indicate a phase shift of 0 degrees (the two time series are perfectly in phase; down-pointing arrows indicate a time shift of 90 degrees. The scales (periods in the decomposed signal) corresponding to the diurnal signal are located between ~ 0.8 -1.2 days.

Fig. 5-4 shows the range of possible seepage velocities for the simulated example for physical properties of the sediment-water system in Tab. 5-1. The range of physical properties was chosen based on values reported in the literature (Hatch et al., 2006; Keery et al., 2007; Shanafield et al., 2011). Physical properties of water were not expected to exert a substantial effect on the seepage estimates, and are considered as constants. A large variability in the amplitude ratio is apparent for the lower range of

seepage velocities between -1 to 0 m d^{-1} . This already suggests that for small seepage velocities, the uncertainty associated with unknown physical properties of the system is large. For instance, for an amplitude ratio $A_r = 0.2$, the corresponding seepage velocity may lie anywhere within the interval from -0.8 m d^{-1} to $+0.1 \text{ m d}^{-1}$ (Fig. 5-4-B). The same holds true for the time lags (Fig. 5-4-A). Note that by definition, the positive sign of the seepage velocity indicates downward water movement through the sediments (losing stream), whereas the negative sign indicates upward fluxes of water (gaining stream). Fig. 5-4-A also indicates that it is not possible to derive the direction of flow based on the time lag only.

The idea is to estimate the range of seepage velocities from the wavelet-derived (Eq. 11) time lags and amplitude ratios determined from the CWCF (Eq. 12), and finding the corresponding seepage velocities in the look-up table.

To observe the performance of our approach, the simulated time lags and the amplitude ratios were compared with the wavelet-derived values (Fig. 5-2-B). There appears to be a small discrepancy between the simulated and wavelet-derived time lags at the beginning and the end of the time series, which is caused by the edge effects of the wavelet transform. Nevertheless, outside the COI, there is a good degree of agreement between the simulated and the wavelet-based estimates of both the time lags and the amplitude ratios. As for the amplitude ratios, there is underestimation of the ratios for negative velocities and overestimation for positive velocities (Fig. 5-2-B). This bias is then inevitably translated into biased estimates of seepage velocities as well. Despite this caveat of the small error introduced by the CWCF as a proxy of the real amplitude ratios, the novelty and added values of the CWCF (Eq. 12) and the instantaneous time lag (Eq. 11) over Fourier-based techniques is that the amplitude ratios and the time lags are determined at the same temporal resolution as is the sampling rate of the thermometers (e.g. 30-minute intervals). Other authors identify peaks (daily maxima and minima) to calculate the time lags and amplitude ratios (Goto et al., 2005; Hatch et al., 2006; Keery et al., 2007; Shanafield et al., 2011), but the sub-diurnal variation of seepage rates is lost by using only daily extremes. The novelty of our approach is that we can capture the finer variability of seepage velocities at temporal scales less than one day. Another added value of having fine-scale estimates of seepage velocities is that we can compare them to other surrogate measurements (e. g. groundwater levels measured in the riparian zone with high temporal resolution).

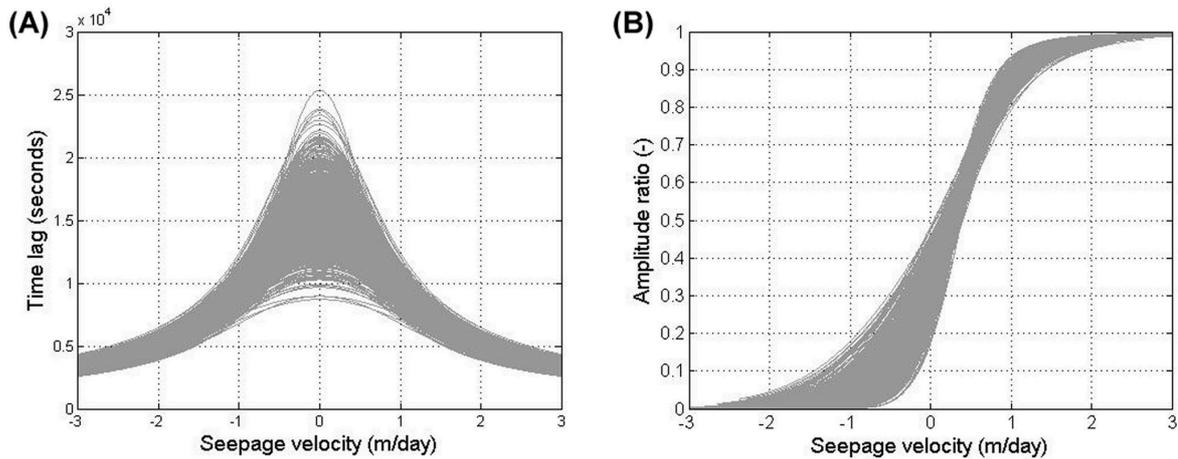


Fig. 5-4 Seepage velocities and the theoretical time lags (A) and amplitude ratios (B), simulated for varying thermal sediment properties, porosity and sensor spacing. The input parameters used to generate the graph with 1000 simulation runs are listed in Tab. 5-1. Positive velocities indicate losing conditions (downward water fluxes), and negative velocities indicate gaining conditions (upward water fluxes).

5.4.2 Field measurements

Apart from testing our approach on synthetic data, the above outlined procedure was also applied to the real field data with temperature measurements taken in the Mess Stream, Luxembourg.

The continuous wavelet power spectrum of the temperatures obtained by the shallower thermometer Fig. 5-5-A at depth z_1 (sensor T_s) exhibits a relatively strong power specifically over the period of 0.8 to 1.3 days. The time series is non-stationary, which is also discernable from the wavelet power spectrum (Fig. 5-5-A) and the cross-spectra between the shallower and the temperature series measured by the shallower and the deeper thermometers (Fig. 5-5-B). The colour bar indicates the “strength” of wavelet power. The more “red” it appears in the scalogram, the more power the spectra contains at that particular scale. The arrows show the direction of the phase difference. Right-pointing arrows show that the first time series leads the other by 90 degrees. Left-pointing arrows would indicate the opposite case, i.e. the second series leads the first series by 90 degrees. The non-stationarity of the spectrum is apparent from the altering strong and weak wavelet spectra within the range of daily scales. The seasonal effect is visible the most. The 1-day periodicity exhibits weaker energies during winter-spring seasons than in the summer months, which we explain by the influence of incoming solar radiation and the ambient air temperature

producing higher differences between daily maxima and minima of temperature in the summer season than in the winter. It should be noted that there are also other phenomena that can likely affect the non-stationarity of the signal, such as seasonally changing physical properties of the water-sediment matrix, e.g. the growth of biofilms and macrophytes, scouring and sedimentation (Genereux et al., 2008). Therefore the assumption of stationary boundary conditions for the conventional Fourier analysis may not always be satisfied at field conditions.

The time lags and amplitude ratios, which are input variables into the model (Eq. 1 through Eq. 6) have been used to calculate the seepage velocities. While there might be a signal in the diurnal range of scales of the CWT, if it cannot be rejected as being a result of noise, we cannot guarantee that it represented the diurnal component of the raw temperature signal. Therefore only time lags and amplitude ratios corresponding to energies in the CWT and WXT scalograms with confidence levels above 95% were used to calculate seepage velocities. Applying this criterion, we obtained an intermittent series of seepage velocities (Fig. 5-6), since some parts of the temperatures could not be accepted as being statistically significant. Testing the raw temperature signal against a background noise (white-noise) is important to have confidence in derived seepage estimates.

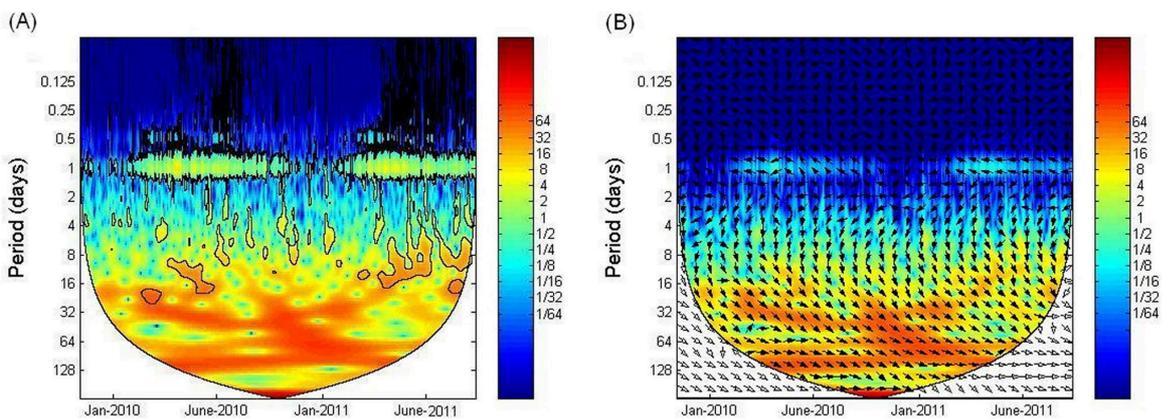


Fig. 5-5 A) The wavelet power spectrum for temperature time series of temperature measured with sensor T_s . A strong diurnal cycle can be seen in the wavelet power spectrum. Sub-daily frequency components are strongly attenuated, which is indicated as diminishing red-yellow colour and eventually turning blue at scales below 0.8 days. A strong seasonal effect on the magnitude of daily temperature fluctuations is apparent, i.e. weaker amplitudes in the winter seasons and stronger amplitudes in the summer seasons. Note that the cone of influence does not affect the wavelet power spectrum at scales corresponding to the diurnal signal (period \sim 0.8-1.2 days); (B) Cross-wavelet spectra of temperature measured by the deeper and shallower sensors (T_d , T_s).

Further, we were interested in calculating all possible values of seepage velocities that would arise due to unknown physical properties of the sediment-water matrix. In this way we could estimate the range of seepage velocities and calculate the mean values and standard deviations. We allowed the physical properties of the streambed sediments to vary over defined intervals following the Gaussian distribution (Tab. 5-1). Then we calculated the theoretical amplitude ratios and time lags for the defined interval of seepage velocities from ~ -3 to $+3$ m d^{-1} (Fig. 5-2). From such a look-up table, the real seepage velocities were obtained and plotted in Fig. 5-6. The raw temperature time series of the two sensors is shown in Fig. 5-6-A.

For the analysed time series, the estimated seepage velocities based on the amplitude ratio were always negative (Fig. 5-6-B), indicating gaining conditions prevailing in the Mess Stream. For the seepage velocities based on the time lag only absolute values could be obtained (Fig. 5-6-C). The uncertainty associated with the seepage velocities is expressed as a standard deviation to the average values of seepage velocities calculated by the Monte Carlo analysis. The standard deviation of the estimated seepage velocities ranges from 0.2 to 0.3 m d^{-1} for the amplitude ratio and from 0.1 to 0.4 m d^{-1} for the time lag. Seepage velocities (mean values) range from -0.7 to -2.5 m d^{-1} for the amplitude ratio and from 0.1 to 3.0 m d^{-1} (absolute values) for the time lag. Although the uncertainty may appear to be quite high, the uncertainty of seepage velocities estimated from thermal records is much smaller compared to conventional Darcy flux estimates using piezometric data (Keery et al., 2007; Lautz, 2010). Since we cannot verify the assumption of vertically moving water in the streambed as required by the original analytical model of Stallman (1965), we anticipate that a lateral flow component might exist in the system. This violation of the vertical flow assumption for the calculation routine introduces an additional error in the estimated seepage fluxes but still allows the relative comparison of the obtained velocities (Lautz, 2010). Also Cuthbert and Mackay (in revision) claim, that the heat flow does not have to be strictly vertical as a prerequisite for applying the Stallman approach. However, they state that significant errors can stem from non-uniform (convergent/divergent) flow fields and/or hydrodynamic dispersion even within uniform flow fields.

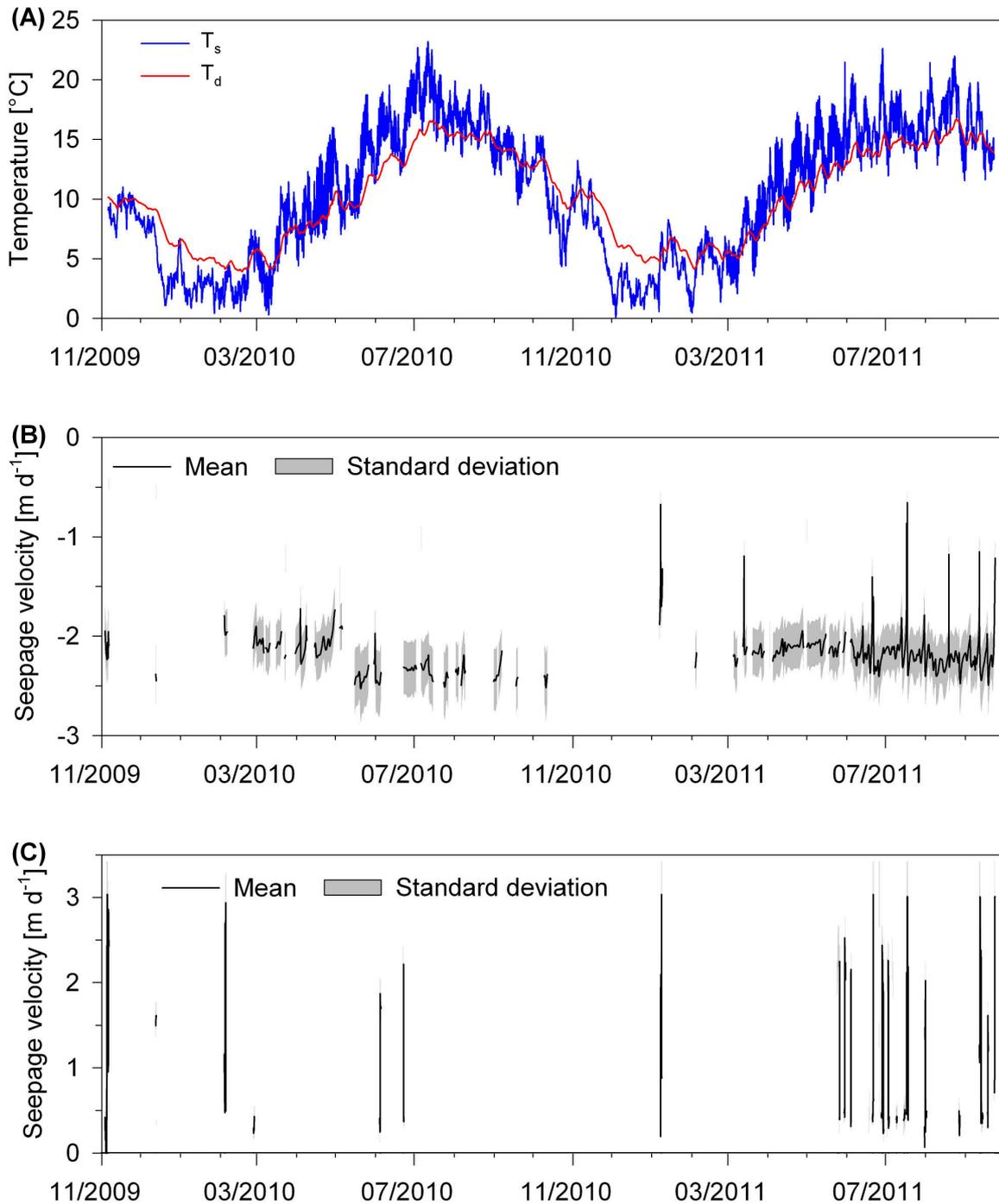


Fig. 5-6 Raw temperature data (A) and seepage velocities (mean \pm standard deviation) calculated from the temperature oscillations; amplitude ratio (B) and time lag (C). Note that the velocities in (C) are only absolute values and do not indicate a flow direction. The distance between the sensors is 0.13 m.

Since we did not carry out piezometric measurements within the stream channel, we cannot compare our results directly with hydraulic data and the resulting Darcy velocities. However, we can compare the obtained seepage velocities with Darcy velocities that are calculated from the hydraulic gradient between the stream and the

riverine groundwater 1.0 m from the bank (Fig. 5-1). The comparison of the velocities is plotted in Fig. 5-7. It is obvious that the absolute seepage velocities based on the temperature measurements are more than one magnitude higher than the Darcy velocities. Despite the discrepancy in the data, both Darcy velocities and temperature-based seepage velocities demonstrate the dominance of gaining stream conditions. The hydraulic data therefore confirms the seepage flow direction obtained from the temperature records. Only during flood events (mostly during winter) the hydraulic gradient between stream and riverine groundwater is reversed for a short time and losing stream conditions are documented (Fig. 5-7).

Due to the aforementioned setup of the measuring equipment the different velocities are not directly comparable and also the uncertainty of the Darcy velocities is quite high. Engelhardt et al. (2011) calculated horizontal infiltration velocities in a riverbank using Darcy's law with a mean value of 0.06 m d^{-1} and an error of 0.04 m d^{-1} . They also found that vertical Darcy velocities in the streambed at the same field site were much higher, reaching maximum values up to 5.3 m d^{-1} .

The seepage velocities obtained from the temperature data appear to be quite high, especially when considering the fine grained sediment which is found in the riverbank (Fig. 5-1). A study of Langhoff et al. (2006) measured seepage fluxes with seepage meters in the streambed of a sandy river between 0.09 and 1.3 m d^{-1} and Hatch et al. (2006) calculated mean seepage rates based on thermal records of up to 1.3 m d^{-1} .

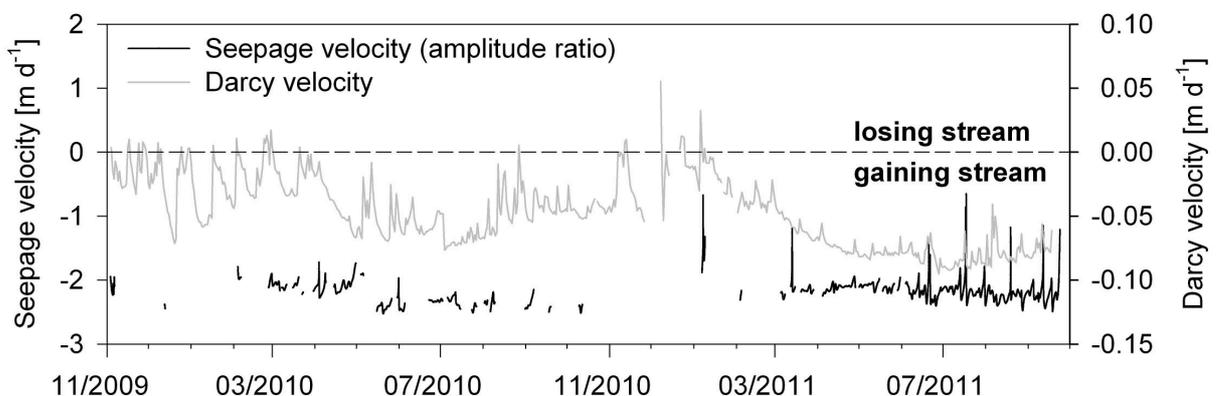


Fig. 5-7 Comparison of seepage velocities (based on the amplitude ratio) determined from temperature records with Darcy velocities in the vicinity of the stream calculated from hydraulic measurements.

The analysis of the temperature data from the two temperature sensors using wavelet analysis delivers good results as a daily component of the signal could be extracted and used to calculate seepage rates. It has to be mentioned that other temperature sensors were installed at the field site in the riverbank at greater depth and distance from the bank which showed seasonal temperature oscillations. But as no daily component could be identified when analysing the time series these data is not presented in this study. The topic of stationarity or non-stationarity of temperature signals for the quantification of surface water and groundwater exchange was addressed by Anibas et al. (2009). They state that there are times of the year where stationarity can be assumed when calculating water fluxes although non-stationary conditions are observed in the thermal records. The method presented in this study, however, allows the use of non-stationary temperature time series for the calculation of seepage rates.

5.5 Conclusions

We used the continuous wavelet transform for band-pass filtering of inherently non-stationary time series of temperature records in order to obtain the diurnal temperature signal (scale (period) > 0.8) and use it as a tracer of the vertical movement of water in the streambed sediments. Our objective was to calculate sub-daily estimates of seepage velocities using only temperature measurements from streambed sediments. The seepage velocity was derived from the one-dimensional analytical solution of Stallman (1965). To extract the diurnal cycle from the raw temperature records, we introduced the method of CWT as an alternative band-pass filter. While several techniques based on the Fourier transform are traditionally applied as band-pass filters to extract desired frequency component from raw data, the major advantage of the wavelet analysis lies in its capability to handle non-stationary time series where conventional Fourier transform is not suitable. This is especially important when dealing with longer time series for which the assumption of stationary conditions may not be satisfied.

First, we tested the appropriateness of the CWT on a set of two synthetic temperature signals from a virtual experiment. The estimated seepage velocities agreed well to the synthetic series. To demonstrate the approach on a real-world example, we then used a temperature time series measured continuously over a two-year period in the streambed sediments of the Mess Stream, Luxembourg, Europe. The results of this study show that the negative values of seepage velocities estimated from the temperature records are in agreement with our previous knowledge obtained from hydraulic observations, i.e. that the Mess is a gaining stream throughout most of the year. Despite the uncertainties in several input parameters required to precisely estimate the seepage velocities applying the Stallman solution, this method confirmed the existence of upward fluxes of water from the hyporheic zone to the stream.

Overall we could demonstrate the use of wavelet analysis for the extraction of diurnal temperature signals from temperature time series. The novelty of our approach is that we can extract seepage velocities with the same temporal resolution as the raw temperature time series, statistically tested for confidence. Therefore, sub-diurnal estimates of seepage velocities can provide a finer insight into the variability of seepage velocity especially in small streams where runoff-events change rapidly and last less than one day.

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Chapter 6

6 Synthesis

In the previous chapters (2-5) the results of field-based studies and laboratory experiments on the hyporheic zone were presented. These investigations were conducted in the course of a PhD-project and culminated in this thesis. Field work was carried out at a site in the Grand Duchy of Luxembourg and laboratory work was carried out at TU Berlin. This study had the following main focuses:

1. Evaluate the use of selected pharmaceutical compounds as anthropogenic indicators for surface water and groundwater interaction.
2. Study the redox-dependent transport and degradation behaviour of selected pharmaceuticals under water saturated conditions.
3. Develop and test a new method to derive seepage rates in the hyporheic zone from temperature measurements.

6.1 Summary and discussion of the main findings

The manuscripts presented in chapters 2 and 3 document the existence of a hyporheic zone in the studied riverbank. Hydraulic measurements in the stream and the riverine groundwater documented changes from effluent to influent aquifer conditions. Therefore, mixing of surface water and groundwater was assumed. To test this assumption, water samples from stream and riverine groundwater were analysed for pharmaceutical compounds. Previous studies that focused on flood events in the stream, regularly detected pharmaceuticals in the surface water (Pailler et al., 2009). The results of this work, however, proved the interaction of water from the two compartments surface water and groundwater. Additionally, gradients with depth for some of the analysed pharmaceuticals were observed in the riverbank. Although effluent aquifer conditions were dominant during the investigated period (10/2009 –

11/2010), the pharmaceuticals were detected in the riverine groundwater. Hence, a preferred infiltration of surface water into the riverbank during flood events was concluded. Furthermore, and supported by hydraulic measurements, it was observed that the extent of the hyporheic zone is dynamic (below 1 m of variation). Altogether, the chosen pharmaceuticals were regarded as characteristic for the field site and suitable as anthropogenic indicators. As expected, the compounds that were classified as mobile (e.g. carbamazepine and sulfamethoxazole) seemed to be more suitable for this application due to their conservative transport behaviour. Additionally, hyporheic interaction was first documented also for a riverbank with a low hydraulic permeability.

In chapter 4 the results of a laboratory column experiment under varying redox-conditions that considered sorption and degradation of selected pharmaceuticals as a combination are presented. The proposed *apparent retardation* therefore was regarded as more appropriate than *retardation* to characterise the mobility of the compounds in the environment. It was shown that changes in nitrate concentrations and resulting specific redox conditions can have a strong influence on the degradation behaviour of the studied pharmaceuticals. As the applied maximum nitrate concentration of 130 mg L^{-1} was already observed in groundwater in Germany, this study is also relevant for groundwater studies on the field scale. Furthermore, the mobility of the studied compounds in very fine-grained sediment, which was already observed on the field scale, was confirmed by the conducted column experiment.

In the manuscript that was introduced as chapter 5 seepage rates in the hyporheic zone were calculated based on temperature measurements. Moreover, the use of continuous wavelet transform to extract the diurnal temperature signal from highly non-stationary time series was demonstrated. It was shown that this method is an alternative to established methods, e.g. using the Fourier transform, especially for its application on non-stationary time series. Furthermore, the detection of effluent/influent aquifer conditions is possible. The seepage rates that were calculated based on the daily temperature signals indicated the dominance of effluent aquifer conditions during the studied period of two years. This was confirmed by calculated Darcy velocities from hydraulic data that was also measured at the field site. However, there was a discrepancy regarding the absolute seepage velocities, which might be caused by insufficient quality of the input data due to installation issues.

This cumulative thesis covers selected aspects of processes that characterise the hyporheic zone. It was shown that the chosen methods are appropriate to describe this compartment at the interface of surface water and groundwater. Although the conducted studies lead to a more comprehensive understanding of this complex system, the results are, at least to some part, site-specific. However, the methods for the investigation of the hyporheic zone that were applied in this work are transferable to other sites.

On the one hand the use of pharmaceuticals as anthropogenic indicators/tracers seems to be a promising method also in other studies (Lapworth et al., 2012; Müller et al., 2012). On the other hand, numerous surveys agreed that an environmental input of pharmaceutical compounds generally should be avoided (Jones et al., 2005; Leal et al., 2010; Wu and Janssen, 2011). However, this work presents a beneficial side effect of the presence of these compounds in the aquatic environment by using them as indicators at low ng L^{-1} -concentrations.

Overall, it seems that an environment free of any contamination by pharmaceuticals is desirable but not achievable, as these compounds are not completely removed during conventional wastewater treatment (Gros et al., 2007). Therefore, studies that aim at predicting environmental concentrations of pharmaceuticals in drinking water resources are needed, e.g. when bank filtrate is used for drinking water production. For instance, Müller et al. (2011) presented a new approach to calculate the predicted environmental concentrations (PECs) for human pharmaceuticals at bank filtration sites based on surface water concentrations. Their method is compound and aquifer specific and realistic values for PECs in groundwater can be obtained with this approach.

However, the behaviour of pharmaceuticals in different sediments and under different geochemical conditions is supposed to be highly variable. The presented column experiment on the transport of selected pharmaceuticals demonstrated the sensitivity of these compounds to different geochemical environments. Moreover, it was documented that the compounds show very different behaviour if the boundary conditions (in this case the specific redox conditions) are varied. To verify the obtained results, however, a rerun of the experiment might be helpful. In addition, column experiments with different sediments but with the same setup and boundary conditions might be helpful. Also a more detailed investigation of the transformation products of the stud-

ied compounds is encouraged (Barbieri et al., 2012; Nödler et al., 2012). This is crucial, since transformation products of pharmaceuticals can have similar pharmacological activities as their parents (de Jongh et al., 2012).

Another approach to study the interaction of surface water and groundwater – and with this also the potential input of pharmaceuticals into groundwater – is the use of temperature as a tracer. Whereas the analysis of water samples for pharmaceuticals on the ng L⁻¹-range delivers point measurements, temperature can be easily measured continuously. Therefore, a combination of these two approaches can yield a more complete dataset and with this also a more comprehensive system-understanding. The method that was introduced in the manuscript was successfully tested by using temperature records, which were measured at the field site. Although the diurnal oscillations of the temperature signal in the riverbank were quite small seepage rates could be calculated. In addition to the two temperature time series that were used for the calculation of seepage rates in the manuscript, there were six more temperature sensors installed at the field site. However, the obtained temperature time series from these six sensors showed only seasonal/long term changes, as the diurnal signal did not propagate that deep into the riverbank. The low amplitude of the temperature signal might be the most plausible explanation for the discrepancy of temperature-based seepage rates and calculated Darcy velocities at the field site. Therefore, the introduced method may be more appropriate for compartments with a higher hydraulic permeability and a deeper propagation of the daily temperature signal. As an alternative to the presented approach, other studies suggest to use the seasonal temperature signal that propagates into the aquifer to estimate infiltration rates and near-river groundwater velocities (Anibas et al., 2011; Molina-Giraldo et al., 2011).

In general, the hyporheic zone is in the focus of current research worldwide (Briggs et al., 2012; Lewandowski et al., 2011b; Westhoff et al., 2011). Moreover, it is "common sense" that this area is of great importance, e.g. for river water quality. However, Wondzell (2011) raised the question, if the hyporheic zone is less important in stream ecosystems than is commonly expected. He stated that, if one considers only the proportion of stream discharge, which is exchanged through the hyporheic zone this area will only play a major role in small streams under low discharge conditions. Nevertheless, when considering all processes that occur in this area, he confirmed the overall importance of the hyporheic zone to stream ecosystems. Research on this

transition zone, which covers a wide range of disciplines (e.g. hydrology, ecology, toxicology, hydrogeology, and water resources), therefore is crucial to assure a sustainable use of the resource water. Moreover, studies on a small scale – like this work – may help to enhance the understanding of processes that are relevant also on the catchment scale.

6.2 Open questions, lessons learned, and recommendations for future studies

Although the results, which were obtained from the presented field and laboratory work, are consistent, some questions still remained unanswered.

One issue that could not be addressed was to gain a precise understanding of the flow paths of the riverine groundwater. The data that was yielded from the installed observation wells and pressure probes did not allow detecting small scale flow patterns in the riverbank, as the measuring network was not fine enough. Therefore, riverine groundwater flow may have had rectangular, parallel, and angled components (relative to the stream) that could not be considered in this work. These components, however, could have influenced the movement and resulting concentration distribution of, e.g. the studied pharmaceutical compounds in the riverbank. Current research confirms the impact of small-scale heterogeneities of streambed and aquifer permeability on surface water and groundwater interaction (Fleckenstein et al., 2006; Kalbus et al., 2009; Lewandowski et al., 2011a). However, the overall impact of heterogeneity on hyporheic flow is not yet fully understood. Therefore, a future research question might be, if the extent of unexpected observations (e.g. concentration distributions of pharmaceuticals in the riverine groundwater) is proportional to the heterogeneity of the riverbank. Hence, this study would have benefited from a finer measuring network. Nevertheless, the obtained results allow a process-supported conceptual understanding of the system surface water/groundwater.

As the sediment material at the field site was very fine grained (high amount of silt and clay), the resulting hydraulic conductivity was also low ($\sim 2.3 \cdot 10^{-6} \text{ m s}^{-1}$). Therefore, also diffusive transport of the pharmaceuticals may have contributed to the overall input of these compounds into the riverbank. In addition, a remobilisation of the pharmaceuticals through desorption may be an explanation for the higher concentra-

tions at shallower depths, which were observed in the shallower parts of the multi-level observation wells. While no sediment samples from the field site were analysed for the studied pharmaceuticals to verify this hypothesis, sediment samples from the column experiment were analysed. These analyses demonstrate that, e.g. for ibuprofen and sulfamethoxazole sorption was negligible. This, however, does not necessarily apply for the other pharmaceuticals, which were studied on the field scale. As the observed low hydraulic permeability will likely be found at other lowland rivers or brooks, the results of this work might also question the often assumed high dynamic in hyporheic zone.

Furthermore, the installed equipment could be optimised. To allow for a more precise distinction between surface water, groundwater, and hyporheic water, an observation well in a greater distance from the stream would have been helpful. However, this was not possible due to administrative and landowner issues. In general, the selection of appropriate measuring equipment and an adequate sampling procedure are crucial for obtaining useful results. Furthermore, sound knowledge of the local hydrogeology is required when studying the hyporheic zone.

Although the field site in Luxembourg had challenging conditions to study hyporheic exchange (e.g. due to the low hydraulic permeability), it was demonstrated that the chosen methods can be used even under these constraints. However, the low exchange of surface water and groundwater resulted in some of the above discussed issues. Altogether, the work could contribute to the understanding of hyporheic interaction especially in low permeable systems.

The results presented in this thesis prove that pharmaceutical compounds can be used as anthropogenic indicators in the hyporheic zone. Furthermore, the findings on redox-dependent transport of selected pharmaceuticals contributed to the overall understanding of the fate of these compounds in the aquatic environment. Also the new method to analyse time series of thermal records for calculating seepage rates and detecting effluent/influent aquifer conditions is transferable to other sites.

Finally, a rough schedule for applying the presented methods as an alternative to the standard methods can be provided. Based on the field work for this thesis, a recommendation for a work flow to use pharmaceuticals and temperature as indicators in the hyporheic zone is suggested as follows:

1. Screen surface water for pharmaceutical compounds (regularly detected in a significant concentration, known transport behaviour, source-specific, e.g. carbamazepine and sulfamethoxazole are proposed for this purpose).
2. Identify potential sources of the detected compounds (e.g. wastewater treatment plants, sewage overflows, agriculture).
3. Install appropriate sampling equipment in the surface water, in the riverbank, and in the aquifer (the measuring network should be fine and high resolution measuring equipment is required, e.g. the CMT multilevel observation wells from Solinst Canada Ltd., which were used in this study, are appropriate).
4. Install sensors to measure temperature changes/gradients across the hyporheic zone (the logging of stream and adjacent groundwater temperature is only recommended if exchange is not expected to be too low, e.g. due to a low hydraulic permeability)
5. Adapt sampling frequency and duration to the respective boundary conditions (seasonal- or event-based sampling, e.g. in this study flood events were identified as most relevant for surface water and groundwater interaction)

6.3 References

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Annex 1

Eidesstattliche Erklärung

Hiermit versichere ich, Stefan Banzhaf, an Eides statt, dass die vorliegende Dissertation in vollem Umfang von mir selbst erstellt wurde. Es wurden keine weiteren als die angegebenen Quellen verwendet.

Berlin, den 24.10.2012

Stefan Banzhaf

Annex 2

Outline of the author's contribution

(Angaben zum Eigenanteil)

The thesis comprises four manuscripts, which are presented in chapters 2 to 5. The author's contribution to each manuscript is described below.

Chapter 2 – first author

Investigative approaches to determine exchange processes in the hyporheic zone of a low permeability riverbank

The concept of the study was developed by the author and co-authors. The collection of field data for this study was done by the author. Additional data was provided by Andreas Krein. The interpretation of the results was done by the author, supported by suggestions of the co-authors Andreas Krein and Traugott Scheytt. Writing and editorial handling of the manuscript were done by the author.

Chapter 3 – first author

Using selected pharmaceutical compounds as indicators for surface water and groundwater interaction in the hyporheic zone of a low permeability riverbank

The concept of the study was developed by the author. The collection of field data for this study was done by the author. Additional data was provided by Andreas Krein. The interpretation of the results was done by the author, supported by suggestions of the co-authors Andreas Krein and Traugott Scheytt. Writing and editorial handling of the manuscript were done by the author.

Chapter 4 – first author

Redox-sensitivity and mobility of selected pharmaceutical compounds in a low flow column experiment

The concept of the study and the design of the laboratory column experiment were developed by the author and co-authors. The author carried out the experiment. Karsten Nödler analysed the pharmaceutical compounds. The interpretation of the results was done by the author, supported by suggestions of the co-authors Karsten Nödler, Tobias Licha, Andreas Krein, and Traugott Scheytt. Writing and editorial handling of the manuscript were done by the author.

Chapter 5 – second author

Seepage rates derived from thermal records using wavelet analysis

The concept of the study was developed by the author and co-authors. Andreas Krein and the author installed the temperature sensors at the field site. Milan Onderka did the calculations of the seepage rates. The interpretation of the results was done by Milan Onderka and the author, supported by suggestions of the co-authors Traugott Scheytt and Andreas Krein. Writing of the manuscript was done by Milan Onderka and the author. Editorial handling of the manuscript was done by the author.

Annex 3

List of publications

Peer-reviewed papers

- Onderka, M., **Banzhaf, S.**, Scheytt, T. & Krein, A. (2013). Seepage velocities derived from thermal records using wavelet analysis. *Journal of Hydrology* 479, pp. 64-74.
- Banzhaf, S.**, Nödler, K., Licha, T., Krein, A. & Scheytt, T. (2012). Redox-sensitivity and mobility of selected pharmaceutical compounds in a low flow column experiment. *Science of the Total Environment* 438, pp. 113-121.
- Banzhaf, S.**, Krein, A. & Scheytt, T. (2012). Using selected pharmaceutical compounds as indicators for surface water and groundwater interaction in the hyporheic zone of a low permeability riverbank. *Hydrological Processes*. doi: 10.1002/hyp.9435
- Banzhaf, S.**, Krein, A. & Scheytt, T. (2011). Investigative approaches to determine exchange processes in the hyporheic zone of a low permeability riverbank. *Hydrogeology Journal* 19 (3), pp. 591-601.
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- Banzhaf, S.** & Scheytt, T. (2009). Effect of an artificial flood wave on the adjacent groundwater aquifer. *Grundwasser* 14 (4), pp. 265-275.
- Janzen, N., **Banzhaf, S.**, Scheytt, T. & Bester, K. (2009). Vertical flow soil filter for the elimination of micro pollutants from storm and waste water. *Chemosphere* 77 (10), pp. 1358-1365.

Conference proceedings

- Banzhaf, S.**, Nödler, K., Licha, T., Krein, A. & Scheytt, T. (2012). Säulenversuche zur Redoxsensitivität und zum Transportverhalten ausgewählter Pharmazeutika. *Kurzfassung in: Liedl, R., Burghardt, D., Simon, E., Reimann, T. & Kaufmann-Knoke (Hg.). Grundwasserschutz und Grundwassernutzung. Tagung der Fachsektion Hydrogeologie in der DGG (FH-DGG). 16. - 20. Mai 2012, Dresden. Kurzfassungen der Vorträge und Poster. Schriftenreihe der DGG, Heft 78, S. 192.*
- Banzhaf, S.**, Onderka, M., Krein, A. & Scheytt, T. (2012). Using wavelet analysis to derive seepage rates from thermal records. *Geophysical Research Abstracts*, Vol. 14, EGU2012-111, EGU General Assembly 2012, Vienna, Austria.

- Banzhaf, S.,** Nödler, K., Licha, T., Krein, A. & Scheytt, T. (2012). Redox-sensitivity and mobility of selected pharmaceutical compounds in a laboratory column experiment. Geophysical Research Abstracts, Vol. 14, EGU2012-70, EGU General Assembly 2012, Vienna, Austria.
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- Banzhaf, S.,** Krein, A. & Scheytt, T.J. (2011). Laboratory column experiment on redox-sensitivity and transport behaviour of selected pharmaceutical compounds. GSA Annual Meeting, 9–12 October 2011, Minneapolis, USA.
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Miscellaneous

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- Banzhaf, S.,** Krein, A. & Scheytt, T. (2010). Austausch von Flusswasser und Grundwasser - Einsatz von Spurenstoffen als Indikatoren in der hyporheischen Zone, Seminarreihe: Regionale Wasserwirtschaft in Theorie und Praxis. Themenschwerpunkt: Neue Stoffe und innovative Technologien in der Abwasserbehandlung und Wasserwirtschaft, Centre de Recherche Public - Gabriel Lippmann, Luxembourg.
- Banzhaf, S.** & Scheytt, T. (2009). Einfluss von Hochwasser auf Strömung und Stofftransport in der hyporheischen Zone. Auftaktworkshop Hyporheisches Netzwerk, IGB, Berlin.

Annex 4

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Annex 5

Curriculum vitae

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04/2009 – 12/2012	PhD student at the Hydrogeology Research Group at TU Berlin, funded by a research grant from the National Research Fund (FNR), Luxembourg
10/2002 – 09/2008	Studies in Applied Geosciences at TU Berlin, focus on hydrogeology, title of diploma thesis: <i>“Einfluss einer Hochwasserwelle auf Strömung und Stofftransport im Grundwasser“</i> (Influence of a flood wave on flow and mass transport in groundwater); final grade: 1.3
10/2001 – 09/2002	Studies in Urban Development at TU Berlin

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04/2009 – 12/2012	Research assistant at the Hydrogeology Research Group at TU Berlin
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