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Investigation of Sorption and Degradation Parameters of Selected Emerging Organic Contaminants under Different Hydrological Conditions

Masterarbeit unter Leitung von PD Dr. Christine Stumpp

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Abstract

Emerging Organic Contaminants (EOCs) are recently getting into focus of research since they are frequently detected in groundwater and other environments. Most abundant EOCs in aqueous environments are pharmaceuticals. Still their transport behaviour including sorption and degradation processes mostly remain unknown. This thesis aimed to investigate sorption and degradation rates for selected pharmaceuticals (Antipyrine, Atenolol, Caffeine, Carbamazepine, Diclofenac, Ketoprofen, Sulfamethoxazole) under both, biotic and abiotic conditions. Furthermore, the impact of different flow velocities on their transport behaviour was studied. Therefore, saturated biotic and abiotic column experiments with a longer pulse of the pharmaceuticals solved in groundwater were conducted. Modelling of the retardation factor and degradation rates was done with the program CXTFIT 2.1. Observed concentrations and recoveries of atenolol and clofibrate were very low and indicating high effects of sorption and degradation on their transport. Clofibric acid as the active metabolite of clofibrate was observed in high concentrations. Diclofenac, caffeine and carbamazepine were also affected by sorption and degradation but to a lesser extent than atenolol and clofibrate. Sulfamethoxazole, ketoprofen and antipyrine were recovered in high amounts and concentrations close to the input concentration revealing less impact of these transport processes. Biodegradation was not observed for any of the compounds. Modelling of sorption and degradation rates revealed a similar order. Compared to the tracer bromide, atenolol showed highest retardation factors (5.6-7.1) and highest degradation rates (7.3-10.8 d^{-1}). For sulfamethoxazole in contrast, low degradation rates (0.1-0.6 d^{-1}) and no sorption was observed. Most of the compounds were not influenced by different flow velocities. Only peak values and recoveries of atenolol were decreasing from the highest flow velocity (1.9 cm^3/min) to the lowest flow velocity (0.7 cm^3/min). This impact was not visible for the modelled degradation rates and retardation factors which reveals that not the flow velocity but the mean transit time was the most important factor influencing its transport. Results of this thesis show the huge variability of the transport behaviour of pharmaceuticals and their metabolites in the environment and provide useful information for later modelling of transport of EOCs in bigger scales.

Keywords: Column experiments, pharmaceuticals, groundwater contaminants, solute transport, sorption, degradation, inverse modelling.

Zusammenfassung

Als Emerging Organic Contaminants (EOCs) wird eine Gruppe von organischen Schadstoffen bezeichnet, die in den letzten Jahren zunehmend im Grundwasser gefunden werden. Die häufigsten EOCs im aquatischen Umfeld sind Arzneimittel, deren Transportverhalten meist noch unbekannt ist. Ziel dieser Arbeit war es, diese Prozesse für ausgewählte Arzneimittel (Antipyrin, Atenolol, Carbamazepin, Coffein, Diclofenac, Ketoprofen, Sulfamethoxazol) im Grundwasser unter biotischen und abiotischen Bedingungen zu untersuchen und mittels ihrer Transportparameter zu quantifizieren. Außerdem sollte der Einfluss verschiedener Fließgeschwindigkeiten auf das Transportverhalten dieser Stoffe analysiert werden. Zu diesem Zweck wurden gesättigte Säulenversuche durchgeführt. Hierbei wurde ein längerer Puls der in Grundwasser gelösten Arzneimittel durch die Säulen geleitet. Die anschließende Modellierung der Durchbruchskurven fand mittels des Programms CXTFIT 2.1 statt. Die Konzentrationen und Rückerhalte von Atenolol und Clofibrat waren gering, was auf einen hohen Einfluss von Sorption und Abbau hinweist. Das Abbauprodukt von Clofibrat, Clofibrinsäure, wurde dagegen in hohen Konzentrationen gemessen. Diclofenac, Coffein und Carbamazepin zeigten ebenfalls Einfluss dieser Prozesse, jedoch in geringerem Maße. Sulfamethoxazol, Ketoprofen und Antipyrin wurden zu sehr großem Anteil rückerhalten, was auf geringen Einfluss von Sorption und Abbau hinweist. Mikrobieller Abbau wurde für keinen der Stoffe beobachtet. Die Modellierung bestätigte diese Beobachtungen. Sowohl die Retardationsfaktoren im Vergleich zum Tracer Bromid (5.6-7.1) als auch die Abbauraten (7.3- 10.8 d^{-1}) lagen für Atenolol höher als für alle anderen modellierten Stoffe. Sehr geringe Abbauraten (0.1-0.6 d^{-1}) und kein Einfluss von Sorption wurden für Sulfamethoxazol erhalten. Für die meisten untersuchten Stoffe konnte kein Einfluss der Fließgeschwindigkeit auf ihren Transport nachgewiesen werden. Die Konzentrationen und Rückerhalte von Atenolol fielen von der höchsten Fließgeschwindigkeit (1.9 cm^3/min) zur niedrigsten (0.7 cm^3/min) ab. Diese Tendenz konnte für die modellierten Abbauraten und Retardationsfaktoren jedoch nicht beobachtet werden, weshalb nicht die Fließgeschwindigkeit sondern die mittlere Verweilzeit Einfluss auf den Transport zu haben scheint. Die Ergebnisse dieser Arbeit zeigen die große Variabilität des Transports der Arzeimittel und ihrer Abbauprodukte im Grundwasser und sind hilfreich für zukünftige Modellierungen in größeren Maßstäben.

Schlüsselwörter: Säulenversuche, Arzneimittel, Grundwasserverunreinigung, Transport gelöster Stoffe, Sorption, Abbau, inverse Modellierung.

1. Introduction

Groundwater is a basic resource needed by humans and other organisms, especially as drinking water. Its pollution, thus, is a threat for all organisms that are depending on this aqueous environment. Indeed, the last years different Emerging Organic Contaminants (EOCs) have been detected in the environment (Mersmann et al., 2002). Since the characteristics of these compounds, including the ecotoxicity and the transport behaviour are often unknown, these compounds are more and more getting into focus of research. They cover diverse organic chemicals including personal care and industrial products but also compounds used in human and veterinary medicine like pharmaceuticals. Some of them are new artificial compounds, which have been increasing in the last years. EOCs also include newfound substances or compounds that are newly assigned to EOCs due to the development in research (Lapworth et al., 2012).

Even if no health risks on humans that are exposed to small amounts of EOCs in water are noted until now, there may be long-term effects that are not yet known (Kümmerer, 2010). The fact that a lot of antibiotic resistances are recently found everywhere in the environment shows one reason why the removal of pharmaceuticals in groundwater is important and more research on the transport behaviour is required (Kümmerer, 2010). This is even more important since groundwater can remain a storage of micropollutants for many years, which is due to low microbial activity, a wide range of redox conditions and especially long residence times in aquifers (Johnson et al., 1998; Lapworth et al., 2012).

Pharmaceuticals are the most often found EOCs in aqueous environments (Lapworth et al., 2012). Their predominant source is wastewater (Mersmann et al., 2002). They are to some extent absorbed or transformed inside the body while some amounts are leaving the body unchanged and thus are present in the waste water (Kümmerer, 2010). Mostly they get into the aquifers via leakages of sewage systems, non-natural groundwater infiltration, bank filtration or via waste water treatment plant effluents (Mersmann et al., 2002; Scheytt et al., 2005). Additionally the produced sewage sludge is used as fertilizer in agriculture (Heberer et al., 1997; Lapworth et al., 2012). There are different methods to remove some of the EOCs during treatment but due to the large variety of EOCs only 3 to 90 % are removed (Heberer, 2002; Lindqvist et al., 2005). The fact that many of these contaminants are new artificial substances or recently detected compounds leads to even higher amounts of EOCs leaving the waste water treatment plants. The release of pharmaceuticals to aqueous environments becomes apparent by looking at the anticonvulsant carbamazepine. Assuming the prescribed daily dose of this drug and that medication is leaving the human body unchanged, the input of carbamazepine into the waste water reaches a maximum of around 108 t per year (67.7 Mio. defined daily doses) in Germany (Schwabe, 2003; Mersmann et al., 2002). The degradation of this substance during treatment was found to be below 10 % (Ternes, 1998). Underlaying these numbers a big part of carbamazepine would leave the German waste water treatment plants and would thus enter the environment. In groundwater samples taken in Europe, carbamazepine was thus found in 42 % of all samples (Loos et al, 2010). Another considerable point is that the transformation of the pharmaceutical compounds does not necessarily lead to the complete mineralization. Sometimes metabolites with even higher toxicity than the original compounds are formed during treatment where many are not known yet (Banzhaf, 2016).

There are four major processes influencing transport of solutes including advection, hydrodynamic dispersion, sorption and degradation (Banzhaf et al., 2016). These transport mechanisms thus might have a huge impact on the mobility and the mass of the EOCs found in the environment, which proves the importance to quantify them (Lapworth et al., 2012). Advection is the main transport process in water and simply leads to the transportation of solutes. Hydrodynamic dispersion includes the two processes mechanical dispersion as well as diffusion. Diffusion plays a minor role at bigger scales or high flow rates while dispersion becomes more important then. Dispersion occurs because of differences in pathways or flow speed and similarly to diffusion is extending the shape of the breakthrough curves (BTC) due to the adaptation of concentration variations (Banzhaf et al., 2016).

Sorption is another factor influencing transport of solutes. Compounds are sorbed onto the matrix surfaces of the saturated and unsaturated zone (Domenico and Schwartz, 1998) which induces a change in hydrochemical equilibrium. Compounds can be partly or fully sorbed depending on their concentration and on the flow velocity. A new equilibrium can be reached when flow velocities are slow enough, otherwise non-equilibrium sorption needs to be considered. Dependent on the strength of the sorption of a compound to the matrix surfaces or if the water composition changes again desorption can happen which leads to a later arrival of the concentration front. Sorption can thus be temporary but also irreversible. The charge and thus the structure of the molecule and the pH are influencing the extent of how strong a solute is sorbed. Solutes that are non-polar mostly have hydrophobic properties and are therefore often less mobile in water (Banzhaf et al., 2016; Schaffer and Licha, 2015). The amount of available surfaces plays a crucial role. Especially organic contents are increasing sorption for non-polar compounds (Delle Site, 2001). However organic compounds often change their charge due to the surrounding pH. Ionic molecules can thus also be sorbed to charged surfaces of the sorbent but are regularly showing a mobile character in comparison to non-polar solutes (Banzhaf et al., 2016). The charge of a molecule in a certain pH and its tendency to sorption in water are often determined with the negative logarithm of the acid dissociation constant (pK_a) and the distribution coefficient between water and octanol (K_{OW}). If the pK_a value of a compound is higher than the pH, the compound is more likely to be neutral; otherwise a polar character is expected. Furthermore, a higher $\log K_{OW}$ of a neutral substance can show a more hydrophobic character (Banzhaf et al., 2016). However, especially the significance of the $\log K_{OW}$ for EOCs in the environment was shown to be questionable (Burke et al., 2013). Thus, experiments are important to quantify the specific sorption behaviour of an organic compound in a specific environment.

Degradation can be chemical, biological and radioactive and lowers the concentration and the whole amount of the compound in the water due to transformation (Fetter, 1988). As a consequence of redox processes, besides mineralization metabolites can be formed with different characteristics than the parent compound (Banzhaf et al., 2016).

The observed concentrations of EOCs in surface and wastewater are much higher than concentrations in groundwater, which implies that besides dilution also retardation and degradation take place (Jurado et al., 2012) although the extent is mostly unknown (Lapworth et al., 2012). There are several established experimental setups to analyse these transport processes of organic contaminants like pesticides or pharmaceuticals in the saturated or unsaturated zone. Most commonly used are batch or column experiments. In general, sorption coefficients determined by batch experiments are often not transferable to the field due to the fact that here equilibrium conditions control the sorption process while in the field or in column studies dynamic or even non-equilibrium conditions are the case. Furthermore, sorption happens much faster. This is partly because of the shaking movement during the batch experiment but also because the ratio of solution to sediment should be much lower to represent natural conditions. Thus, column experiments mostly lead to more realistic results on the transport behaviour of an organic contaminant under groundwater conditions (Banzhaf et al., 2016).

Although batch or column studies are also suitable to analyse the transport of EOCs the awareness and research on organic pollutants like pesticides started much earlier (Kolpin et al., 2002, Lapworth et al., 2012). This is mostly because it took several years to improve the methods to analyse these contaminants. Pharmaceuticals are mostly polar and in small amounts water-soluble chemical substances which are not easy to measure (Kolpin et al., 2002). Due to their chemical properties EOCs can mostly not be investigated by gas chromatography with mass spectrometry like it is possible for well-studied compounds like DDT (dichlorodiphenyltrichloroethane). Nowadays, EOCs are analysed with liquid chromatography with mass spectrometry (LC-MS) (Kolpin et al., 2002).

The development of analytical methods to investigate compounds like EOCs led to some studies on the transport behaviour in sewage sludge (Horsing et al., 2011), and in the unsaturated zone (e.g. Lin and Gun, 2011). Studies on the transport behaviour of EOCs in the saturated zone are still rare. Furthermore, small changes in temperature, amount of oxygen or the redox potential but also different sediments, were found to lead to big changes of the degradation and sorption parameters of a compound under saturated conditions which makes it impossible to transfer results to different settings (Johnson et al., 1998; Gruenheid et al., 2008; Banzhaf et al., 2016). However, all studies outlined the importance of transport processes on the behaviour of pharmaceuticals in the environment. According to batch and saturated column studies of Mersmann et al. (2002) and Scheytt et al. (2005) sorption is strongly influencing the transport behaviour of EOCs in the saturated zone. Im et al. (2016) outlined the importance of biodegradation. They proved that anionic contaminants were more degraded under biotic conditions than in a column with abiotic conditions (Im et al., 2016). Besides the properties of the compound itself, these mechanisms are depending on the properties of the sorbate and also the properties of the groundwater (Banzhaf et al., 2016).

Concerning the sorbate grain-size and thus also the area of the surfaces was found to play an important role. Greenhagen et al. (2014) compared sorption and biodegradation of methamphetamine, acetaminophen and caffeine in a sandy column and a column with fine-grained sediment. The removal of the compounds due to degradation and sorption was lower in the sandy column, which shows the risk of polluted sandy aquifers (Greenhagen et al., 2014). Furthermore, a batch study of Martinez-Hernandez et al. (2014) demonstrated the importance of mineral surfaces since most of the sorption happened here. Additionally, the total organic carbon content and the pH was found to influence the transport of pharmaceuticals in groundwater (Kodesova et al., 2015).

The surrounding conditions, like the redox potential or the amount of oxygen in the water also play an important role on the transport of pharmaceuticals since they can influence the amount of degradation by microbes (Johnson et al., 1998). Gruenheid et al. (2008) showed higher biodegradation rates of sulfamethoxazole with increasing temperature in a saturated column study. Although it might be an important factor, the impact of different pore water velocities and transit times on the transport behaviour of EOCs is nearly unstudied. Knowing the impact of pore water velocities on the sorption and degradation of a compound would for example be useful for the infiltration or direct injection of contaminated water (Teijón et al., 2014). Experiments studying the impact of different flow velocities on EOCs were so far only performed by Teijón et al. (2014). They found no influence on the sorption of naproxen under saturated conditions in a column study. According to these authors their residence times were insufficient in the experiments with higher pore water velocities to see any possible effect (Teijón et al., 2014). Studies that analysed the behaviour of other organic contaminants like benzene under different flow conditions in column studies, reported a decreasing sorption with higher pore water velocities due to shorter interaction periods (Kim et al., 2006). Brusseau (1992) found similar results for dichlorbenzene, tetrachlorethen, naphtalene and p-xylene. Furthermore, the author demonstrated that there is an inverse but not a direct correlation, which according to him would imply that the extrapolation of results of smaller flow rates to higher flow rates is not possible (Brusseau, 1992). Biodegradation might also increase under lower flow velocities because of two reasons: On the one hand, longer interaction periods between the compound and the sediment were also found to lead to higher microbial activity (Murphy et al, 1997). On the other hand, these interactions and thus the transport of organic compounds to the microbes is controlled by diffusion. This was shown in many studies (e.g. Kinzelbach et al., 1991, Harms & Bosma, 1997; Caldwell & Lawrence, 1986; Harms & Zehnder, 1994). Since diffusion is becoming more important in low pore velocities, the limitation due to transport can be overcome and thus biodegradation gets higher under lower flow velocities. The same might be true for abiotic degradation. However, the study of Mendoza-Sanchez et al., 2010 showed that under low pore water velocities biodegradation of organic compounds can be limited due to the fact that lower flow rates lead to a lower stream density of electron donors. This influences the amount of microbial species.

The extent of how much other factors are influencing the transport is of course dependent on the compound itself (Delle Site, 2001). The most often found PCs in the subsurface water area in studies all over the world were found to be carbamazepine, sulfamethoxazole, ibuprofen, caffeine and diclofenac (Lapworth et al., 2012). Sulfamethoxazole is the most often found antibiotic in groundwater samples. Sampling in 164 aquifers in Europe showed sulfamethoxazole in 24.4 % of the taken samples (Loos et al., 2010). No or just little degradation or sorption was found for this antibiotic compound in many different soils like sandy soils or Loess in a batch study (Kodesova, 2015). Here, higher pH was found to have a negative effect on sorption (Kodesova et al., 2015). Thus, this compound seems to be mobile although specific result from controlled experiments in column studies are still missing.

Similar results were found for clofibric acid. Clofibric acid is the active metabolite of the unstable fibric acid clofibrate (Drugbank, 2016). Samples showing high concentrations of clofibric acid in the south of Berlin in deep aquifers led to the assumption of a conservative and mobile behaviour of this compound (Scheytt et al., 1998). It was found to be significantly related to pH, with only little to no sorption in common pH values of most aquifers and no observed degradation under any conditions (Oppel et al., 2004; Mersmann et al., 2002; Scheytt et al., 2004).

Carbamazepine is the most often found PC in groundwater samples all over the world (Lapworth et al., 2012) since it is commonly used as anticonvulsant. Studies found different results on sorption behaviour of this compound. A saturated sandy column study by Mersmann et al. (2002) found significant retardation for carbamazepine but a batch study with 13 different soils of Kodesova et al. (2015) and an incubation experiment of river sediments of Radke et al. (2014) demonstrated really low sorption of carbamazepine. Biodegradation did not play an important role in these studies (Mersmann et al., 2002; Radke et al., 2014). Additionally, transport of carbamazepine seems to be independent of pH (Mersmann et al., 2002).

For Diclofenac as a commonly used analgesic no degradation was observed (Mersmann et al., 2002). Furthermore, the anionic compound was found to strongly interact with the matrix surfaces and thus to be retarded in different studies (Mersmann et al., 2002; Scheytt et al., 2004). This doesn't coincide with a column and batch study of Im et al. (2016), which showed that neutral and cationic species were more sorbed than anionic species.

Atenolol is a β-blocker and was found to be strongly retarded in batch studies of Kodesova et al., (2015) and Barbieri et al. (2012) but also in a column study of Burke et al. (2013). Barbieri et al. (2012) also found biological degradation for atenolol, although first sorption was the predominant process.

Ketoprofen is another commonly used β-blocker. A batch and incubation study of Xu et al. (2009) found just little sorption for ketoprofen in four different soils. Ketoprofen stayed longer in abiotic soils than under biotic conditions, showing biodegradation as one process having an impact on its fate (Xu et al., 2009). However, the total organic carbon content (TOC) was influencing the degradation rates as well as retardation leading to higher biodegradation and sorption with higher TOC.

Antipyrine is an analgesic drug. 0.35 g per year are in average taken by every German (Sadezky et al., 2008). Antipyrine was found in groundwater samples and wastewater effluents for example in Barcelona, Spain (Cabeza et al., 2012) but detailed information on its transport behaviour is still missing (Tan et al., 2013). Wastewater treatment plants could just lower the concentration of antipyrine under biological and aerobic conditions to maximal 70 % of the previous concentration (Zuehlke et al., 2006).

Some contaminants seem to generally be more biodegradable than others like for example caffeine (Benotti and Bronawell, 2009). This EOC is known as a nervous system stimulant also used in medicine but primarily known as lifestyle product (Sigma-Aldrich, 2016). The used amounts of caffeine are high but its occurrence in the environment is comparably low (Benotti and Bronawell, 2009). It is better biodegradable than other compounds used in smaller quantities (Benotti and Bronawell, 2009), although caffeine was found to be relatively mobile in sandy columns (Greenhagen et al., 2014).

Overall the behaviour of EOCs and especially pharmaceuticals in the environment seems to be complex and influenced by many factors. More research on the transport behaviour of EOCs in the saturated zone is required to analyse the fate of EOCs in groundwater and risks of possible groundwater contamination. Saturated column studies dealing with this topic are still rare. Therefore, the specific transport behaviour of many compounds, including sorption and degradation parameters as well as their transformation products in groundwater are still unknown. Furthermore, it still remains to be tested whether different pore velocities are influencing these transport processes.

2. Study Objectives

The aim of this thesis was to analyse the transport behaviour of selected pharmaceuticals in groundwater under different hydrological conditions. The analysed substances in this thesis were antipyrine, atenolol, carbamazepine, caffeine, diclofenac, ketoprofen and sulfamethoxazole.

The following hypothesises were investigated:

- Microbial activity leads to differences in the reactive transport behaviour under biotic conditions compared to abiotic conditions.
- The flow velocity of groundwater is influencing the transport behaviour of the analysed EOCs.
- Clofibrate is in high amounts transformed to its metabolite clofibric acid under both, biotic and abiotic conditions.
- Caffeine and the β-blockers ketoprofen and atenolol are well biodegradable under saturated groundwater conditions.
- Sorption highly influences the transport behaviour of the anti-inflammatory drug diclofenac and the β-blocker atenolol.
- Sulfamethoxazole, carbamazepine and antipyrine do not show any or just little effects of sorption or degradation processes.

In order to analyse the transport behaviour of the pharmaceuticals and to simulate different flow conditions, saturated biotic and abiotic column experiments with different flow velocities were conducted. Results were analysed and modelled to determine their sorption and degradation parameters.

The specific objectives of this thesis were:

1) The investigation of sorption and degradation rates for the selected pharmaceuticals with column experiments under biotic and abiotic conditions.
2) The comparison of these rates for
    a. the different pharmaceuticals to analyse their different transport characteristics under biotic and abiotic conditions.
    b. different flow velocities to analyse the possible impact of different transit times on sorption and degradation.

Thus, this thesis aimed to provide new insights on the transport under different flow conditions of EOCs in the environment.

3. Materials and Methods

3.1. Project and Study Site

The thesis was part of the project "PERSIST" (JPI Water; BMBF, 2015-2017) which deals with the behaviour of EOCs and multiresistant bacteria in the environment, especially in groundwater. The project is a collaboration between the Institute of Groundwater Ecology (IGOE) of the Helmholtz Zentrum München, the University in Nîmes, France and the Catalan Institute for Water Research in Catalonia, Spain. The research includes field experiments at two field sites in the aquifer of Vistrenque, France and the Empordà aquifer, Spain as well as additional laboratory experiments at the IGOE to study the transport of selected compounds and to get information on their retardation and degradation (PERSIST Project, 2015).

The sediment and the used groundwater in this thesis were samples from the aquifer Empordà in Spain (Figure 3.1). It is a fluvio-deltaic region with a multilayer aquifer. The region is extensively used for agriculture, and therefore, manure is strongly influencing the water quality of soil and groundwater recharge. As a consequence, besides high amounts of nitrate different veterinary pharmaceuticals are regularly found in groundwater samples. Even multiresistant bacteria were already detected (PERSIST Project, 2015).

Figure 3.1 shows the field site of Empordá with its groundwater, sediment and surface water (Fluviá river) sampling sites and sites were samples from effluents of waste water treatment plants were taken. All were analysed on its ionic composition, stable isotopes, contamination with EOCs and bacteria. The used sediment and groundwater in these column experiments were taken from a non-contaminated area of the aquifer, to imitate natural conditions in the columns but without any previous contamination during the column experiments. The water was taken in March 2016 from a well at point P-VE01 in 9 m depth and an altitude of 4 m (Coordinates: UTM X: 505706, Y: 4666972). The sediment was taken close to it from an altitude of 9.5 m in a depth of 3 m (Coordinates X: 503576, Y: 4668805).

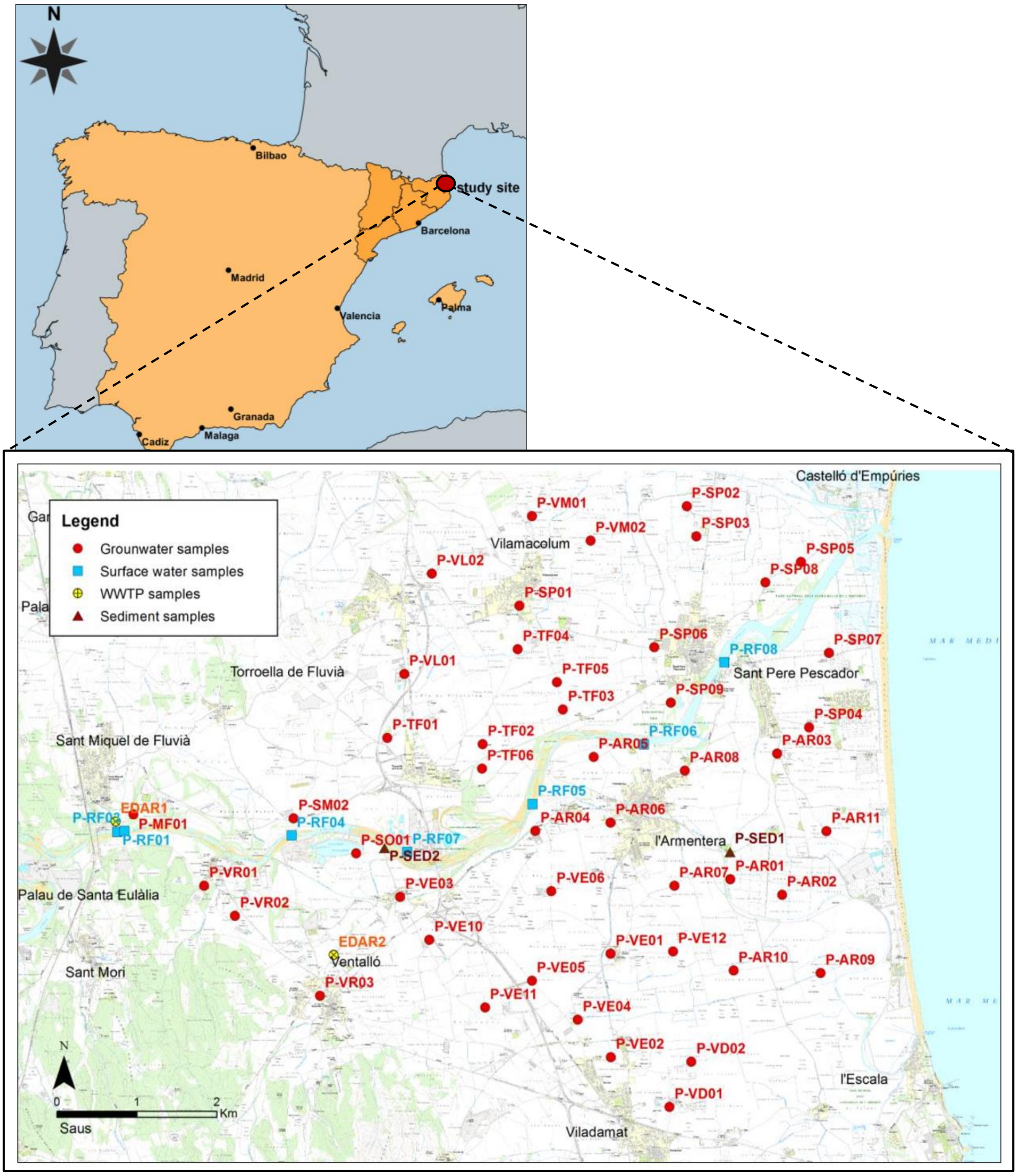

Figure 3.1: Field site of Empordá with groundwater sampling points (red points), surface water sampling points (blue squares), sediment sampling sites (dark red triangle) and sites where samples from waste water treatment plant effluents were taken (WWTP, yellow points with cross). Some of the groundwater and surface water sampling was afterwards repeated monthly for some points (PERSIST Project, 2015).

3.2. Sediment Properties

The sediment was previously sieved to a grain diameter of 4 mm. The grain size distribution was determined by sieve analysis using DIN 18683 (Durner and Nieder, 2003). The resulting curve was used to determine the grain size distribution (German grain size system, Table 3.1) and compared to data observed in Spain. The sediment was dominated by the coarse and medium sand fraction.

Table 3.1: Grain-size distribution of the used Sediment from Emporda, Spain.

Category	**Diameter [mm]**	**Portion [%]**
Coarse sand	2-0.63	41.1
Medium sand	0.63-0.2	45.6
Fine sand	0.2-0.063	11.47
< Fine sand	<0.063	1.83

Furthermore the hydraulic conductivity k_f [L/T] was calculated (Table 3.2) according to the approach of Beyer (Beyer, 1964):

$$k_f = C_{sort} * {d_{10}}^2 \tag{1}$$

C_{sort} is an empirical sorting coefficient (here 0.0092) depending on the coefficient of grain uniformity U:

$$U = \frac{d_{60}}{d_{10}} \tag{2}$$

d_{60} and d_{10} are the grain diameters in mm where 60% or 10 % of the material have a smaller size which was 0.642 mm and 0.168 mm in this case. The formula may be used for d_{10} ranging from 0.06 mm to 0.6 mm and U between 1 to 20 (Beyer, 1964), which was the case here. k_f was calculated as $2.6 \cdot 10^{-4}$ m/s.

The pH of the sediment of 7.68 (Table 3.2) was measured in a 0.01M $CaCl_2$ solution at 21.8 °C water temperature with a pH-electrode with temperature sensor (pH 3110 Set 2 with pH electrode Sentix 41).

Table 3.2: Measured and calculated properties of the used sediment. For TC and TOC mean and standard deviation (3 samples) are shown

k_f [m/s]	$2.6 \cdot 10^{-4}$
$\mathrm{pH_{CaCl2}}$	7.68
TC [%]	2.54 ± 0.26
TOC [%]	1.24 ± 0.25

The total amount of carbon TC and the amount of total organic carbon TOC (Table 3.2) was analysed using a TOC analyser of Shimadzu (TOC-5050). Three samples were analysed for TOC as well as for TC by burning the samples in 1000 °C and measuring the released CO_2. For removing non-organic carbon a few drops of a 8M HCl solution were added to the TOC samples before drying and finally burning them together with the TC samples in the analyser. The sediment contained carbon of 2.54 ± 0.26 %. With 1.24 ± 0.25 % approximately half of it was organic carbon.

3.3. Groundwater Properties

The used groundwater was analysed on its components using ion chromatography. The results are shown in Table 3.3. The HCO_3^--content was obtained by titration with HCl and methyl orange as indicator. Since there were 0.14 mg/l bromide naturally occurring in the groundwater, this background concentration was subtracted from the observed bromide concentrations during the experiments. Eventual changes in nitrate and sulfate during the experiments due to changes in redox conditions were observed by analysing all samples for this two compounds. The electrical conductivity of the groundwater after sampling in Spain was 1337 µS/cm at a water temperature of 16.6 °C. pH was determined to be 7.27.

Table 3.3: Water analysis of the used groundwater from Emporda, Spain. Mean and standard deviation (3 samples) are given here.

Ion	**Amount [mg/l]**
Li^+	0.01 ± 0
Na^+	33.86 ± 0.23
K^+	2.83 ± 0.04
Mg^{2+}	20.88 ± 0.22
Ca^{2+}	151.91 ± 0.97
NH_4^+	0 ± 0
NO_2^-	0 ± 0
NO_3^-	36.05 ± 0.05
Cl^-	59.22 ± 0.59
Br^-	0.14 ± 0.01
HPO_4^{2-}	0 ± 0
SO_4^{2-}	325.53 ± 0.46
HCO_3^-	140.32± 0

3.4. Experimental Design

3.4.1. Packing and Properties of the Columns

The experiments were carried out using stainless steel columns to ensure that no sorption to the column material is possible, which could eventually falsify the results. Each experiment was done in a biotic column (EB) and an abiotic control column (EA) to distinguish biological from chemical degradation. The columns were packed with the sandy sediment of the Spanish aquifer Empordá by bit by bit packing weighted portions of the sediment into the column and waiting for saturation with water before starting with the next portion. To prevent air inclusions and to pack equally a rubber hammer was used. By knowing the weight of the sediment packed into each column, the volume of the sediment V_{Sed} could be calculated. Therefore, the density of quartz sand of 2.66 g/cm^3 was assumed. The volume of the water V_{Water} could then be calculated out of the difference between V_{Tot} and V_{Sed}. The porosity n was calculated with

$$n = \frac{V_{Water}}{V_{Tot}} \tag{3}$$

Table 3.4 shows the dimensions of the columns as well as the volumes of water and sediment and the resulting total porosities.

Table 3.4: Dimensions of the columns as well as the volumes of water and sediment and the resulting total porosity.

Column	**EA**	**EB**
Internal Diameter [cm]	9	
Height [cm]	50	
A [cm^2]	63.62	
V_{Tot} [cm^3]	3181	
V_{Water} [cm^3]	921.46	972.59
V_{Sed} [cm^3]	2259.40	2208.27
n [%]	28.97	30.58

3.4.2. Experimental Setup

For saturated conditions, groundwater with a constant flow rate was pumped from the bottom to the top of the stainless steel columns with a peristaltic pump (Figure 3.2). The columns were flushed with natural groundwater from Empordá until a hydrochemical equilibrium between water and sediment was assumed to be reached. To ensure abiotic conditions in column EA, the groundwater in this column always contained a concentration of 0.05 g/l sodium azide (NaN_3). With the start of every experiment a pulse of approximately 1.1 l of a tracer solution including the selected EOCs and tracers solved in groundwater was added and pumped through the column. Afterwards the tank was switched and approximately 4.4 l of pure groundwater (including 0.05 g/l NaN_3 for EA) were pumped through the column. At the outlet a fraction collector collected samples in test vials for defined intervals. Between the experiments, the columns were flushed with water for two pore volumes to ensure that no tracers are still sorbed to the sediment surfaces. Due to a lack of groundwater from Spain the flushing was firstly done with distilled water. However, to prohibit density effects Spanish groundwater was used for some hours at the end of the cleaning process.

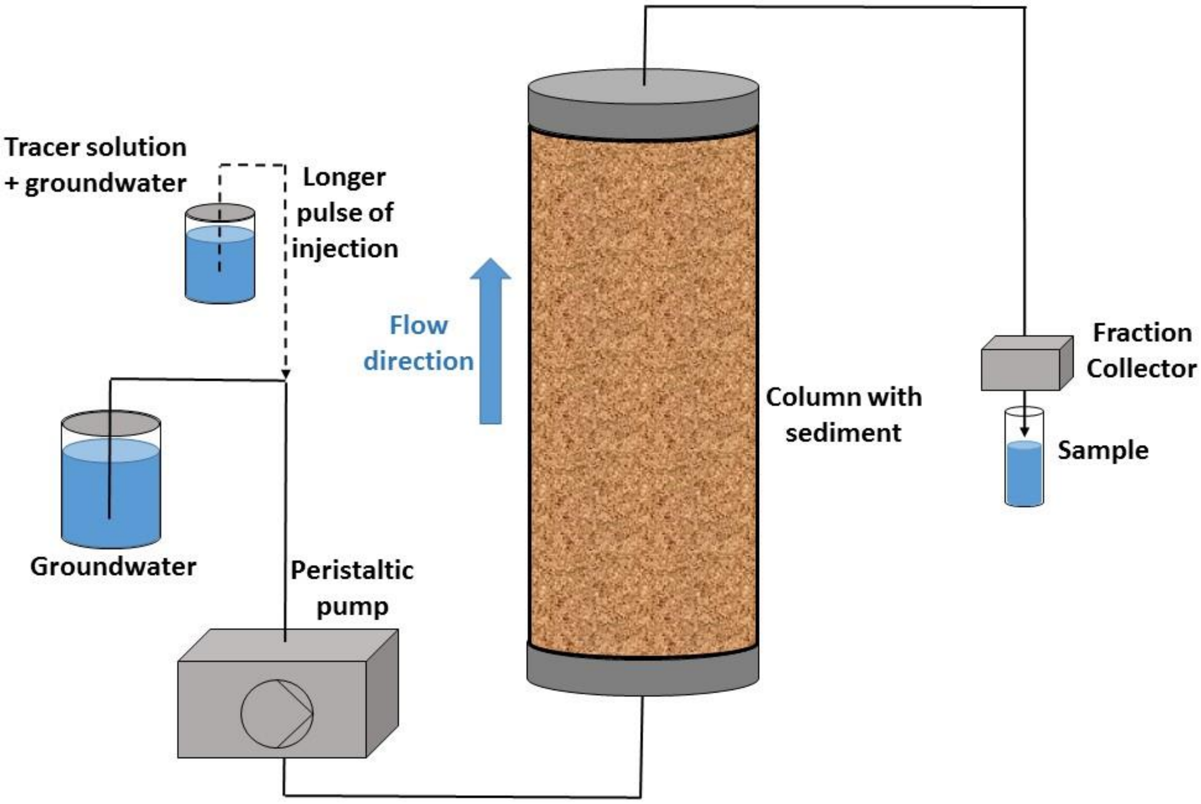

Figure 3.2: Experimental setup of the column experiments.

3.4.3. The Three Experiments

Three different flow rates were tested for each compound starting by the fastest flow rate. By changing the flow rates of the groundwater through the column, different pore water velocities and transit times could be tested and the influence of different residence times in the biotic and abiotic column on the transport behaviour of the pharmaceuticals could be analysed. The flow rates were determined by collecting the outflow over 10 minutes and weighing it. This was done until the wanted flow rate was reached. Due to the small difference in the porosity of the two columns the velocities were slightly different.

An overview of the three experiments is given in Table 3.5. The sample intervals were adjusted to always sample approximately the same amount of water in each vial. For each experiment and each column around 5.5 l were running through the column and thus at least 360 samples were taken per experiment. The pore velocities v_p [L/T] were calculated out of the measured flow rate with

$$v_p = \frac{Q}{A * n} \tag{4}$$

where Q is the measured flow rate [L^3/T] and A the area of the column opening [L^2]. The pore velocities were just used as first measure before the modelling.

Table 3.5: The measured flow rates and calculated pore velocities, sample interval, sample volume, the volume of the tracer applied, the application time of the tracer and the total running time of each experiment.

	Experiment 1		**Experiment 2**		**Experiment 3**	
Column	**EA**	**EB**	**EA**	**EB**	**EA**	**EB**
Q [cm^3/min]	1.86	2.02	1.28	1.37	0.71	0.76
v_p [cm/min]	0.101	0.104	0.070	0.070	0.039	0.039
Sample interval [min]	8		11.5		20.7	
Sample volume [cm^3]	14.9	16.1	14.8	15.7	14.7	15.6
V_{Tracer} [l]	1.10	1.18	1.06	1.13	1.05	1.12
T_{Tracer} [h]	10.08		13.82		24.5	
T_{Total} [h]	48		69		124.2	

3.4.4. Used Pharmaceuticals and Tracers

Table 3.6: Properties of the used EOCs.

Pharmaceutical	CAS-Reg. No.	Empirical Formula	Use	Solubility$_{H2O}$ [mg/ml]	pK$_a$ (20°C)	LogK$_{ow}$
Antipyrine	60-80-0 [a]	$C_{11}H_{12}N_2O$ [a]	Analgesic [a]	47.4 **[b]	-	1.22 **[c]
Atenolol	29122-68-7 [a]	$C_{14}H_{22}N_2O_3$ [a]	Beta-blocker [a]	0.429 **[b]	9.67 **[c]	0.43 **[c]
Carbamazepine	298-46-4 [a]	$C_{15}H_{12}N_2O$ [a]	Anticonvulsant [a]	0.152 **[b]	15.96 **[c]	2.77 **[c]
Clofibrate	637-07-0 [a]	$C_{12}H_{15}ClO_3$ [a]	Fibric acid [a]	0.029 **[b]	-	3.4 **[c]
Clofibric acid *	882-09-7 [d]	$CIC_6H_4OC(CH_3)_2CO_2H$ [d]	Metabolite of Clofibrate [a]	0.5825 [e]	3.2 [e]	2.84 [f]
Caffeine	58-08-2 [a]	$C_8H_{10}N_4O_2$ [a]	Nervous system stimulant [a]	11.0 **[b]	14 [g]	-0.55 **[c]
Diclofenac	15307-86-5 [a]	$C_{14}H_{11}Cl_2NO_2$ [a]	Anti-inflammatory [a]	0.0045 **[b]	4 **[c]	4.26 **[c]
Ketoprofen	22071-15-4 [a]	$C_{16}H_{14}O_3$ [a]	Beta-adrenergic blocker [a]	0.0213 [b]	2.88 **[c]	3.61 **[c]
Sulfamethoxazole	723-46-6 [a]	$C_{10}H_{11}N_3O_3S$ [a]	Antibiotic [a]	0.459 **[b]	6.16 **[c]	0.79 **[c]

*not added to tracer cocktail

**predicted values

[a] Drugbank, 2016

[b] calculated with ALOGPS (VCCLAB, 2005; Tetko et al., 2005)

[c] calculated with Chemaxon, 2016

[d] Sigma-Aldrich, 2016

[e] Bayer-AG, 2001

[f] Henschel et al., 1997

[g] Moffatt et al., 1986

Table 3.6 shows the used EOCs and the metabolite of clofibrate, clofibric acid. Clofibric acid was not added to the tracer solution. Besides the pharmaceuticals shown in Table 3.6 the conservative tracers bromide added as potassium bromide and uranine were used. They were all ordered from Sigma-Aldrich, Steinheim (Germany). Because most of the organic contaminants are hardly water-soluble compounds (see Table 3.6) a small amount of methanol needed to be added to create a solution of groundwater and pharmaceuticals. Table 3.7 shows the composition of the tracer cocktails used in the three experiments.

Every tracer cocktail contained 1.5 l of water (containing 0.05 g/l sodium azide for EA) of which around 1.1 l were flowing through the column. A concentrated mix solution was made with all EOCs besides caffeine solved in methanol in a concentration of 1 g/l. 0.225 ml of this solution were added to the tracer bottle resulting in a total methanol concentration of approximately 0.12 g/l in the tracer bottle and a concentration of every EOC of around 150 µg/l. Since caffeine is soluble in water it was added separately in a concentration of around 200 µg/l. The conservative tracer uranine was added in a concentration of around 83 µg/l as well as 4.45 g/l bromide.

Table 3.7: Calculated concentrations of all compounds in the tracer solution.

Compounds	**Calculated concentration in tracer [mg/l]**
Bromide	4476
EOCs (besides caffeine)	0.15
Caffeine	0.2
Uranine	0.083
NaN_3 (just for EA)	50
Methanol	120

3.5. Sample Analysis

3.5.1. Uranine Analysis

For uranine analysis 0.3 ml of each test vial were transferred to a spectrometer plate using a pipette. Additionally samples of the tracer bottles were also analysed. The uranine analysis was then done using a fluorescence spectrometer (Perkin-Elmer Victor 3 1420 Multi Label Counter, Xenon lamp). Excitation and emission wavelength show a specific difference of 25 nm for uranine. Therefore the wavelength range scanned by the machine was set between 485 nm and 535 nm. Each measurement took 0.1 s which made the analysis really fast. To transfer fluorescein counts of the machine to concentration values, a calibration curve with known concentrations was created (see Appendix).

3.5.2. Analysis of Bromide, Sulfate and Nitrate

For the analysis of bromide, vials were filled with 1.5 ml of every sixth filtrated sample (0.2 µm filter) and two filtrated samples of the tracer bottles and then analysed using ion chromatography (Dionex ICS-1100). The measurement of each sample took 15 minutes. Additionally NO_3^- and SO_4^{2-} were analysed in all samples to get information on oxygen content and redox potential.

3.5.3. EOC Analysis

In order to analyse the concentrations of the compounds in each sample taken by the fraction collector, the samples were analysed with Liquid Chromatography- Mass Spectrometry (LC-MS) (3200 QTRAP LC-MS/MS System) using a Kinetex column (2,6 µm C18 100 A, 150 x 3 mm, Phenomenex, Aschaffenburg, Germany). Therefore 1.5 ml of every sixth sample and two samples from the tracer bottles were transformed to small vials using a 0.2 µm filter and stored in the fridge at 4°C until measurement started. Depending on their properties, some compounds needed to be measured in a positive and some in a negative mode. To not keep samples outside of the fridge for too long, samples for the two modes were taken separately. All compounds besides Clofibric acid, Diclofenac and Ketoprofen were analysed in the positive mode, the other three in the negative mode. Every sample took 28 min (negative mode) and 34 min (positive mode) for analysis. More details on the methods and its parameters are shown in the appendix.

3.6. Mass and Recovery Calculation

After analysis, some parameters were calculated out of the resulting breakthrough curves (BTCs) to characterize the transport behaviours additionally to the later modelling results.

The injected mass M_{inj} of each compound was calculated with

$$M_{inj} = \frac{C_{inj}}{V_{inj}} \tag{5}$$

C_{inj} is the measured concentration of the compound in the tracer bottle [ML^{-3}] and V_{inj} the total volume injected [L^{-3}] determined by weighing the tracer bottles before and after the experiment. With this the total recovery R of each compound could be calculated:

$$R = \frac{\int_0^\infty C(t) * Q(t)}{M_{inj}} * 100 \tag{6}$$

$C(t)$ is the concentration [ML^{-3}] and $Q(t)$ the flow velocity [L^3T^{-1}] per sample and interval. Recoveries where calculated until the last taken sample (1. Exp.: after 48 h, 2. Exp.: after 69 h, 3. Exp.: after 124 h) and thus after approximately a recovery of 5.4 l of water in each experiment. Depending on the different analysis methods (e.g. positive or negative mode) and velocities, this slightly varied.

3.7. Modelling

To quantify sorption and degradation of the EOCs and to model the BTCs of the conservative tracers, the program CXTFIT 2.1 was used which is based on the convection-dispersion equation (CDE). The program provides options for direct and inverse modelling. The inverse modelling can be done for different types of models including the deterministic equilibrium CDE and the deterministic non-equilibrium CDE. Therefore, the objective function, which is build up of the squared differences of observed and fitted concentrations, is minimized by a nonlinear least-squares inversion procedure (Toride et al., 1995).

3.7.1. Equilibrium CDE

The equilibrium CDE assumes equilibrium conditions for transport including sorption and retardation without any immobile water regions (Toride et al., 1995):

$$R_f \frac{\partial c_r}{\partial t} = D \frac{\partial^2 c_r}{\partial x^2} - v_p \frac{\partial c_r}{\partial x} - \mu c_r + \gamma(x) \tag{7}$$

with R_f as retardation factor [-], c_r as volume-averaged or resident concentration of the liquid phase [ML^{-3}], t as time [T], D as dispersion coefficient [L^2 T^{-1}], x as distance [L], and µ [T^{-1}] is a first-order decay coefficient while γ [T^{-1}] is a zero-order production coefficient (Toride et al., 1995).

The retardation factor R_f and the first-order decay coefficient for biodegradation μ are here determined as (Toride et al., 1995):

$$R_f \approx 1 + \frac{\rho_b}{\theta} * K_d \tag{8}$$

$$\mu = \mu_l + \frac{\rho_b \mu_S}{\theta} * K_d \tag{9}$$

where ρ_b is the soil bulk density of the sediment [ML^{-3}], K_d the empirical distribution constant [M^{-1} L^3], θ the volumetric water content [L^{3}L^{-3}] *and* μ_L and μ_S the first-order degradation coefficients in the liquid and the solid phase [T^{-1}]. v_p and D as well as R_f and μ can be fitted in CXTFIT 2.1. The input concentration and the duration of injection are needed start values and can be optimized as well.

3.7.2. The Non-Equilibrium CDE

The non-equilibrium CDE is available as a two region physical non equilibrium and a two site chemical non-equilibrium version. The chemical non-equilibrium differs between adsorption regions in equilibrium and the one where first-order kinetics are taking place while the physical non-equilibrium varies between immobile and mobile water zones that have different portions on transport. Exchange is assumed to happen as first-order process.

The physical and chemical non-equilibrium transport equation can be shown as one dimensionless equation (Toride et al., 1995):

$$\beta R_f \frac{\partial C_1}{\partial T} = \frac{1}{P}\frac{\partial^2 C_1}{\partial Z^2} - \frac{\partial C_1}{\partial Z} - \omega(C_1 - C_2) - \mu_1 C_1 + \gamma_1(Z) \tag{10}$$

$$(1-\beta) R_f \frac{\partial C_2}{\partial T} = \omega(C_1 - C_2) - \mu_2 C_2 + \gamma_2(Z) \tag{11}$$

Where β is a partitioning coefficient [-], ω a mass transfer coefficient [-], Z a dimensionless distance [-], T a dimensionless time [-]. The subscript 1 and 2 for concentration C, the first-order decay coefficient μ and the zero- order production coefficients γ stand for the equilibrium and non-equilibrium sites. P is the Peclet number [-].

The pore water velocity v_p is calculated with

$$v_p = \frac{\theta_m v_m}{\theta} \tag{12}$$

With $\theta_m$as the mobile volumetric water content [L^3L^{-3}] and v_m as the pore water velocity of the mobile phase [LT^{-1}].

The above mentioned input concentration and duration of tracer injection, D, R_f and v_p as well as β, ω and μ for the liquid and adsorbed phase can be fitted in the model.

3.7.3. Estimation Procedure and Further Parameter Calculations

The conservative tracer bromide almost behaves like water and was thus used to estimate dispersivity and pore velocity without the influence of sorption and retardation. Since uranine is undergoing sorption to small amounts and is photodegradable the parameters were mainly taken from the BTC of bromide. First, the data of bromide was modelled using the equilibrium CDE with resident concentration (first type) and R_f set to 1 and μ set to 0. It was estimated that the recovery of bromide was 100 % and therefore the input concentration was adapted and used as fixed input parameter for the modelling. Thus D, v_p and the application time $T_{appl.}$ were fitted to the data. v_p was first optimized for all experiments but then sometimes adjusted manually to always keep the proportions between the pore velocities. $T_{appl.}$ was fitted for EB and then fixed for EA, due to problems in the ion chromatographic analysis for EA (see error analysis).

D and v_p as estimated parameters were then in a second step taken as fixed values for the EOCs, just leaving R_f und μ as fitting parameters by still using the equilibrium CDE.

The equilibrium version was used for bromide and the EOCs because modelling with the non-equilibrium version led to over-parametrization showing different but unrealistic results dependent on the start values. Furthermore, realistic parameter combinations showed highest possible values of the partitioning coefficient β and low values of the mass transfer coefficient ω. This revealed that the exchange between mobile and immobile water regions was negligible, according to the model. Additionally, almost the same values for D and v_p were achieved for both, the equilibrium and the non-equilibrium version when modelling bromide BTCs. Therefore, the equilibrium version was used for the whole modelling.

Out of the modelled parameters D and v_p some other parameters were calculated. The modelled D was used to calculate the dispersivity α [L]:

$$\alpha = \frac{D}{v_p} \tag{13}$$

Furthermore by knowing v_p and Q the effective porosity n_{eff} was calculated:

$$n_{eff} = \frac{Q}{A \cdot v_p} \tag{14}$$

Knowing v_p the mean transit time t_0 of every experiment and column could then be calculated with

$$t_0 = \frac{x}{v_p} \tag{15}$$

4. Results

4.1. Conservative Tracers

Figure 4.1 shows the normalized breakthrough curves and the recoveries of the two conservative tracers uranine and bromide for column EA (left side) and EB (right side). The first experiment of both columns is shown in the first line, the third of each column at the bottom. Although a longer pulse was applied, there was no plateau reached in the columns. The shape of the BTCs compared between the columns and the tracers was slightly different. The maximum C/M-ratios and recoveries of bromide were little higher in the biotic columns. For bromide they ranged between 0.74 and 0.78 l^{-1} for EA and 0.76 and 0.88 l^{-1} for EB. Its recoveries were around 76 to 81 % for EA while between 95 to 102 % were recovered for the biotic column EB.

Uranine showed lower recoveries and C/M-ratios in comparison to bromide. The maximum C/M-ratios reached for uranine ranged between 0.58 and 0.63 l^{-1} for EA and between 0.66 and 0.72 l^{-1} for EB. The recoveries of uranine for the biotic column decreased with lower flow velocities from 84 to 73 % while for EA almost the same recoveries were achieved for all experiments ranging from 73 to 75 %.

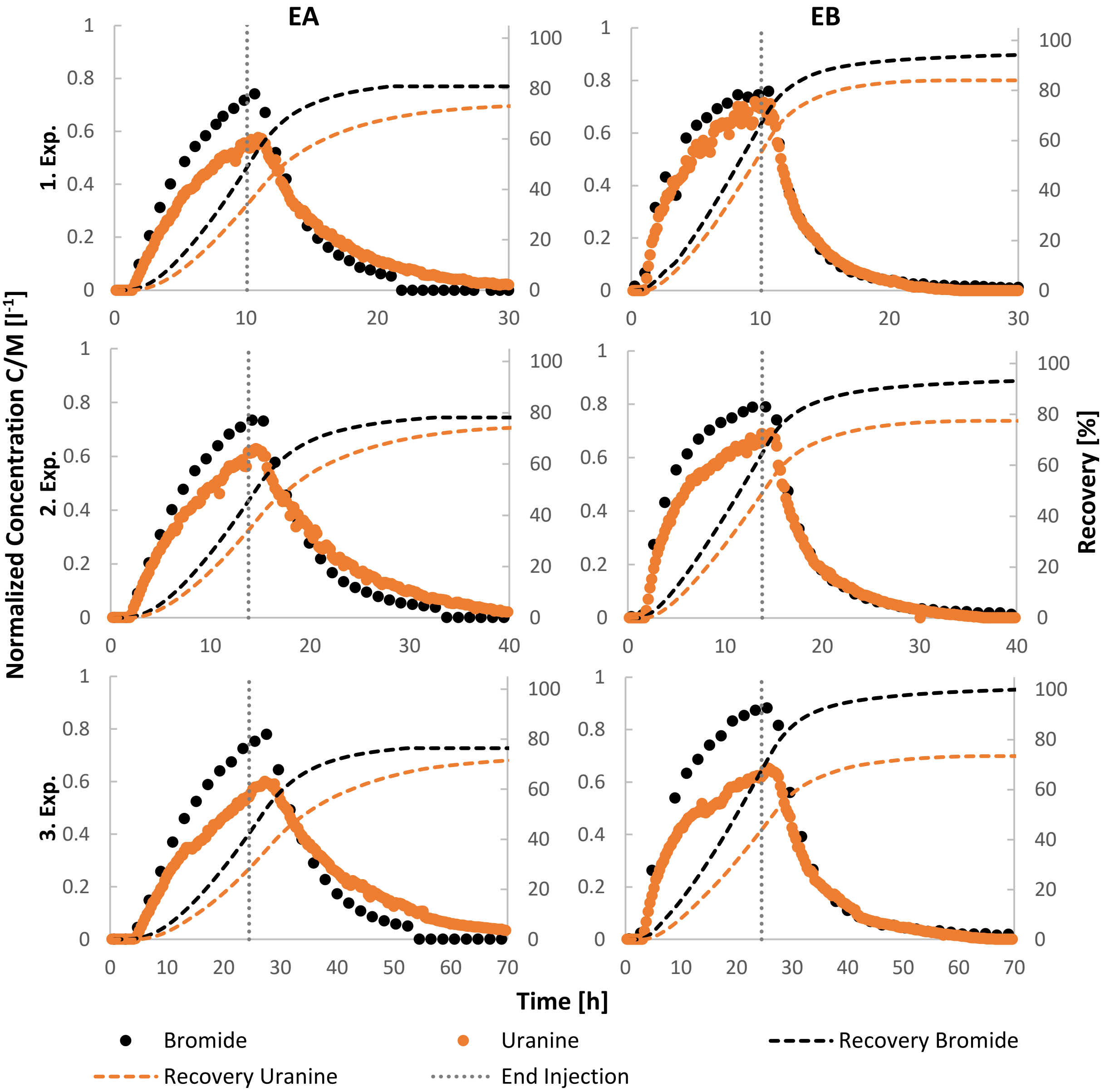

Figure 4.1: BTCs (points, left axis) and recoveries (broken line, right axis) of the two conservative tracers bromide (black) and uranine (orange) of column EA (left side) and EB (right side) of the three experiments in each column starting with the first experiment in the first line. The concentrations were normalized with the mass injected in every experiment. The end of injection is shown with the grey vertical pointed line.

4.2. EOCs

4.2.1. BTCs

The BTCs of antipyrine, atenolol, caffeine, carbamazepine, diclofenac, ketoprofen and sulfamethoxazole for the different experiments in the two columns are shown in Figure 4.2. and 4.3. Atenolol had the lowest maximum ratios and most retarded peak of all compounds. In both columns the maximum C/M-ratios decreased with slower flow velocities from 0.21 to 0.1 l^{-1} in EB and from 0.09 to 0.04 l^{-1} in EA. Like for the conservative tracers the maximum ratios reached were higher in the biotic column than in the abiotic. The BTCs of caffeine and carbamazepine were similar compared to each other. There were no effects of the different flow velocities visible but again the maximum ratios were higher for the biotic column. Caffeine showed maximum C/M ratios between 0.54 and 0.59 l^{-1} for EB and 0.44 to 0.51 l^{-1} for EA. For carbamazepine values between 0.55 and 0.59 l^{-1} were reached for the peak of column EB and between 0.44 to 0.50 l^{-1} for EA. Diclofenac displayed maximum ratios between 0.59 and 0.67 l^{-1} for EB and between 0.47 and 0.54 l^{-1} for EA. A higher peak for the biotic column and no big differences between the different experiments were observed. Thus, diclofenac as well as caffeine and carbamazepine all showed distinct lower maximum C/M-values than bromide. Furthermore, a small retardation of the peak was observable for all three compounds compared to bromide. In contrast, antipyrine, ketoprofen and sulfamethoxazole showed high maximum ratios close to the one of bromide and no or only a small delay of the peak. There was no effect of different flow velocities noticeable in both columns. Antipyrine had maximum C/M-ratios between 0.69 and 0.74 l^{-1} for EB and 0.65 and 0.73 l^{-1} for EA which were thus little lower than the maximum values reached for bromide. Ketoprofen showed similar highest values between 0.76 and 0.78 l^{-1} for EB and 0.64 and 0.73 l^{-1} for EA. Thus, the peak of EB was again higher than EA. For sulfamethoxazole the maximum ratios were mostly even higher with values ranging from 0.75 to 0.83 l^{-1} for EB and 0.75 to 0.81 l^{-1} for EA.

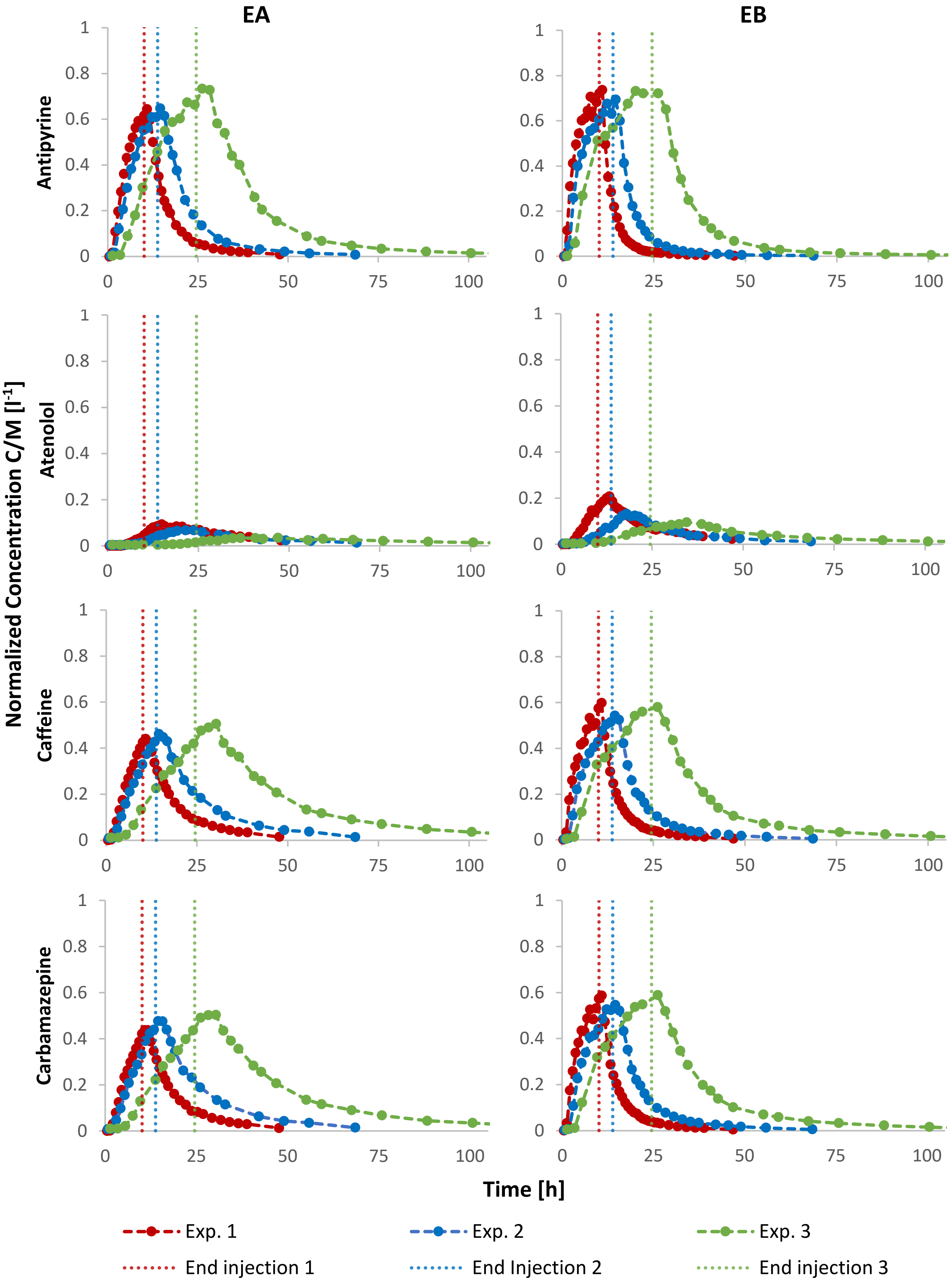

Figure 4.2: BTCs of the compounds antipyrine, atenolol, caffeine and carbamazepine of the two columns EA (left) and EB (right) for the experiment 1 (red), experiment 2 (blue) and experiment 3 (green). The concentrations were normalized with the mass injected in every experiment. The end of every injection is shown as pointed line in the same colour than the experiment.

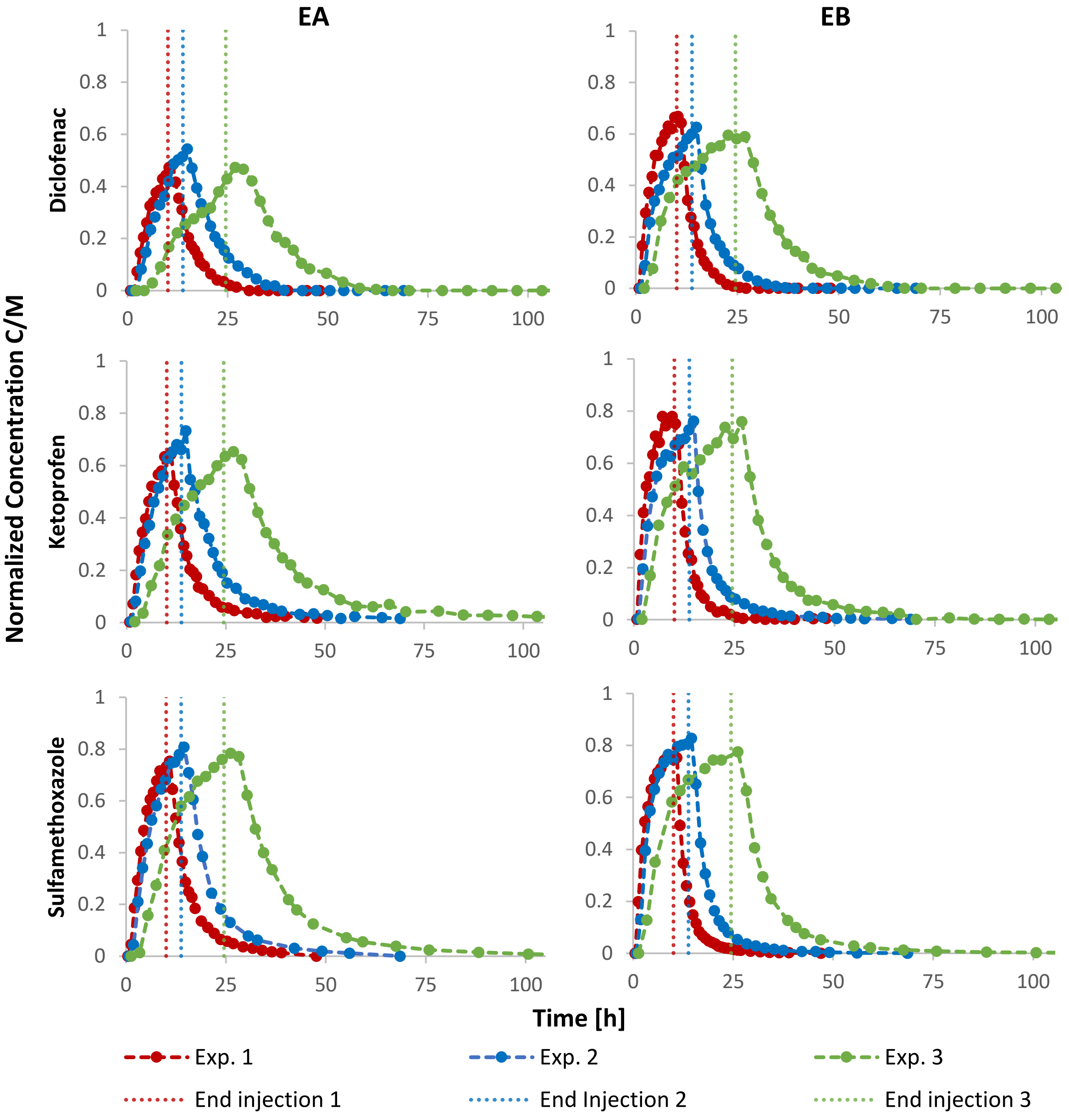

Figure 4.3: BTCs of the compounds diclofenac, ketoprofen and sulfamethoxazole of the two columns EA (left) and EB (right) for the experiment 1 (red), experiment 2 (blue) and experiment 3 (green). The concentrations were normalized with the mass injected in every experiment. The end of every injection is shown as pointed line in the same colour than the experiment.

The BTCs of clofibrate and its active metabolite clofibric acid are shown in Figure 4.4. The total mass used in the experiments could not be determined for both compounds. The samples of clofibrate, that were taken out of the tracer bottle already showed low or variable concentrations when analysed. The same was visible for the concentrations of clofibrate during the experiments. The observed concentrations were low, not showing any clear peaks. In contrast, its metabolite clofibric acid was detected in higher amounts. The peak of clofibric acid arose around the same time than bromide. Since the input concentration of clofibrate could not be analysed the highest possible produced amount of clofibric acid could also not be determined. Maximum concentrations measured were increasing from 112 to 137 µg/l with decreasing flow velocity for the column EB. The concentrations in the column EA were showing closer values for the three experiments between 102 and 106 µg/l.

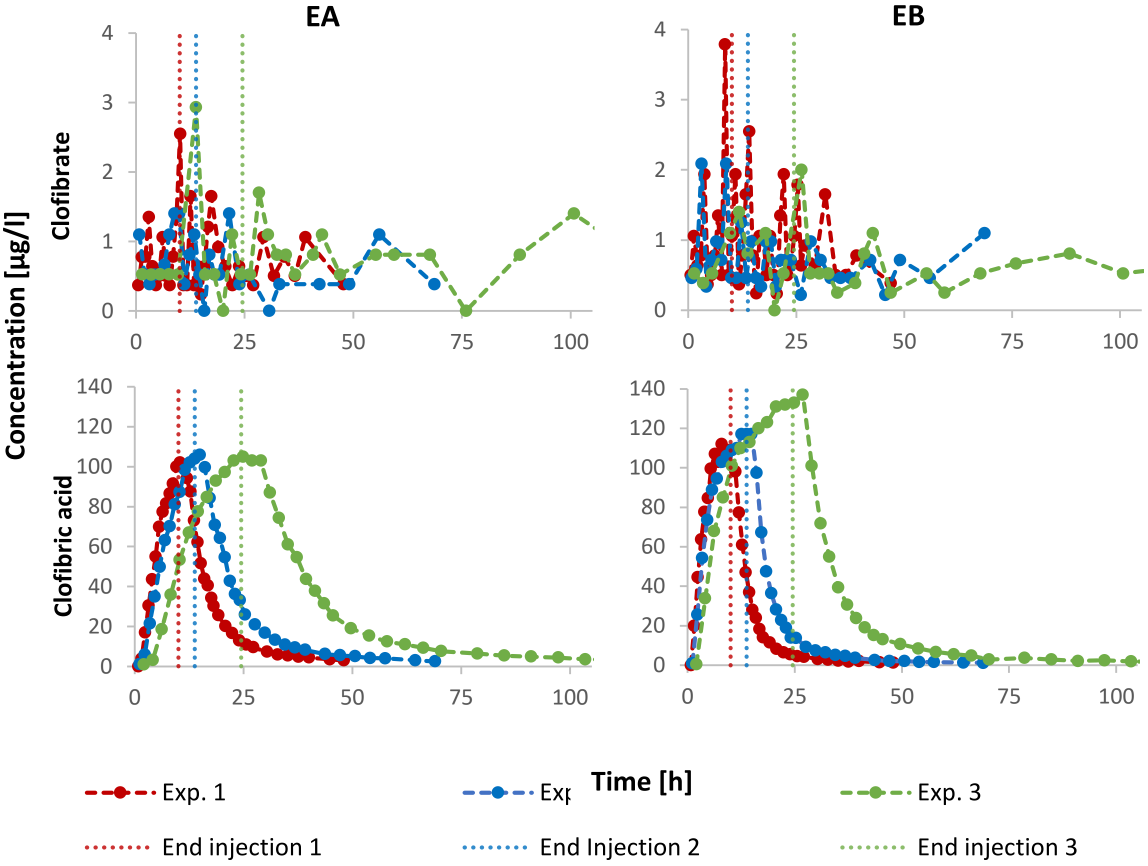

Figure 4.4: BTCs of clofibrate (first line) and clofibric acid (second line) of the two columns EA (left) and EB (right) for experiment 1 (red), experiment 2 (blue) and experiment 3 (green). The end of every injection is shown as pointed line in the same colour than the experiment.

4.2.2. Recoveries

Figure 4.5 shows the recoveries of all used compounds besides clofibrate until the last taken sample and thus recovery of approximately 5.4 l of water in every experiment. Concentrations of all compounds where at zero or close to it at that point (see Figures 4.2 and 4.3). Results mostly matched with the results of the BTCs described before. Sulfamethoxazole, ketoprofen and antipyrine had the highest recoveries with almost the same values for both columns. For sulfamethoxazole, recoveries were slightly getting smaller with lower flow velocities from 99 to 91% for EB and 99 to 93 % for EA. Ketoprofen showed values ranging from 86 to 100 % for EB and 84 to 88 % for EA but no effect of flow velocity was visible. The recoveries for antipyrine were also high with values from 81 to 92 % for the biotic and 86 to 89 % for the abiotic column without any big difference between the experiments. They were followed by caffeine, carbamazepine and diclofenac. Values of caffeine and carbamazepine were again similar. Caffeine displayed recoveries from 71 to 80 % for EB and 69 to 74 % for EA while carbamazepine recoveries were between 72 to 79 % for EB and 68 to 74 % for EA. Both showed no big differences between the two columns or between the different experiments. For diclofenac differences between the two

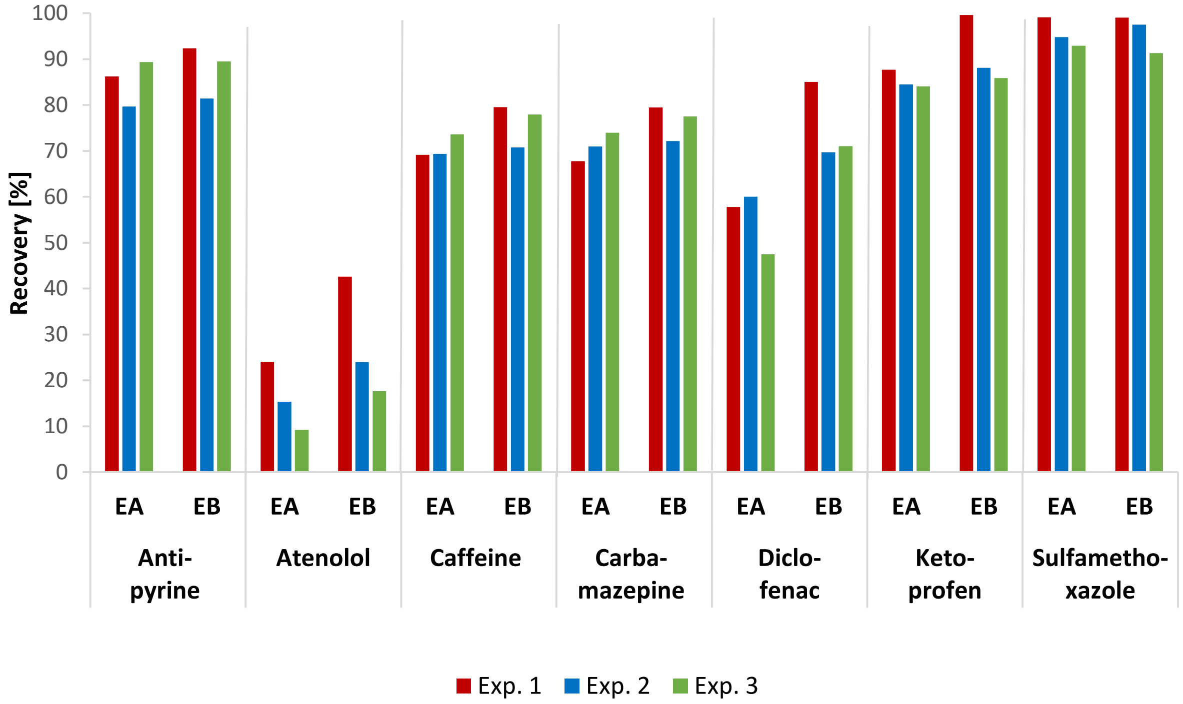

Figure 4.5: Recoveries of the compounds antipyrine, atenolol, caffeine, carbamazepine , diclofenac, ketoprofen and sulfamethoxazole for experiment 1 (red), experiment 2 (blue) and experiment 3 (green) for both columns at the end of the experiments after 5.4 l of water were collected.

columns were larger between 70 and 85 % for EB and 48 and 60 % for EA. Atenolol recovery was low and showed higher recoveries for higher flow velocities. The recoveries of the column EB were dropping from 43 % for the first experiment to 18 % for the last experiment. For the column EA recoveries were generally lower starting from 24 to 9 %.

4.3. Nitrate and Sulfate

Normalized nitrate and sulfate concentrations during the experiments are shown in Figure 4.6. The input concentrations in the tracer bottles were always around 340 mg/l for sulfate and around 35 mg/l for nitrate. During the first experiment, sulfate stayed constantly around the input concentration for both columns while nitrate concentrations were increasing from only 50 % of the input concentration to 85 % at the end of the experiment. In the second experiment of both columns, nitrate and also sulfate showed a general increase of concentrations from the beginning until the end of the experiment. Sulfate started around 80 % and then increased until the input concentration was

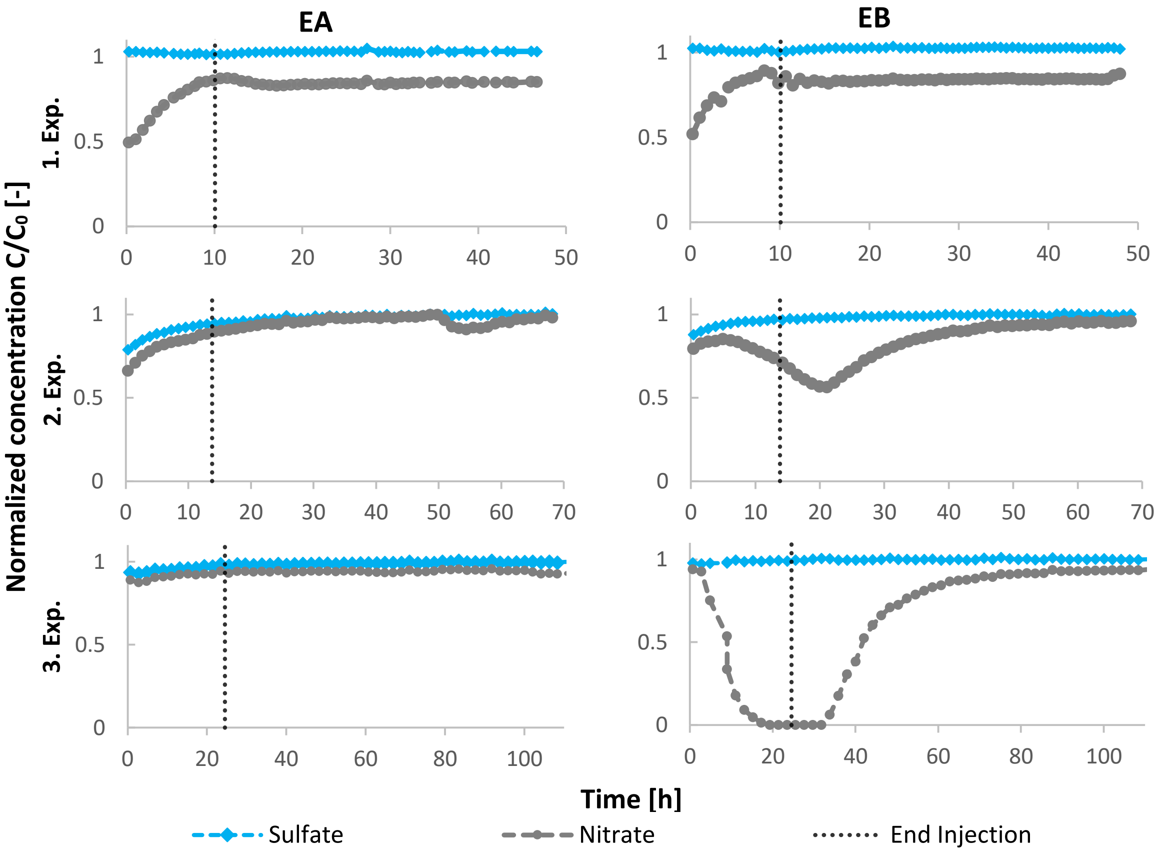

Figure 4.6: Normalized nitrate (grey) and sulfate (blue) concentrations during the three experiments for column EA (left) and EB (right). The end of injection is shown as black pointed line. Concentrations were normalized with the input concentrations measured in the tracer bottle.

reached. Nitrate in the abiotic column started at 66 % of the input concentration. However, for the biotic column concentrations were decreasing for the first 22 h from 80 % to even 57 %. Afterwards the concentrations increased until nearly the input concentration was reached.

Figure 4.7 shows the nitrate concentrations for column EB and the BTCs of Atenolol and Clofibric acid. The drop in concentration in the second experiment of column EB occurred when most of the PCs already reached their peak but was in time with the breakthrough of atenolol.

In the third experiment of column EB nitrate disappeared totally after 20 h. The water stayed without nitrate until 34 h after the start of the tracer injection. Nitrate concentrations were already around 0 % before atenolol completely broke through (Figure 4.7). The concentrations increased again after concentrations of atenolol decreased. In the abiotic column nitrate stayed constantly close to the input concentration during the whole experiment as well as sulfate in both columns.

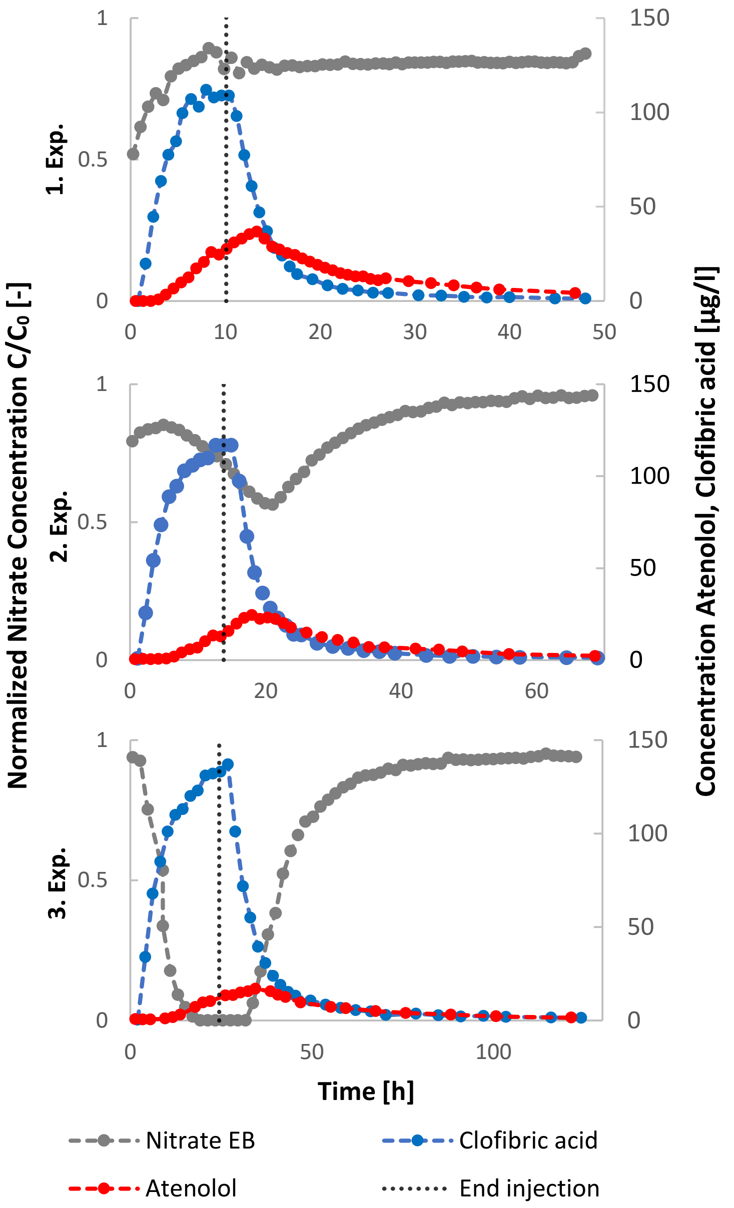

Figure 4.7: Normalized nitrate concentration (grey) of column EB and BTCs of atenolol (red) and clofibric acid (blue) for the three experiments.

4.4. CXTFIT Modelling

4.4.1. Optimized Parameters Bromide

Table 4.1 shows the parameters that were achieved by fitting the bromide data. As quality criterions R^2 and NRMSE (normalized root-mean-square error) were used. For better comparisons thus the RMSE was normalized with the mean of the observations of every compound. The fitted application time $T_{appl.}$ was about 16, 23 and 29 min lower than the measured application time (605 min, 829 min, 1470 min). Generally, v_p as well as D were higher for EB than for EA. Although fits were good in general indicated by R^2 and NRMSE, the pore velocity was always higher than calculated before (EA: 0.101 cm/min, 0.07 cm/min, 0.039 cm/min; EB: 0.104 cm/min, 0.07 cm/min, 0.039 cm/min).

Table 4.1: Modelled pore velocity v_p, dispersion coefficient D, application time $T_{appl.}$ and NRMSE and R^2 of bromide of the three experiments for both columns.

	Experiment 1		**Experiment 2**		**Experiment 3**	
Column	**EA**	**EB**	**EA**	**EB**	**EA**	**EB**
v_p [cm/min]	0.178	0.234	0.123	0.162	0.068	0.090
D [cm^2/min]	2.03	4.63	1.38	2.79	0.51	1.27
$T_{appl.}$ [min]	589.3		805.7		1441	
NRMSE [-]	0.06	0.17	0.07	0.11	0.08	0.09
R^2 [-]	0.992	0.990	0.993	0.996	0.987	0.996

The modelled values were used to calculate the effective porosity n_{eff}, the mean transit time t_0, as well as the dispersivity α (Table 4.2). The modelled pore water velocities led to an effective porosity of 13 % for EB and 16 % for EA. Due to the lower effective porosity in EA the mean transit time t_0 was thus higher in this column than in EB. The dispersivity α was calculated using the dispersion coefficient D of every experiment. Generally, the dispersivity for EB was higher than for EA. For EB, the values decreased from 19.4 to 14.1 cm from the first to the last experiment. For EA dispersivities of the two fastest experiments ranged around 11.4 cm and then for the last experiment dropped to 7.5 cm.

Table 4.2: Dispersivity α, the effective porosity n_{eff} and the resulting mean transit time t_0 in all experiments and both columns. All parameters were calculated out of the modelling results.

	Experiment 1		**Experiment 2**		**Experiment 3**	
Column	**EA**	**EB**	**EA**	**EB**	**EA**	**EB**
α [cm]	11.4	19.4	11.3	17.2	7.5	14.1
n_{eff} [%]	16.5	13.3	16.4	13.3	16.4	13.3
t_0 [min]	282	209	407	308	737	559

4.4.2. Fits Bromide and EOCs

Fits of bromide, carbamazepine and atenolol for the first experiment in column EB are shown in Figure 4.8. All others are shown in the appendix. Although sometimes the peak or the tailing was not fitted perfectly, in general good fits for all the compounds were achieved.

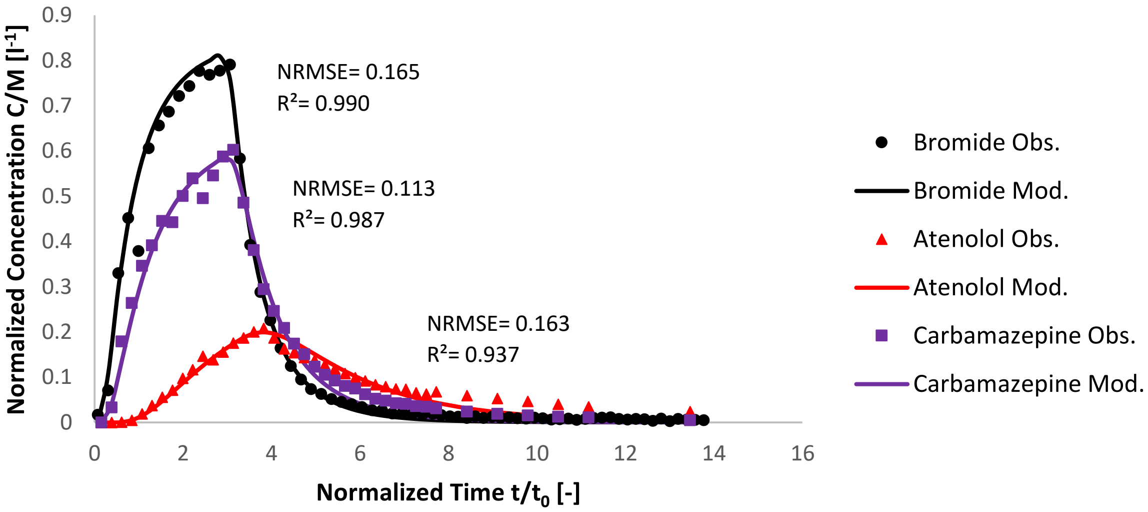

Figure 4.8: Fits of bromide (black), carbamazepine (purple) and atenolol (red) with their NRMSE and R^2 *for column EB for the first experiment. The time was normalized with the modelled* t_0*. The concentration was normalized with the mass injected.*

Figure 4.9 shows the same BTCs of bromide, atenolol and sulfamethoxazole of Figure 4.2 and 4.3, but here the time was normalized with the modelled t_0 (others see appendix). Using this normalized time it became more obvious that there were no big differences between the curves of the different experiments of one compound. The only exception was atenolol as already mentioned above. Furthermore, its retardation became more obvious here, while for other compounds there was no big retardation observable. According to the modelled t_0 around two effective pore volumes were applied as tracer for EA and 2.7 for EB.

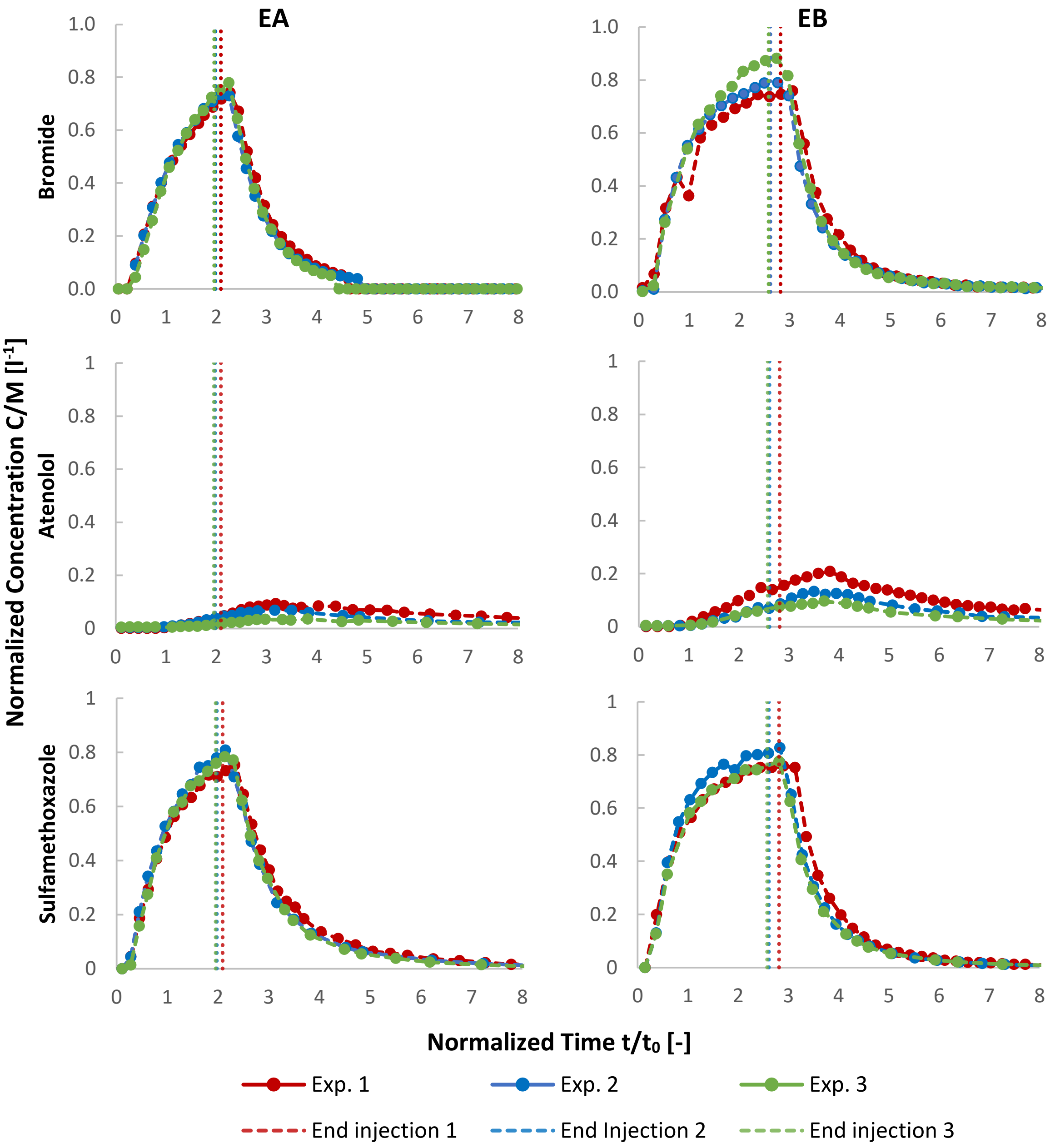

Figure 4.9: BTCs of bromide (first line), atenolol (second line) and sulfamethoxazole (third line) including the modelled application times T_{app} as vertical pointed lines in matching colours of the experiment for column EA (left) and EB (right). The time was normalized using the modelled t_0 of every experiment. Concentrations were normalized with the mass injected.

4.4.3. Modelled Retardation Factors

The results of the modelling for the retardation factor R_f for the EOCs and the conservative tracer uranine is shown in Figure 4.10. Clofibrate could not be modelled. Uranine had a higher retardation factor than some of the EOCs with values ranging between 1.25 to 1.30 for EB and 1.39 to 1.46 for EA. Thus EA showed higher values for R_f. Values of some compounds were close to one and therefore close to the BTC of bromide. These compounds were antipyrine, sulfamethoxazole and ketoprofen in all experiments and both columns. For these compounds no differences of R_f between the experiments were observable. For sulfamethoxazole R_f even ranged between 0.94 and 1 for EB and 1.01 and 1.10 for EA with little higher retardation for EA. Ketoprofen showed values around 1.05 and 1.13 for EB and between 1.18 and 1.24 for EA. Thus, values in the abiotic column were slightly higher. Antipyrine values ranged between 1.16 and 1.24 for EB and 1.21 and 1.27 for EA. This three compounds were followed by diclofenac, caffeine and carbamazepine. Diclofenac displayed a retardation factor of 1.35 and 1.41 for EB and 1.48 and 1.54 for EA and thus slightly higher values for EA. Very close values were observed for caffeine and carbamazepine with R_f ranging between 1.65 and 1.84 for EB and 1.81 and 1.95 for EA for carbamazepine. Values of caffeine ranged between 1.67 and 1.87 for EB and 1.83 and 1.97. R_f was

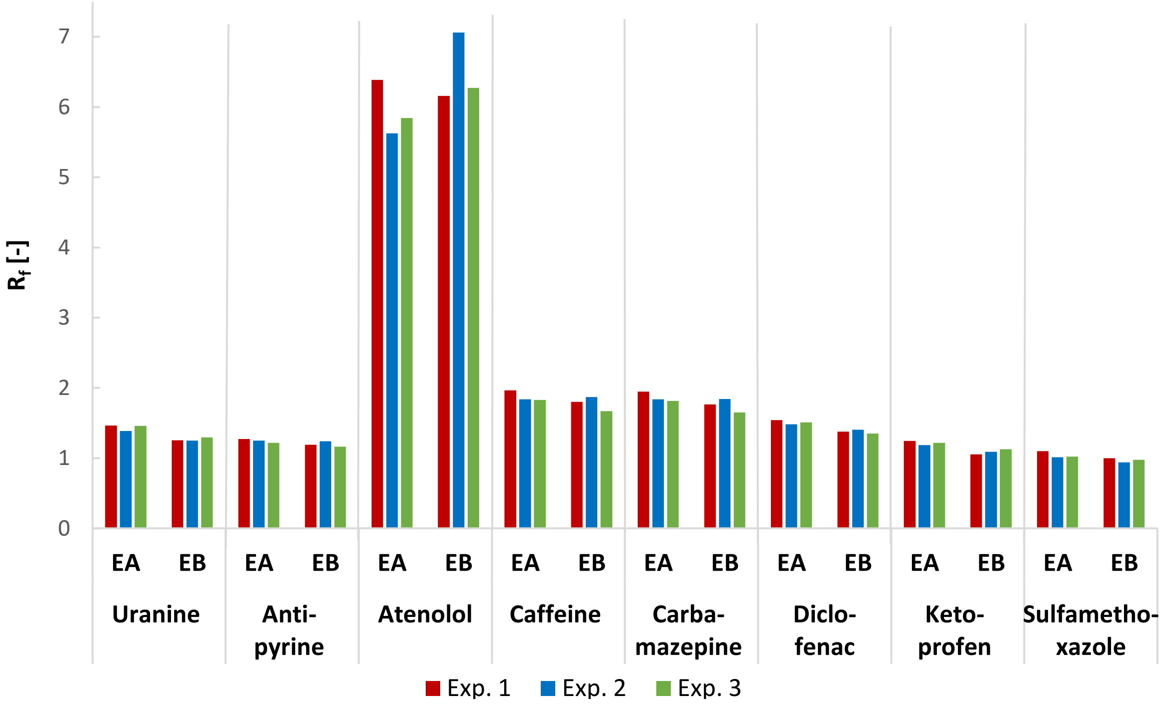

Figure 4.10: Modelled retardation factor R_f for uranine and the EOCs antipyrine, atenolol, caffeine, carbamazepine, diclofenac, ketoprofen and sulfamethoxazole for the column EA and EB for all three experiments.

slightly getting smaller with lower flow velocities in the column EA for both compounds. Atenolol had the highest values of all compounds. Values ranged from 6.16 to 7.06 for EB and from 5.63 to 6.39 for EA but did not show any effect of different flow velocities.

4.4.4. Modelled Degradation Rates

Degradation rates (Figure 4.11) generally showed a higher variability than the retardation factors observed. However, they revealed a similar order with degradation rates of uranine that were dropping from 1.27 to 0.86 d^{-1} for EB and from 2.15 to 0.85 d^{-1} for EA. Ketoprofen, sulfamethoxazole and antipyrine showed low values for μ. The degradation rates of sulfamethoxazole were ranging from 0.09 to 0.29 d^{-1} for EB and 0.33 to 0.59 d^{-1} for EA. Ketoprofen ranged from 0.15 to 0.75 d^{-1} for EB and 0.70 and 1.49 d^{-1} for EA. For both compounds values were slightly decreasing with flow velocity for EA and were in general little higher in EA than in EB. Antipyrine did not show any differences or any tendency between the columns or the experiment and ranged from 0.37 to 1.09 d^{-1} for EB and 0.45 to 1.17 d^{-1} for EA. These compounds were again followed by caffeine, carbamazepine and diclofenac. Caffeine and carbamazepine showed a decrease of μ with decreasing flow

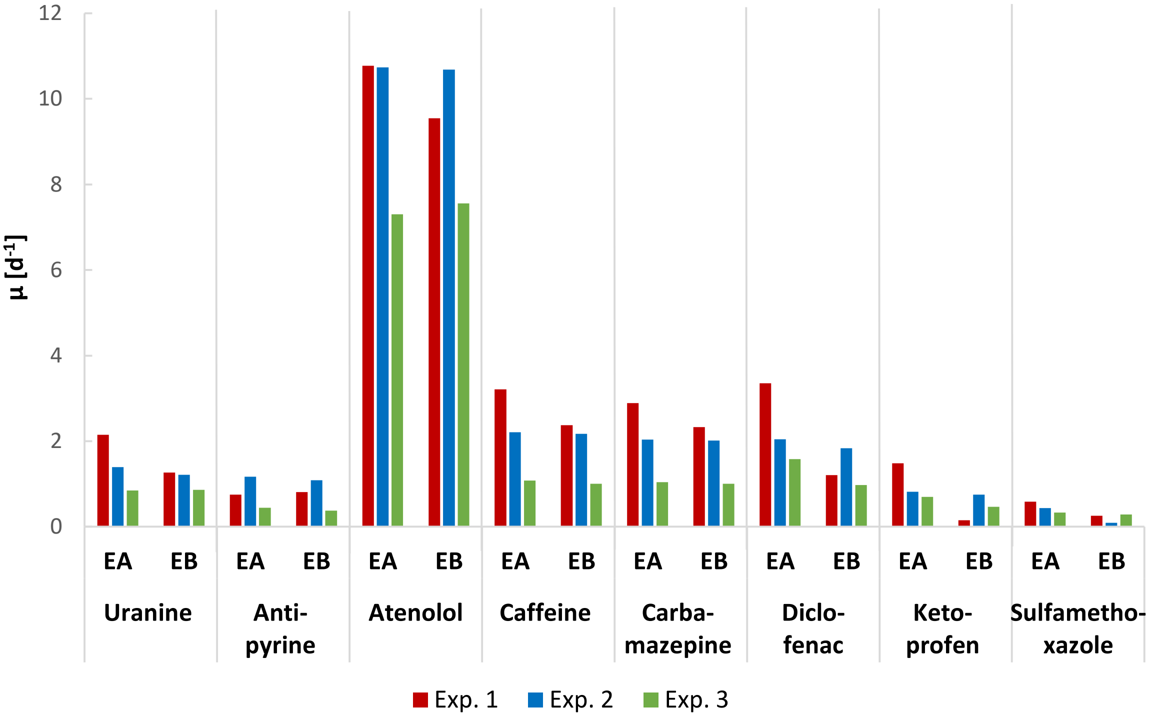

Figure 4.11: Modelled degradation rate μ for uranine and the EOCs antipyrine, atenolol, caffeine, carbamazepine, diclofenac, ketoprofen and sulfamethoxazole for column EA and EB for all three experiments.

velocity but no differences between the columns. Caffeine dropped from 2.38 to 1.00 d^{-1} for EB and from 3.21 to 1.08 d^{-1} for EA. Carbamazepine started with 2.33 and then dropped to 1.01 d^{-1} for EB and decreased from 2.89 to 1.04 d^{-1} for EA. The same tendency was observed for diclofenac in column EA with values that decreased from 3.36 to 1.58 d^{-1} while EB ranged between 0.98 and 1.83 d^{-1}. Values were mostly higher for EA. Atenolol showed the highest degradation rates of all compounds with similar values in both columns and no effect of flow velocity. Degradation rates ranged from 7.56 to 10.68 d^{-1} for EB and 7.30 to 10.76 d^{-1} for EA.

5. Discussion

5.1. Hydrodynamics

The columns contained high amounts of immobile water since according to the model just 57 % (EA) and 44 % (EB) of the total porosity was effective porosity. This led to much higher modelled values of the pore water velocity than calculated. For EA, the pore velocities were about 1.8 times higher, for EB even a factor of 2.3 was separating the modelled from the calculated pore velocities. Column EA thus showed higher amounts of mobile water which led to the lower modelled pore water velocities compared to EB.

The transport was hardly influenced by dispersion in both columns. This led to the early increase of the concentrations measured at the outlet shortly after the start of injection. Dispersivities (8-19 cm) were really high compared to other studies. Modelled dispersivities of a column study of Burke et al. (2013) in a medium sandy sediment were around 0.41 cm and hence much lower. The modelled dispersion coefficients and thus also the dispersivities were lower for EA than for EB. The dispersivity α is an aquifer property, which is not dependent on flow velocity. Thus, around the same values were previously expected for each experiment of every column. However, α decreased with lower flow velocities in most experiments. There are some possible explanations for this tendency to lower α with lower flow velocity. On one hand lower flow velocities could have led to other preferable flow paths in the column and therefore to different dispersivities. On the other hand, the porous system of the sediment could also have been changed due to the different flow velocities which then also led to different pathways in the sediment. However, this changes and also the generally high values for the dispersivity compared to other studies could at least partly be attributed to the uncertainties of the model.

5.2. Comparison of Transport Parameters of the Analysed EOCs

The results demonstrated partly different but also similar behaviour of the different EOCs. Sulfamethoxazole mostly showed the highest C/M-ratios of all compounds and basically no retardation, high recoveries always above 91 % and low degradation rates. Since degradation rates were little higher for EA no biological degradation could be observed. In total, sulfamethoxazole was thus found to be very mobile with sorption or degradation not playing an important role. The results of this column study fit with the results of the batch study of Kodesova et al. (2015). These authors classified sulfamethoxazole as a mobile and persistent compound due to very low sorption. Negligible sorption was also found in batch experiments with different soils of Lin and Gan (2011). However, based on their incubation experiments they also observed biodegradation of sulfamethoxazole with half-lifes between 9 and 18 days in aerobic and unaerobic environments (Lin and Gan, 2011).

Ketoprofen also showed very high C/M ratios and low retardation between 1.05 and 1.24 as values for R_f for both columns. The recovery was high between 84 and 100 %. Since modelled degradation rates were also low, the transport behaviour of the β-blocker ketoprofen was thus not much influenced by sorption or degradation. Since degradation rates were even higher for EA than for EB, the lost mass could not be led back to biological degradation. Thus, ketoprofen in this study was observed to be a mobile compound. A batch and incubation study with four different soils of Xu et al. (2009) also found very little sorption. However, they found degradation, especially biodegradation to be present and increasing with higher TOC content (Xu et al., 2009). Sandy loam having a comparable amount of organic matter (1.93 %) than in this study was there found to show quite high degradation rates of ketoprofen but only little retardation. This is contrary to this study since biodegradation could not be observed here.

No biological degradation was also found for antipyrine. Also other abiotic processes of degradation were little according to the quite high recoveries between 81 and 92 % and low modelled degradation rates. Sorption was also small with R_f ranging from 1.16 to 1.27. To conclude, sorption or degradation did not play a key role for antipyrine and therefore this compound could, according to this study, be present in water for a long time. Since studies on antipyrine and its behaviour in the environment are still mostly missing, there is no comparable study. Anyhow, the fact that biodegradation in wastewater treatment plants was found to be low (Zuehlke et al., 2006) is in agreement with these findings.

Diclofenac showed slightly higher retardation factors between 1.35 and 1.54 compared to sulfamethoxazole, ketoprofen and antipyrine. Recoveries were between 70 and 85 % for column EB and between 48 to 60 % for EA and thus mostly lower than for the previous compounds. The lower recoveries for EA and also higher modelled degradation rates for this column in comparison to EB leads to the fact that probably biological degradation did not influence the transport of diclofenac. However, other abiotic factors leading to degradation were according to the lower recoveries and the higher degradation rates in comparison to the previous compounds influencing the behaviour of diclofenac in groundwater. But still it seems to be mobile to some extent. There are variable results of previous studies which are not always in line with these findings. Some authors found even higher influence of sorption on the transport of diclofenac. In the column study of Mersmann et al. (2002) reversible sorption was found with a calculated R_f of 2.6 but negligible degradation. Scheytt et al. (2004) also showed a big influence of sorption on its transport. However, other studies observed even more persistent behaviour for diclofenac under unaerobic conditions, showing its probably high mobility in groundwater (Lin and Gan, 2011; Xu et al., 2009b). Under aerobic conditions both studies found high biodegradation and very low sorption with maximum half-lifes of 20.44 d (Lin and Gan, 2011; Xu et al., 2009b). Therefore, the behaviour of diclofenac seems to be hardly dependent on the surrounding conditions like the aerobic status.

Caffeine and carbamazepine were found to be similarly influenced by sorption and degradation. The modelled retardation factor R_f ranged between 1.65 and 1.97 for both compounds and thus higher sorption than for the compounds before was observed. Recoveries were lower than for sulfamethoxazole, ketoprofen and antipyrine ranging between 69 and 80 % for both columns. Furthermore, there was no difference between the columns observable. Thus, the lower recoveries and higher degradation rates in both columns compared to the other compounds cannot be led back to biological retardation but to other abiotic degradation processes.

Results for carbamazepine from other studies are quite variable ranging from very high sorption in a column study (Mersmann et al. ,2002) with R_f calculated as 2.8 to very low sorption found by other incubation and batch experiments (Kodesova et al., 2015; Radke et al., 2014). However, these studies also never found biodegradation (Mersmann et al., 2002; Radke et al., 2014). Gottschall et al. (2012) observed quite long half-lifes of 46 days in biosolids. Thus especially the sorption behaviour of carbamazepine might be variable dependent on the surrounding conditions. Especially the sediment might play a key role (Lapworth et al., 2012; Mersmann et al., 2012).

Caffeine was found to be mobile in a column study with sandy sediment of Greenhagen et al. (2014). However many other studies found a huge impact of biodegradation on its transport (Benotti and Bronawell, 2009; Lin et al., 2010). A batch study of Lin et al. (2010) found half-lifes of 1.5 d and irreversible sorption and biodegradation as factors hardly influencing transport of caffeine. Although sorption was influencing its transport in this study, biodegradation could not be observed.

Atenolol showed different behaviour in comparison to the other compounds. Recoveries were very low ranging from 18 to 43 % for EB and only 9 to 24 % for EA. Thus, this compound was degraded to very high amounts also visible at the highest modelled degradation rates of all compounds. Similar to the other pharmaceuticals this degradation was probably not due to the activity of microbes but due to abiotic processes like irreversible sorption. Modelled degradation was similar in both columns but with even lower recoveries for EA. Its retardation factors were the highest of all compounds. R_f was ranging between 5.63 and 7.06 showing a high tendency to sorption to the matrix surfaces for both columns. Due to the high retardation factor next to degradation also sorption played an important role for this compound. High sorption and degradation rates were also found by other studies (Kodesova et al., 2015; Barbieri et al., 2012; Burke et al., 2013). Burke et al. (2013) observed a retardation factor higher than 6 in their column experiments which fits to the findings here.

Clofibrate was only detectable in a few samples and just in very small amounts. Therefore, recoveries of this compound were very low but could not be calculated because the input mass in the tracer was not always measurable. If there were measurable concentrations in the samples of the tracer bottles they were very variable and differing within the samples of the same bottle. Therefore, and because it was nearly not detectable during the experiments, it could also not be modelled. Due to the fact, that its active metabolite clofibric acid was found in high amounts in both columns clofibrate was probably transformed to clofibric acid in very short time via hydrolysis. The detected maximum concentrations of clofibric acid higher than 100 µg/l showed that probably most of clofibrate added was transformed to clofibric acid. The fact that the BTCs of clofibric acid occured around the same time as bromide leads to the assumption that the transformation to clofibric acid happened very fast. Transformation however occurred inside the column since in samples of the tracer bottles clofibric acid was just found in negligible amounts. Mersmann et al (2002) did a column study on clofibric acid. He calculated a retardation factor of 1.1 for clofibric acid and recovered nearly the total input mass. To conclude, the metabolite clofibric acid is probably not significantly influenced by sorption or degradation processes like proved in many different studies under various conditions (Mersmann et al., 2002; Oppel et al., 2004; Scheytt et al., 2004). Due to the fact that clofibrate is leaving the human body as clofibric acid to approximately 95 to 99 % after treatment (Drugbank, 2016), the finding of these huge amounts of clofibric acid was not surprising and thus here the metabolite clofibric acid is probably the compound to care about.

These findings are partly contrary to the pK_a and $logK_{ow}$ values which are sometimes used as a first measure for the sorption behaviour of a compound (Banzhaf et al., 2016). Since besides atenolol, caffeine and carbamazepine all analysed EOCs show a lower pK_a at 20 °C than the pH of the water and of the sediment it would according to this values be estimated that they would be rather ionic and thus more mobile than the other three compounds that would be neutral according to this value. Besides the fact that for clofibrate and antipyrine no pK_a values are available, this estimates would partly be in line with the findings in this study. However, carbamazepine and diclofenac showed similar behaviour in this study but show very different pK_a values. According to the $logK_{ow}$ as measure for the hydrophobic or hydrophilic tendency of a compound (Banzhaf et al., 2016) a less mobile transport behaviour would be estimated for most of the compounds besides atenolol, sulfamethoxazole and caffeine. The lowest mobility would be assumed for diclofenac according to its high K_{ow}. Thus besides for sulfamethoxazole all findings would be contrary to the pK_a values and mostly also to the findings in this study. This shows that values like the pK_a and especially the $logK_{ow}$ should not be used to characterize the mobility of EOCs since, as mentioned before their behaviour not only depends on the pH or the compound itself, but also on the sediment and other surrounding conditions. Burke et al. (2013) also showed that the $logK_{ow}$ is an inadequate measure to estimate transport of EOCs.

According to the results of the experiments and the followed modelling the EOCs can be separated into three groups.

Clofibric acid, sulfamethoxazole, ketoprofen and antipyrine were found to be quite conservative with especially sulfamethoxazole showing a behaviour comparable to the behaviour of the conservative tracer bromide. These three compounds can thus be estimated to show a mobile transport behaviour at least in sandy aquifers comparable to the sediment used in this study. Once brought into the water via waste water treatment plants or other sources, they could thus be found in the water for long time and could be transported over long distances.

Caffeine, carbamazepine and also diclofenac could be classified into a second group. Degradation and sorption were leading to a lower concentration of these compounds in the environment according to this study. However, to some extent they were still mobile.

The third group contains atenolol and clofibrate. According to the results in this study they can be estimated to not be mobile and to be sorbed or degraded. But this does not necessarily mean that the environmental contamination is negligible for this compounds. The example of clofibrate and its metabolite clofibric acid shows that this can lead to metabolites which can be even more mobile than the parent compound, showing the same or even higher toxic effects. Transformation products of atenolol or other compounds were not analysed and thus there is no information on the fate and behaviour of potential metabolites of the other compounds.

Remarkable is that none of the compounds analysed in this study showed biodegradation. This is in contrast to other studies mentioned above (e. g. Lin et al., 2010, Xu et al., 2009, Lin and Gan, 2011) but also in contrast to the observed drop in nitrate for the second and third experiment. This is further discussed below.

5.3. Comparison of Transport Parameters for the Different Flow Velocities

Most of the compounds showed no influence of flow velocity on their transport behaviour by looking at the modelled retardation factors and degradation rates. Retardation factors of all three experiments showed really close values for all compounds besides atenolol. However, the degradation rates of caffeine and carbamazepine, as well as uranine were decreasing with decreasing flow rate. For compounds like diclofenac, ketoprofen and sulfamethoxazole this effect was just visible for the abiotic column. This cannot be explained by biotic degradation. Furthermore, due to the fact that the degradation rates as well as the recoveries cannot be separated into the impact of irreversible sorption and abiotic transformations it is not possible to determine what exactly is causing this decrease of degradation rates for these compounds. Nevertheless, this would lead to the assumption that abiotic degradation processes in the case of caffeine and carbamazepine decreased with deceasing flow velocity. However, since the BTCs and the recoveries were not showing any tendency this cannot clearly be confirmed.

Atenolol was the only compound that showed the impact of different transit times by looking at the peak values of the BTCs and the recoveries with decreasing flow velocities. The maximum C/M-ratios decreased with lower flow velocity which was also leading to lower recoveries. This implies that the impact of transport processes which were lowering the concentration of atenolol in water, were increasing with lower flow velocities. There was no effect observable for the modelled retardation or degradation rates. However, different studies proved that not the flow velocity but the interaction time and thus, the mean transit time is the most important factor influencing transport (Knorr et al., 2016; Kim et al., 2006; Brusseau, 1992). Assuming this, degradation rates and retardation factors should not change over time, while absolute values like recoveries should change with interaction times. This could explain why no effects of flow velocity were observed for the modelled degradation rates or retardation factors of atenolol while recoveries and maximum C/M-ratios decreased with slower flow velocity since the interaction time increased. The studies of Brusseau (1992) and Kim et al. (2006) who analysed this correlation for other organic contaminants like benzene or naphthalene found clear results. Both demonstrated a decreasing sorption with higher pore water velocities due to shorter interaction periods (Brusseau, 1992; Kim et al., 2006). To conclude, the lower recoveries for atenolol under lower flow velocities can either be explained with an increase of irreversible sorption or abiotic degradation. Maybe even both processes were increasing under lower flow velocities. Longer interaction times and a higher impact of diffusion under lower flow velocities were also found to lead to higher biodegradation (e.g. Murphy et al., 1997; Kinzelbach et al., 1991). However, biodegradation was not observed for any of the compounds in this study and thus no effect of different flow velocities on biodegradation could be determined. Therefore, the drop of nitrate concentrations for the second and third experiment was surprising. Nitrate and sulfate are used as electron acceptors by microbes under absence of oxygen when degradation of organic material is taking place. Since this effect was increasing with lower flow velocities this implies that biodegradation took place and increased with decreasing flow velocity.

The time when the concentrations decreased in the second experiment of the biotic column fits to the BTC of atenolol. Atenolol could also be responsible for the decrease of nitrate in the third experiment. Nitrate was probably totally consumed before atenolol reached the peak. A clear explanation for the general decrease in nitrate during the experiment, although no visible biological degradation took place, could not be found but there are some possible explanations for this.

Barbieri et al. (2012) observed biological degradation of atenolol after 5 to 10 days of their batch study of 87 days, together with a decrease of nitrate. The first 10 days only sorption was influencing the transport of atenolol. Therefore, the observed drop in nitrate for the second and third experiment in EB could be an indicator of the biodegradation of atenolol. Since recoveries for EB in this study were not observed to be lower than for EA biodegradation of atenolol could have happened at the irreversibly sorbed amounts of atenolol thus leading to the same recoveries at the outlet in both columns.

Another explanation would be the presence of methanol in the tracer cocktail. Although the amount of methanol added was kept very low due to density effects that were observed before the experiments started, the amount of methanol in comparison to atenolol or clofibric acid was high. The calculated concentration of methanol in 1.5 litres of tracer was around 0.12 g/l while the calculated concentration of every EOC was only around 0.00015 g/l. Methanol could have been favoured for biodegradation by microbes instead of the EOCs and thus led to the decrease of nitrate. This would also explain why no biological degradation was observed for the EOCs added in these experiments. Howard et al. (1991) found half-lifes of methanol in groundwater of 1 to 7 days with biodegradation as the most important factor.

Besides atenolol, high transformation of clofibrate to clofibric acid was observed in both columns. Its active metabolite clofibric acid was in column studies of Mersmann et al. (2002) and Scheytt et al. (1998) found to lower the redox potential during breakthrough under biotic conditions. Scheytt et al. (1998) observed a decrease of the redox potential from +500 mV to -250 mV. They assumed that the presence of clofibric acid leads to changes of the chemical environment catalysed by microbes (Scheytt et al., 1998). The presence of clofibric acid could have led to a decrease of the redox potential and thus to nitrate reducing conditions. This would explain why almost no biological degradation was found for all compounds since these conditions would have lowered the ability of microbes for degradation. Assuming this under absence of clofibric acid, more degradation would have been possible. This would be in line with findings of other studies mentioned above, that found high biodegradation rates for some of the compounds analysed in this study. The fact that this decrease in nitrate was higher for lower flow rates and not visible for the fastest flow rate could lead to the assumption that the fastest flow rate was too fast to show any effect of the clofibric acid breakthrough on the redox potential catalysed by microbes. Looking at the studies that observed the influence on redox potential for clofibric acid the used flow velocities in the experiments of Scheytt et al. (1998) were around 1.17 cm^3/min and therefore little lower than the flow rates of the second experiment in this study. Mersmann et al. (2002) also used flow rates between 0.92 and 1.23 cm^3/min and thus lower than the first experiment.

5.4. Error Analysis

5.4.1. Methanol as Solvent

Methanol was used because most of the EOCs were not soluble in water. The amount of used methanol was kept very low because pre-experiments showed that probably a density effect due to methanol leads to a faster flow through of the tracer cocktail with methanol than without. Due to the fact the pre-experiments done without EOCs and methanol in the used columns showed the same fast breakthrough of uranine and bromide than in the shown experiments with methanol it can be assumed, that the used amount of methanol was low enough to prevent a density effect in the columns.

However as mentioned above methanol is well biodegradable and thus is able to stimulate the biological degradation (Howard at al., 1991). It is therefore possible that even this low amounts of methanol added were leading to biodegradation of methanol instead of the EOCs. Since most of the used EOCs are hardly water soluble an organic solvent is needed to make sure that they are transported into the column. It is difficult to overcome this problem. As long as solvable amounts of the EOCs in pure water are still possible to be analysed with LC-MS, lower concentrations could be used to prevent the use of an organic solvent like methanol.

5.4.2. Uranine as conservative Tracer

While bromide was found to be a good tracer uranine showed much lower recoveries and according to the modelling it was also retarded and degraded to some amounts. Degradation rates between 0.85 and 2.15 d^{-1} as well as retardation factors between 1.25 and 1.46 were higher than the rates of some of the analysed EOCs like sulfamethoxazole and ketoprofen. In other studies, uranine was found to be influenced by photodegradation with a half-life of 11 hours and to small amounts also by sorption (Leibundgut et al., 2009; Koeniger et al., 2010). Due to this it might not be the perfect tracer for column studies where a good and reliable conservative tracer is essential for comparison and especially modelling. Deuterium would have been a better and more conservative tracer but could not be analysed in the presence of organic compounds. However, due to the really fast and easy analysis of uranine it is very useful for fast estimates during the experiments.

5.4.3. NaN_3 and Ion Chromatographic Analysis

As visible in Figure 4.1 bromide concentrations and also recoveries in the column EA were always lower than in EB. This was due to the analysis of bromide with ion chromatography. An additional peak arose close to the bromide peak due to NaN_3 or transformation products (Figure 5.1). This peak made the separation of the peaks and thus bromide and also nitrate analysis extremely difficult. For other experiments another method or substance for sterilization of the columns should be used. This could for example be done with autoclavation of the sediment (Burke et al., 2013).

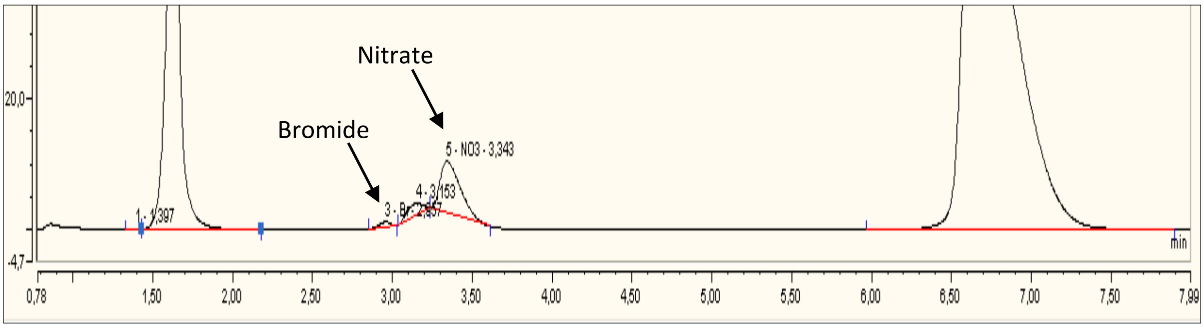

Figure 5.1: Output of the ion chromatography of one sample of the antibiotic column showing the additional peak between the peak of bromide and nitrate due to the presence of NaN_3.

5.4.4. Measurement of Oxygen, Redox Potential and pH

It was shown that the transport behaviour of EOCs in groundwater is strongly dependent on the surrounding conditions. Especially the pH but also the amount of oxygen and resulting redox conditions are important factors (Johnson et al., 1998). Although the anions in the solution were analysed and gave some ideas of redox conditions in the column more information would have been important. The use of ports for oxygen and redox potential measurement in the columns was not possible due to the column type without ports. However, pH, redox potential and amount of oxygen could have been measured at the entrance and the outlet of each column over time.

6. Conclusion

Coming back to the hypothesises, some can be confirmed while some need to be rejected. As expected, sulfamethoxazole and antipyrine were barely influenced by sorption and degradation and thus, these compounds can be present in groundwater for long time. However, since carbamazepine was sorbed and degraded the hypothesis that carbamazepine is not influenced by any of these processes needs to be rejected. Previously it was also expected that diclofenac and atenolol will highly be influenced by sorption. In general, both compounds showed sorption as one process influencing their transport. However, atenolol was much more sorbed than diclofenac. Both compounds were also influenced by abiotic degradation processes. The hypothesis that clofibric acid as the active metabolite of clofibrate is detected in the samples under both, biotic and abiotic conditions can be confirmed. Clofibric acid was observed in high amounts while concentrations of clofibrate were low, which shows that not only the compound itself but also its metabolites are important to consider during analysis. Since biodegradation was not observed for any of the compounds, the hypothesis that caffeine as well as ketoprofen and atenolol are well biodegradable cannot be confirmed. However, sorption and abiotic degradation influenced the transport of caffeine, while ketoprofen was barely influenced by these processes.

To conclude some compounds can be estimated to be very mobile in groundwater like clofibric acid, sulfamethoxazole, ketoprofen and antipyrine, while concentrations of caffeine, carbamazepine and diclofenac were lower at the outlet and together with their modelled transport parameters indicating that sorption and degradation were affecting their transport. Atenolol and clofibrate were recovered in very low amounts and thus sorbed or degraded.

Although some findings were in line with other studies, especially with regard to expected biodegradation of compounds, like caffeine or atenolol differences were observed. Furthermore, values of the pK_a or $logK_{ow}$ were shown to mostly not be useful for the estimation of transport of EOCs. This shows that the behaviour of a compound in one sediment with a special grain-size and pH does not necessarily lead to the same behaviour in another sediment. The mobility of some EOCs like for example carbamazepine might be very variable depending on the pH or the sediment and therefore might be difficult to predict. However, according to this study, sorption and degradation for most analysed EOCs might not be influenced by different flow velocities. Caffeine and carbamazepine degradation rates were decreasing with lower flow velocities. However, no clear statement is possible here since the BTCs or recoveries as well as the retardation factors did not show any impact. Therefore, the previous hypothesis, that transport of EOCs might be influenced by flow velocities cannot be confirmed. Atenolol was obviously not primarily influenced by the flow velocities, but by the different transit times showing lower recoveries with longer mean transit times, while modelled degradation rates did not show any impact. This leads to the fact that the explained effects are most likely due to abiotic degradation or irreversible sorption, which might have increased due to longer interaction times.

The drop in nitrate concentrations, which was increasing with lower flow velocities, revealed that biodegradation happened inside the column and was also influenced by different pore water velocities. Therefore, the hypothesis that microbial activity leads to differences in the reactive transport behaviour under biotic conditions compared to abiotic conditions cannot completely be rejected. The fact that no biodegradation was observed for the analysed EOCs might be due to the presence of clofibric acid. This on one hand, might have lowered the redox conditions inside the column and thus did not allow much microbial activity. On the other hand, the use of methanol might have led to the biological degradation of methanol instead of the EOCs. Furthermore, biodegradation might have happened at the irreversibly sorbed compounds. To ensure that the presence of methanol or clofibric acid did not influence the results further experiments are necessary, where also the amount of oxygen, redox potential and the pH during the experiment should be measured.

7. Outlook

This thesis proved that the behaviour of EOCs in groundwater is variable depending on the compound itself but also on the surrounding conditions and thus difficult to characterize. Furthermore, different chemicals might interact and influence the transport of each other like here discussed for clofibric acid. It is therefore also important to consider the combination of different EOCs in water (Kümmerer, 2010). More research, especially on possible metabolites of the EOCs is necessary. These are sometimes more mobile than the original compound like for clofibric acid. This is also important with regard to possible more efficient treatments of EOCs in the wastewater to minimize the biggest source of pharmaceuticals in the environment. Additionally, grouping the substances according to their behaviour in water would lead to the possibility to take some compounds as indicators for other compounds, that are transported in a same way (Jekel et al., 2015). Since some of the EOCs were in thiss study, but also in other studies shown to be very mobile, they could be tracked over long distances like for example sulfamethoxazole. Persistant compounds might stay in the groundwater for long time and are also present in drinking water. Therefore, threshold values for groundwater contamination concerning EOCs are required (Lapworth et al., 2012).

The upscaling of these and other findings to the catchment scale is therefore difficult, since the behaviour of EOCs in the environment is hard to predict. Furthermore, it depends on the different combinations of EOCs and surrounding conditions, like the type of sediment and pH. However, this thesis provides insides to the behaviour of the analysed pharmaceuticals in sandy aquifers and could thus be useful for the later modelling of comparable regions.

8. References

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9. Appendix

9.1. List of Abbreviations

BTC	Breakthrough Curve
CDE	Convection-Dispersion Equation
CXTFIT	Program used for modelling transport parameters of solutes (Toride et al., 1995)
DDT	Dichlorodiphenyltrichloroethane
EA	Abiotic column Empordá
EB	Biotic column Empordá
EOC	Emerging Organic Contaminants
Exp. 1	Experiment 1
Exp. 2	Experiment 2
Exp. 3	Experiment 3
LC-MS	Liquid Chromatography coupled Mass Spectrometry

9.2. List of Symbols

9.2.1. Symbols

Symbol	**Name**	**Unity**
A	Area of the column opening	[L^2]
C_{inj}	Concentration of the compound in the tracer bottle	[ML^{-3}]
C_{sort}	Empirical sorting coefficient	[-]
C_1	Concentration for the equilibrium sites	[ML^{-3}]
C_2	Concentration for the non-equilibrium sites	[ML^{-3}]
c_r	Volume-averaged or resident concentration of the liquid phase	[ML^{-3}]

D	Dispersion coefficient	[L^2 T^{-1}]
d_{10}	Grain diameter where 10 % have a smaller size	[L]
d_{60}	Grain diameter where 60 % have a smaller size	[L]
K_d	Empirical distribution constant	[L^3 M^{-1}]
K_{OW}	Distribution coefficient between water and octanol	[-]
k_f	Hydraulic conductivity	[L T^{-1}]
$\mathrm{Log}K_{OW}$	Logarithm of the distribution coefficient between water and octanol	[-]
M_{inj}	Injected mass	[M]
n	Porosity	[-]
n_{eff}	Effective porosity	[-]
P	Peclet number	[-]
pK_a	Logarithm of the acidic dissociation constant	[-]
Q	Flow rate	[L^3 T^{-1}]
R	Total recovery	[-]
R_f	Retardation factor	[-]
T	Dimensionless time	[-]
T_{Total}	Total duration of the experiments	[T]
T_{Tracer}	Application Time of the tracer	[T]
TC	Total carbon	[-]
TOC	Total organic carbon	[-]
t	Time	[T]
t_0	Mean transit time	[T]
U	Coefficient of grain uniformity	[-]

V_{inj}	Total volume injected	$[L^{-3}]$
V_{Sed}	Volume of the Sediment	$[L^{3}]$
V_{Tot}	Volume of the Sediment	$[L^{3}]$
V_{Tracer}	Volume of the Tracer injected	$[L^{3}]$
V_{Water}	Volume of the Water	$[L^{3}]$
v_m	Pore water velocity of the mobile phase	$[LT^{-1}]$
v_p	Average pore water velocity	$[LT^{-1}]$
x	Distance	[L]
Z	Dimensionless distance	[-]

9.2.2. Greek Symbols

α	Dispersivity	[L]
β	Partitioning coefficient	[-]
γ	Zero-order production coefficient	$[T^{-1}]$
γ_1	Zero-order production coefficient for the equilibrium sites	$[T^{-1}]$
γ_2	Zero-order production coefficient for the non-equilibrium sites	$[T^{-1}]$
θ	Volumetric water content	$[L^{3}L^{-3}]$
θ_m	Mobile volumetric water content	$[L^{3}L^{-3}]$
μ	First-order decay coefficient	$[T^{-1}]$
μ_L	First-order degradation coefficient in the liquid phase	$[T^{-1}]$
μ_S	First-order degradation coefficient in the solid phase	$[T^{-1}]$
μ_1	First-order decay coefficient for the equilibrium sites	$[T^{-1}]$
μ_2	First-order decay coefficient for the non-equilibrium sites	$[T^{-1}]$
ρ_b	Soil bulk density	$[ML^{-3}]$

ω	Mass transfer coefficient	[-]

9.3. Recoveries

Table A.1: Recoveries of antipyrine, atenolol, caffeine and carbamazepine in all experiments and both columns

	Antipyrine		Atenolol		Caffeine		Carbamazepine	
	EA	**EB**	**EA**	**EB**	**EA**	**EB**	**EA**	**EB**
Exp. 1	86.2 %	92.4 %	24.1 %	42.6 %	69.1 %	79.6 %	67.7 %	79.4 %
Exp. 2	79.7 %	81.4 %	15.4 %	24.0 %	69.4 %	70.7 %	71.0 %	72.2 %
Exp. 3	89.3 %	89.5 %	9.2 %	17.6 %	73.6 %	77.9 %	74.0 %	77.5 %

Table A.2: Recoveries of diclofenac, ketoprofen and sulfamethoxazole in all experiments and both columns

	Diclofenac		Ketoprofen		Sulfamethoxazole	
	EA	**EB**	**EA**	**EB**	**EA**	**EB**
Exp. 1	57.8 %	85.0 %	87.7 %	99.6 %	99.1 %	99.0 %
Exp. 2	60.0 %	69.7 %	84.5 %	88.1 %	94.8 %	97.5 %
Exp. 3	47.5 %	71.0 %	84.1 %	85.9 %	92.9 %	91.3 %

9.4. BTCs of EOCs with Normalized Time

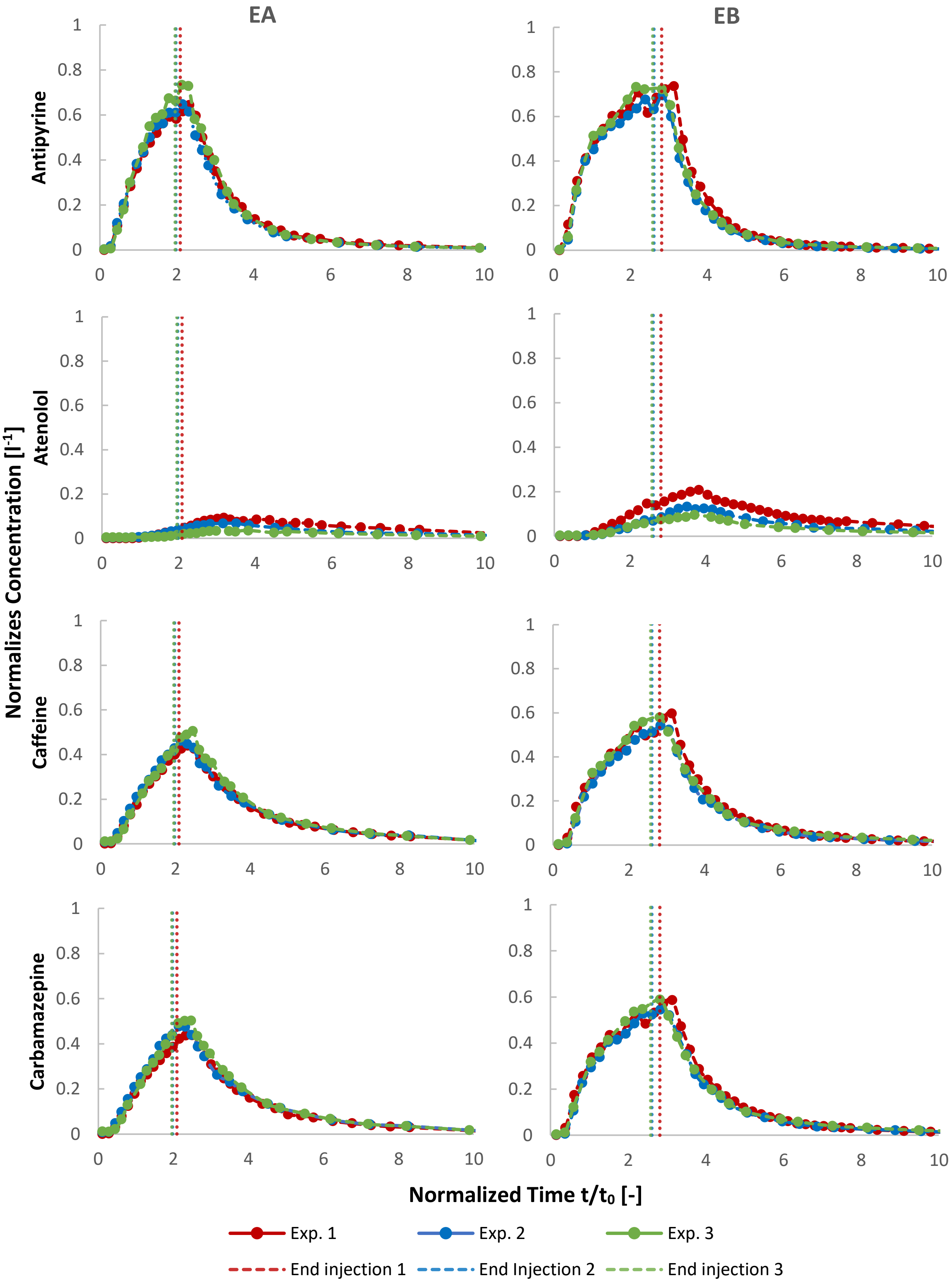


Figure A.1: BTCs of antipyrine, atenolol, caffeine and carbamazepine including the modelled application times T_{app} as vertical broken lines in matching colours of the experiment for column EA (left) and EB (right). The time was normalized using the modelled t_0 of every experiment. Concentrations were normalized with the mass injected.

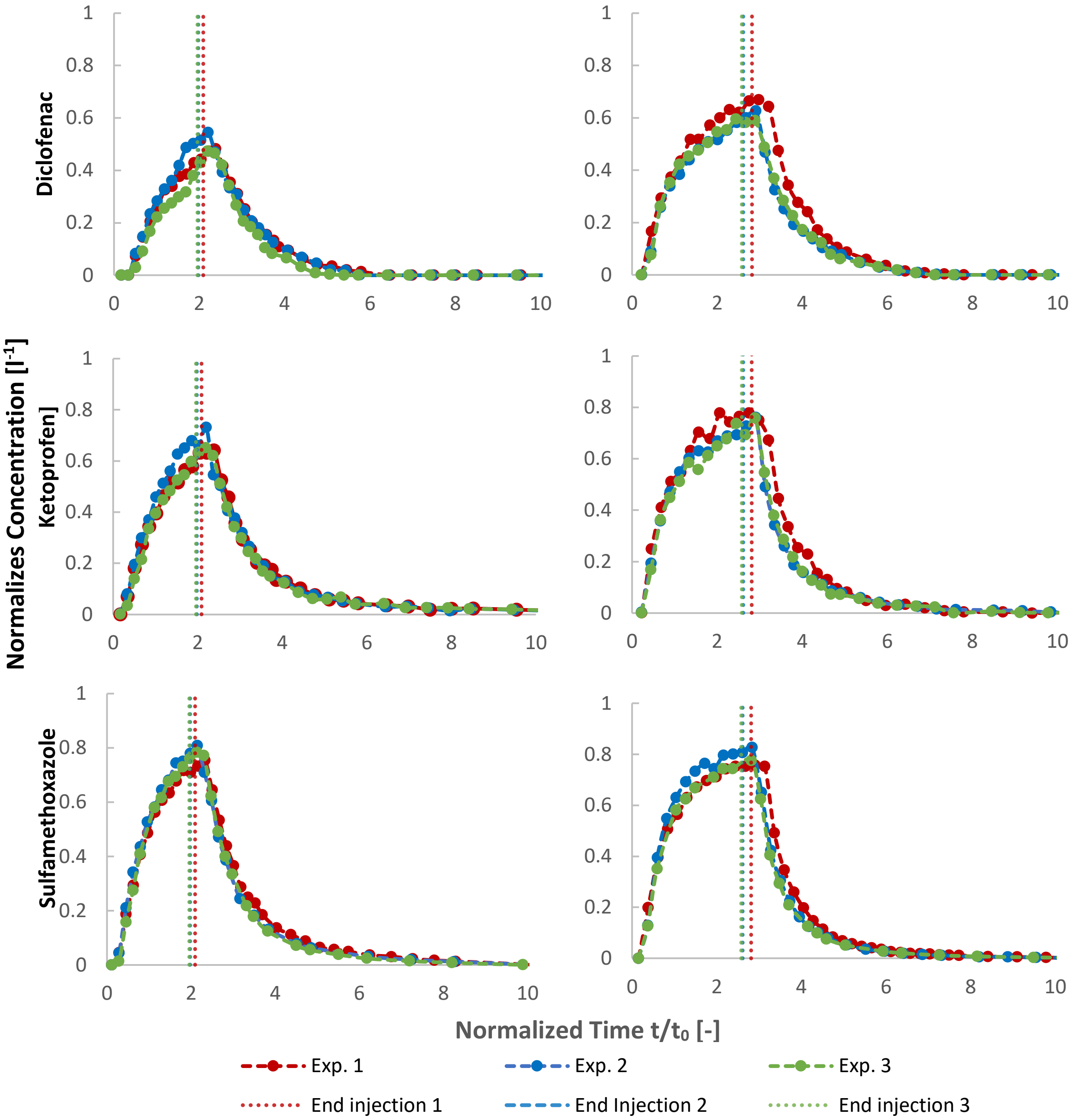


Figure A.2: BTCs of diclofenac, ketoprofen and sulfamethoxazole including the modelled application times T_{app} as vertical broken lines in matching colours of the experiment for column EA (left) and EB (right). The time was normalized using the modelled t_0 of every experiment. Concentrations were normalized with the mass injected.

9.5. Modelled Parameters

9.5.1. EA

*Table A.3: Modelled parameters for the conservative tracers of all modelled EOCs for the first experiment in column EA. Fixed values are marked with *.*

Compound	v [cm/min]	D [cm²/min]	T [min] *	R [-]	μ [d⁻¹]	NRMSE	R²
Bromid	0.1775	2.028	589.3			0.058	0.992
Uranine	0.1775	2.028	589.3	1.463	2.15	0.192	0.977
Antipyrine	0.1775	2.028	589.3	1.273	0.75	0.109	0.985
Atenolol	0.1775	2.028	589.3	6.386	10.78	0.276	0.840
Caffeine	0.1775	2.028	589.3	1.967	3.21	0.184	0.941
Carbamazepine	0.1775	2.028	589.3	1.948	2.89	0.168	0.952
Diclofenac	0.1775	2.028	589.3	1.541	3.36	0.101	0.989
Ketoprofen	0.1775	2.028	589.3	1.244	1.49	0.150	0.971
Sulfamethoxazole	0.1775	2.028	589.3	1.099	0.59	0.126	0.980

*Table A.4: Modelled parameters for the conservative tracers of all modelled EOCs for the second experiment in column EA. Fixed values are marked with *.*

Compound	v [cm/min] *	D [cm²/min]	T [min] *	R [-]	μ [d⁻¹]	NRMSE	R²
Bromid	0.1228	1.383	805.7			0.067	0.993
Uranine	0.1228	1.383	805.7	1.389	1.39	0.289	0.953
Antipyrine	0.1228	1.383	805.7	1.251	1.17	0.096	0.986
Atenolol	0.1228	1.383	805.7	5.626	10.74	0.248	0.895
Caffeine	0.1228	1.383	805.7	1.84	2.21	0.173	0.943
Carbamazepine	0.1228	1.383	805.7	1.84	2.04	0.166	0.948
Diclofenac	0.1228	1.383	805.7	1.483	2.04	0.124	0.985
Ketoprofen	0.1228	1.383	805.7	1.188	0.82	0.167	0.966
Sulfamethoxazole	0.1228	1.383	805.7	1.013	0.44	0.092	0.987

*Table A.5: Modelled parameters for the conservative tracers of all modelled EOCs for the third experiment in column EA. Fixed values are marked with *.*

Compound	v [cm/min] *	D [cm^2/min]	T [min] *	R [-]	μ [d^{-1}]	NRMSE	R^2
Bromid	0.06783	0.5112	1442			0.082	0.987
Uranine	0.06783	0.5112	1442	1.46	0.85	0.264	0.964
Antipyrine	0.06783	0.5112	1442	1.218	0.45	0.132	0.976
Atenolol	0.06783	0.5112	1442	5.846	7.30	0.385	0.631
Caffeine	0.06783	0.5112	1442	1.829	1.08	0.189	0.937
Carbamazepine	0.06783	0.5112	1442	1.813	1.04	0.181	0.944
Diclofenac	0.06783	0.5112	1442	1.51	1.58	0.143	0.983
Ketoprofen	0.06783	0.5112	1442	1.219	0.70	0.183	0.959
Sulfamethoxazole	0.06783	0.5112	1442	1.023	0.33	0.126	0.980

9.5.2. EB

*Table A.6: Modelled parameters for the conservative tracers of all modelled EOCs for the first experiment in column EB. Fixed values are marked with *.*

Compound	v [cm/min] *	D [cm^2/min]	T [min]	R [-]	μ [d^{-1}]	NRMSE	R^2
Bromid	0.239	4.63	589.3			0.165	0.990
Uranine	0.239	4.63	589.3	1.26	1.27	0.103	0.996
Antipyrine	0.239	4.63	589.3	1.19	0.81	0.098	0.993
Atenolol	0.239	4.63	589.3	6.16	9.55	0.163	0.937
Caffeine	0.239	4.63	589.3	1.80	2.38	0.122	0.984
Carbamazepine	0.239	4.63	589.3	1.76	2.33	0.113	0.987
Diclofenac	0.239	4.63	589.3	1.38	1.20	0.071	0.995
Ketoprofen	0.239	4.63	589.3	1.05	0.15	0.073	0.995
Sulfamethoxazole	0.239	4.63	589.3	1.00	0.26	0.076	0.996

*Table A.7: Modelled parameters for the conservative tracers of all modelled EOCs for the second experiment in column EB. Fixed values are marked with *.*

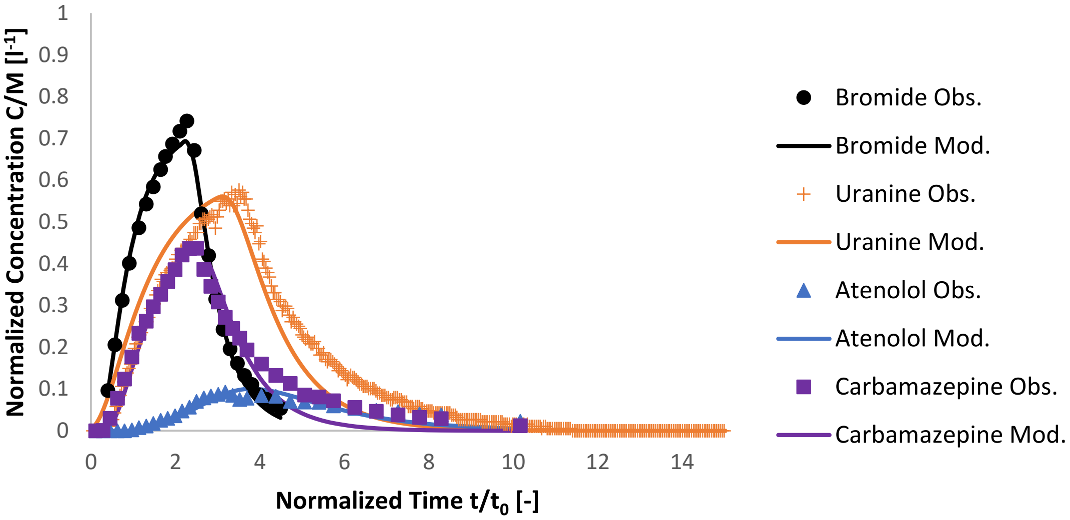
Compound	**v [cm/min]**	**D [cm²/min]**	**T [min]**	**R [-]**	**μ [d⁻¹]**	**NRMSE**	**R²**
Bromid	0.1622	2.788	805.7			0.108	0.996
Uranine	0.1622	2.788	805.7	1.25	1.22	0.099	0.996
Antipyrine	0.1622	2.788	805.7	1.24	1.09	0.081	0.994
Atenolol	0.1622	2.788	805.7	7.06	10.68	0.149	0.964
Caffeine	0.1622	2.788	805.7	1.87	2.17	0.095	0.989
Carbamazepine	0.1622	2.788	805.7	1.84	2.01	0.087	0.991
Diclofenac	0.1622	2.788	805.7	1.41	1.84	0.094	0.992
Ketoprofen	0.1622	2.788	805.7	1.09	0.75	0.100	0.991
Sulfamethoxazole	0.1622	2.788	805.7	0.94	0.09	0.065	0.996

*Table A.8: Modelled parameters for the conservative tracers of all modelled EOCs for the third experiment in column EB. Fixed values are marked with *.*

Compound	**v [cm/min] ***	**D [cm²/min]**	**T [min]**	**R [-]**	**μ [d⁻¹]**	**NRMSE**	**R²**
Bromid	0.08951	1.265	1441			0.092	0.996
Uranine	0.08951	1.265	1441	1.30	0.86	0.131	0.994
Antipyrine	0.08951	1.265	1441	1.16	0.37	0.078	0.994
Atenolol	0.08951	1.265	1441	6.27	7.56	0.178	0.944
Caffeine	0.08951	1.265	1441	1.67	1.00	0.120	0.982
Carbamazepine	0.08951	1.265	1441	1.65	1.01	0.110	0.985
Diclofenac	0.08951	1.265	1441	1.35	0.98	0.101	0.991
Ketoprofen	0.08951	1.265	1441	1.13	0.47	0.118	0.988
Sulfamethoxazole	0.08951	1.265	1441	0.98	0.29	0.0703	0.995

9.6. Modelled Curves

9.6.1. EA



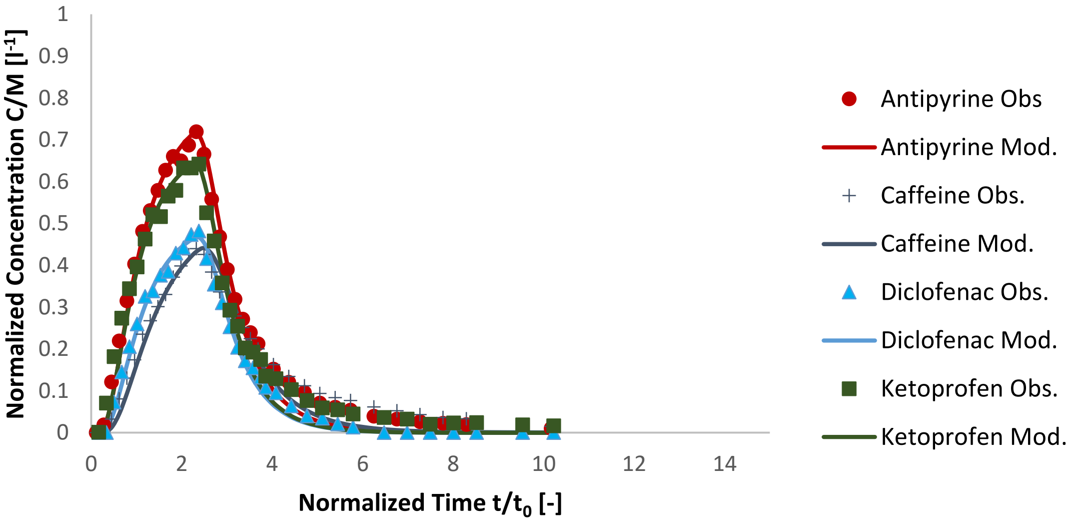


Figure A.3: Observed and modelled BTCs for the first experiment of column EA of bromide, uranine, atenolol, carbamazpine (top) and antiprine, caffeine, diclofenac, ketoprofen and sulfamethoxazol (bottom). Quality criterions can be seen in parameter tables above.

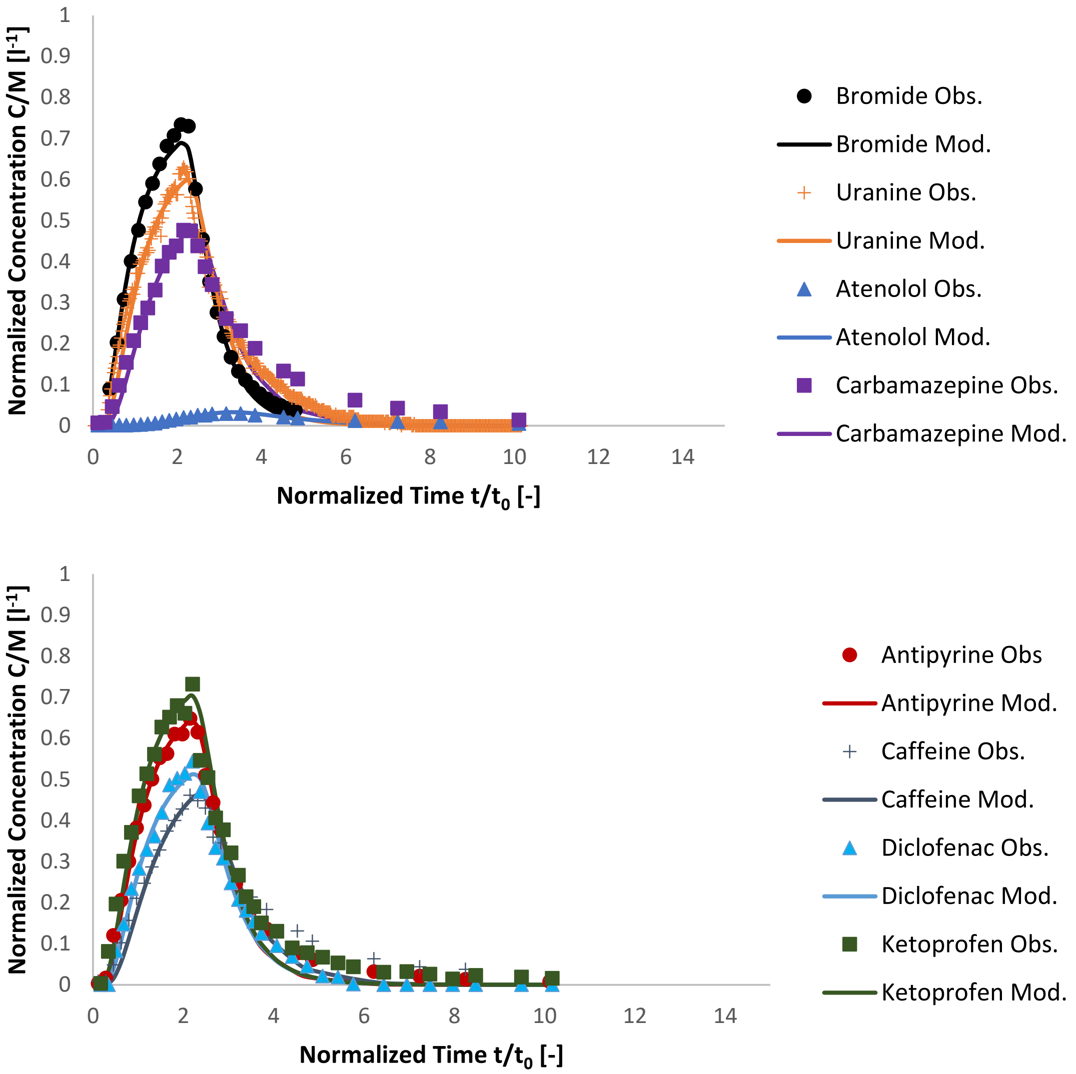


Figure A.4: Observed and modelled BTCs for the second experiment of column EA of bromide, uranine, atenolol, carbamazpine (top) and antiprine, caffeine, diclofenac, ketoprofen and sulfamethoxazol (bottom). Quality criterions can be seen in parameter tables above.

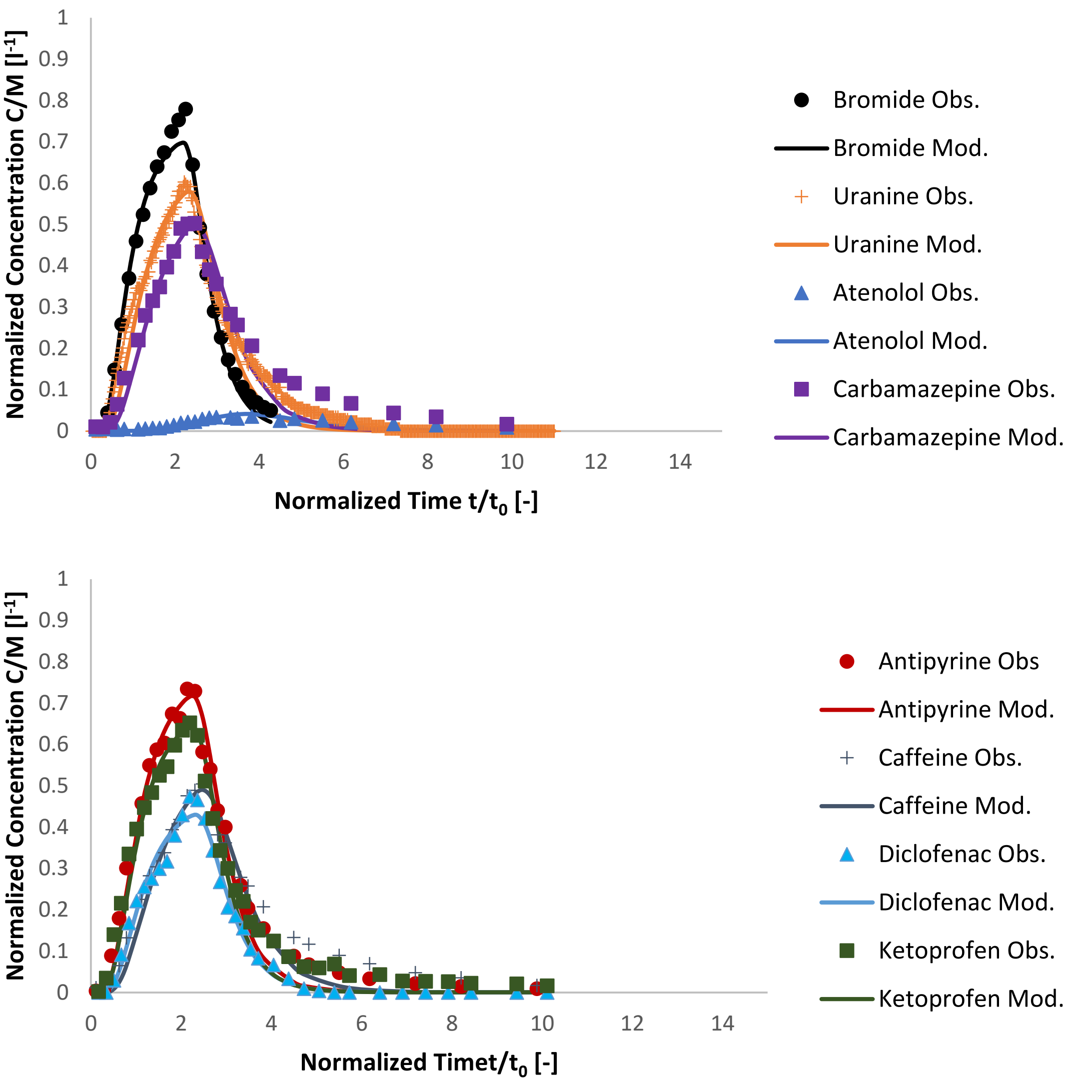
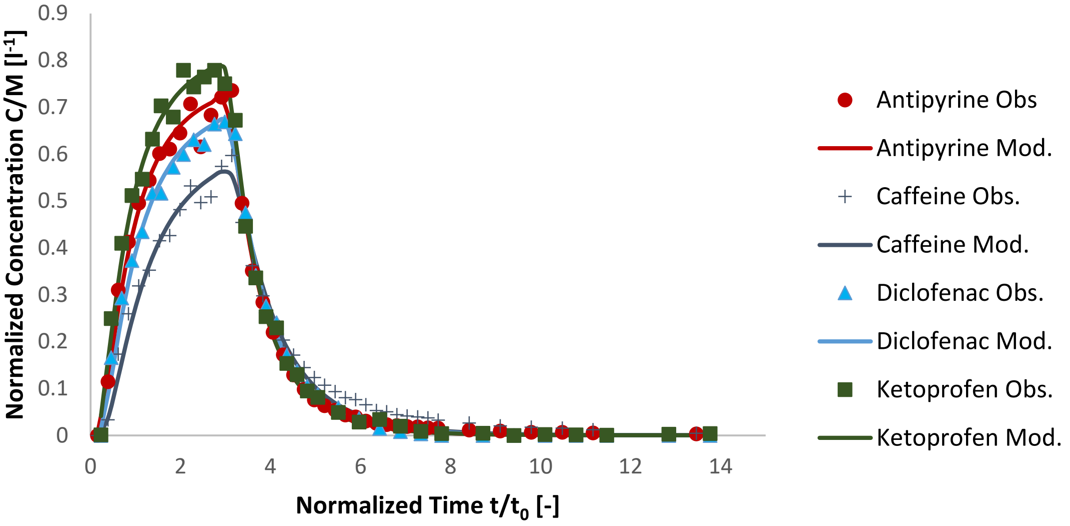


Figure A.5: Observed and modelled BTCs for the third experiment of column EA of bromide, uranine, atenolol, carbamazpine (top) and antiprine, caffeine, diclofenac, ketoprofen and sulfamethoxazol (bottom). Quality criterions can be seen in parameter tables above.

9.6.2. EB



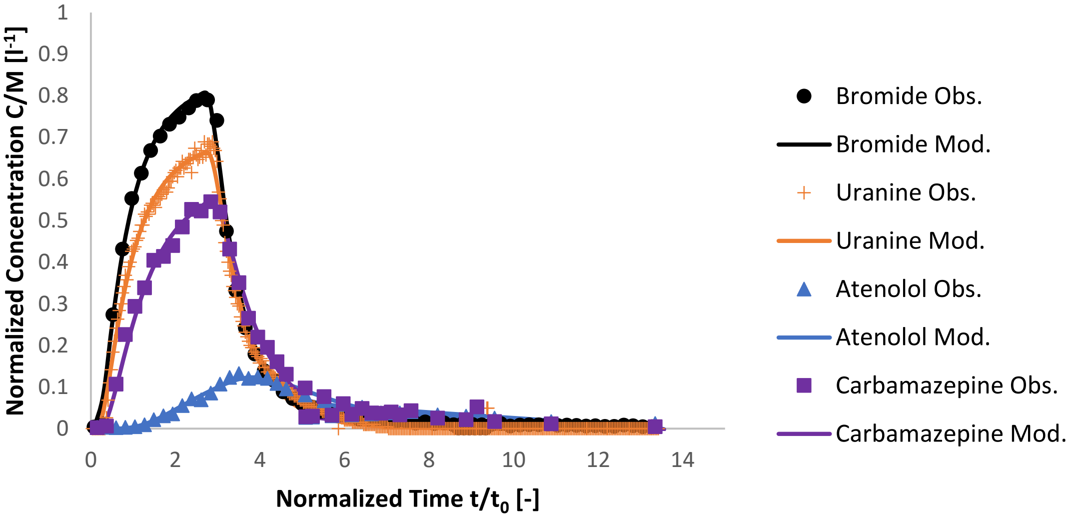
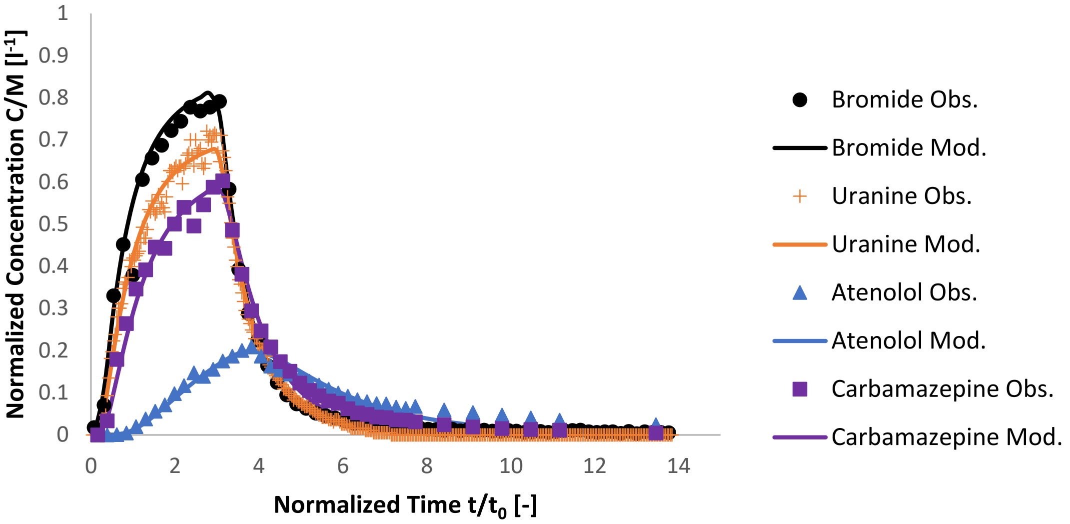


Figure A.6: Observed and modelled BTCs for the first experiment of column EB of bromide, uranine, atenolol, carbamazpine (top) and antiprine, caffeine, diclofenac, ketoprofen and sulfamethoxazol (bottom). Quality criterions can be seen in parameter tables above.



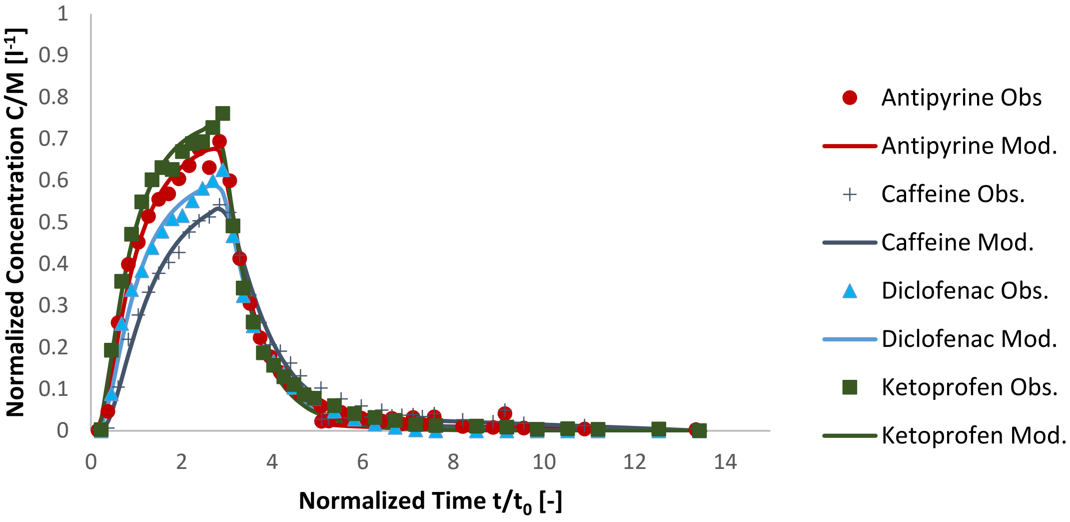


Figure A.7: Observed and modelled BTCs for the second experiment of column EB of bromide, uranine, atenolol, carbamazpine (top) and antiprine, caffeine, diclofenac, ketoprofen and sulfamethoxazol (bottom). Quality criterions can be seen in parameter tables above.

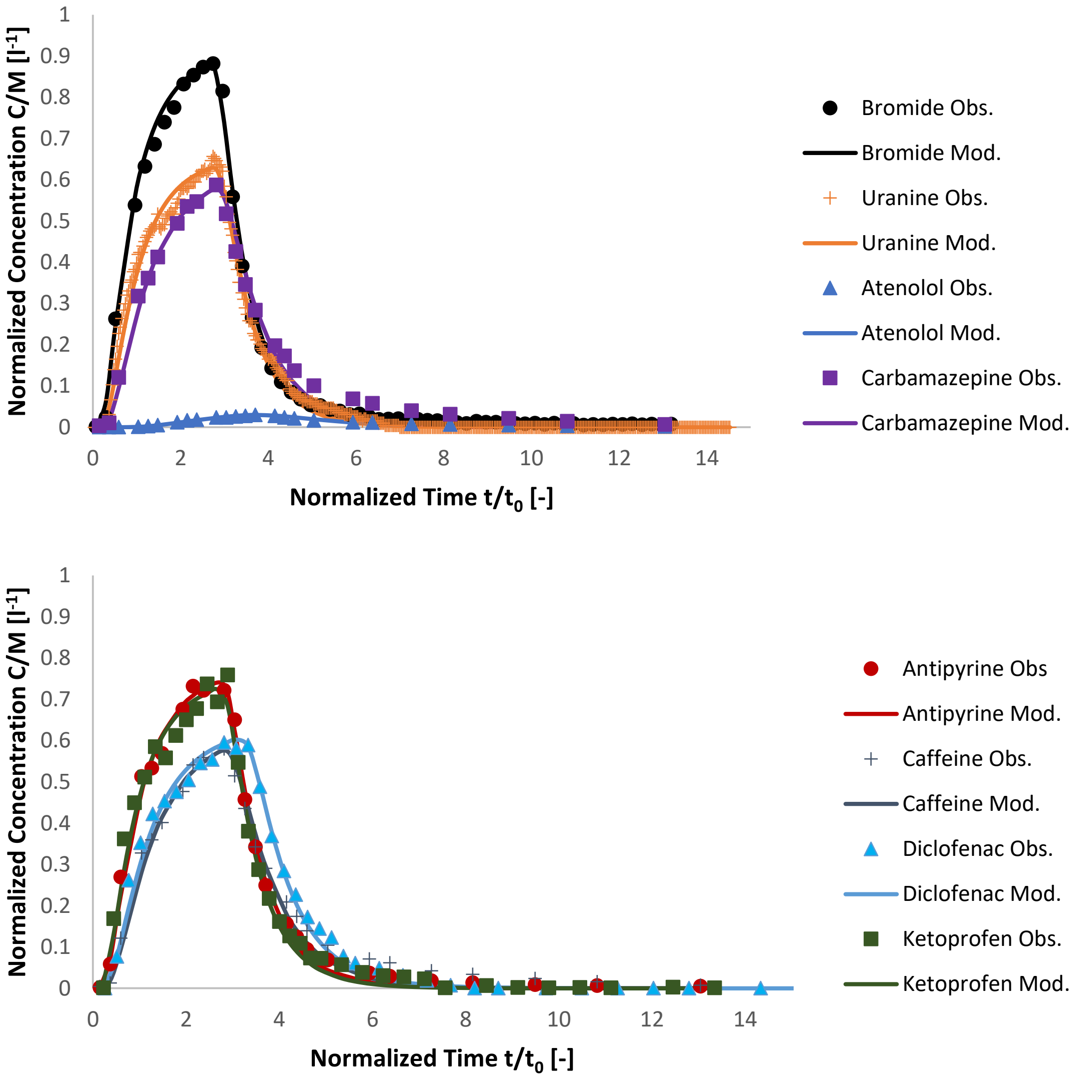


Figure A.8: Observed and modelled BTCs for the third experiment of column EB of bromide, uranine, atenolol, carbamazpine (top) and antiprine, caffeine, diclofenac, ketoprofen and sulfamethoxazol (bottom). Quality criterions can be seen in parameter tables above.

9.7. Uranine Calibration Curve

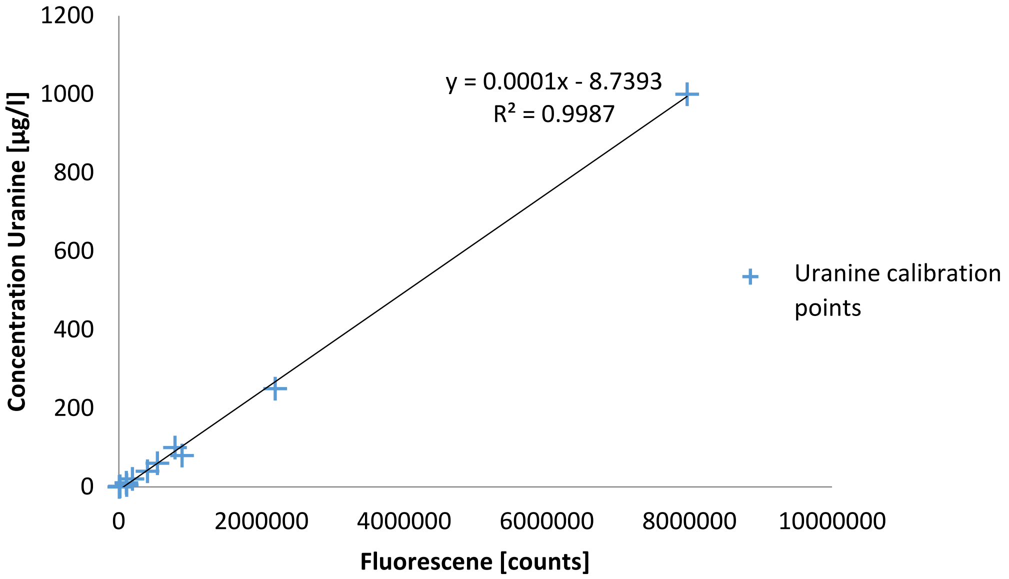


Figure A.9: Calibration curve of uranine.

9.8. LC-MS Analysis

9.8.1. Positive Mode

Column: Kinetex 2,6 µm C18 100 A, 150 x 3 mm, Phenomenex, Aschaffenburg, Germany

Flow rate: 250 µl/min

Injection volume: 25 µl

Solvents: (A) 10 mM formic acid (377 µl/l) / ammonium formate (630,6 mg/l) (pH 3,2), (B) Methanol

Gradient: 0-1 min A:B = 10:90; 1-28 min A:B = 0:100; 28-29 min A:B = 0:100; 29-31 min A:B = 10:90; 31-34 = 10:90

Table A.9: LC-MS parameters used by the machine for analysis in the positive mode.

Compound	MW	DP	EP	CEP	Q1	Q3	CE	CXP
Antipirine	188,20	41	11,5	14,5	189,2	104,2	31	4
Atenolol	266,34	36	12	20	267,2	145,0	39	4
Azithromycin	749,98	51	11,5	24	749,6	591,4	31	8
Caffeine	194,19	81	12	16	194,1	179,1	33	4
Carbamazepine	236,27	36	6	16	237,2	194,2	27	4
Ciprofloxacine	331,35	46	12	22	332,2	231,0	43	4
Clofibrate	242,70	26	12	14	243,1	115,1	13	4
Ofloxacine	361,37	36	12	20	362,2	261,1	31	4
Sulfamethaxazole	253,30	31	4,5	16	254,1	156,2	19	4

Table A.10: Source and gas parameters used by the machine for analysis in the positive mode.

Parameter	TEM	CUR	IS	GS1	GS2	CAD
Value	350	25	1500	40	40	5

9.8.2. Negative Mode

Column: Kinetex 2,6 µm C18 100 A, 150 x 3 mm, Phenomenex, Aschaffenburg, Germany

Flow rate: 250 µl/min

Injection volume: 25 µl

Solvents: (A) Acetonitrile, (B) 5 mM ammonium acetate / ammonim hydroxide (pH 8)

Gradient: 0-15 min A:B = 100:0; 15-20 min A:B = 40:60; 20-25 min A:B = 0:100; 25-28 min A:B = 100:0

Table A.11: LC-MS parameters used by the machine for analysis in the negative mode.

Compound	MW	DP	EP	CEP	Q1	Q3	CE	CXP
Clofibric acid	214,65	-21	-11,5	-	127	150	-20	-2
Diclofnac	296,15	-16	-8	-	293,9	250,1	-12	-4
Ketoprofen-d3	257,31	-31	-9,5	-	252,9	209,2	-8	-4

Table A.12: Source and Gas parameters used by the machine for analysis in the negative mode.

Parameter	TEM	CUR	IS	GS1	GS2	CAD
Value	350	40	-4500	40	40	3

10. Ehrenwörtliche Erklärung

Hiermit erkläre ich, dass die Arbeit selbstständig und nur unter Verwendung der angegebenen Hilfsmittel angefertigt wurde.

Ort, Datum

Unterschrift