

On the possibility of using organic molecules in the characterization of subsurface processes

Dissertation

zur Erlangung des Doktorgrades

der Mathematisch-Naturwissenschaftlichen Fakultäten

der Georg-August-Universität zu Göttingen

vorgelegt von

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aus Dresden

Göttingen 2013

D 7

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Tag der mündlichen Prüfung: 4. April 2013

Short Summary

Nowadays, tracer tests represent an important part in the repertoire of hydro(geo)logical characterization techniques. For determining hydromechanical parameters of and flow properties within a reservoir or an aquifer, conservative tracer compounds are usually the applied chemicals of choice. This means that these compounds behave inert and, thus, interact only negligibly during their residence time in the investigated geosystem. In contrast, the use of non-conservative organic molecules as tracers is a novel approach. Here, additional information on subsurface processes may be provided when the molecules interact in a known way with certain components of the considered system. However, the interpretation of the tracer behavior requires a sufficient *a priori* knowledge on processes and influence factors affecting the tracer transport. Since sorption is probably the most relevant physicochemical transport process for numerous organic solutes in the subsurface, the systematic investigation of sorption processes including their relation to molecular properties and boundary conditions was a main focus of the presented cumulative thesis. In addition, the derived implications on tracer transport were directly incorporated into the design of a new reactive reservoir tracer for geological storage of CO₂.

In order to get a general overview on the sorption of organic compounds with different functionalities, the pH-dependent transport of several ionizable pharmaceuticals (acids, bases, zwitter) was investigated by using sediment column experiments. The sorption coefficients were determined and compared with two correlation approaches. As a result, a strong pH-dependence of sorption was found for all compounds with pK_a values in or near the studied pH range. However, an appropriate prediction of sorption was only feasible for neutral and anionic (acidic) compounds. In contrast, the sorption of cationic (bases) and zwitter-ionic compounds was stronger than expected indicating the occurrence of additional electrostatic sorption mechanisms, which are not considered in the conventional concepts.

Consequently, cation exchange processes were expected to have a significant influence on the retardation of organic cations in the subsurface. The dominating role of cation exchange processes was demonstrated for two cationic beta-blockers in column experiments. Higher concentrations of inorganic cations in solution led to lower sorption of the organic cation due to increased competition for the negatively charged sorbent exchange sites. The contribution of non-hydrophobic interactions to the overall sorption was estimated with >99%. Due to the importance of cation exchange, more influence factors have to be considered for the successful prediction of the transport of organic cations in the subsurface.

As a first step towards the systematic consideration of further influence factors, the role of competing inorganic cations on the sorption of organic cations was studied in batch experiments. Sorption isotherms for the cationic beta-blocker metoprolol on sediment were obtained for varying background concentrations of competing inorganic ions. The obtained data showed that the influence of competing Ca^{2+} on the sorption of metoprolol is stronger than for Na^+ . The found correlation between the Freundlich sorption coefficient and the concentration of competing inorganic ions allows the prediction of metoprolol sorption within the investigated range of boundary conditions. Furthermore, the contribution of sorptive interactions to the organic carbon of the sediment was determined to be negligible. Therefore, the results improve the process understanding and help to improve predicting the subsurface transport of organic cations.

Eventually, the concept and the design of a new reactive tracer (KIS tracer) intended for the characterization of interfacial areas during injections of supercritical CO_2 into deep saline aquifers is presented. Due to an interface-sensitive hydrolysis reaction with known kinetics the temporal study of the CO_2 /brine interfacial area is feasible. Based on the findings from previous investigations, the conservative organic anion naphthalenesulfonate was selected as base structure for the ester synthesis (esterification) and, thus, also as hydrolysis product. Beside the definition of required tracer properties, first promising compounds were synthesized, tested in the laboratory, and evaluated with a newly developed macroscopic model. Furthermore, the numerical forward modeling of the tracer behavior is exemplarily described for several hypothetical functions of the interfacial area change. The first results are promising and provide first insight into the potential of KIS tracers.

Kurzfassung

Tracertests stellen heute einen integralen Bestandteil im Repertoire der hydro(geo)logischen Charakterisierungstechniken dar. Insbesondere konservative Stoffe werden zur Bestimmung von hydraulischen Reservoir- und Aquiferparametern eingesetzt. Diese Stoffe verhalten sich weitestgehend inert und unterliegen somit nur vernachlässigbaren physikochemischen Wechselwirkungen während ihrer Verweilzeit im untersuchten Geosystem. Im Gegensatz dazu stellt der Einsatz nicht-konservativer organischer Stoffe als Tracer einen relativ neuen Ansatz dar, welcher das Potential birgt, zusätzliche Informationen zu ablaufenden Untergrundprozessen zu gewinnen, sofern die Wechselwirkungsarten und somit das Tracerverhalten bekannt sind. Folglich ist die genaue Kenntnis potentieller Transportprozesse und deren Abhängigkeiten eine unabdingbare Voraussetzung für eine erfolgreiche Interpretation dieser Tracer. In diesem Zusammenhang ist die Sorption an Festphasen für zahlreiche gelöste organische Verbindungen der wohl bedeutendste physikochemische Transportprozess. Aus diesem Grund ist die systematische Untersuchung von Sorptionsprozessen und deren Abhängigkeiten von den Moleküleigenschaften bzw. Randbedingungen ein Hauptbestandteil der hier vorgestellten, kumulativen Dissertationsschrift. Die aus den Sorptionsuntersuchungen abgeleiteten Schlussfolgerungen wurden in die Entwicklung eines neuen, reaktiven Reservoir-Tracers für die geologische Speicherung von CO₂ mit einbezogen.

Um einen Überblick über das Sorptionsverhalten organischer Verbindungen mit unterschiedlichen Funktionalitäten zu gewinnen, wurde zunächst der pH-abhängige Stofftransport mehrerer dissozierbarer Arzneimittelwirkstoffe (Säuren, Basen, Zwitter) mit Hilfe von Sedimentsäulenexperimenten untersucht. Hierzu wurden die Sorptionskoeffizienten bestimmt und mit den vorausberechneten Ergebnissen zweier Korrelationsansätze verglichen. Eine starke pH-Abhängigkeit zeigte die Sorption für alle Moleküle mit einem pK_s-Wert im oder nahe des untersuchten pH-Bereiches. Eine zufriedenstellende Vorhersage war nur für neutrale und anionsche

(saure) Verbindungen möglich. Im Gegensatz dazu war die Sorption der kationischen (basischen) und zwitter-ionischen Verbindungen stärker als erwartet. Als Ursache dafür kann das Auftreten zusätzlicher, elektrostatischer Sorptionsmechanismen angesehen werden, welche in den konventionellen Korrelationsansätzen nicht berücksichtigt werden.

Somit konnte unter anderem erwartet werden, dass auch Kationenaustausch einen signifikanten Prozess für die Retardation organischer Kationen im Untergrund darstellt. Mit zwei kationischen Beta-Blockern durchgeführte Säulenversuche belegen die dominierende Rolle von Kationenaustauschprozessen. Steigende Konzentrationen anorganischer Kationen führen aufgrund der verstärkten Konkurrenz um die Austauschplätze des Sorbens zu einer geringeren Sorption der organischen Kationen. Der Beitrag nicht-hydrophober Wechselwirkungen zur Gesamtsorption konnte mit >99% abgeschätzt werden. Aufgrund der großen Bedeutung von Kationenaustauschprozessen sollten weitere Einflussfaktoren berücksichtigt werden, um den Transport organischer Kationen zuverlässig vorhersagen zu können.

Daher wurde anschließend der Einfluss konkurrierender anorganischer Kationen auf die Sorption organischer Kationen in Wasser/Sediment-Batchtests systematisch untersucht. Die bei verschiedenen Hintergrundkonzentrationen an anorganischen Kationen aufgenommenen Sorptionsisothermen des kationischen Beta-Blockers Metoprolol zeigten eine deutlich stärkere Beeinflussung der Sorption durch Ca^{2+} als durch Na^+ . Durch die gefundene Korrelation zwischen dem Freundlich-Koeffizienten und der Konzentration anorganischer Kationen wird eine Vorhersage der Metoprolol-Sorption im Bereich der untersuchten Randbedingungen möglich. Zudem konnte der Beitrag sorptiver Wechselwirkungen zum organischen Kohlenstoff des Sediments als vernachlässigbar bestimmt werden. Insgesamt liefern die erzielten Ergebnisse einen weiteren wichtigen Beitrag zur Prozessbeschreibung der Sorption und helfen somit, die Vorhersage des Stofftransportes organischer Kationen im Untergrund zu verbessern.

Im letzten Teil der Arbeit werden das Konzept und die Entwicklung eines neuen, reaktiven Tracers (KIS-Tracer) zur Charakterisierung von Grenzflächen während Injektionen von überkritischem CO_2 in tiefe saline Aquifere beschrieben. Durch eine

Hydrolysereaktion an der CO₂/Wasser-Grenzfläche mit bekannter Kinetik wird ein Zusammenhang zur zeitlichen Änderung der Grenzflächengröße geschaffen. Basierend auf den vorangegangenen Untersuchungen zur Sorption, wurde das konservative, organische Anion Naphthalinsulfonat als Basisstruktur für die Tracersynthese (Veresterung) und somit auch als gewünschtes Hydrolyseprodukt ausgewählt. Neben der Definition notwendiger Tracereigenschaften wurden bereits erste Verbindungen synthetisiert, im Labor getestet und mit einem neuentwickelten, makroskopischen Modell ausgewertet. Abschließend wurde das Tracerverhalten exemplarisch für verschiedene hypothetische Funktionen der zeitlichen Grenzflächenänderung numerisch modelliert. Die bisher erzielten Ergebnisse sind sehr vielversprechend und gewähren einen ersten Einblick in das Potential von KIS-Tracern.

Danksagung

Zuallererst möchte ich mich bei meinen beiden Betreuern Prof. Dr. Martin Sauter und Dr. Tobias Licha für die Bereitstellung des spannenden Forschungsthemas sowie die umfangreiche Unterstützung bei der Anfertigung meiner Arbeit bedanken. Mein besonderer Dank gilt dabei Dr. Tobias Licha, welcher mir während meiner gesamten Promotionszeit stets mit konstruktiver Kritik und wertvollen Ratschlägen zur Seite gestanden hat. Hervorzuheben sind die oft intensiv und teilweise kontrovers geführten, fachlichen Diskussionen, welche mich stets motivierten mich mit großer Freude noch tiefer in die Thematik einzuarbeiten und bestimmte Zusammenhänge auch aus einem anderen Blickwinkel zu betrachten. Vielen Dank für diese einzigartige und beileibe nicht selbstverständliche Betreuung. Ich möchte mich ebenfalls bei allen weiteren Mitgliedern der Prüfungskommission: Prof. Dr. Eckhard Worch, Prof. Dr. Hans Ruppert, Dr. Chicgoua Noubactep und Dr. Jürgen Niemeyer, bedanken. Prof. Dr. Eckhard Worch danke ich insbesondere für die Übernahme des Koreferates und die stets sehr anregenden Diskussionen während meiner Besuche in Dresden.

Des Weiteren danke ich allen Kollegen der Angewandten Geologie, vor allem aber meinen Bürokollegen Dr. Karsten Nödler, Dr. Martin Nottebohm und Enrico, welche mir immer für Diskussionen und Gespräche jeglicher Art zur Verfügung gestanden haben. Ich freue mich sehr darüber, dass sich aus der kollegialen Beziehung ein freundschaftliches Verhältnis entwickelt hat, welches – da bin ich mir sicher – auch in Zukunft erhalten bleiben wird. Anke von Gaza und Mechthild Rittmeier danke ich für die Messung unterschiedlichster Parameter sowie für die Unterstützung bei meinen praktischen Arbeiten im Labor. Dr. Krzysztof Idzik und Dr. Eike-Fabian Sachs danke ich für die Hilfestellungen bei der chemischen Synthese.

Meinen Ko-Autoren danke ich für die experimentelle Unterstützung, das Einbringen guter Ideen und konstruktiver Vorschläge, ohne die ich meine Arbeit nicht so reibungslos und effizient hätte fertig stellen können. An dieser Stelle möchte ich mich, zusätzlich zu den bereits genannten Kollegen, noch bei Dr. Hilmar Börnick für

die unzähligen Diskussionen und Telefongespräche sowie bei Norman Boxberger und Anne Niedbala für die Durchführung zahlreicher Laborversuche bedanken. Friedrich Maier danke ich für die numerische Modellierung und die oft erkenntnisreichen Diskussionen physikalischer Sachverhalte.

Meiner lieben Freundin Yukey danke ich für ihre Fürsorge und hingebungsvolle Unterstützung während der vergangenen zweieinhalb Jahre. 감사합니다! 谢谢!

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Chapter 1

1 Introduction

1.1 Motivation and background

1.1.1 *Organic molecules in hydrogeological systems*

To date, more than 69 million inorganic and organic substances have been registered at the Chemical Abstract Service (CAS, 2012). More than 40 million of these substances can be assigned to the class of organic compounds. The vast number of known and the theoretically unlimited number of not yet described organic molecules merely implies the existing large variety of different structures, properties, and thus, conceivable applications.

In aquatic environments two main groups of dissolved organic compounds are found: (1) compounds originating from biomass and/or metabolic processes (e.g., all kinds of organic matter: hydrocarbons, humic substances, etc.) representing the background level of natural substances and (2) compounds from anthropogenic origin (e.g., industrial chemicals, pesticides, pharmaceuticals, etc.).

The latter have been detected in virtually all surface and subsurface water bodies during the last decades (Daughton and Ternes, 1998; Halling-Sørensen, 1998; Heberer, 2002; Kolpin et al., 2002; Schwarzenbach et al., 2006). On the one hand, certain threshold concentrations of these compounds might have adverse effects in terms of water quality, since specific (eco)toxicological risks from single compounds or mixtures are often unknown (DeLorenzo et al., 2001; Schwarzenbach et al., 2006). Therefore, the occurrence, environmental behavior, and risk assessment of these chemicals including their respective transformation products are typical research topics in environmental sciences.

On the other hand, the deliberate introduction of selected compounds with desired properties from the huge pool of available organic compounds into aquifers holds the immense potential to gain insight into the properties of hydro(geo)logical systems and the therein occurring processes. Chemical substances that are intentionally applied for investigating certain elements of aquifer systems are termed as (*hydrogeological*) *tracers* and are described in more detail in the following chapter.

1.1.2 *Organic molecules and their application as tracers in geosystems*

The application of various organic molecules as tracers has been proven as a useful instrument in the characterization of groundwater systems. In this work, a *tracer* is defined as a chemical compound that is intentionally introduced into a hydrogeological system (e.g., aquifer or georeservoir) having a temporally and spatially well-known input function. Due to the relation of the input function (e.g., Dirac pulse, step or continuous input) with the observed system response function (breakthrough curve) quantitative and system-specific information can be gained (Käss, 2004).

In Table 1.1 an impression of the wide spectrum of tracers including their possible applications, processes, and required properties is given. Depending on their physicochemical and chemical behavior, respectively, tracers can principally be differentiated in conservative and non-conservative tracers (Goldscheider et al., 2008). Conservative tracers are considered as physically and chemically inert (ideal tracers) to the greatest possible extent. Classically, they are applied for tracking connectivities and flow paths; analyzing travel times, groundwater drift, and flow velocities; determining recharge and discharge as well as for estimating hydromechanical aquifer properties (e.g., dispersivity, porosity) (Flury and Wai, 2003). In contrast, non-conservative tracers underlie physicochemical processes or chemical reactions during their transport. Therefore, they may provide unique information on physicochemical aquifer properties and the water chemistry (Ptak et al., 2004; Divine and McDonnell, 2005; Luhmann et al., 2012).

Table 1.1 Compilation of tracers used in hydrological geosciences.

Tracer type	Injection phase	Application / Target parameters	Underlying Processes	Exemplary compound classes	Most relevant tracer properties
Conservative					
Conservative tracers					
Ionic tracers	Aq.	Hydromechanical properties (porosity, dispersion, matrix diffusion, arrival times)	None	Organic and inorganic anions (salts, fluorescent dyes)	Anionic, highly water-soluble, non-sorptive, low log D , low pK_a
Tritium tracers	Non-aq. (non-aq.)	Plume migration, arrival times	None	Isotopically labeled water	Molecular weight > 18 g mol ⁻¹
Temperature (heating/cooling)	Aq. (non-aq.)	Groundwater flow, thermal conductivity	Thermal conduction, advection / convection	Perfluorocarbons (McCallum et al., 2005)	Inert, non-polar (no partitioning into water)
Pressure	Aq. (non-aq.) (gas.)	Permeability, hydraulic conductivity, leakage, arrival times	Pressure stimulation / response	None	None
Colloidal tracers (particle tracers)					
Microorganisms	Aq.	Hydraulic connection, groundwater drift, mixing, transport of microorganisms	None, (adsorption, coagulation size exclusion)	Bacteria, bacteriophages, yeasts, animal viruses, colored or fluorescently labeled spores (<i>Lycopodium clavatum</i>) (Keswick et al., 1982; Becker et al. 2003)	
Microspheres / nanoparticles	Aq.	Hydraulic connection, groundwater drift, mixing	None, (adsorption, coagulation, size exclusion)	Fluorescently labeled polystyrene or latex microspheres (Becker et al., 1999; 2003), artificial DNA labeled microspheres (Sharma et al., 2012), fluorescent silica nanobeads (Agenet et al., 2011)	
Retardation					
Partitioning tracers (equilibrium tracers)					
Sorptive tracers	Aq.	Organic carbon content, retardation, (degradation)	Non-ionic sorption processes, (degradation)	Organic, hydrophobic compounds	Neutral molecules, moderate log K_{ow}
Ion exchange tracers	Aq.	Surface charge, ionic strength, exchange area, retardation, (degradation)	Cation exchange, (anion exchange)	Inorganic (Dean et al., 2012) and organic cations (bases) (Leecaster et al., 2012; Reimus et al., 2012)	Ionic molecules; low log D , high pK_a
Interfacial tracers	Aq.	Interfacial area between immiscible phases	Adsorption on interface	Liquid/liquid interface: (anionic) surfactants (Saripalli et al., 1997; 1998), liquid/gas interface: high molecular weight alcohols (Kim et al., 1998; Rao et al., 2000)	Amphiphil, ions with long alkyl chain or other non-polar substructures
Volume-sensitive tracers	Aq., non-aq., gas.	Residual saturation of two phases	Partitioning between two phase volumes	Alcohols (Annable et al., 1998), phenols (Bennett and Larter, 1997; Bennett et al., 2003), (noble) gases (Vulava et al., 2002), fluorocarbons (Deeds et al., 1999), radioisotopes (Hunkeler et al., 1997; Semprini et al., 2000; Davis et al., 2002)	Moderate phase partitioning coefficients, low molecular weight
Reaction					
Tracer with chemical reaction (non-equilibrium tracers)					
Kinetic interface-sensitive tracers (KIS tracer)	Non-aq.	Interfacial area and development with time	Hydrolysis at interface	Non-polar, hydrophobic esters (Schaffer et al., 2013)	High log K_{ow} , reaction products anionic, suitable reaction rates
Thermo-sensitive tracers	Aq.	Reservoir temperature, temperature gradients	Temperature-dependent hydrolysis	Polar, anionic esters (Nottebohm et al., 2012)	Low log D , low pK_a , suitable reaction rates
Reactive esters for partitioning	Aq.	Residual saturation of immiscible phases	<i>In-situ</i> generation of volume-sensitive partitioning tracers due to hydrolysis	Esters (reaction to alcoholic esters and alcohols) (Tomich et al., 1973; Myers et al., 2012)	Water soluble, suitable hydrolysis rates of esters and partitioning coefficients of the reaction products
Biogeochemical reactive tracers	Aq.	Transformation rates for certain domain, <i>in-situ</i> microbiological activity	Biological and/or chemical decay	Inorganic electron acceptors or donors (O ₂ , NO ₃ ⁻ , SO ₄ ²⁻ , H ₂) (Stok et al., 1997), low weight alcohols, benzoate, sugars (Rao et al., 2000), caffeine (Hillebrand et al., 2012)	Labile (easily biodegradable) or reactive
Aq. = aqueous phase, non-aq. = non-aqueous phase, gas. = gaseous phase, log K_{ow} = n -octanol/water distribution coefficient, log D = pH-dependent n -octanol/water distribution coefficient of all species of ionizable organics, pK_a = logarithmic acidity constant					

In general, extensive knowledge on the reactive or non-reactive behavior of any applied tracer is the indispensable prerequisite for the successful qualitative and quantitative interpretation of tracer tests. However, basically all molecules are influenced to some degree by physical, chemical or biological processes. This means that fully ideal tracers do not really exist. Even tracers, which are supposed to behave conservatively, may interact to some extent with aquifer materials or with the water chemistry during their transport in the subsurface. Hence, for several commonly selected fluorescent dyes, for instance, sorption (Smart and Laidlaw, 1977; Kasnavia et al., 1999; Geyer et al., 2007), biodegradation (Benischke et al., 2007; Goldscheider et al., 2008) and precipitation (Geyer et al., 2007; Licha et al., 2013) were reported. These limitations may be detected and mitigated by conducting multi-tracer tests with different “potentially conservative” compounds and comparing their breakthrough curves. For non-conservative tracers, which are intended to interact in a designated way within the aquifer, this approach is usually not feasible and the exact knowledge on (potential) processes is even more essential in order to avoid misinterpretations. However, the actual occurring compound-specific processes and their dependences are often unknown and cannot yet be predicted.

In order to overcome these limitations, the thorough study of the relative role of all involved processes and their influence factors affecting the tracer transport is necessary. The possibility, extent and nature of appearing processes are strongly connected to the molecule structures and thus its molecular properties. If this interplay is exactly understood, organic molecules can be a powerful tool for the purposeful and explicit characterization of subsurface processes, too. As a consequence, the additional use of non-conservative tracers to commonly applied conservative tracers has the potential to significantly increase the informative value of tracer tests.

1.1.3 Subsurface processes affecting the fate of organic molecules

Prior to discussing specific processes affecting the fate of solutes in the subsurface, the term *subsurface process* has to be defined. Here, *subsurface processes* include all phenomena/effects leading to spatial and/or temporal concentration changes of a considered solute in the subsurface. The term *transport processes* is often used

equivalently in the literature (Adam et al., 2000) and can be mathematically described based on the principle of mass conservation for a considered substance by means of the advection-dispersion model including source terms. This yields to the following equation for the general three-dimensional case:

$$\begin{aligned} & \textcircled{1} \quad \textcircled{2} \quad \textcircled{3} \quad \textcircled{4} \\ \frac{\partial c}{\partial t} = & -\bar{\mathbf{v}} \cdot \bar{\nabla} c + \bar{\nabla} (D_{Disp.} \bar{\nabla} c) + \bar{\nabla} (D_{Diff.} \bar{\nabla} c) + \frac{\partial q}{\partial t} \quad \text{with} \quad (1.1) \\ \bar{\mathbf{v}} = & \begin{pmatrix} \bar{v}_x \\ \bar{v}_y \\ \bar{v}_z \end{pmatrix}, D_{Disp.} = \begin{pmatrix} D_{Disp.,xx} & D_{Disp.,xy} & D_{Disp.,xz} \\ D_{Disp.,yx} & D_{Disp.,yy} & D_{Disp.,yz} \\ D_{Disp.,zx} & D_{Disp.,zy} & D_{Disp.,zz} \end{pmatrix}, \text{ and } D_{Diff.} = \begin{pmatrix} D_{Diff.,xx} & D_{Diff.,xy} & D_{Diff.,xz} \\ D_{Diff.,yx} & D_{Diff.,yy} & D_{Diff.,yz} \\ D_{Diff.,zx} & D_{Diff.,zy} & D_{Diff.,zz} \end{pmatrix} \end{aligned}$$

where c is the solute concentration, t is time, $\bar{\mathbf{v}}$ is the mean pore water velocity, $D_{Disp.}$ is the hydromechanic dispersion tensor, $D_{Diff.}$ is the pore diffusion tensor, and q is the concentration in co-existing phases (e.g., solids or immiscible liquid phases).

As a consequence, subsurface processes can be generally divided into two categories: (1) system/fluid-specific and (2) compound-specific processes. The former includes all hydromechanical mass flux processes in Eq. (1.1). Advection and hydromechanical dispersion (1st and 2nd term) belong clearly to this group. Despite the fact that diffusion (3rd term) is also a pure physical process, it cannot be fully attributed to the first category, since molecular and, thus, diffusion coefficients depend on the size and the weight of a molecule, respectively (Worch, 1993). Usually, these hydrodynamical processes can be investigated with tracer compounds showing a (almost ideal) conservative behavior. In conclusion, physically driven transport processes are well understood, can be measured, and sufficiently described by means of mathematical equations.

The latter comprises all processes, which lead to a chemical or physicochemical alteration of the respective solutes during their subsurface transport (4th term). The source/sink term can be split further according to the relevant processes. This considers typical processes, such as dissolution or precipitation according to the solubility product; chemical reactions with other solutes or with mineral surfaces; chemical and microbial degradation as well as sorption. Therefore, the explicit description/formulation of these processes summarized in the fourth term of Eq. (1.1) is much more challenging.

The systematic study of sorption processes and their relevance for hydrogeological systems is a main focus of the presented thesis. *Adsorption* is a surface process and can be defined as a net enrichment of chemical species from a fluid phase on the surface of a liquid or a solid (Sposito, 1998; Worch, 2012). In this work, the terms *adsorption* and *(geo)sorption* are used interchangeably, because the distinction between absorption and adsorption is not always obvious in heterogeneous natural systems. This is especially true for complex geosorbents, such as organic matter in aquifer materials (Worch, 2012). Depending on the nature of a sorption process in the subsurface, hydrophobic (non-polar) interactions with the sorbent organic matter (SOM) and electrostatic (polar) interactions with minerals, oxides, and SOM surfaces can be distinguished. Hydrophobic sorption results from a decrease in entropy by the sorption of solutes on hydrophobic surfaces and can be explained by the occurrence of unspecific van-der-Waals interactions (dipole and/or induced-dipole interactions). As a consequence, the more hydrophobic the solute the higher is its affinity to migrate from the (polar) aqueous phase to the (non-polar) solid phases. This sorption process is often described as partitioning process of solutes between water and SOM. The additional use of general or compound class-specific correlations based on the *n*-octanol-water distribution coefficient $\log K_{ow}$ (e.g., Karickhoff et al., 1979; Sabljic et al., 1995) or the water solubility (Razzaque and Grathwohl, 2008) as polarity measures commonly allows a sufficient prediction for the sorption behavior (partitioning coefficients) of neutral organic compounds.

For charged species of organic molecules the situation is much more complex, since electrostatic interactions additionally to hydrophobic interactions must be expected. Depending on the degree of dissociation and protonation of solutes with ionizable functional groups (bases, acids, zwitter-ionics, amphoteres), respectively, several sorption mechanisms and, thus, transport properties for each species come into question. The probably most relevant electrostatic sorption mechanisms are ion exchange, surface complexation, hydrogen bonding, ligand exchange, cation bridging, and charge-transfer or electron donor-acceptor mechanisms (Senesi, 1992; Tolls, 2001; Cunningham et al., 2004; Kah and Brown, 2007; Worch, 2012). The adequate mathematical description of these (partially overlapping) interactions is more complicated than for hydrophobic interactions, since the role and extent of these sorption mechanisms are affected to a greater extent by the ambient

groundwater chemistry (e.g., pH, ionic strength, etc.) and sorbent properties (e.g., surface area, surface charges, etc.). Furthermore, the existence and the type of relationship between the observed sorption and these influencing factors are often unknown. Therefore, the subsurface behavior of ionizable compounds can normally not be reliably predicted and requires extensive further research.

1.2 Scope, objectives, and further outline of the thesis

Due to the large number of organic compounds associated with different functionalities and molecular properties, the study of their individual interactions within the subsurface bears the potential to gain specific information about the underlying processes. For this purpose, the systematic investigation and description of existing relations between molecule properties and occurring processes is vital to understand the behavior of organic compounds in the subsurface. *Vice versa*, if the behavior of an organic molecule in the subsurface is known, conclusions on the existence and role of involved processes affecting the molecule's fate can be drawn. Thus, sufficient knowledge on processes is the prerequisite to interpret tracer data and to get valuable implications for the development and selection of new tracer substances.

However, a complete evaluation of all conceivable processes and organic molecules is obviously impossible within a single study. The presented work, therefore, can be considered as the successful and consequent continuation of current research. It claims to contribute to an overall understanding of the transport behavior of organic molecules in the subsurface by relating subsurface processes, especially sorption processes, with their molecule properties. Eventually, the gained understanding is used for supporting the development of new, chemically reactive tracers for process studies.

In the beginning, ionizable organic molecules with different chemical character (different functional groups and physicochemical properties) were investigated with respect to their transport and sorption behavior. Consecutively, the most relevant sorption processes of cationic compounds were identified and studied separately. Furthermore, a new tracer class for the sequestration of CO₂ into deep saline aquifers

is proposed and first results gained from controlled laboratory experiments are presented. For the tracer development the previous findings on sorption of charged organics were taken into account. A more detailed outline is presented in the following.

Chapter 2 presents the screening of the pH-dependent transport behavior of eight frequently prescribed human pharmaceuticals in sediment column experiments. The selected pharmaceuticals bear different ionizable functional groups, which can be protonated or deprotonated depending on the water pH. Therefore, the investigation included neutral, anionic, cationic, and zwitter-ionic molecules. Thus, differences in their transport behavior were expected. The experimentally obtained sorption coefficients were compared with predicted values derived from two different regressions ($\log K_{OW}$ - $\log K_{OC}$ correlations) considering the sorbate speciation in solution. Beside the detection of a significant pH-dependence on sorption for all charged compounds, a strong retardation was measured for several substances despite their high polarity. The measured data confirmed a good match for the prediction of sorption only for acidic and neutral compounds. Cationic compounds retarded much stronger than expected, which was attributed to additional ionic interactions (e.g., cation exchange processes), which are not considered in the applied correlations.

Chapter 3 deals with the identification of the relevant sorption processes of organic cations by conducting column experiments using the beta-blockers atenolol and metoprolol as example compounds. The sorption behavior of these compounds onto different sediments and under varying background concentrations of inorganic cations was compared. Due to decreasing sorption of the beta-blockers with increasing concentrations of inorganic cations, cation exchange could be identified as the dominating sorption process whereby the contribution of hydrophobic interactions to the overall sorption was determined to be negligible. Thus, meaningful predictions of organic cation sorption with commonly applied models like $\log K_{OW}$ - $\log K_{OC}$ correlations are not possible and new, more complex approaches considering further boundary conditions are unavoidable.

In **Chapter 4** the identified cation exchange processes of organic cations are studied systematically in order to improve the quantitative process description. For this

purpose, the influence of competing Na^+ and Ca^{2+} cations on the sorption process of the monovalent organic cation metoprolol onto a natural sediment was investigated by determining Freundlich sorption isotherms for different electrolyte and metoprolol concentrations. The similar isotherm non-linearity indicates that the relevant sorption mechanisms did not change over several orders of magnitude. Freundlich sorption coefficients were correlated with the concentration of the competing inorganic ions allowing the prediction of metoprolol sorption at different electrolyte concentrations. Eventually, the presented work represents a first stepping stone for a general and systematic understanding of occurring sorption processes for organic cations. The results will contribute to the development of predictive models for the subsurface transport of organic cations.

In **Chapter 5** the concept and the development of a new reactive tracer type for the characterization of interfacial areas between water and supercritical CO_2 during CO_2 injections into deep saline aquifers is presented (KIS tracer). Starting from the definition of tracer requirements, an exemplary methodology for a suitable target molecular design is described and first promising ester compounds were synthesized. The gained experience on sorption and transport of charged organic molecules (especially organic anions) from the previous investigations were considered for the selection of suitable compound structures during the molecular design. The interface behavior of the novel compounds was tested in analog laboratory experiments and evaluated with a macroscopic numerical model. Based on the experimentally determined interface mass flux for the combined phase transfer and subsequent reaction, several interface expansion scenarios were predicted by forward modeling.

Chapter 6 summarizes the conclusions with respect to the focus of the thesis and gives an outlook for future research activities.

In **Appendix A** additional information regarding Chapter 2 is presented.

In **Appendix B** additional information regarding Chapter 3 is presented.

In **Appendix C** additional information regarding Chapter 4 is presented.

In **Appendix D** a complete list of journal articles, conference contributions, and miscellaneous publications authored or co-authored by me and related to the presented work are listed.

Since this thesis is a cumulative dissertation including published journal articles, cited literature is listed separately at the end of each chapter.

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Chapter 2

2 Sorption influenced transport of ionizable pharmaceuticals onto a natural sandy aquifer sediment at different pH

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Citation:

Schaffer, M., Boxberger, N., Börnick, H., Licha, T., Worch, E., 2012. Sorption influenced transport of ionizable pharmaceuticals onto a natural sandy aquifer sediment at different pH. *Chemosphere* 87 (5), 513–520.

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Abstract

The pH-dependent transport of eight selected ionizable pharmaceuticals was investigated by using saturated column experiments. Seventy-eight different breakthrough curves on a natural sandy aquifer material were produced and compared for three different pH levels at otherwise constant conditions. The experimentally obtained K_{OC} data were compared with calculated K_{OC} values derived from two different $\log K_{OW}$ - $\log K_{OC}$ correlation approaches. A significant pH-dependence on sorption was observed for all compounds with pK_a in the considered pH range. Strong retardation was measured for several compounds despite their hydrophilic character. Besides an overall underestimation of K_{OC} , the comparison between calculated and measured values only yields meaningful results for the acidic and neutral compounds. Basic compounds retarded much stronger than expected, particularly at low pH when their cationic species dominated. This is caused by additional ionic interactions, such as cation exchange processes, which are insufficiently considered in the applied K_{OC} correlations

2.1 Introduction

In the past decades the occurrence of numerous polar anthropogenic trace compounds, particularly residues from pharmaceuticals and their metabolites, were detected in the aquatic environment (Halling-Sørensen et al., 1998; Daughton and Ternes, 1999; Heberer, 2002). These hydrophilic and poorly degradable organics are able to survive wastewater treatment (Stumpf et al., 1999; Lindqvist et al., 2005; Reemtsma et al., 2006) and enter into the water cycle (Ternes, 1998; Heberer, 2002; Nödler et al., 2010; Nödler et al., 2011). The ubiquitous occurrence of pharmaceuticals is caused by their high consumption, e.g. for the anticonvulsant and mood stabilizing drug carbamazepine a worldwide annual consumption of 1,000 tons was estimated (Zhang et al., 2008).

The interface between water and natural solids (e.g., sediments in aquifers, river bank filtration, and soil aquifer treatment sites) plays an important role in the elimination of these compounds from the aqueous phase. In particular, the occurrence of sorption and degradation processes at the solid/water interfaces are known to be main attenuation processes (Katayama et al., 2010). Numerous environmentally relevant pharmaceuticals contain one or more dissociable functional groups (acidic/basic). Therefore, these compounds are in dissociation equilibrium and ionic depending on the pH. Particularly for compounds with logarithmic acid dissociation constants pK_a in the typical groundwater pH range (pH = 5–8), a highly pH-dependent sorption behavior can be expected (Kah and Brown, 2007; Franco and Trapp, 2008; Franco et al. 2009).

Different authors demonstrated a strong pH-dependence for the sorption of several ionizable compounds, e.g. Figueroa et al. (2004) for tetracycline, Vasudevan et al. (2009) for ciprofloxacin, and ter Laak et al. (2006) for three further antibiotics. In most cases, however, the experiments are limited to batch experiments under equilibrium conditions. Flow-through experiments with focus on pH under more realistic flow and sediment packing conditions are rarely available. Based on column experiments, a strong pH-dependence on the transport was shown, e.g. for nalidixic acid on aquifer sand by Lorphensri et al. (2007) and for 32 organic acids on soil organic matter by Tülp et al. (2009).

The objective of the presented study was the screening of pH effects on the sorption of further frequently used ionizable pharmaceuticals under dynamic conditions. For this purpose, ten column experiments with eight selected pharmaceuticals in natural sandy aquifer sediment were conducted and the resulting 78 breakthrough curves were compared. All physical and hydromechanical parameters were kept constant, only the pH was varied. The subsequent evaluation of the obtained breakthrough curves allows the determination and comparison of retardation factors and sorption coefficients K_{OC} at different pH values. Additionally, the sediment was characterized to assess the influence of pH on the sorbent. As a result, the most important occurring processes and dependencies could be identified and compared, such as the role of speciation and the characteristics of the sediment. Additionally, the validity of two different K_{OC} correlation approaches for the investigated compounds was studied. Furthermore, these results provide the basis for an improved understanding of sediment/water interactions and a more precise prognostic modeling of the sorption of ionizable compounds in further research.

2.2 Theory and calculations

The sorption influenced transport of medium to non-polar organic pollutants through porous media is often adequately predicted by means of compound (class) specific or unspecific $\log K_{OW}$ - $\log K_{OC}$ correlations (Chiou et al., 1979; Karickhoff, 1981; Sabljic et al., 1995). K_{OW} is the compound specific *n*-octanol/water distribution coefficient as polarity indicator and can be received for every compound of interest from literature data. K_{OC} is the organic carbon normalized sorption coefficient and the practically applied parameter from these correlations in the retardation concept. The solid/water distribution coefficient K_d for the considered compound is normalized to the fraction of organic carbon f_{OC} in the solid phase yielding K_{OC} :

$$K_{OC} = \frac{K_d}{f_{OC}} \quad (2.1)$$

If the distribution coefficient K_d , the bulk density ρ , and the effective porosity n_e are known, the retardation factor R can be calculated under the assumption of a linear sorption isotherm with:

$$R = 1 + \frac{\rho}{n_e} \cdot K_d \quad (2.2)$$

As a consequence, significant retardation for non-polar compounds with high $\log K_{OW}$ and hence also high $\log K_{OC}$ can be expected in the subsurface. For ionizable compounds an extended concept considering the pH-dependent speciation of the sorbates within the water phase was applied. Here, the pH-dependent *n*-octanol/water distribution coefficient $\log D$ was introduced into the correlation instead of $\log K_{OW}$:

$$\log K_{OC} = A \cdot \log D + B \quad (2.3)$$

In this work, *A* and *B* are empirical parameters for non-hydrophobic compounds with values of 0.52 and 1.02 (Sabljić et al., 1995), respectively. The corresponding $\log D$ for alkaline or acidic compounds can be calculated from $\log K_{OW}$ and the acidity constant pK_a for every pH level (Scherrer and Howard, 1977):

$$\log D_{acid} = \log K_{OW} + \log \left(\frac{1}{1 + 10^{pH - pK_a}} \right) \quad (2.4)$$

$$\log D_{base} = \log K_{OW} + \log \left(\frac{1}{1 + 10^{pK_a - pH}} \right) \quad (2.5)$$

Thus, the concentration for the anionic species of acids relative to its conjugate neutral species increases with increasing pH. Simultaneously, $\log D$ decreases resulting in lower $\log K_{OC}$ and thus *R*. In contrast, bases become cationic due to the increasing protonation at decreasing pH values. Additionally, two recent non-linear K_{OC} regressions for organic acids and bases were used (Franco and Trapp, 2008):

$$\log K_{OC(acid)} = \log \left(\frac{10^{0.54 \cdot \log K_{OW} + 1.11}}{1 + 10^{pH - 0.6 - pK_a}} + \frac{10^{0.11 \log K_{OW} + 1.54}}{1 + 10^{pK_a - pH + 0.6}} \right) \quad (2.6)$$

$$\log K_{OC(base)} = \log \left(\frac{10^{0.37 \cdot \log K_{OW} + 1.70}}{1 + 10^{pK_a - pH}} + \frac{10^{pK_a^{0.65} \cdot f^{0.14}}}{1 + 10^{pH - pK_a}} \right) \quad \text{with} \quad f_{pH=7} = \frac{D_{base} + D_{acid}}{1 + D_{base} + D_{acid}} \quad (2.7)$$

The parameter *f* expresses a diffusion limiting factor. For calculating the pH-dependent K_{OC} values for bases with Eq. (2.7) Franco and Trapp's (2008) suggestion was adopted to use the variable sediment pH instead of the fixed, optimal regression $pH_{opt} = 4.5$. However, Franco et al. (2009) showed that the implementation of pH into

these regressions is only expedient for acids to predict the pH effect on sorption. The K_{OC} of zwitter-ionic compounds can not be calculated.

The application of the modified empirical K_{OC} correlation in Eq.(2.3) has its limitations. These limitations apply particularly to compounds having several functional groups (e.g., zwitter-ions) with more than one pK_a . Furthermore, the general transferability of the K_{OC} concept to ionizable compounds is questionable as only non-polar interactions and partitioning to the sediment total organic carbon content TOC are considered (Sabljić, 1989). Nevertheless, a strong correlation between $\log K_{OC}$ and $\log K_{OW}$ was found for cationic bases in an earlier study (Franco and Trapp, 2008). Consequently, this must lead to an underestimation of K_{OC} and K_d for ionizable organic compounds (Tolls, 2001; Cunningham et al., 2004; Kah and Brown, 2007) when additional processes are involved such as ion exchange, cation bridging, surface complexation, and hydrogen bonding. These additional processes and their relative importance depend on the nature of the sorbent (sediment) (Nicholls and Evans, 1991; Tolls, 2001; Kwon and Armbrust, 2008; Figueroa-Diva et al., 2010). As such, additional properties of the sediment other than TOC have to be considered. These are specific surface area, pH, cation exchange capacity (CEC), charge properties and the mineral composition of the sediment.

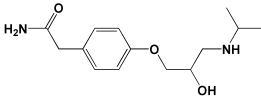
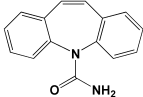
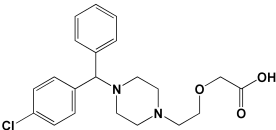
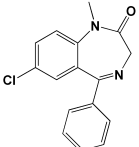
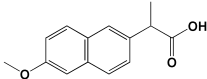
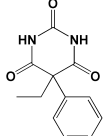
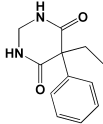
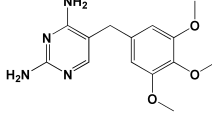
2.3 Materials and methods

2.3.1 Pharmaceuticals

For the column studies eight human pharmaceuticals (3 bases, 4 acids, 1 zwitter) with a wide range of pK_a values were selected (Table 2.1). Therefore, the presence of differently charged species (cation, anion, zwitter-ion) in the experiments is guaranteed and the investigation of pH effects becomes feasible. The investigated compounds included the beta blocker atenolol, the tranquilizer diazepam, the non-steroidal anti-inflammatory drug naproxen, and the anticonvulsant phenobarbital from Fagron (Barsbüttel, Germany); the anticonvulsants carbamazepine and primidone from Sigma-Aldrich (Steinheim, Germany); the antihistamine cetirizine from KSK-Pharma (Berghausen, Germany); and the antibiotic trimethoprim from Fluka (Neu-Ulm, Germany). All compounds had a purity >98%. Compound

concentrations from the experiments were determined using high pressure liquid chromatography and UV detection (details see Appendix A1).

Table 2.1 Chemical properties, structures and speciation of the sorbates.

Compound Detect. wavelength λ	Structure	pK_a^a (Character ^c)	$\log K_{OW}^a$	Species ^d at pH =		
				4	6	8
Atenolol $\lambda = 227$ nm		$9.2 \pm 0.4^*$ (B)	0.1 ± 0.28	+	+	+, 0
Carbamazepine $\lambda = 232$ nm		$-0.49 \pm 0.2^*$ (B)	2.67 ± 0.38	0	0	0
Cetirizine $\lambda = 232$ nm		2.2^b 2.9^b 8.0^b (A/B)	1.62 ± 0.63	+, +/-	+/-	+/-, -
Diazepam $\lambda = 232$ nm		$3.4 \pm 0.1^*$ (B)	2.96 ± 0.55	+, 0	0	0
Naproxen $\lambda = 215$ nm		4.8 ± 0.3 (A)	3.0 ± 0.24	0, -	-	-
Phenobarbital $\lambda = 243$ nm		7.6 ± 0.1 (A)	0.53 ± 0.26	0	0	-
Primidone $\lambda = 215$ nm		12.3 ± 0.4 (A)	0.4 ± 0.52	0	0	0
Trimethoprim $\lambda = 225$ nm		$7.2 \pm 0.1^*$ (B)	0.79 ± 0.38	+	+	+, 0

^a SciFinder Scholar 2007 predicted values, calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (1994–2011 ACD/Labs), unless otherwise noted; all $\log K_{OW}$ values refer to the neutral species.

^b van Balen et al., 2001.

^c Character of ionizable functional group: (A) acidic, (B) basic, (A/B) acidic and basic functional groups (zwitter).

^d Charge of the occurring relevant species at certain pH according to their pK_a : (0) neutral, (+) cation, (-) anion, (+/-) zwitter.

* All pK_a values given for bases refer to pK_a values for the conjugate acid (protonated species).

2.3.2 Sediment

A fluvial river bed sediment from a former tributary of the Elbe River close to the city of Torgau, Germany was used for the experiments. The grain size fractions of clay (0.7%, <2 μm) and silt (3.5%, <63 μm) of this coarse medium sand (>95%, 63–2,000 μm) are very low (Amiri et al., 2005). Before column packing, the sediment was sieved and the homogenized fraction <2 mm was used. The clay and silt fraction <63 μm consists mainly of quartz (10%) and the layered silicate minerals mica (muscovite, illite, biotite, 35%), kaolinite (40%), and chlorite (<5%). Quartz, muscovite, illite, and chlorite minerals possess points of zero charge (PZC) lower than 4 and provide therefore negatively charged surfaces over the entire considered pH range. Mainly due to carboxylic groups ($\text{p}K_a = 4\text{--}5$), the solid organic matter also represents an important source for variable negative charges. As a consequence, sorption and exchange of cations is possible at even lower pH levels. Measured sediment properties are listed in Table 2.2 and further information on sediment characterization methods are available in Appendix A2.

Table 2.2 Physicochemical properties of the used sorbent and column experimental conditions.

Sorbent and bulk properties		Column conditions for all runs	
BET [$\text{m}^2 \text{g}^{-1}$]	1.9	L [cm]	25
pH (CaCl_2) [-]	5.85	A [cm^2]	9.2
pH (H_2O) [-]	6.20	Q [$\text{cm}^3 \text{min}^{-1}$]	0.82
ρ_b [g cm^{-3}]	1.78 \pm 0.03	v_f [m d^{-1}]	1.28
ρ_s [g cm^{-3}]	2.65	v_w [m d^{-1}]	3.77
n_e [-]	0.340 \pm 0.02	c_0 [$\mu\text{g L}^{-1}$]	500
f_{OC} [mg g^{-1}]	2.33 (0.23%)		
$\text{CEC}_{\text{pH}=8.1}$ [$\text{cmol}_c \text{kg}^{-1}$]	1.36		
$\text{CEC}_{\text{pH}=6.2}$ [$\text{cmol}_c \text{kg}^{-1}$]	0.74		

BET = specific surface area, ρ_b = bulk density, ρ_s = solid density, n_e = effective porosity, f_{OC} = fraction of organic carbon, CEC = cation exchange capacity at certain pH, L = column length, A = cross-sectional area of column, Q = flow, v_f = filter velocity, v_w = porewater velocity, c_0 = initial concentration

2.3.3 *Water matrix*

Elbe river water, sampled in Dresden, Germany was filtered (cellulose nitrate, $<0.45\ \mu\text{m}$) to remove all suspended or colloidal substances and used for the experiments. The dissolved organic carbon DOC ranged between 4.6 and 7.5 mg L^{-1} . Natural pH of the river water was around 7.5 and was adjusted with NaOH or HCl to the pH levels of 4, 6, and 8. The stability of pH was controlled over time at the inflow and outflow of the columns. After one week equilibration time, a mixture of the eight pharmaceuticals was added to the reservoir. Due to initial concentrations of $c_0 = 500\ \mu\text{g L}^{-1}$ the investigation and direct measurement without concentration steps prior to chemical analysis was possible.

2.3.4 *Column experiments*

Stainless steel columns with dimensions of $250 \times 34\ \text{mm}$ were used for the experiments. Hydromechanical properties of the columns were kept constant for every single experiment and did not change over time (Table 2.2). The bulk parameter n_e was calculated from the breakthrough curves of a conservative Cl^- tracer (NaCl) before and after the experiments. In order to guarantee saturated conditions the water was pumped in up-flow direction. All column experiments were carried out at a constant temperature of $10\ ^\circ\text{C}$.

During the experiments the columns were purged with water, containing the pharmaceutical mixture, and the breakthrough behavior of each pharmaceutical was measured over time. The samples were taken with respect to the required temporal resolution. All experiments were verified by repeating each experiment at least three times, except for trimethoprim at $\text{pH} = 8$ which was not repeated. The breakthrough curves and the hydraulic and sediment parameters of all experiments at the same pH level were averaged before modeling to reduce statistical uncertainties caused by sediment heterogeneities. The evaluation of the obtained experimental breakthrough curves was achieved by an iterative parameter-fitting procedure based on the one-dimensional, analytical solution of the advection-dispersion-equation under equilibrium conditions. In addition, two sink terms for sorption and degradation processes are implemented (Van Genuchten, 1982; Wexler, 1992). The

optimization parameters of this model are R , the effective dispersivity α_{eff} , and a first-order kinetic degradation rate. Possible effects caused by sorption kinetics are included in α_{eff} already (Rahman et al., 2003; Worch, 2004).

Initially, K_d was derived in Eq. (2.2) from the modeled R of the breakthrough curves. Afterwards, K_{OC} was calculated by the use of Eq. (2.1). These experimental K_{OC} values were compared with calculated values on the basis of the correlation in Eq. (2.3) by the use of $\log K_{OW}$ from literature and with Eq. (2.4) and Eq. (2.5) calculated $\log D$, respectively. Additionally the experimental results were compared with the correlation results obtained from Eq. (2.6) and (2.7) (Franco and Trapp, 2008).

2.4 Results and discussion

All K_{OC} values derived from the column experiments are given in Figure 2.1 and the corresponding breakthrough curves are shown in Figure 2.2. The comparison of measured with correlated data after Franco and Trapp (2008) is given in Figure A1 (see Appendix A).

2.4.1 Acidic compounds

Two acidic compounds (naproxen, phenobarbital) with their anionic species occurring in the investigated pH range were investigated. A general low retardation was measured for phenobarbital. R ranges between 1.6 at pH = 4 and 1.1 at pH = 8. The appearing weak pH-dependence is caused by a hydroxyl group due to a lactam-lactim tautomerization in the barbituric substructure. This group leads to the resulting pK_a and becomes deprotonated with increasing pH. The increasing anionic character makes the molecule more polar, thus resulting in a decrease in retardation. The comparison of the measured and calculated K_{OC} values shows moderate differences. At this point, it is obvious that the relative error of the measured K_{OC} is considerable at small R around 1 (see Eq. 2.2).

A higher retardation and pH-dependence was observed for naproxen. R decreases from 7.7 at pH = 4 to 1.4 at pH = 8. The increasing deprotonation of the carboxyl group with increasing pH changes the molecule to the hydrophilic anionic form.

Except at pH = 8, where the $\log D$ seems underestimated, accordance between experimental and calculated K_{OC} was found. In general, the two investigated acidic compounds seem to confirm the expected transport behavior received from the modified K_{OC} concept as well as from the regression of Franco and Trapp (2008).

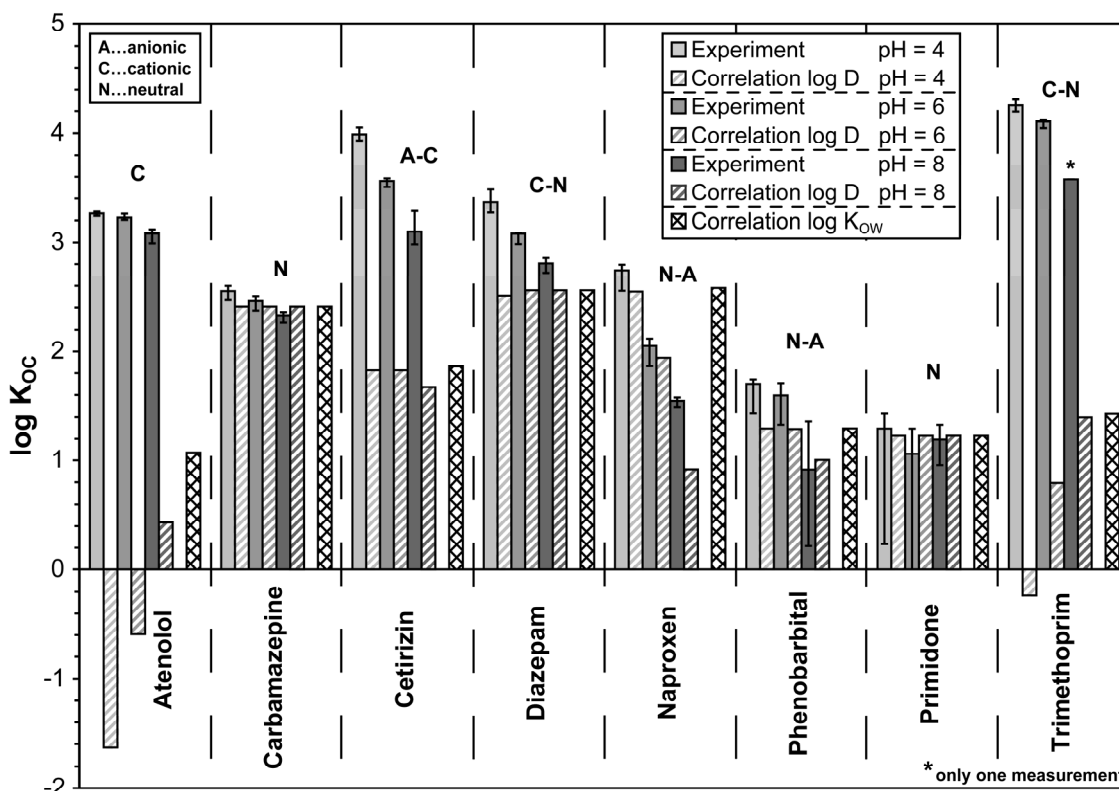


Fig. 2.1 Average from column experiments derived $\log K_{OC}$ values (uniform columns) compared with estimated $\log K_{OC}$ values (hatched columns) calculated with a modified $\log K_{OW} - \log K_{OC}$ correlation after Sabljic et al. (1995) for all compounds at pH = 4, pH = 6, and pH = 8. Error bars indicate the range of experimentally derived $\log K_{OC}$ for at least three measurements, except for TRI at pH = 8.

2.4.2 Neutral compounds

The validity of the K_{OC} concept together with no pH-dependence of the retardation was expected for the two neutral compounds primidone and carbamazepine because of their pK_a values being far beyond the investigated pH range.

Primidone has shown low retardation as well as its main metabolite phenobarbital. For all considered pH levels, R remains around 1.2. No dependence from pH could be detected. A theoretically possible deprotonation of the hydroxyl group due to a

lactam-lactim tautomerization cannot occur at the experimental pH values. So, the molecule stays in its neutral form and is very mobile because of its low $\log K_{OW}$.

According to the higher $\log K_{OW}$, R between 5.3 at pH = 4 and 3.6 at pH = 8 were found for carbamazepine. Because of its very low pK_a , only the neutral form of carbamazepine is the clearly dominating species at all investigated pH levels. Despite this, a weak pH-dependence was registered. The weak decrease in retardation for carbamazepine with increasing pH originates from the significantly higher $\log K_{OW}$ compared to primidone. The probability for hydrophobic interactions with the sediment decreases with rising pH due to the increasing deprotonation of the functional groups (mainly carboxyl and hydroxyl groups) on the sediment organic matter with increasing pH. As these interactions dominate the sorption process for carbamazepine (Scheytt et al., 2005) and other neutral compounds with higher $\log K_{OW}$ their retardation decreases, too. In contrast, the influence of the pH-dependent sediment charge on the sorption of the very polar compound primidone seems to be negligible. As expected, the two applied correlations gave similar and acceptable results for neutral compounds.

2.4.3 Alkaline compounds

Strongest retardations and therefore highest $\log K_{OC}$ values were observed for the cationic compounds atenolol, diazepam, and trimethoprim. In contrast to organic acids, the nitrogen bearing functional groups in these compounds are protonated and thus ionic below their pK_a . An increase of pH leads to a shift of the dissociation equilibrium in favor of the neutral species. Hence, the hydrophobicity and $\log D$ values increase with rising pH. However, the pH-dependent retardation of the compounds investigated in this study shows an inverted image. R decreased from 23.3 to 15.8 for atenolol, from 29.4 to 8.8 for diazepam and from 219.6 to 47.0 for trimethoprim with increasing pH from 4 to 8. Despite of the non-protonated, neutral species becoming the dominating species the retardation decreases with increasing pH. Therefore, the modified K_{OC} concept fails to predict the sorption behavior of these alkaline substances. Even worse, the implementation of $\log D$ intended to correct for neutral/charged species distribution further enhances the differences between estimated and measured $\log K_{OC}$ data. Much better results were obtained by

using the specific correlation for bases from Franco and Trapp (2008). In contrast to the modified K_{OC} concept, at least the trend of decreasing sorption with increasing pH could be reproduced. Nevertheless, absolute K_{OC} values are still underestimated.

An additional sorption process has to be responsible for the increasing sorption of the cationic species. The existence and dominating role of cation exchange processes on the retardation was earlier reported for the beta-blocker atenolol (Yamamoto et al., 2009) as well as for the antibiotic trimethoprim (Bekçi et al., 2006; Qtaitat, 2004). This is plausible since the composition of the sediment (TOC, minerals) gives evidence for the presence of negatively charged surfaces at all here investigated pH levels (see Chapter 2.3.2). Also, Figueroa et al. (2004), Carmosini and Lee (2009), and Vasudevan et al. (2009) could highlight the importance of cation exchange processes for the cationic species of tetracycline antibiotics and the fluoroquinolone ciprofloxacin on negatively charged surfaces. Therefore, the shown similar behavior is likely for the further investigated basic compound diazepam. Atenolol at pH = 8 is the only substance which was noticeably biodegraded (to 80% of c_0) during the experiments (Fig. 2.2).

2.4.4 Zwitter-ionic compounds

The zwitter-ionic character of cetirizine in the considered pH range is caused by two basic reacting tertiary amine groups with pK_a of 2.2 and 8.0, respectively and one acidic carboxyl group with pK_a of 2.9. At pH values close to 4 and 8, cetirizine occurs as a monovalent cation and a monovalent anion, respectively. The $\log D$ value changes minimally between pH = 4 and pH = 8 (van Balen et al., 2001) and only a weak pH-dependence may be expected. But in contrast to this presumption, a strong pH-influence associated with a much higher retardation was observed. The reason for such behavior might be explained by a combination of the above-mentioned effects. At low pH the cationic species with positive partial charges are dominating. Therefore, the affinity to negative charged sediment surfaces is high and the molecules are able to sorb due to cation exchange. With increasing pH the positive charges of cetirizine becomes weaker because of an increased deprotonation. As a result, the sorption due to cation exchange is reduced and the retardation factors decrease drastically from 130 at pH 4 to 16 at pH 8.

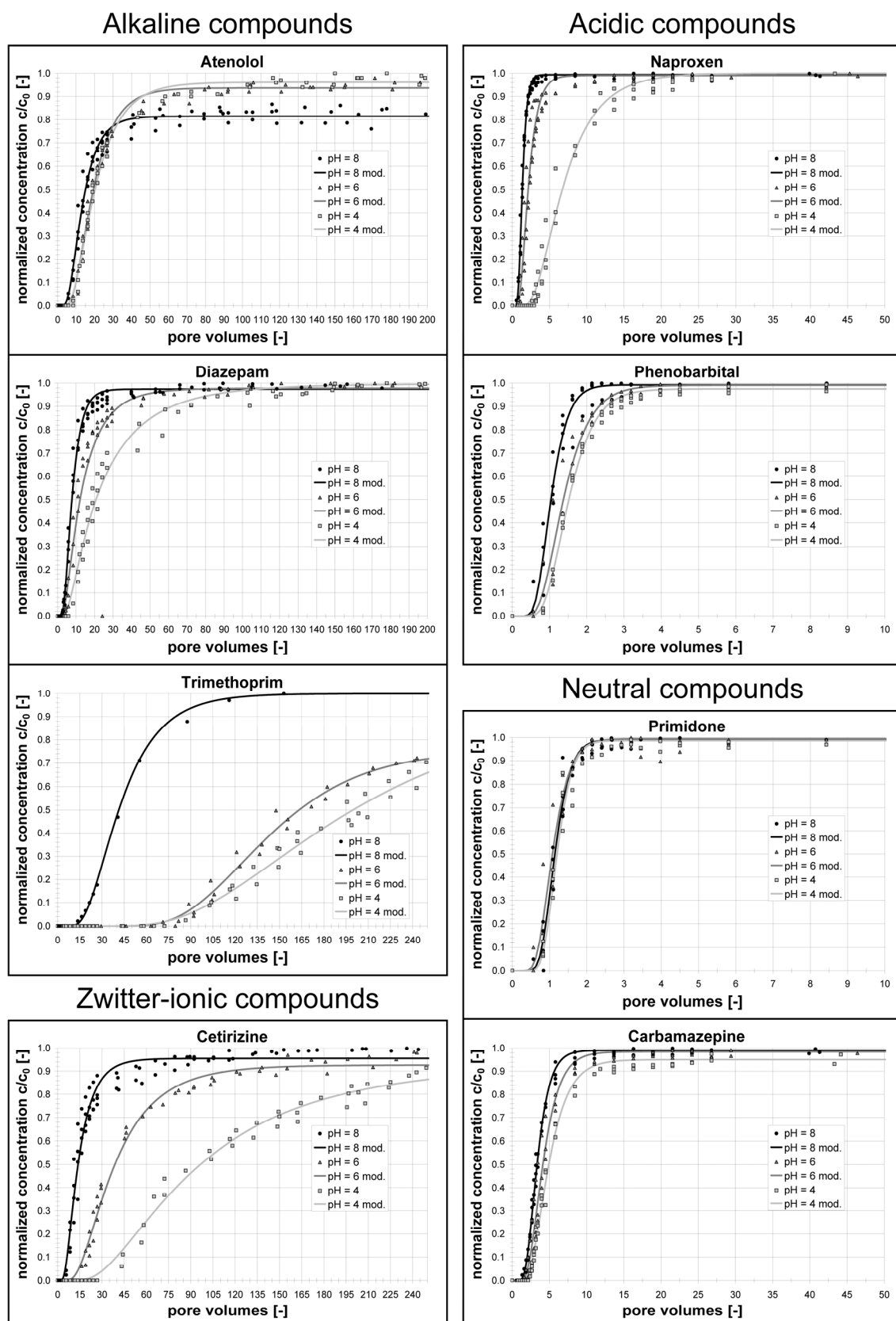


Fig. 2.2 Experimental and modeled breakthrough curves for eight pharmaceuticals at pH = 4, pH = 6, and pH = 8 showing the pH-dependence for different compounds and a wide spectrum of pK_a . Concentrations c of the breakthrough curves were normalized with the initial concentration c_0 . Pore volumes were calculated by normalizing the experiment duration to the breakthrough time of the Cl^- tracer.

2.5 Summary and conclusions

As expected, a strong pH-dependence of the transport behavior was observed for the majority of the investigated compounds. When analyzed outside the considered pH range ($pK_a > 9$ or $pK_a < 3$) the compounds atenolol, carbamazepine, and primidone, with very high and low pK_a values, respectively, occur mainly as one species. Therefore, no or only a weak dependence from pH was registered. Retardations of all compounds were significant, except for primidone and phenobarbital. Despite of the low sediment TOC, R ranged between 3 and 248.

According to the literature (Tolls, 2001; Kah and Brown, 2007; Lorphensri et al., 2007; Yamamoto et al., 2009; Figueroa-Diva et al., 2010) it was established that the prediction of mobility applying $\log K_{OW}$ - $\log K_{OC}$ correlations has considerable limitations for ionizable compounds. Large differences and an overall underestimation between measured and calculated K_{OC} values were obtained for the majority of the applied substances. Only for the neutral compounds carbamazepine and primidone the K_{OC} concept gave confident results.

The weak pH-dependence of the neutral compound carbamazepine was explained with a decrease of non-polar interactions with increasing pH due to the deprotonation of the functional groups on the sediment TOC. The implementation of $\log D$ instead of $\log K_{OW}$ into the calculation of $\log K_{OC}$ or the use of the correlation after Franco and Trapp (2008) enhances the prediction particularly for the acidic, partially anionic compounds naproxen and phenobarbital.

In contrast, the organic bases atenolol, trimethoprim and the zwitter-ion cetirizine with partially positive charges have shown much higher retardations than calculated from $\log K_{OW}$ and have therefore the most substantial differences to the predicted K_{OC} values. The integration of $\log D$ amplifies these differences. The reason is that in the $\log D$ concept only the speciation in solution is considered and additional occurring polar interactions to the sorbent are neglected. Particularly, the dominating role of cation exchange processes as a sorption process on negatively charged surfaces must be considered, even for sediments with very low CEC. Therefore, a general strong retardation of organic cations can be expected in non-tropic, permanently charged sediments and soils with higher pH, such as the used sediment, as they usually have negative net surface charges (Sollins et al., 1988). Due to the preferable

results achieved from Franco and Trapp (2008) it is more reliable to predict the sorption of organic bases with this regression. Nevertheless, considerable differences to the measured data still exist.

Moreover, it can be concluded that the pH-dependent speciation has a bigger influence on the cation sorption than the pH induced charge variation of the sediment. Furthermore, the development and dynamics of sediment surface charges due to chemical processes are essential for estimating the transport behavior. As ion exchange and other polar interactions are possible sorption processes for the ionic species, further boundary conditions should be considered, like competition with other ions, interactions to dissolved organic matter, and specific sorption mechanisms.

The investigation has shown that the pH has a significant influence on the retardation of ionizable organic compounds. As a consequence, it can be noted that already small changes in the pH will have a big influence on the mobility of ionizable organic compounds. Hence, changes of pH caused by variations in, e.g. land use or climatic conditions might have considerable effects on the transport and retardation of organic pollutants. For this purpose, it is also essential to know that dominating sorption mechanisms can change from hydrophobic to ionic interactions and *vice versa* in dependence of the pH and sediment types. Simple prognostic models based on hydrophobic interactions like the K_{OC} concept are not able to consider these effects. The more complex model approach of Franco and Trapp (2008) gives better but still unconvincing results and shows the limitations of empirical correlations. Therefore, new mechanistic, process-based approaches, considering further relevant boundary conditions, are necessary.

2.6 Acknowledgment

The presented study was funded by the European Commission (contract number 518118-1, GABARDINE, "Groundwater Artificial Recharge Based on Alternative Sources of Water: Advanced Integrated Technologies and Management").

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Chapter 3

3 Role of cation exchange processes on the sorption influenced transport of cationic beta-blockers in aquifer sediments

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Citation:

Schaffer, M., Börnick, H., Nödler, K., Licha, T., Worch, E., 2012. Role of cation exchange processes on the sorption influenced transport of cationic β -blockers in aquifer sediments. *Water Research* 46 (17), 5472–5482.

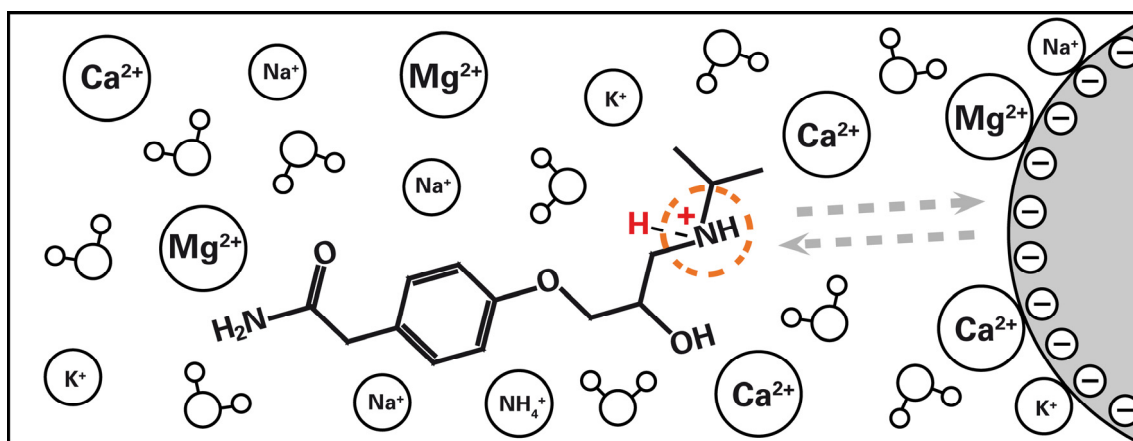
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Abstract

The influence of cation exchange processes on the transport behavior of the cationic beta-blockers atenolol and metoprolol was investigated by applying saturated laboratory column experiments. Breakthrough curves using natural sediments under different competitive conditions were generated and resulting sorption coefficients were compared. For the cationic species of atenolol (at pH = 8), the existence and dominating role of cation exchange processes were demonstrated by varying calcium concentrations. No effect of atenolol concentration on its retardation was observed within a wide concentration range. The breakthrough curve comparison of atenolol and the more hydrophobic metoprolol under constant conditions showed a significantly stronger retardation for metoprolol than for atenolol. However, additional non-polar interactions cannot explain the observed differences as they are determined to be negligible for both compounds. Due to the dominating role of cation exchange processes for the cationic species on overall sorption, a simple prediction of beta-blocker transport in the subsurface by using K_{OC} values derived from $\log K_{OW}$ - $\log K_{OC}$ correlations is not feasible.

Graphical abstract

3.1 Introduction

During the last decades numerous pharmaceuticals and their metabolites have been detected in different parts of the water cycle (Ternes, 1998; Halling-Sørensen et al., 1998; Daughton and Ternes, 1999; Heberer, 2002). Frequently consumed beta-blockers (e.g., metoprolol, atenolol, sotalol, and propranolol) cannot be completely eliminated by conventional wastewater treatment (Ternes, 1998; Maurer et al., 2007). Therefore, these compounds are commonly detected in surface water and even in groundwater samples (Ternes, 1998; Sacher et al., 2001; Heberer, 2002; Cleuvers, 2005; Nödler et al., 2011).

The knowledge of interactions of these compounds with geosorbents in aquifers or during riverbank filtration and soil aquifer treatment is essential to assess their fate in the environment. Besides the chemical and biological degradation processes, sorption on environmental surfaces is the major transport influencing process for numerous anthropogenic trace compounds (Katayama et al., 2010).

Typically, beta-blockers are weak organic bases with acidity constants $pK_a > 9$ for β_1 -selective blockers (pK_a of the conjugate acid). Therefore, at typical groundwater pH conditions (pH = 4–8) the molecules are protonated and the cationic species clearly dominate. For charged species, the classical K_{OC} concept for predicting the retardation in the subsurface by means of $\log K_{OW}$ - $\log K_{OC}$ correlations (Chiou et al., 1979; Karickhoff, 1981; Sabljic et al., 1995) is usually not feasible (Tolls, 2001; Kah and Brown 2007; Schaffer et al., 2012). The very recent studies from Hyland et al. (2012) and Schaffer et al. (2012) highlight the limitations of the K_{OC} concept and the need of a mechanistic understanding to predict the sorption behavior of charged compounds, since the specific mechanisms of the observed sorption are still unclear and electrostatic interactions are not yet quantitatively predictable.

Particularly for cationic organic compounds, the calculated distribution coefficients K_d solely derived from organic carbon normalized sorption coefficients K_{OC} are generally underestimated. This is because additional sorption processes (e.g., ion exchange, cation bridging, surface complexation, ligand exchange, hydrogen bonding) and pH effects (speciation, variable surface charges) are not sufficiently considered in this concept (Tolls, 2001; Cunningham et al., 2004; Kah and Brown, 2007; Schaffer et al., 2012).

Previous studies covering the groundwater pH range (Zachara et al., 1986; Figueroa et al., 2004; ter Laak et al., 2006; Franco and Trapp, 2008; Franco et al., 2009) showed above the mineral's point of zero charge in general an increased sorption for organic bases with decreasing pH. This means the higher the positively charged fraction of these molecules, the more important sorption becomes. Therefore, several authors came to the conclusion that sorption of the cationic species (particularly cation exchange) must be a significant sorption mechanism for a variety of organic bases in the cationic form (Zachara et al., 1986; Brownawell et al., 1990; Nicholls and Evans, 1991; Li et al., 2001; Bi et al., 2006; Carmosini and Lee, 2009). Fábrega et al. (1998, 2001) proposed two diagnostic modeling approaches based on numerically optimized sorption coefficients to describe competitive cation exchange for aromatic amines. In the case of beta-blockers, the occurrence of relevant cation exchange processes was also to be expected in sorption studies by Yamamoto et al. (2009), Ramil et al. (2010), and Schaffer et al. (2012).

Despite this state of knowledge, virtually all available studies dealing with the sorption of beta-blockers were carried out under fixed hydrochemical boundary conditions. The capability of cation exchange and its dependence on further influence factors (e.g., effects of pH, ionic strength and ionic composition) are often not systematically considered in the determined sorption coefficients (Yamamoto et al., 2005; Kibbey et al., 2007; Maurer et al., 2007; Barron et al., 2009; Ramil et al., 2010; Stevens-Garmon et al., 2011, Hyland et al., 2012). Furthermore, these studies are generally limited to batch experiments, which do not allow an explicit separation of sorption and degradation processes for easily degradable compounds like atenolol.

Therefore, this study focuses on the evaluation of the importance of cation exchange processes for the worldwide highly consumed beta-blockers atenolol and metoprolol. In total, three different sediments were studied using saturated column experiments. These novel experiments were conducted under different competitive conditions with respect to Ca^{2+} concentrations. The influence of competing Ca^{2+} on beta-blocker retardation was determined by comparing resulting distribution coefficients. Additionally, desorption behavior is reported. Furthermore, the generally expected non-transferability of results from column experiments conducted with high concentrations to experiments using environmentally relevant

concentrations was examined. These experiments are believed to make a valuable contribution to this current discussion. Finally, the comparison of two structural related compounds allows assessing the relevance of possible additional hydrophobic interactions on the transport of beta-blockers.

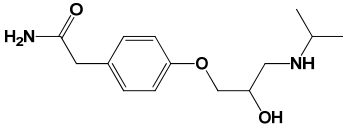
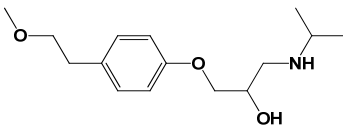
3.2 Materials and methods

3.2.1 Chemicals

Atenolol from Fagron (Barsbüttel, Germany) and metoprolol (tartrate salt) from Sigma-Aldrich (Steinheim, Germany) were used in the experiments. Their purity was >99%. For the HPLC-MS/MS analysis the analytical standard atenolol-D₇ from Sigma Aldrich (Steinheim, Germany) was used as internal standard. Atenolol acid was purchased from LGC Promochem (Wesel, Germany).

Atenolol and metoprolol are structurally related, featuring a basic reacting secondary amine group (Table 3.1). The sole difference between both compounds is that atenolol bears a more hydrophilic carboxamide group instead of a methoxy group. Hence, the neutral species of atenolol has a significantly lower *n*-octanol/water distribution coefficient $\log K_{OW}$ than the neutral species of metoprolol.

Table 3.1 Chemical properties and structures of the sorbates.

Compound	Structure	$pK_a^{a,b}$	$\log K_{OW}^{a,c}$	$\log K_{OW}^{+,a,d}$	$\log D_{pH=8.0}^e$
Atenolol		9.54	0.22	<-2.0	-1.2
Metoprolol		9.63	1.95	-1.10	0.09

^a Caron et al. (1999).

^b All pK_a values refer to pK_a values for the conjugate acid (protonated species).

^c All $\log K_{OW}$ values refer to the neutral species.

^d All $\log K_{OW}^+$ values refer to the cationic species.

^e All $\log D$ values refer to the neutral and cationic species at pH = 8. SciFinder Scholar 2007 predicted values, calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (1994–2012 ACD/Labs).

3.2.2 Sorbents

Three fluvial riverbed sediments were used for the experiments. Sediment S1 was sampled in 1 m depth in a former tributary of the Elbe river close to the city of Torgau, Germany. It is a medium quartz sand with a very small clay and silt fraction (<63 μm) of 4%. Main components of this fraction are quartz and the layered silicate minerals mica (muscovite, illite, biotite), kaolinite, and chlorite (Amiri et al., 2005; Schaffer et al., 2012). These minerals possess points of zero charge in the low pH range. Therefore, the surface is negatively charged at the considered pH (pH = 8) and cation exchange on these mineral surfaces is potentially possible.

The other two sediments S2 and S3 are from different aquifer layers within the Pleistocene and Holocene fluvial fan of the Gallikos river close to Thessaloniki, Greece. Sediment S2, sampled in around 3 m depth, is a coarse sand with a clay and silt fraction of 13% and sediment S3, sampled in approx. 5 m depth, is a medium sand with a clay and silt fraction of 6%, respectively. Both sediments consist mainly of quartz, feldspars (plagioclase, microcline), and the layered silicate minerals muscovite, smectite, chlorite, and biotite. Especially the clay minerals smectite and chlorite can provide high cation exchange capacities (CEC).

Further, even small fractions of solid organic matter can also provide negative charges originating from the deprotonation of carboxylic groups ($\text{p}K_a$ around 4–5). All sediments used in this study are from aquifers and contain, therefore, in general a low fraction of total organic carbon f_{oc} . While the f_{oc} of sediment S1 is around two to three times higher than for sediment S2 and S3, respectively, sediment S1 has a lower CEC than the two other sediments.

To reduce heterogeneities in the column filling, all sediments were sieved and the homogenized fractions <2 mm were used. Measured sediment properties are listed in Table 3.2 and further information on sediment characterization methods are given in Chapter 3.2.5.3.

3.2.3 Model water

Tap water from Dresden, Germany was used as base matrix for the experiments. The pH was constant between 7.9 and 8.1 (bicarbonate buffered) for all experiments and

was only controlled at the column outlet over time. The dissolved organic carbon DOC ranged slightly between 1.7 and 2.1 mg L⁻¹. According to the experimental requirements, different amounts of inorganic salts (NaCl, CaCl₂, KCl, KNO₃, MgCl₂, Na₂SO₄, NaHCO₃) and beta-blocker (atenolol, metoprolol) were added. The performed experiments and the resulting concentrations of inorganic cations and beta-blockers are listed in Table 3.3. All experiments were carried out at a constant temperature of 10 °C in a climatic chamber.

Table 3.2 Physicochemical properties of the used sediments and column experimental conditions.

Sorbent and bulk properties				Column conditions for all runs	
<u>Sediment</u>	<u>S1</u>	<u>S2</u>	<u>S3</u>		
BET [m ² g ⁻¹]	1.9	6.3	nd	<i>L</i> [cm]	25
pH (CaCl ₂) [-]	5.85	7.78	8.01	<i>A</i> [cm ²]	9.2
pH (H ₂ O) [-]	6.20	8.10	8.77	<i>Q</i> [cm ³ min ⁻¹]	0.40–0.50
ρ_b [g cm ⁻³]	1.76	1.94	1.50±0.1	v_f [m d ⁻¹]	0.62–0.78
n_e [%]	35	29	38±2	v_w [m d ⁻¹]	1.91–2.43
f_{oc} [%]	0.23	0.11	0.07	c_0 [µg L ⁻¹]	1–30,000
CEC [cmol _c kg ⁻¹]	1.36	3.09	4.40		

BET = specific surface area, ρ_b = bulk density, n_e = effective porosity, f_{oc} = fraction of organic carbon, CEC = potential cation exchange capacity at pH = 8.1, *L* = column length, *A* = cross-sectional area of column, *Q* = volumetric flow rate, v_f = filter velocity, v_w = pore water velocity, c_0 = initial concentration of beta-blocker, nd = not determined

3.2.4 Column experiments

The column experiments were carried out in stainless steel columns with dimensions of 250 × 34 mm. In order to ensure saturated column conditions, the water was pumped upwards. All hydraulic parameters of the columns were kept constant within every experiment. The column packing with different grain-size distributed sediments (Table 3.2) leads to different hydromechanical properties between the experiments. The effective column porosities n_e of all experiments were calculated

from the conductivity breakthrough curves $\kappa(t)$ (microprocessor conductivity meter LF 537 with flow-through cell LDM/S, WTW) of a conservative Cl^- tracer (NaCl):

$$n_e = \frac{Q \cdot t_{id}}{A \cdot L} \quad \text{with} \quad t_{id} = t_{max} - \frac{\int_0^{t_{max}} \kappa(t) dt}{\kappa_0 - \kappa_b} \quad (3.1)$$

The ideal breakthrough time t_{id} of the tracer (center of gravity) was calculated after a cubic spline interpolation of the measured data points. Here, A denotes the cross-sectional area of the column, t_{max} the duration of the experiment, κ_0 the initial conductivity of the tracer and κ_b the background conductivity of the water at the column outlet before tracer addition.

During the experiments the columns were fed with water (lab pump RHSY Jr., Fluid Metering Inc.), containing different concentrations of the respective beta-blocker and inorganic cations (Table 3.3). Samples were taken with a fraction collector (Retriever II, Teledyne Isco) in a temporal resolution of 45 min with the aim of atenolol and metoprolol breakthrough curve determinations. Samples volumes were at least 20 mL. Due to the high temporal sampling resolution, not all taken samples were analyzed.

All experimentally obtained breakthrough curves were inversely modeled with analytical solutions of the one-dimensional advection-dispersion-equation. For this purpose, the CXTFIT code (Toride et al., 1995) implemented in the software STANMOD (Version 2.07) was used. The model includes sink terms for sorption and degradation (assumption of first-order rate law). The numerically optimized parameters are the retardation factor R , the dispersivity α , and the first-order degradation rate constant λ . In case of unsatisfactory modeling results ($R^2 < 0.99$) with the chemical equilibrium model, the two-site chemical non-equilibrium model was used to improve fit quality (Table B2). Selected replicates of the experiments can be found in the Appendix B (Table B1 and B2, Fig. B1–B3).

The experiments were classified into sub-groups from group A to group D (Table 3.3) with respect to their experimental focus.

Table 3.3 Concentrations of beta-blockers and inorganic main cations for each experiment.

Exp. (Sorbens)	Description	Water matrix	Target c_0 of beta- blockers	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
			[$\mu\text{g L}^{-1}$]	[mg L^{-1}]	[mg L^{-1}]	[mg L^{-1}]	[mg L^{-1}]
<u>Atenolol</u>							
A1(S1)	Breakthrough	Tap water	500	8	2	3	47
A2(S1)	Breakthrough	Tap water + CaCl ₂	500	7	2	3	430
A3(S2)	Breakthrough	Tap water	500	8	2	3	41
A4(S2)	Breakthrough	Tap water + CaCl ₂	500	8	2	3	400
<u>Metoprolol</u>							
B1(S1)	Desorption	Tap water	0	8	2	3	48
B2(S1)	Desorption	Tap water + CaCl ₂	0	8	2	3	421
B3(S2)	Desorption	Tap water	0	7	2	3	42
B4(S2)	Desorption	Tap water + CaCl ₂	0	8	2	3	405
C1(S3)	Breakthrough	Tap water + salt mix	1	732	41	90	80
C2(S3)	Breakthrough	Tap water + salt mix	500	743	40	90	81
C3(S3)	Breakthrough	Tap water + salt mix	5,000	726	40	93	82
C4(S3)	Breakthrough	Tap water + salt mix	30,000	726	40	93	82
D1(S3)	Breakthrough	Tap water + salt mix	500	726	40	93	82

3.2.4.1 Experiments A: Different concentrations of Ca²⁺

The effect of inorganic ions on the transport of atenolol due to different competitive conditions was studied here. After equilibrating the columns for at least 1 week (pH, DOC = const.), atenolol was added to the reservoir containing the model water and breakthrough curves were recorded (experiments A1 and A3). Subsequently, atenolol-free water was used for a complete desorption of the columns (see Section 3.2.4.2). Next, the breakthrough experiment was repeated using the same column (A2 and A4) at identical experimental conditions. But in contrast to the previous breakthrough curves, the reservoir contained besides atenolol additional CaCl₂. Thus, the concentration of Ca²⁺ was increased by a factor of ten (from around 40 to 400 mg L⁻¹). Eventually, the breakthrough curves with and without CaCl₂ addition

were compared. The experiments were conducted with two different sediments (S1 and S2) at initial atenolol concentrations of $c_0 = 500 \mu\text{g L}^{-1}$.

3.2.4.2 Experiments B: Desorption

As mentioned above, an intermediate desorption step was inserted between the two breakthrough experiments A1/A2 and A3/A4, respectively. After the breakthrough (A1 and A3) was completed, atenolol-free tap water was used for desorbing atenolol from the columns (experiments B1 and B3). The decreasing atenolol concentrations at the outflow were measured over time. When the atenolol concentrations reached around 5% of c_0 , the Ca^{2+} concentrations were increased tenfold from around 40 to 400 mg L^{-1} by adding CaCl_2 to the reservoir (experiments B2 and B4). The declining curves for atenolol were observed until it could no longer be detected ($c < 12 \mu\text{g L}^{-1}$).

3.2.4.3 Experiments C: Different concentrations of atenolol

In contrast to the experiments with different Ca^{2+} concentrations (experiments A1–A4), the influence of different atenolol concentrations and thus varying ratios of organic to inorganic cations was investigated (experiments C1–C4). The concentrations of inorganic cations were kept constant and the columns were refilled with sediment S3 for each atenolol concentration. After at least 1 week equilibration time, atenolol was added together with NaCl (conservative tracer) to the reservoir and the breakthrough curves were determined. Atenolol concentrations were varied in a wide range between $c_0 = 1 \mu\text{g L}^{-1}$ and $c_0 = 30,000 \mu\text{g L}^{-1}$.

3.2.4.4 Experiment D: Comparison with metoprolol

For comparing the influence of two structurally similar molecules with different hydrophobicity but equal $\text{p}K_a$ on the sorption influenced transport, the breakthrough behavior of metoprolol was investigated in experiment D1. Setup, methodology, and concentrations are equal to experiment C2 (see Section 3.2.4.3).

3.2.4.5 Determination of sorption coefficients

Due to the fact that the simple application of linear free-energy relationships ($\log K_{OW}$ - $\log K_{OC}$ correlations) for hydrophobic partitioning is not expected to be applicable for the investigated cationic compounds at $\text{pH} = 8$ (see Section 3.1), organic carbon normalized sorption coefficients $K_{OC} = K_d/f_{OC}$ were not compared. Instead, the distribution coefficients K_d were used directly for the quantitative comparison of the obtained breakthrough curves. Assuming a linear sorption isotherm (or ion exchange isotherm), K_d was calculated from R of the respective modeled breakthrough curve, n_e obtained from the conservative tracer test and the bulk density ρ with:

$$K_d = \frac{n_e}{\rho}(R - 1) \quad (3.2)$$

Thus, K_d represents R normalized to the bulk properties. This implies that K_d can be used as effective parameter for the comparison of column experiments even when conducted with different sediments.

The relative contribution of electrostatic (ionic) interactions to the sorption process was estimated as follows: The hydrophobic proportions, derived from the classical K_{OC} concept, were subtracted from K_d . This can be done as the obtained K_d represents the sum of all involved sorption processes (Schwarzenbach et al., 2003). Therefore, K_d can be separated into contributions from ionic (K_d^+) and hydrophobic (K_d^0) interactions:

$$K_d = K_d^0 + K_d^+ \quad (3.3)$$

It is assumed that K_d^0 can completely be described by hydrophobic partitioning of the sorbates to the fraction of organic carbon of the sorbent. Considering both sorbate species, K_d^0 is a function of K_{OC}^0 , K_{OC}^+ , f_{OC} and the degree of protonation α :

$$K_d^0 = (1 - \alpha)(K_{OC}^0 \cdot f_{OC}) + \alpha(K_{OC}^+ \cdot f_{OC}) \quad \text{with} \quad \alpha = \frac{1}{1 + 10^{\text{pH} - \text{p}K_a}} \quad (3.4)$$

K_{OC} values for the neutral species (K_{OC}^0) can be calculated from $\log K_{OW}$ - $\log K_{OC}$ correlations and with the values in Table 3.1, e.g. after Sabljic et al. (1995) for non-hydrophobic compounds with:

$$\log K_{OC} = 0.52 \cdot \log K_{OW} + 1.02 \quad (3.5)$$

Due to the lack of specific $\log K_{OW}$ - $\log K_{OC}$ correlations for predicting the hydrophobic partitioning of organic cations Eq. (3.5) was slightly modified. The $\log K_{OW}^+$ determined by Caron et al. (1999) (Table 3.1) was used instead of $\log K_{OW}$ to derive the K_{OC} values for the cationic species (K_{OC}^+).

3.2.5 Chemical analysis

3.2.5.1 Beta-blockers

All samples of the experiments with $c_0 \geq 500 \mu\text{g L}^{-1}$ were analyzed by high-performance liquid chromatography with UV detection (HPLC, Merck-Hitachi) using a diode array detector (DAD L-4500, Merck-Hitachi). A $150 \times 3 \text{ mm}$ C18-HPLC reversed phase column (Gemini-NX $3 \mu\text{m}$ C18 110A, Phenomenex) was used for chromatographic separation. The separation was operated at $29 \text{ }^\circ\text{C}$ with an injection volume of $100 \mu\text{L}$. Before injection all samples were filtered with a cellulose nitrate filter ($<0.45 \mu\text{m}$, Sartorius, Göttingen) to remove all suspended particles. Samples with $c > 500 \mu\text{g L}^{-1}$ were diluted with ultrapure water to the calibration range ($c = 25\text{--}500 \mu\text{g L}^{-1}$) prior to analysis. The linearity for all calibrations was $R^2 > 0.99$.

The atenolol samples were analyzed with a detection wavelength of 223 nm and a constant flow rate of 0.5 mL min^{-1} . Eluent A was acetonitrile (HPLC grade, Mallinckrodt Baker, Griesheim, Germany) and eluent B was water (HPLC grade, Mallinckrodt Baker, Griesheim, Germany) containing 5 Vol.-% acetonitrile and $2.45 \mu\text{mol L}^{-1}$ acetic acid (p.a., Merck, Darmstadt, Germany). The elution was performed isocratically by using $19\% \text{ A}$ and $81\% \text{ B}$ for 8 min .

The metoprolol samples ($c_0 = 500 \mu\text{g L}^{-1}$) were analyzed with a detection wavelength of 227 nm and a constant flow rate of 0.3 mL min^{-1} . Eluent A was acetonitrile and eluent B was an aqueous 10 mM NH_4HCO_3 (p.a., Mallinckrodt Baker, Griesheim, Germany) buffer with $\text{pH} = 8.8$. The elution was performed isocratically by using $20\% \text{ A}$ and $80\% \text{ B}$ for 8 min .

The atenolol samples of the experiment with $c_0 = 1 \mu\text{g L}^{-1}$ were analyzed by a method based on solid phase extraction (SPE) and high-performance liquid chromatography coupled with tandem-mass spectrometric detection (HPLC-MS/MS). The instrumentation, sample pretreatment and analysis followed the method of Nödler

et al. (2010). In contrast to this, a sample volume of 20 mL was spiked with 1 mL phosphate buffer and 10 μL ($m = 100 \text{ ng}$) of the internal atenolol- D_7 standard solution and filled up to 25 mL with ultrapure water. The sample solution was pre-concentrated by using the SPE on Oasis HLB (6 mL, 500 mg) from Waters (Eschborn, Germany). Afterwards, the compounds were eluted by methanol and ethyl acetate and the extract was evaporated to dryness at 40 °C with a gentle stream of nitrogen. The analytes were re-dissolved in 0.5 mL of aqueous 5 mM ammonium acetate solution, containing 4% methanol, resulting in a total pre-concentration factor of 40.

3.2.5.2 Analysis of inorganic cations

For the analysis of inorganic cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) an ion chromatographic system DX-500 (Dionex) with conductometric detection and a 250 \times 3 mm cation exchange column (IonPac CS16, Dionex) were used. The separation was performed isocratically at 44 °C with a 35 mM methanesulfonic acid eluent.

3.2.5.3 Sediment analysis

The specific surface areas of the sediments were determined with the N_2 adsorption/desorption BET method (DIN ISO 9277, 2003) by using the Autosorb-1-C (Quantachrome) surface analyzer. Sediment pH values were measured according to the international norm DIN ISO 10390 (2003) with ultrapure water and a 0.01 M CaCl_2 solution. The determination of the total organic carbon (TOC) content was carried out by dry combustion of the previously with 4 M HCl treated sediment at 900 °C in a total organic carbon analyzer (Dohrmann Boat Sampler 184 S / Rosemount Dohrmann DC 70). The potential CEC (at pH = 8.1) was measured in accordance with DIN ISO 13536 (1997). The mineralogical constitutions were characterized by macroscopic observation and combined X-ray diffractometry-thermoanalysis (Siemens diffractometer D5000, Netzsch STA 409 PG Luxx).

3.3 Results and discussion

The obtained sorption coefficients of all experiments can be found in Table 3.4. The modeled parameters and column conditions of the tracer tests as well as for the experiments are listed in Table B1 and B2 in the Appendix B.

3.3.1 Experiments A: Different concentrations of Ca^{2+}

A tenfold increase of the Ca^{2+} concentration resulted for sediment S1 and S2 in a reduction close to one half of the retention times for atenolol (Fig. 3.1 and Fig. 3.2). Comparing experiment A1 with A2, K_d decreased for sediment S1 from 3.5 L kg^{-1} ($R = 18.5$) to 1.3 L kg^{-1} ($R = 7.4$). The same behavior was observed for sediment S2, as K_d decreased from 3.2 L kg^{-1} ($R = 22.4$) in experiment A3 to 1.7 L kg^{-1} ($R = 12.1$) in experiment A4. Apparently, Atenolol was biodegraded in both experiments (around 15–30% of c_0).

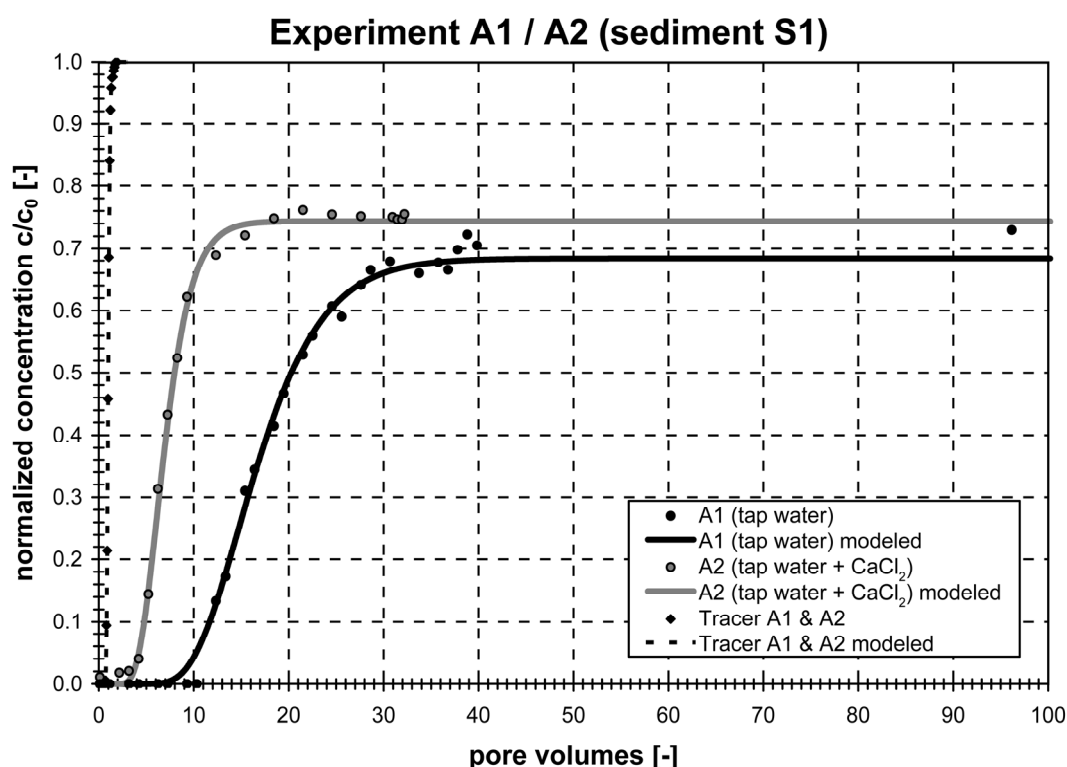


Fig. 3.1 Experimental and modeled breakthrough curves (including tracer tests) of atenolol for sediment S1 with and without CaCl_2 addition (Ca^{2+} concentrations of 40 and 400 mg L^{-1}). Concentrations c of the breakthrough curves were normalized with the initial concentration c_0 . Pore volumes were calculated by normalizing the experiment duration to the ideal breakthrough time of the Cl^- tracer.

Increased competition with inorganic cations leads to a weaker atenolol sorption onto the sediment. The effect can solely be explained by the existence of cation exchange processes, which were already expected from Yamamoto et al. (2009), Ramil et al. (2010), and Schaffer et al. (2012). Higher Ca^{2+} concentrations lead to a shift of the exchange equilibrium in favor of the double charged Ca^{2+} and as a consequence the probability for atenolol sorption on exchange sites decreases. According to Eq. (3.3–3.5), the contributions of hydrophobic partitioning to K_d are estimated to be $<0.0030 \text{ L kg}^{-1}$ for sediment S1 and $<0.0015 \text{ L kg}^{-1}$ for sediment S2. Thus, ionic interactions are clearly dominating even at high concentrations of competing inorganic ions.

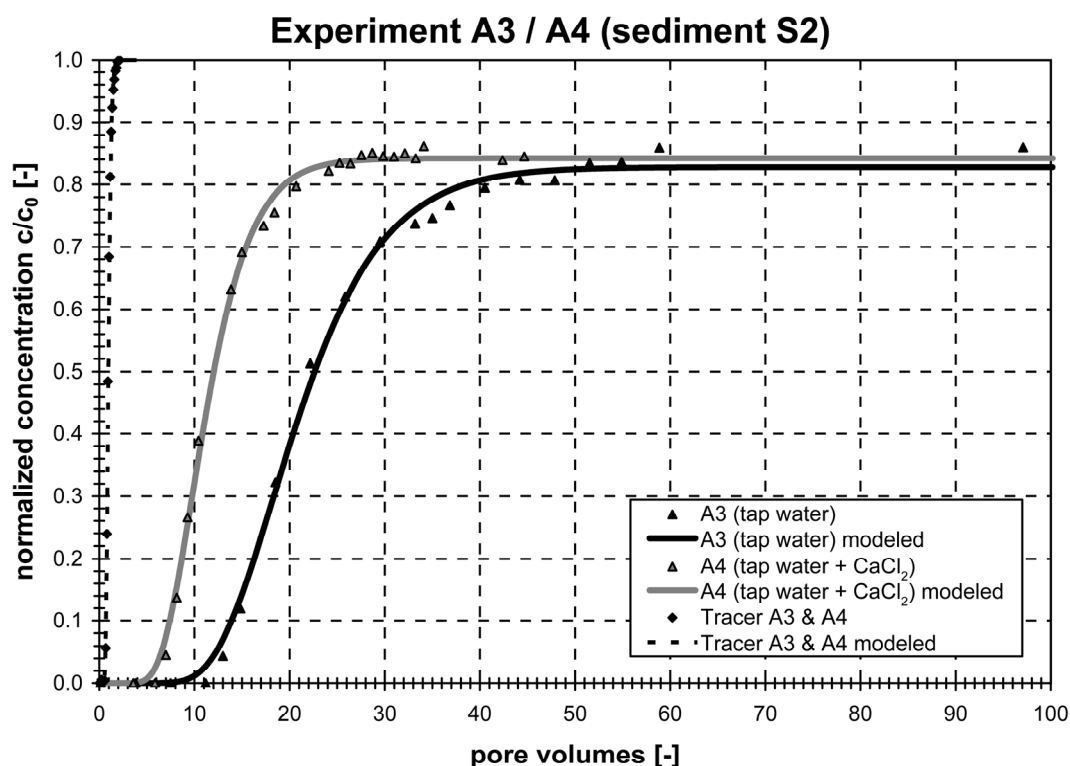


Fig. 3.2 Experimental and modeled breakthrough curves (including tracer tests) of atenolol for sediment S2 with and without CaCl_2 addition (Ca^{2+} concentrations of 40 and 400 mg L^{-1}). Concentrations c of the breakthrough curves were normalized with the initial concentration c_0 . Pore volumes were calculated by normalizing the experiment duration to the ideal breakthrough time of the Cl^- tracer.

Despite differences in the sediment properties, the sorption behavior is very similar for both sediments. Neither the differences in f_{OC} nor in CEC seem to have a noticeable effect. Barron et al. (2009) found considerable differences for the $\log K_{OC}$

values of atenolol and metoprolol between two sorbents (soil and sludge). Further, they report similar to Hyland et al. (2012), and Schaffer et al. (2012) the limitations of the K_{OC} concept for ionizable compounds. Here, it can be confirmed that K_{OC} is not a suitable parameter for comparing and predicting the sorption behavior of organic cations in different aquifers and sediments, since electrostatic interactions are not considered in this approach (Tolls, 2001; Cunningham et al., 2004; Kah and Brown, 2007; Schaffer et al., 2012). As a consequence, the formally calculated K_{OC} changes with the boundary conditions (e.g., ionic strength, pH). In this study, the log K_{OC} decreased from 3.2 to 2.7 (experiment A1/A2) and from 3.5 to 3.2 (experiment A3/A4).

3.3.2 Experiments B: Desorption

Desorption with tap water led to similar curves for both sediments (experiments B1 and B3, Fig. 3.3). After horizontally reflecting the desorption curves, their shapes are qualitatively symmetrical compared to the breakthrough curves in experiment A1 and A3, respectively. Therefore, the sorption behavior is likely to be fully reversible.

The quantitative modeling of the desorption curves with CXTFIT under equilibrium conditions led to similar results for R and K_d when comparing sorption and desorption (Table 3.4 and Table B2). The observed higher values for α in case of desorption compared to sorption are expected to be caused by kinetic effects (Rahman et al. 2003, Worch, 2004). As initial condition in the desorption model the columns were assumed to be in sorption equilibrium with atenolol ($c(x, t_0) = 0.73$ for experiment B1 and 0.85 for experiment B3) and as upper boundary condition the columns were fed with water containing no atenolol ($c_0 = 0$).

Afterwards (experiments B2 and B4), the addition of CaCl_2 resulted in an increase in atenolol concentration (small peak) for both sediments (Fig. 3.3). Due to the higher competition with Ca^{2+} , a new desorption equilibrium is established resulting in an increased desorption. Therefore, strong evidence for cation exchange as the main retardation process for the cationic species of beta-blockers on natural surfaces is apparent.

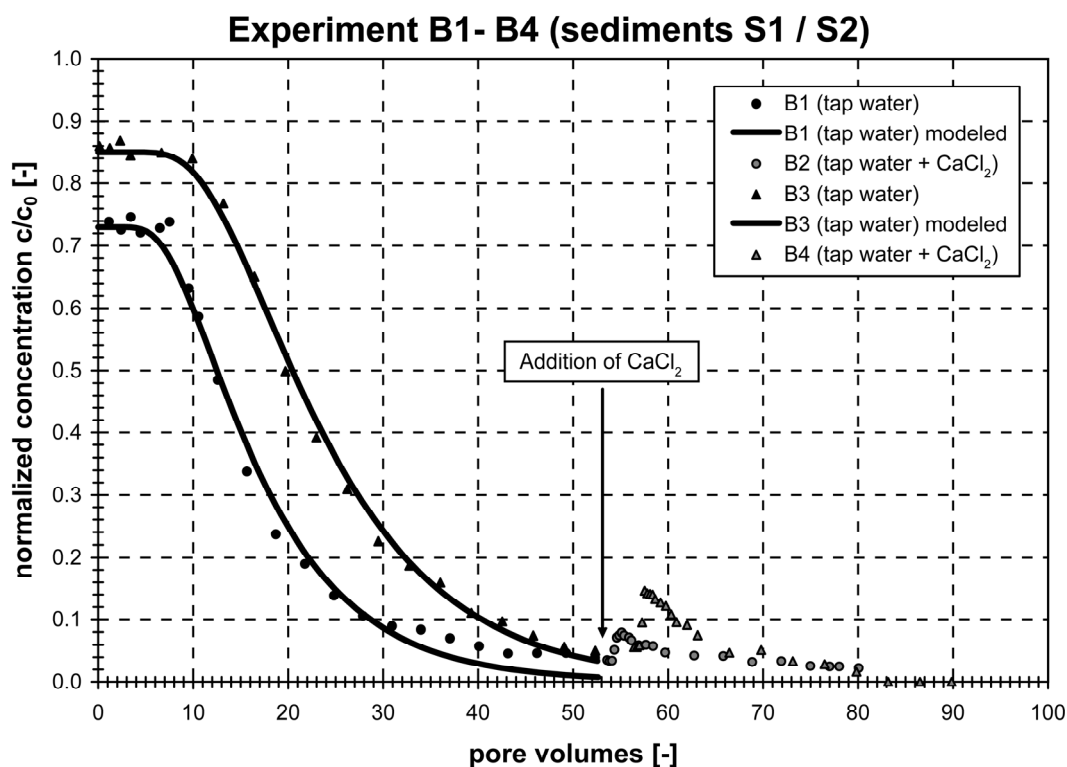


Fig. 3.3 Experimental and modeled desorption curves of atenolol for sediments S1 and S2 with CaCl_2 addition after 53 pore volumes (Ca^{2+} concentrations of 40 and 400 mg L^{-1}). Concentrations c of desorption curves were normalized with the initial concentration c_0 of the previous breakthrough curves. Pore volumes were calculated by normalizing the experiment duration to the ideal breakthrough time of the Cl^- tracer.

3.3.3 Experiments C: Different concentrations of atenolol

No significant influence on the transport behavior of atenolol could be observed despite several orders of magnitude difference in atenolol concentrations at identical conditions (Fig. 3.4). R varied between 4.3 for $c_0 = 500 \text{ } \mu\text{g L}^{-1}$ in experiment C2 and 5.4 for $c_0 = 1 \text{ } \mu\text{g L}^{-1}$ in experiment C1. Due to the independence from the column bulk properties, the obtained K_d values are virtually equal. K_d was 0.8 L kg^{-1} for C1 and C2, 0.9 L kg^{-1} for C3, and 1.0 L kg^{-1} for C4. As with experiments A1–A4, some biodegradation was observed. In experiment C1 the presence of the atenolol metabolite atenolol acid (Radjenović et al., 2008) was confirmed by LC-MS/MS analysis with atenolol acid as reference substance.

The K_d values are considerably lower compared to experiment A3 and A4 with a similar sediment. This is due to increasing concentrations of inorganic cations (ionic strength) resulting in stronger competition at the sorbent. Therefore, the sorption of atenolol to the available exchange sites decreases.

In contrast, K_d values are equal at constant ionic strength. This implies that even at very high concentrations of inorganic cations the affinity of atenolol to the sorbent is independent from its concentration. At the investigated conditions, the calculated K_d^0 of $<0.001 \text{ L kg}^{-1}$ indicates that around 99.9% of the observed total sorption is caused by ionic interactions. Thus, the underlying sorption mechanism is not changing and a linear sorption behavior can be expected over a wide concentration range ($1\text{--}30,000 \mu\text{g L}^{-1}$). Hence, the influence of the concentration ratio of atenolol to inorganic cations on the transport of atenolol is negligible at all environmentally relevant concentrations. Absolute concentrations of involved cations are rather important, since these define the competitive system. Therefore, it is postulated that only very high molar atenolol concentrations in the range of the inorganic cation concentrations should have a noticeable influence on the exchange equilibrium and thus on the transport behavior of beta-blockers.

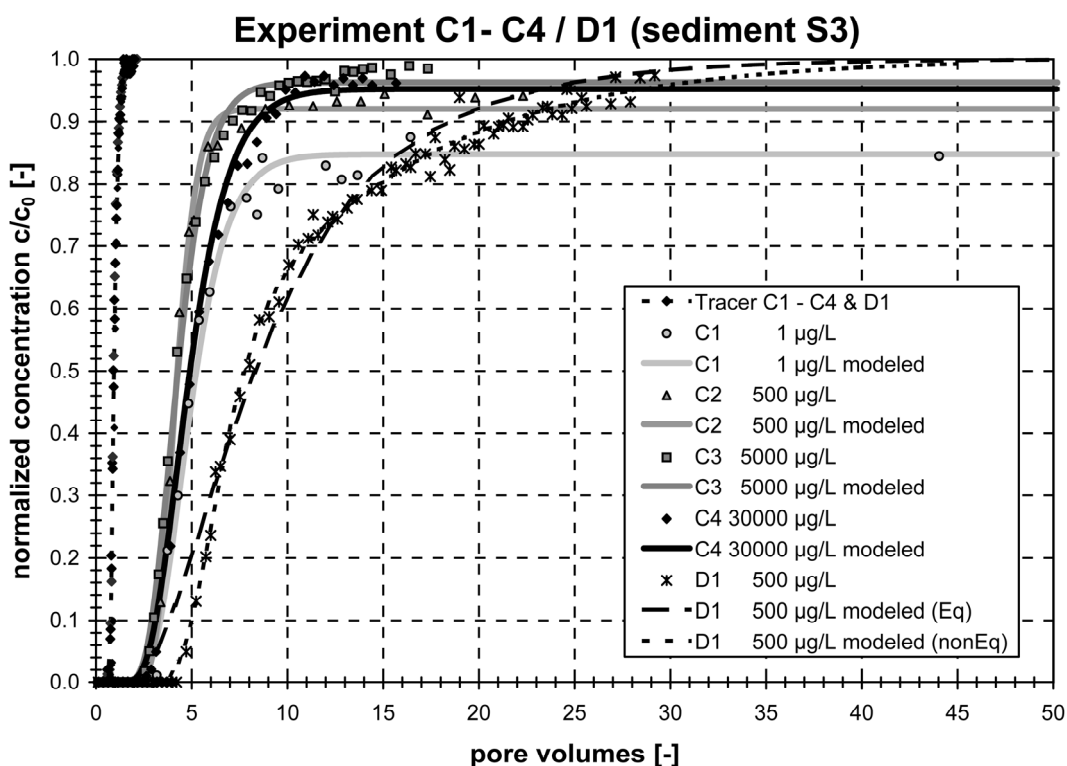


Fig. 3.4 Experimental and modeled breakthrough curves (including tracer tests) for different concentrations of atenolol (C1–C4) and metoprolol (D1, Eq = chemical equilibrium model, nonEq = chemical non-equilibrium model) in sediment S3 at constant ionic strength. Concentrations c of the breakthrough curves were normalized with the initial concentration c_0 . Pore volumes were calculated by normalizing the experiment duration to the ideal breakthrough time of the Cl^- tracer.

Table 3.4 Distribution coefficients and calculated relative proportion of cation exchange.

Exp.	ρ_b [g cm ⁻³]	K_d [L kg ⁻¹]	lower	upper	f_{oc} [g g ⁻¹]	K_d^0 [L kg ⁻¹]	K_d^+ [L kg ⁻¹]	lower	upper	K_d^+/K_d [%]
			K_d [L kg ⁻¹]	K_d [L kg ⁻¹]				K_d^+ [L kg ⁻¹]	K_d^+ [L kg ⁻¹]	
A1	1.76	3.48	3.04	3.97	0.0023	0.0030	3.48	3.04	3.97	99.91
A2	1.76	1.28	1.12	1.45	0.0023	0.0030	1.27	1.12	1.45	99.76
A3	1.94	3.20	2.80	3.67	0.0011	0.0014	3.20	2.80	3.66	99.96
A4	1.94	1.66	1.47	1.88	0.0011	0.0014	1.66	1.47	1.88	99.91
B1	1.76	3.40	2.92	3.95	0.0023	0.0030	3.40	2.92	3.95	99.91
B3	1.94	3.61	3.19	4.08	0.0011	0.0014	3.61	3.19	4.08	99.96
C1	1.74	0.80	0.70	0.92	0.0007	0.0009	0.80	0.69	0.92	99.89
C2	1.72	0.75	0.66	0.85	0.0007	0.0009	0.75	0.66	0.85	99.88
C3	1.68	0.86	0.76	0.96	0.0007	0.0009	0.86	0.76	0.96	99.89
C4	1.74	1.00	0.89	1.13	0.0007	0.0009	1.00	0.89	1.13	99.91
D1_Eq	1.69	2.21	1.94	2.51	0.0007	0.0037	2.20	1.93	2.51	99.83
D1_nonEq	1.69	2.32	2.06	2.60	0.0007	0.0037	2.31	2.06	2.60	99.84

Exp. = experiment, ρ_b = bulk density, K_d = observed distribution coefficient (including 95% confidence limits of R and 5% error for ρ_b and n_e respectively), f_{oc} = fraction of organic carbon, K_d^0 = calculated distribution coefficient attributed to non-polar interactions, K_d^+ = determined distribution coefficient attributed to cation exchange, Eq = equilibrium model, nonEq = non-equilibrium model

3.3.4 Experiment D: Comparison with metoprolol

At $c_0 = 500 \mu\text{g L}^{-1}$ and comparable concentrations of inorganic cations, the breakthrough curve of metoprolol (Fig. 3.4) showed a significantly higher retardation ($R = 10.8$) when compared with atenolol ($R = 4.3$). The obtained K_d of 2.3 L kg^{-1} for metoprolol in experiment D1 was three times higher than in experiment C2 for atenolol ($K_d = 0.8 \text{ L kg}^{-1}$). Biodegradation was not detected (100% of c_0 were retrieved).

The higher sorption of metoprolol compared to atenolol is in accordance with the results of Barron et al. (2009) and Ramil et al. (2010) who also found significantly higher K_d values for metoprolol. However, only around 0.15% of the obtained K_d of metoprolol can be attributed to non-polar hydrophobic partitioning ($K_d^0 = 0.004 \text{ L kg}^{-1}$). Although, partitioning of metoprolol is stronger than for atenolol

(four times higher K_d^0 at pH = 8) it can still be neglected for the prediction of transport parameters in aquifers sediments. This is caused by the very low TOC of these sediments while simultaneously the fraction of the cationic species is very high. Hence, cation exchange is still the controlling sorption process. Despite the similar molecular structure of both molecules, considerable differences remain. The obtained electrostatic contribution of $K_d^+ = 0.8$ of atenolol is significantly lower than for metoprolol with $K_d^+ = 2.3$. This might be caused by several factors, e.g., different molecular geometry and charge density distributions, slightly different pK_a values, and uncertainties caused by the applied $\log K_{ow}$ - $\log K_{oc}$ correlations.

3.4 Conclusions

The transport and sorption behavior of the cationic beta-blockers atenolol and metoprolol in natural aquifer sediments were studied under saturated conditions using column experiments. By means of the application of different sediments and variable concentrations of inorganic cations and beta-blockers, the influence of cation exchange on the transport of protonated organic bases could be characterized. As a result, a first insight into the relevance and the relative contribution of cation exchange processes on the sorption influenced transport of beta-blockers was gained. Eventually, the obtained results offer a better understanding of relevant processes, which have to be considered in future modeling approaches in terms of cationic organics. The major conclusions of the presented study are:

- The dramatically decreased sorption of atenolol at increased Ca^{2+} concentrations indicates that cation exchange processes are highly relevant and play a major role for the transport of cationic beta-blockers in aquifers.
- The desorption curves support the significant role of cation exchange processes on sorption and lead to the expectation that sorption of beta-blockers is fully reversible.
- Due to cation exchange as dominating sorption mechanism, the sole application of $\log K_{ow}$ - $\log K_{oc}$ correlations for non-ionic and hydrophobic compounds is insufficient for cationic beta-blockers. Therefore, the commonly

determined K_d and K_{OC} values in sorption studies at $\text{pH} < \text{p}K_a$ are not transferable to other competitive systems and thus not representative for systems with different concentrations of inorganic cations.

- No influence of the atenolol concentration on the sorption (K_d values) was observed even at comparably high concentrations of competing inorganic cations.
- As a consequence, a variation in the main cation composition in the water phase bears the possibility of beta-blocker remobilization or accelerated transport, e.g. during salt water intrusions in coastal aquifers.

3.5 Acknowledgments

This work partly pertains to a research project jointly funded by Energie Baden-Württemberg (EnBW, Karlsruhe) and by the German Ministry for Environment, Nature Conservation and Nuclear Safety (BMU, project key: 0325111B), with operational support from local Energy and Water Supply Plants (EWB). Further, we acknowledge the German Federal Ministry of Education and Research (promotional reference No. 02WRS1277A, AGRO: "Risikomanagement von Spurenstoffen und Krankheitserregern in ländlichen Karsteinzugsgebieten") for the financial support. The authors would also like to thank Zahra Fona, Susann Kutzner and Anne Niedbala for carrying out several experiments and parts of the sediment analysis.

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Chapter 4

4 Influence of competing inorganic cations on the ion exchange equilibrium of the monovalent organic cation metoprolol on natural sediment

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Citation:

Niedbala, A., Schaffer, M., Licha, T., Nödler, K., Börnick, H., Ruppert, H., Worch, E., 2013. Influence of competing inorganic cations on the ion exchange equilibrium of the monovalent organic cation metoprolol on natural sediment. *Chemosphere* 90(6), 1945–1951.

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Abstract

The aim of this study was to systematically investigate the influence of the mono- and divalent inorganic ions Na^+ and Ca^{2+} on the sorption behavior of the monovalent organic cation metoprolol on a natural sandy sediment at $\text{pH} = 7$. Isotherms for the beta-blocker metoprolol were obtained by sediment-water batch tests over a wide concentration range ($1\text{--}100,000 \mu\text{g L}^{-1}$). Concentrations of the competing inorganic ions were varied within freshwater relevant ranges. Data fitted well with the Freundlich sorption model and resulted in very similar Freundlich exponents ($n = 0.9$), indicating slightly non-linear behavior. Results show that the influence of Ca^{2+} compared to Na^+ is more pronounced. A logarithmic correlation between the Freundlich coefficient K_{Fr} and the concentration or activity of the competing inorganic ions was found allowing the prediction of metoprolol sorption on the investigated sediment at different electrolyte concentrations. Additionally, the organic carbon of the sediment was completely removed for investigating the influence of organic matter on the sorption of metoprolol. The comparison between the experiments with and without organic carbon removal revealed no significant contribution of the organic carbon fraction (0.1%) to the sorption of metoprolol on the in this study investigated sediment. Results of this study will contribute to the development of predictive models for the transport of organic cations in the subsurface.

4.1 Introduction

A large number of anthropogenic organic compounds detected in the aquatic environment (Daughton and Ternes, 1999; Schwarzenbach et al., 2006) are bases with corresponding logarithmic acid constants pK_a above the common pH range of natural freshwaters. Therefore, these bases are protonated and thus positively charged. The most common (micro)-contaminants with these properties belong to the groups of industrial precursors (e.g., alkyl amines), pesticides (e.g., fungicides), pharmaceuticals and cationic surfactants. Despite their high polarity, sorption to environmental surfaces, such as soils, riverbed and aquifer sediments can play a significant role for the removal of these compounds from the aqueous phase, because a variety of these geosorbents (e.g., clays, organic matter) possess a negative surface charge (Kibbey et al., 2007; Schaffer et al., 2012a). Hence, sorption may be a significant attenuation process for organic bases during riverbank filtration, soil aquifer treatment, and artificial groundwater recharge.

In contrast to neutral compounds and the anionic species of organic acids, the experimentally determined distribution coefficients or organic carbon normalized sorption coefficients K_{OC} of organic cations are usually higher than estimated merely from *n*-octanol/water distribution coefficients K_{OW} and $\log D$, respectively (Tolls, 2001; Kah and Brown, 2007; Schaffer et al., 2012a; 2012b). The reason is that pH effects and additional electrostatic contributions to the overall sorption of organic cations (e.g., ion exchange, hydrogen bonding, formation of surface complexes, etc.) cannot be taken into account by predicting the sorption only by means of linear-free energy relationships for hydrophobic partitioning ($\log K_{OW}$ - $\log K_{OC}$ correlations).

For several basic pesticides Weber et al. (2004) reported empirical compound-specific correlations for K_d with selected soil properties (organic matter, clay content, pH). However, this approach only gave poor fit qualities suggesting a more complex sorption mechanism for basic pesticides. An extended predictive semi-empirical model based on regressions for organic bases was proposed by Franco and Trapp (2008) and Franco et al. (2009). This recent modeling approach allows considering the pH dependent speciation of the sorbates in solution and generally improves the prediction for basic compounds (Franco and Trapp, 2008; Franco et al., 2009; Schaffer et al., 2012a). However, the obtained results are still not valid for all compounds and

at different boundary conditions (Schaffer et al., 2012a). This is because ionic interactions and especially cation exchange processes are not explicitly considered therein. Schaffer et al. (2012b) demonstrated the dominating role of cation exchange processes for two cationic beta-blockers at pH = 8 and quantified their contribution to the whole sorption process with >99%. Consequently, sorption of organic cations onto environmental media mainly depends on (1) the organic molecule (e.g., hydrophobicity, type and location of protonated moiety, molecule size), (2) the composition of the aqueous phase (e.g., pH, ionic content) and, (3) the composition and type of the sorbent (e.g., clay content and type, organic matter) (Calvet, 1989; Limousin et al., 2007). As the influencing variables are numerous, it is necessary to address them individually. In this study, the influence of the ionic composition of the aqueous phase (No. 2) is addressed. Strong effects of competing inorganic cations were earlier shown by Brownawell et al. (1990), Nicholls and Evans (1991), Polubesova et al. (1997), Laird and Fleming (1999), Bilgiç (2005), Sassman and Lee (2005), Bi et al. (2006), ter Laak et al. (2006), Schaffer et al. (2012b), and Droge and Goss (2012). In general, a reduced sorption for organic cations on different geosorbents with increasing concentrations of competing cations was observed.

Sorption models considering cation exchange or binding as surface complexes to negatively charged sites were introduced and applied for different organic cations by several authors (e.g., Nir et al., 1986; Margulies et al., 1988; Brownawell et al., 1990; Rytwo et al., 1995; Fábrega et al., 1998; 2001). The common drawback of these models is, however, the use of an inverse optimization procedure. That means the models are non-predictive since the solutions are best fitted into measured isotherm data. To date, the influence of changing boundary conditions, including sorption in different competitive systems, cannot be modeled predictively.

The prerequisite for creating suitable models for competitive sorption of organic cations based on mechanistic principles is the understanding of all involved processes and their dependences from boundary conditions together with a sufficient mathematical description. Beside the pH, which determines the speciation of the sorbates and the variable surface charges, knowledge on the competition from inorganic cations is most essential. Among the few studies available today, Bäuerlein et al. (2012) and Droge and Goss (2012) recently demonstrated and quantified the

changed sorption behavior of organic cations caused by competition with different inorganic cations on ion exchange polymers and organic matter, respectively. Brownawell et al. (1990), Nicholls and Evans (1991), Figueroa et al. (2004), ter Laak et al. (2006), Bi et al. (2006), Schaffer et al. (2012b) investigated semi-quantitatively the sorption of organic cations by deliberately varying background electrolyte concentrations. Further studies with main focus on competitive sorption between organic and inorganic cations, especially conducted with natural sediments are not yet available.

Therefore, the aim of this study is the systematic investigation of cation exchange processes for organic cations on natural sediment. Isotherms for the basic beta-blocker metoprolol were obtained over a wide concentration range (1–100,000 $\mu\text{g L}^{-1}$) starting from environmentally relevant concentrations on a sandy aquifer material at $\text{pH} = 7$. Solely the concentrations of the competing inorganic cations Na^+ and Ca^{2+} in solution were varied within relevant ranges of freshwater. Isotherm parameters were calculated, compared, and related to the type and concentration of the considered inorganic cation. Additionally, the influence of complete organic carbon removal from the sediment on the sorption of metoprolol is reported. The experiments shall provide further information on the boundary conditions for the cation exchange equilibrium of organic cations. Due to the systematic consideration and quantitative description of the influence of competing cations, valuable contributions for future model developments are expected.

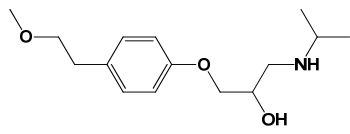
4.2 Materials and methods

4.2.1 Chemicals

Metoprolol (physicochemical properties shown in Table 4.1) as tartrate salt was purchased from Sigma-Aldrich (Steinheim, Germany) with a minimum content of 99%. One of its major metabolites metoprolol acid and the internal reference standard metoprolol- D_7 were purchased from LGC Promochem (Wesel, Germany). All other used fine chemicals were of high purity (>98%, analytical grade) and were purchased from VWR (Darmstadt, Germany). Ultrapure water for the preparation of

all solutions was obtained from a combined water purification system consisting of Elix 5 and Milli-Q Gradient A10, both from Millipore (Schwalbach, Germany).

Table 4.1 Physicochemical properties of the sorbate and sorbent.

Compound	Structure	^{a, b} pK_a	^{a, c} $\log K_{ow}$	^{a, d} $\log K_{ow}^+$	^e $\log D_{pH=7}$
Metoprolol	 CAS number 37350-58-6	9.63	1.95	-1.10	-0.81

Mineral composition of the sorbent			Physicochemical properties of the sorbent	
Mineral class	Qualitative	Quantitative [% w/w]		
Silicates	Quartz	40	pH (H ₂ O)	8.8
	Hornblende	3	pH (CaCl ₂)	8.1
	Actinolite	1	TOC (%)	0.1
	Diopside	1	CEC (cmol _c kg ⁻¹)	4.4
Phyllo-silicates	Muscovite	9		
	Smectite	6		
	Chlorite	4		
Feldspars	Biotite	2		
	Plagioclase	20		
	Microcline	11		
	Orthoclase	3		

TOC = total organic carbon, CEC = potential cation exchange capacity at pH = 8.1.

^a Caron et al. (1999).

^b pK_a value refers to pK_a value for the conjugate acid (protonated species).

^c $\log K_{ow}$ value refers to the neutral species.

^d $\log K_{ow}^+$ value refers to the cationic species.

^e $\log D$ value refers to all species at pH = 7. SciFinder Scholar 2007 predicted values, calculated using Advanced Chemistry Development (ACD/Labs) Software V 11.02 (1994–2012 ACD/Labs).

4.2.2 Sorbent

The sediment used originates from a Pleistocene and Holocene alluvial fan, which is part of a shallow aquifer in Sindos, Northern Greece. The sediment can be assigned to the texture class of medium sand. The homogenized bulk sediment (<2 mm) was

used in all experiments. Preliminary experiments with various particle size fractions of the sediment exhibited no significant differences in sorption (Fig. C1).

Selected physicochemical properties of the sediment are listed in Table 4.1, further can be found in Schaffer et al. (2012b) (denoted as sediment S3). Additionally, the mineral composition of the bulk sediment was determined by powder X-ray diffraction (XRD) with a Philips X'Pert MPD diffractometer (PANalytical, Almelo, Netherlands), equipped with a PW 3373/00 Cu LFF X-ray tube and a PW 3050/10 goniometer. The dominant mineral classes are silicates, feldspars, and phyllosilicates (Table 4.1). Among the detected mineral phases, the clay minerals chlorite and smectite are expected to bear the highest potential for sorption and cation exchange, respectively, of organic cations due to their high cation exchange capacities (CEC). Several minerals in the sediment provide a much lower CEC, but should also carry negative net surface charges under typical groundwater pH conditions, since their point of zero charge (pH_{pzc}) is low ($\text{pH}_{\text{pzc}} < 5$; Scheffer and Schachtschabel, 2010). In addition, the total organic carbon (TOC) content of the sediment is very low, which is vital for separating electrostatic interactions from hydrophobic partitioning.

The pH of the sediment was adjusted over a two week period with 1 M HCl to $\text{pH} = 7$ in order to ensure stable pH conditions during the batch experiments and the sole existence of the cationic metoprolol species. Afterwards, the sediment was washed with pure water and dried at $40\text{ }^{\circ}\text{C}$ for 24 h. The final pH was confirmed by measuring the pH in its aqueous suspension.

For a subsample of the aquifer material, the organic matter of the sediment was completely removed with the method after Gao et al. (1998) using 30% H_2O_2 . This was done to assess the contribution of organic matter on the sorption of metoprolol. The TOC of the sediment, before and after treatment with H_2O_2 was determined with a TOC-L analyzer (Shimadzu, Duisburg, Germany) utilizing the suspension method combined with catalytic oxidation at $680\text{ }^{\circ}\text{C}$.

4.2.3 Model water

For the isotherm determination, solutions with six different concentrations of metoprolol between $3.7\text{E-}06$ and $3.7\text{E-}01$ mmol L^{-1} ($1\text{--}100,000$ $\mu\text{g L}^{-1}$) were prepared in ultrapure water. Different competitive conditions were realized by adding defined amounts of NaCl or $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ to the metoprolol containing solutions. The target concentrations of each inorganic cation were 0.37, 3.7, and 37 mmol L^{-1} . The selected concentrations cover almost entirely the typical stream water concentration ranges in Europe for Na^+ ($c = 0.01\text{--}175$ mmol L^{-1} , median: 0.28 mmol L^{-1}) and Ca^{2+} ($c = 0.006\text{--}14.8$ mmol L^{-1} , median: 1 mmol L^{-1}) (Salminen et al., 2005). An overview of all applied concentrations and corresponding activities is given in Table 4.2.

Table 4.2 Freundlich regression parameters of all batch experiment series.

Water matrix	Added electrolyte			Freundlich regression parameters							
	c	$\log c$	$\log a$	$\log K_{Fr}$	lower $\log K_{Fr}$	upper $\log K_{Fr}$	n	lower n	upper n	R^2	SSE
	[mmol L^{-1}]				[L kg^{-1}] ⁿ			[-]		[-]	[-]
pure water		-		1.20	1.10	1.30	0.92	0.86	0.98	0.9962	9.9E-02
			-	1.20	1.10	1.30	0.92	0.86	0.99	0.9963	9.8E-02
pure water + NaCl	0.37	-0.43		1.04	0.95	1.13	0.87	0.83	0.91	0.9989	1.6E-02
			-0.44	1.05	0.96	1.14	0.87	0.83	0.91	0.9989	1.6E-02
pure water + NaCl	3.7	0.57		0.98	0.91	1.06	0.91	0.88	0.94	0.9994	9.5E-03
			0.54	1.01	0.94	1.08	0.91	0.88	0.94	0.9994	9.6E-03
pure water + NaCl	37	1.57		0.78	0.67	0.90	0.93	0.89	0.98	0.9986	2.2E-02
			1.49	0.86	0.75	0.96	0.93	0.89	0.98	0.9986	2.2E-02
pure water + CaCl_2	0.37	-0.43		0.97	0.88	1.06	0.91	0.88	0.95	0.9990	1.5E-02
			-0.50	0.98	0.89	1.07	0.92	0.88	0.95	0.9990	1.5E-02
pure water + CaCl_2	3.7	0.57		0.76	0.60	0.93	0.92	0.85	0.99	0.9970	4.7E-02
			0.38	0.81	0.65	0.97	0.92	0.85	0.99	0.9970	4.7E-02
pure water + CaCl_2	37	1.57		0.50	0.16	0.84	0.89	0.75	1.03	0.9869	1.9E-01
			1.13	0.60	0.27	0.93	0.89	0.75	1.03	0.9869	1.9E-01

SSE = sum of squared errors, see Eq. (C2)

4.2.4 Batch-equilibrium experiments

Isotherms were determined using the batch equilibrium method. Every isotherm point represents the average of three experiments (triplicate). As observed in preliminary tests an experimental duration of 72 h was found sufficient to ensure equilibrium conditions without any mass loss due to biotransformation. The latter was further monitored by the absence of the transformation product metoprolol acid. Only when the sediment-water batch tests were carried out for more than 5 days significant concentrations of metoprolol acid were detected (around 5–10% of c_0 from metoprolol). All batch experiments were conducted with a constant sediment-to-liquid ratio of 1:10 ($m:V$) in 40 mL glass vials with PTFE-lined caps or 100 mL glass bottles (both borosilicate glass), if pre-concentration with solid phase extraction (SPE) prior to analysis was necessary ($c_0 = 1$ and $10 \mu\text{g L}^{-1}$). The metoprolol solutions containing the respective electrolyte were added to the dry sediment. The vials were sealed and shaken in a horizontal shaker (KS 501D, IKA, Staufen, Germany) with 250 rpm at 20 ± 1 °C. After the equilibration time, both phases were separated by centrifugation in glass centrifuge tubes for 10 min at 4,000 rpm (Centrifuge 5804, Eppendorf, Hamburg, Germany).

After analysis, the sorbed amount q_{eq} [M M^{-1}] was calculated from the mass loss of metoprolol in the solution with:

$$q_{eq} = \frac{V_0 (c_0 - c_{eq})}{m_A} \quad (4.1)$$

where c_{eq} [M L^{-3}] is the equilibrium concentration in the aqueous phase, c_0 [M L^{-3}] is the initial concentration in the aqueous phase, V_0 [L^3] is the volume of aqueous phase, and m_A [M] is the mass of the sorbent.

4.2.5 Chemical analysis

4.2.5.1 Analysis of metoprolol and metoprolol acid

The samples were kept frozen at -18 °C until analysis. SPE was used for samples with the lowest initial concentrations of metoprolol ($1 \mu\text{g L}^{-1}$, $10 \mu\text{g L}^{-1}$) and conducted according to Nödler et al. (2010) by using Oasis HLB cartridges (6 mL, 500 mg; Waters, Eschborn, Germany). Prior to extraction, samples were spiked with 250 ng of the

internal standard metoprolol-D₇. Samples with higher initial concentrations of metoprolol were diluted into the operating range of the linear calibration curve (2.5–1,000 µg L⁻¹) and spiked with the same amount of internal standard. The quantification of metoprolol and metoprolol acid was performed by HPLC-ESI-MS/MS as described in Barbieri et al. (2012). Before analysis, all samples, sample extracts (from SPE), and standard solutions were centrifuged at 1500 rpm (Christ RVC 2-18, Fisher Scientific, Schwerte, Germany) for 30 min at room temperature. Nine concentration levels (2.5–1,000 µg L⁻¹) were used for the calibration and the correlation coefficients exceeded 0.99.

4.2.5.2 Analysis of inorganic cations

The determination of inorganic cations (Na⁺, K⁺, Mg²⁺, Ca²⁺) was conducted by using a DX-500 Ion Chromatography System with conductometric detection and electrochemical suppression (Dionex, Sunnyvale, USA). This isocratic system runs with 20 mM methanesulfonic acid as the eluent with a flow rate of 0.45 mL min⁻¹ at a temperature of 44 °C. Separation was achieved by using an IonPac CS12 column system (200 × 3 mm, 5 µm; Dionex).

4.3 Results and discussion

4.3.1 Role of organic matter

The organic carbon measurements confirmed the complete removal of organic matter from the sediment below the analytical detection limit of TOC = 100 µg g⁻¹. The comparison of sorption between TOC-free and untreated sediment allows investigating the contribution of organic matter on the sorption of the cationic metoprolol species.

The sorbed amount of metoprolol on the sediment was 571.7±34.5 µg kg⁻¹ (95% confidence intervals) before and 546.1±11.5 µg kg⁻¹ after H₂O₂ treatment. Thus, no significant difference was detected. As a consequence, sorption onto organic carbon (partitioning, complexation and sorption on sites with variable charges) can be neglected for this sediment and coulomb forces between the cation and the

negatively charged surfaces control the sorption of metoprolol at pH=7. Furthermore, the data confirm the results from Schaffer et al. (2012b) who highlighted the dominating role of cation exchange and the minor influence of organic matter for the sorption of atenolol and metoprolol on aquifer sediments low in TOC fraction relative to other exchange sites (e.g., clays).

4.3.2 Influence of competing inorganic ions

All sorption data fitted well with the Freundlich sorption model (Fig. 4.1, Table 4.2) and were evaluated applying a linear least-square regression of the linearized Freundlich equation (for more details see Appendix C2, Figs. C2–C8):

$$\log q_{eq} = \log K_{Fr} + n \cdot \log c_{eq} \quad (4.2)$$

where K_{Fr} is the Freundlich coefficient and the Freundlich exponent n describing the isotherm's non-linearity. For low concentrations in the environmentally relevant range the data may be approximated with a linear isotherm. However, in order to describe all investigated concentrations with one equation the Freundlich model was used. This model is commonly employed for the description of sorption (including ion exchange) on heterogeneous sorbents with different sorption sites, such as the used bulk sediment (Sposito, 1980; Schwarzenbach et al., 2003; Droge and Goss, 2012). Freundlich behavior for organic cation sorption onto geosorbents was also observed by Baker und Luh (1971), Zachara et al. (1986), Brownawell et al. (1990), Nicholls and Evans (1991), Kulshrestha et al. (2004), Sassman and Lee (2005), Burgos and Pisutpaisal (2006), ter Laak et al. (2006), Bäuerlein et al. (2012), Droge and Goss (2012). The obtained average of $n = 0.9$ indicates that sorption of metoprolol to the aquifer material is slightly non-linear in the investigated concentration range. Very similar values for n between all experiments allow the direct comparison of K_{Fr} for all isotherms (Table 4.2). Furthermore, identical binding mechanisms to the exchange sites under Na^+ and as well as under Ca^{2+} competition can be assumed due to the same isotherm non-linearity. Comparable n were reported for the sorption of several organic cations onto organic matter (Pahokee peat) by Droge and Goss (2012). The values in their study ranged between $n = 0.75$ and $n = 0.96$.

From the thermodynamic point of view, the use of activities instead of concentrations would be more appropriate (Trapp et al. 2010). Nevertheless, the comparison of the isotherms plotted against c_{eq} with the isotherms plotted against the equilibrium activity of metoprolol a_{eq} (using Davies activity coefficients) in solution revealed no significant difference for $\log K_{Fr}$ and n (Fig. 4.1, Table 4.2).

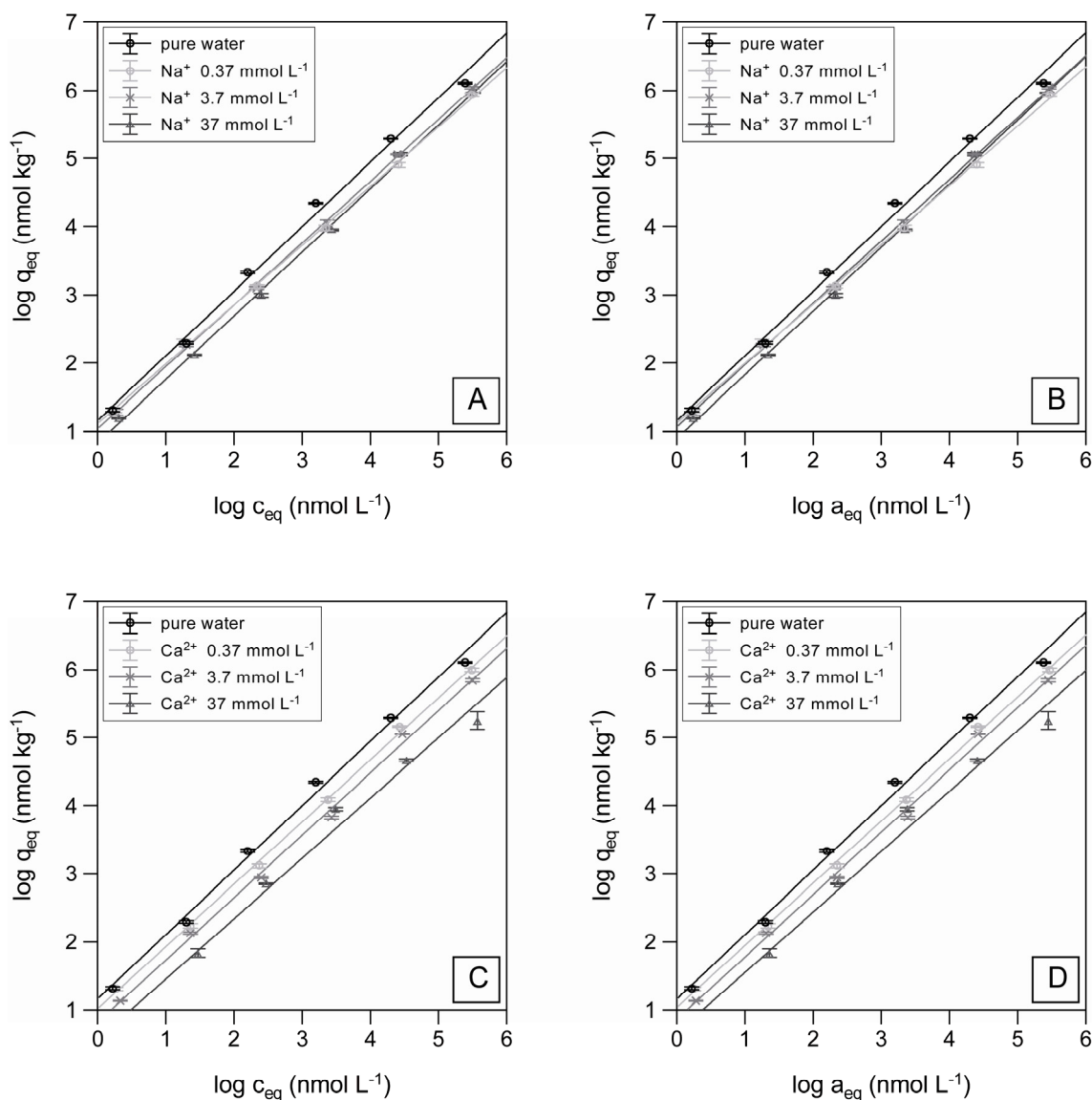


Fig. 4.1 A–B: Freundlich sorption isotherms of metoprolol on sandy aquifer sediment from water with various Na⁺ concentrations or Na⁺ activities at pH = 7.0; **C–D:** Freundlich sorption isotherms of metoprolol on sandy aquifer sediment from water with various Ca²⁺ concentrations or Ca²⁺ activities at pH = 7.0. Data points represent the average of batch triplicates. Error bars show the range of measured minimum and maximum values.

In general, decreasing sorption of metoprolol to the aquifer material with increasing concentrations of Na^+ and Ca^{2+} was observed compared to the reference isotherm using pure water. According to the cation exchange theory, the free inorganic cations in solution compete with metoprolol for the negatively charged surface sites. For equal molar concentrations of Na^+ and Ca^{2+} , the sorbed amounts of metoprolol under Ca^{2+} competition are significantly smaller than for Na^+ . This confirms the expected behavior from the theory as Ca^{2+} cations should have a higher affinity to exchange sites than Na^+ due to their higher valence. Furthermore, the larger shifts (y-axis) of the Ca^{2+} isotherms than for the Na^+ isotherms at increasing concentrations also demonstrate the more efficient displacement of exchangeable cations from the exchanger with Ca^{2+} than with Na^+ (Fig. 4.1).

In order to compare and quantify the role of competing Na^+ and Ca^{2+} on the exchange equilibrium, the obtained sorption coefficients were correlated with the inorganic cation concentrations in solution (Fig. 4.2). Figure 4.2A shows $\log K_{Fr}$ as a function of the logarithmized concentration $\log c$ and Figure 4.2B as a function of the logarithmized activity $\log a$. For both considered inorganic cations a linear correlation for the logarithmized variables was found. Similar dependences between electrolyte concentration and sorption coefficients were observed earlier by Figueroa et al. (2004) for the cationic species of oxytetracycline on clay, and for several organic cations on exchange polymers (Bäuerlein et al., 2012), and on organic matter (Droge and Goss, 2012).

As mentioned above, the influence of Ca^{2+} on the exchange equilibrium of metoprolol is stronger than for Na^+ . At equal molar concentrations of Ca^{2+} and Na^+ K_{Fr} of metoprolol suffering Ca^{2+} competition is lower than for Na^+ competition. Figure 4.2 investigates how this difference is maintained with rising concentrations of Na^+ and Ca^{2+} . Surprisingly, Ca^{2+} still shows almost twice the effect than Na^+ , although the classical ion exchange equation would suggest an inverted image (Droge and Goss, 2012). The comparison of the regression lines shows that the slopes differ by a factor of around two (1.82). Furthermore, the influence (slope) for Ca^{2+} is in the same order of magnitude (-0.28 vs. -0.23) compared to the results reported by Schaffer et al. (2012b). There, the sorption of atenolol on a very similar sediment was investigated under varying Ca^{2+} concentrations (1 to 10 mmol L^{-1}) in a column experiment.

The hypothetical point of intersection of the Na^+ and Ca^{2+} regression lines reflecting a reference point below which competition should have no further influence was calculated with $\log c = -1.27$ ($c = 0.054 \text{ mmol L}^{-1}$) and $\log K_{Fr} = 1.17$ ($K_{Fr} = 14.85$). This point corresponds very well with the measured $\log K_{Fr} = 1.2$ ($K_{Fr} = 15.85$) in pure water and thus without competition.

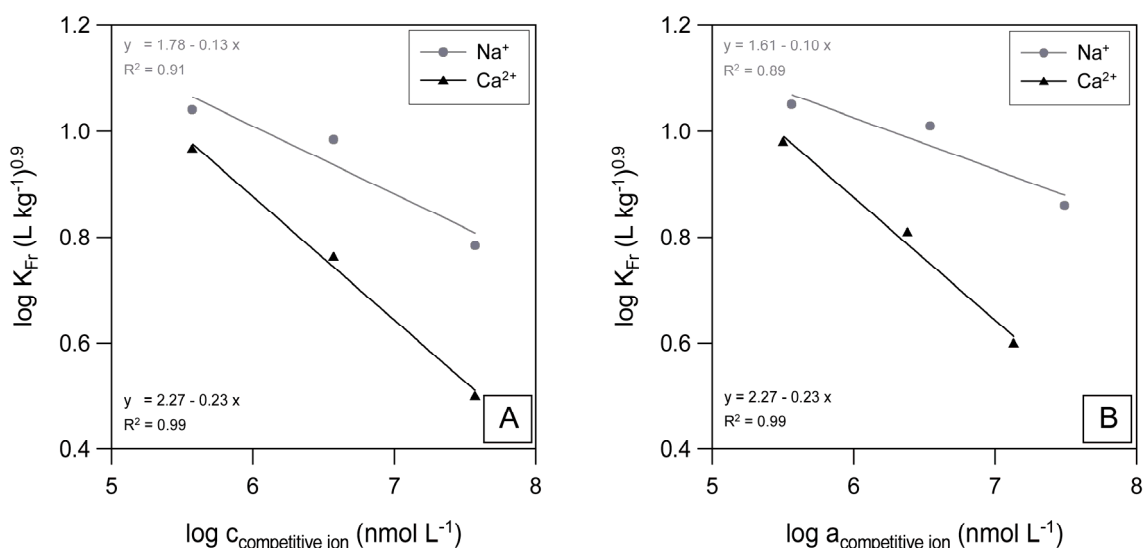


Fig. 4.2 A: Relation between the Freundlich coefficients $\log K_{Fr}$ and the concentration of the competing ions Na^+ and Ca^{2+} ; B: Relation between the Freundlich coefficients $\log K_{Fr}$ and the activity of the competing ions Na^+ and Ca^{2+} .

Finally, the comparison between $\log K_{Fr}$ expressed as a function of a (Fig. 4.2B) instead of a function of c leads to very similar results. The dependencies are identical and only the slope ratio of 2.36 between Ca^{2+} and Na^+ differs slightly. Thus, the use of concentrations instead of activities for simplifying the isotherm evaluation is reasonable within the considered concentration range and allows a better comparability with literature data.

4.4 Summary and conclusions

Batch equilibrium sorption experiments with metoprolol as organic cation onto natural sediment were carried out under different competitive conditions with respect to the background concentrations of the inorganic cations Na^+ and Ca^{2+} . All obtained isotherms could be characterized sufficiently by the application of the

Freundlich sorption model in the investigated concentration range. Furthermore, the role of organic matter on organic cation sorption was tested. Due to the systematic and defined variation of Na^+ and Ca^{2+} concentrations and the constancy of all other parameters, the direct evaluation of competition between inorganic and organic cations was possible. Two logarithmic relationships were found in this systematic study. Eventually, the results are an important step for understanding and predicting the sorption of organic cations. On the basis of the results presented in this study, the following conclusions can be drawn:

- The investigations on the sediment's organic carbon demonstrate that for natural sediments low in organic carbon relative to other constituents potentially acting as cation exchangers (e.g., clays) the sorption of the cationic metoprolol species can be neglected.
- Competitive sorption isotherms generally show a decreasing sorption of metoprolol with increasing background concentrations of the inorganic cations Na^+ and Ca^{2+} . Additionally, a decrease of $\log K_{Fr}$ values with increasing concentrations of competing cations was found. These results confirm that cation exchange is the main mechanism for metoprolol sorption onto geosorbents low in organic carbon at $\text{pH} < \text{p}K_a - 1$.
- Isotherms show that the influence of Ca^{2+} compared to Na^+ on the sorption of metoprolol is more pronounced with increasing concentrations.
- For all experiments a similar Freundlich coefficient of $n = 0.9$ was found. This may be attributed to identical binding mechanisms and the sorption onto the same sorption sites.
- The evaluation of sorption data based on either activity or concentration leads to very similar results. Thus, the concentration commonly used to interpret isotherm data seems to be an adequate approximation. It certainly simplifies data evaluation within the investigated electrolyte concentration range and allows data comparison between different authors even when they have not stated the full water chemistry but evaluated isotherms based on concentrations.

- Finally, this study showed a logarithmic correlation between the Freundlich coefficient K_{Fr} and the concentration/activity of the inorganic competing ions (Na^+ and Ca^{2+}). This enables the sorption behavior prediction for metoprolol on the investigated sediment at different competing concentrations.

4.5 Acknowledgments

This work partly pertains to a research project jointly funded by Energie Baden-Württemberg (EnBW, Karlsruhe) and by the German Ministry for Environment, Nature Conservation and Nuclear Safety (BMU, project key: 0325111B), with operational support from local Energy and Water Supply Plants (EWB). Further, we acknowledge the German Federal Ministry of Education and Research (promotional reference No. 02WRS1277A, AGRO: "Risikomanagement von Spurenstoffen und Krankheitserregern in ländlichen Karsteinzugsgebieten") for the financial support.

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Chapter 5

5 A new generation of tracers for the characterization of interfacial areas during supercritical carbon dioxide injections into deep saline aquifers: Kinetic interface-sensitive tracers (KIS tracer)

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Citation:

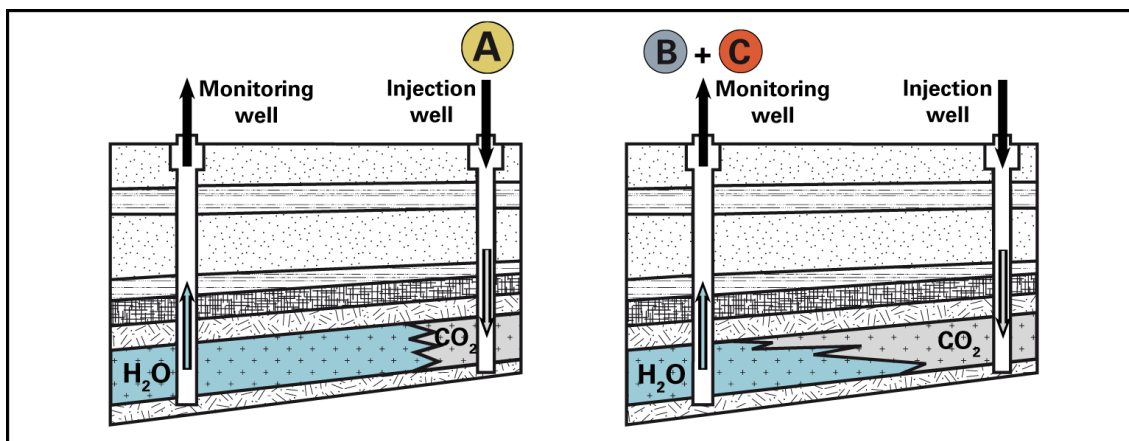
Schaffer, M., Maier, F., Licha, T., Sauter, M., 2013. A new generation of tracers for the characterization of interfacial areas during supercritical carbon dioxide injections into deep saline aquifers: Kinetic interface-sensitive tracers (KIS tracer). *International Journal of Greenhouse Gas Control* 14, 200–208.

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Abstract

The storage of supercritical carbon dioxide in deep saline aquifers requires new techniques to assess plume spreading, storage efficiencies and operational strategies after and during injections. In this work, a new class of reactive tracers (KIS tracers) planned to be used for the characterization of interfacial areas between supercritical CO_2 and formation brine is presented. The implementation of a time-dependent hydrolysis reaction at the interface enables to investigate the development of the CO_2 /brine interface. Besides the basic concept for these novel tracers and the methodology for a suitable target molecular design, the desired tracer properties as well as the exemplary synthesis of first promising compounds are presented here. Additionally, the first experimental results of an analog study in a static two-phase batch system are shown and evaluated with a newly developed macroscopic model. Subsequently, the numerical forward modeling of different functions for the interfacial area change is described. The first results are promising and show the potential for new applications of KIS tracers after further research.

Graphical abstract

Nomenclature

c	concentration of reaction product in water phase
c_0	initial concentration of reaction product in water phase
c_a	tracer concentration in scCO ₂
c_i	tracer concentration at interface
$c_{i,max}$	tracer concentration at saturated interface
k_1	hydrolysis reaction rate constant in water (one-phase system)
k_a	effective hydrolysis reaction rate constant (two-phase system)
m	slope of a line
p	pressure
p_c	pressure at critical point
pH	pH value
pK_a	logarithmic acid dissociation constant
q	specific mass flux across interface
scCO ₂	supercritical carbon dioxide
t	time
A	interfacial area size
A_{eff}	effective interfacial area
A_{scCO_2}	reactive Tracer in scCO ₂ phase (reactant)
B_{H_2O}	reaction product 1 in water phase
C_{H_2O}	reaction product 2 in water phase
D	diffusion coefficient
D_{H_2O}	diffusion coefficient in water
D_{scCO_2}	diffusion coefficient in scCO ₂
D_{OW}	pH-dependent <i>n</i> -octanol/water distribution coefficient
$E_T(30)$	empirical solvent polarity indicator (based on solvatochromism)
K_L	Langmuir sorption coefficient
K_{OW}	<i>n</i> -octanol/water distribution coefficient
NAPL	non-aqueous phase liquid
T	temperature
T_c	temperature at critical point
V	volume of water phase
λ	fluorescence: excitation wavelength → emission wavelength

5.1 Introduction

The storage of CO₂ into geological formations, such as unmineable coal beds, depleted oil or gas reservoirs, sedimentary basins and deep saline aquifers is recently one of the most promising technologies to mitigate anthropogenic greenhouse gas emissions into the earth's atmosphere (Lackner, 2003; Bachu and Adams, 2003; IPCC, 2005, 2007). Deep saline aquifers are considered as the most potential sequestration sites of CO₂ due to their large storage capacities and wide presence compared with other geological sequestration alternatives (Lackner, 2003; IPCC, 2005). The global storage capacity of these aquifers is estimated to be in the order of up to 10 teratons (IEA, 2001; Bachu and Adams, 2003).

When CO₂ is injected as supercritical fluid (scCO₂) above its critical point ($p_c = 7.39$ MPa, $T_c = 31.1$ °C) it has a lower density than the formation brine. Therefore, it is buoyant with respect to the brine and flows unevenly upwards until it reaches the top of the aquifer, usually represented by overlying and sealing caprocks. At this point the CO₂ is able to continue the migration only in lateral direction. Here, four trapping mechanisms play a major role (IPCC, 2005): (1) structural and stratigraphic trapping: hindrance of vertical CO₂ migration by impermeable caprock (static trapping) or very slow CO₂ migration over long distances in open systems (hydrodynamic trapping); (2) capillary or residual trapping: retention of CO₂ by capillary forces as immobile phase in the pore space, disconnection from initial plume at the edges; (3) solubility trapping: dissolution of CO₂ in brine, decreasing solubility with increasing temperature and salinity of brine (20–60 g L⁻¹); (4) geochemical trapping: reaction of dissolved CO₂ in reservoir leads to formation of HCO₃³⁻/CO₃²⁻ species (ionic trapping) or precipitation of carbonate minerals at rock surfaces (mineral trapping) at higher pH.

Due to the different time scales ($t_{(1)} = t_{(2)} < t_{(3)} \ll t_{(4)}$) dissolution and mineral trapping processes can be neglected during and shortly after the injection (IPCC, 2005; Juanes et al., 2007; Ide et al., 2007). Therefore, several authors assume sharp interfaces for the existing three-phase system scCO₂/brine/rock in their modeling approaches (Juanes et al., 2007; MacMinn and Juanes, 2009; Dentz and Tartakovsky, 2009). This approximation appears to be plausible from the physicochemical point of view, since as a result of the low solubility between the phases a very high concentration

gradient exists between them. More concisely, a several angstroms thick interphase is formed due to the diffusion of scCO₂ into the brine phase (Tewes and Boury, 2005).

To assess the fate of CO₂ during and after injection into these aquifers, an understanding of spreading, mixing and plume migration is fundamental. Particularly, knowledge on the size, the amount, and the shape of the injected CO₂ plume is important to provide more information on the trapping effectiveness in the formation.

Dissolution of scCO₂ into the brine is limited by the interfacial area. Thus, numerous subsequent chemical processes (e.g., mineral dissolution, precipitation) are also directly affected. Therefore, the extent of the interfacial area between injected scCO₂ and brine is of great interest. The larger the interface, the larger is the reacted or dissolved mass. In most cases, it is desired to maximize this area to increase the storage effectiveness in terms of long-term trapping. During injections the interfacial area increases with time due to mixing, spreading and dispersive processes (Dentz and Carrera, 2005; Dentz and Tartakovsky, 2009). Therefore, novel tracers, which are able to describe and to characterize the spatial and temporal development of the plume and its interface in the reservoir, are required.

Up to now, such time-dependent tracers for reservoir studies are not available. Current studies are limited to equilibrium tracers. On the one hand, volume-sensitive partitioning tracers are used to quantify the amount or the saturation of immiscible hydrophobic phases (e.g., NAPLs or scCO₂) in porous multiphase systems under equilibrium conditions. Frequently used compounds are (Noordman et al., 2000): alcohols (Dwarakanath and Pope, 1998), gases (e.g., SF₆ and Kr; Vulava et al., 2002), fluorinated hydrocarbons (McCallum et al., 2005; Wells et al., 2007) and naturally occurring isotopes (e.g., ²²²Rn; Hunkeler et al., 1997). On the other hand, so-called "interfacial tracers" exist (Saripalli et al., 1998; Setarge et al., 1999; Annable et al., 1998). Anionic surfactants, such as linear alkylbenzenesulfonates (Saripalli et al., 1998; Kim et al., 1999), which adsorb exclusively on the interface between the water and the non-aqueous phase are applied. Hence, these tracers are interface-sensitive. But similarly to conventional partitioning tracers, a thermodynamic equilibrium between water and liquid/liquid-interface is assumed. Therefore, the application is only useful

in static time-independent systems. Furthermore, these tracers are dissolved in the water phase and cannot be injected together with the scCO₂ phase.

The work presented provides first insight into the development of novel reactive tracers, termed as kinetic interface-sensitive tracers (KIS tracer). These tracers have the potential to overcome above-mentioned deficits by describing the plume and interface development with time. This is obtained by the implementation of an intended and well studied hydrolysis reaction of the tracer molecule, which allows an irreversible chemical reaction at the scCO₂/water interface. Due to the reaction kinetics controlling the phase transfer a time-dependent component is integrated. In CO₂ sequestration reservoirs, the tracers may help to provide additional information on the following issues:

- Effect of pressure stimulation on mixing
- Plume spreading, characterization of interfacial area and area change
- Identification of fingering effects
- Estimation of residual scCO₂ saturation
- Assessment of storage capacity and effectiveness
- Optimization of operational strategies, management of injection wells

5.2 Theory – conceptual model

5.2.1 Application of KIS tracers during CO₂ injections

Before the CO₂ injection, the KIS tracer (A_{scCO_2}) is dissolved in supercritical or mixed with liquid CO₂. Afterwards, the mixture is injected simultaneously through the injection well into the brine saturated aquifer. The tracer reacts at the brine/scCO₂ interface to highly water soluble reaction products B_{H_2O} and C_{H_2O} . Subsequently, these products are measured in the water phase over time (monitoring well). Due to the spreading of the scCO₂ plume, the interfacial area increases with time (Fig. 5.1). The larger the interface (reaction surface) between both phases, the higher is the mass of the reaction products in the water phase. The high water solubility leads to negligible back-partitioning of the reaction products into the scCO₂ phase. Because of the implemented interface-sensitive hydrolysis reaction with known kinetic

parameters, it is possible to establish a correlation between time, concentration in water phase, and interfacial area size for given reservoir conditions (T , p , pH). For the field evaluation and interpretation of the time-dependent interface development, these correlations may be integrated as specific reaction terms into a flow and transport model of the reservoir.

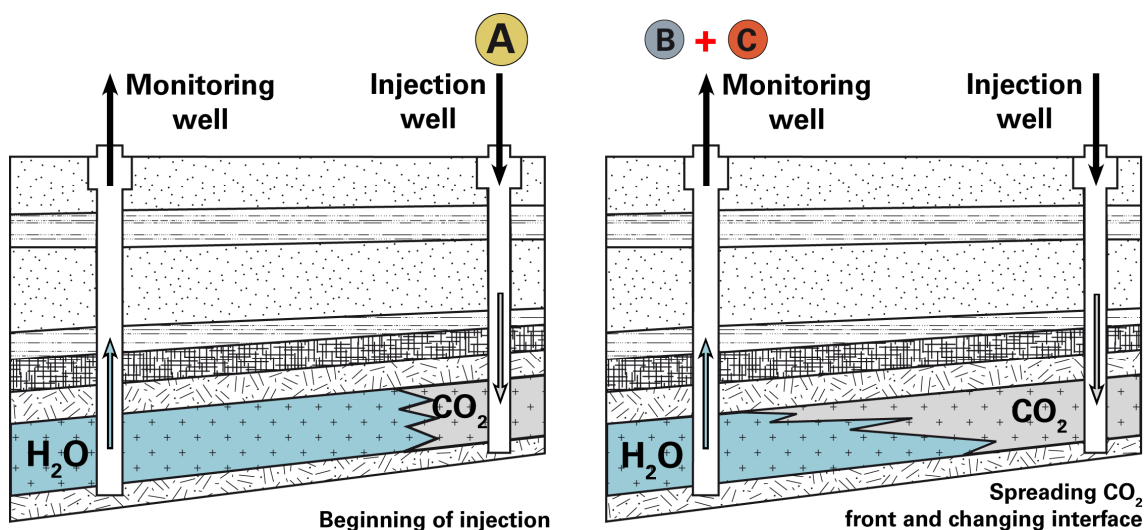


Fig. 5.1 Injection well: Injection and spreading of scCO₂ together with dissolved KIS tracer. Monitoring well: Measurement of KIS tracer reaction products in the brine.

5.2.2 Underlying processes

The basis of KIS tracers is an interface-sensitive hydrolysis reaction at the scCO₂/brine interface. Here, the tracer substance A_{scCO_2} reacts irreversibly into two reaction products B_{H_2O} and C_{H_2O} in the presence of water (H₂O) at the interface:



The parameter k_1 depends on the physical and chemical conditions (e.g., T and pH) at the point of reaction and expresses the reaction rate constant of the hydrolysis reaction. Due to the presence of two mobile phases, several underlying physicochemical processes influencing the mass transfer from scCO₂ to the brine phase and the reaction speed have to be taken into account as well (Fig. 5.2):

(1.) Dissolution of tracer in scCO₂ and diffusion toward the interface. A_{scCO_2} is dissolved and evenly distributed into the scCO₂ phase. This assumption is reasonable because

the diffusion coefficients in scCO₂ are one order of magnitude higher than in water (e.g., for phenol $T = 35\text{--}55\text{ }^\circ\text{C}$: $D_{\text{scCO}_2} = 1\text{--}3\text{E}\text{--}08\text{ m}^2\text{ s}^{-1}$ (Lai and Tan, 1995) and $D_{\text{H}_2\text{O}} = 0.5\text{--}2\text{E}\text{--}09\text{ m}^2\text{ s}^{-1}$ (Niesner and Heintz, 2000)). Thus, a fast transport without limitations (small transport resistance) to the interface is expected.

(2.) Adsorption at the interface. The surface active tracer molecules A_{scCO_2} are assumed to accumulate at the interface (energy minimization) and saturate the interface after an initial time. This adsorption process normally follows a non-permeable monolayer isotherm type, such as a Langmuir or Frumkin isotherm (Benjamin, 1997). The absolute amount of adsorbed molecules depends linearly on the interfacial area. Due to an excess of dissolved A_{scCO_2} in the supercritical phase, the interface is assumed to be permanently saturated. Therefore, the concentration of A_{scCO_2} at the interface can be expected to remain constant.

(3.) Reaction at the interface. After adsorption at the interface, A_{scCO_2} reacts in contact with water. The envisaged hydrolysis reaction (see Section 5.3.1) of an ester with water follows a (pseudo)-first order kinetics (Nottebohm et al., 2012). Due to the constant interface concentration, the reaction kinetics simplifies to (pseudo)-zero order kinetics with linear behavior. Thus, the reaction kinetics is the limiting step for phase transfer across the interface.

(4.) Phase transfer. The highly water soluble reactions products $B_{\text{H}_2\text{O}}$ and $C_{\text{H}_2\text{O}}$ are distributed into the brine due to diffusion and thus away from the interface. Therefore, the concentrations of $B_{\text{H}_2\text{O}}$ and $C_{\text{H}_2\text{O}}$ increase proportionally to the decrease of A_{scCO_2} and can be measured in the water phase.

In addition to the interface-sensitive part of mass transfer across the interface, partitioning between both phases also has to be taken into account. Despite the low polarity and water solubility of A_{scCO_2} small amounts of A_{scCO_2} may partition into the brine phase. The resulting reaction in the water phase follows first order kinetics and would lead to an exponential increase of $B_{\text{H}_2\text{O}}$ and/or $C_{\text{H}_2\text{O}}$ in the water phase. Hence, the superposition of interface reaction and partitioning results in a non-linear function. *Vice versa*, a low back-partitioning of the polar and highly water soluble reaction products $B_{\text{H}_2\text{O}}$ and $C_{\text{H}_2\text{O}}$ into the scCO₂ phase may also occur. Because of the increasing complexity, it is desirable to be able to neglect or to minimize partitioning effects within the data evaluation. To estimate and compare the tendency for

partitioning between both phases at reservoir conditions the *n*-octanol/water distribution coefficient K_{OW} was used as a model parameter due to similar solvent hydrophobicities of *n*-octanol and $scCO_2$ ($\log K_{OW(scCO_2)} = 2.85$ (50 °C, 143 bar; Nakaya et al., 2001), $\log K_{OW(n-octanol)} = 2.88$ (25 °C, 1 bar; SciFinder, 2012). Furthermore, Timko et al. (2004) showed for non-acidic compounds, such as the KIS tracers, that the $\log K_{OW}$ is correlated to the $scCO_2$ /water partitioning behavior.

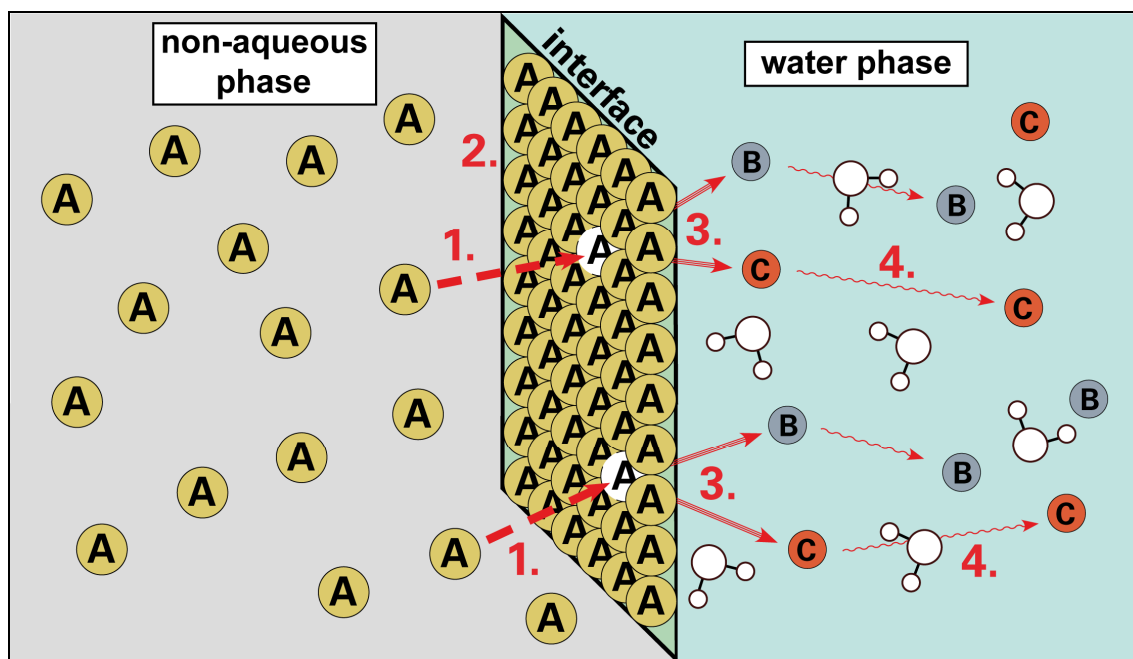


Fig. 5.2 Schematic representation of all involved processes at the $scCO_2$ /water interface during KIS tracer application.

5.3 KIS tracer design

Molecular target design has been established as a methodology for producing molecules with desired properties or effects especially in the field of pharmaceutical, biochemical (Kuntz et al., 1994) and material sciences (Kang and Zhang, 2000). Due to the exploitation and combination of well studied structural elements and molecular properties (e.g., functional groups, substructures, and homologs) novel tailor-made compounds with controlled structures and properties are conceivable and can be synthesized for a magnitude of applications. During the molecular design quantitative structure-property relationships (QSPR) can be used as a tool for predicting molecule properties for the molecule selection/modification and to

transfer their chemical behavior to unknown systems. In this work for instance, the relation of the molecule structure to the $\log K_{OW}$ value was used to estimate the water/scCO₂ partitioning behavior of the synthesized esters (see Section 5.3.2).

Up to now, the molecular design of tracer substances for environmental studies has not yet been considered. This also applies to challenging tracer tests in CO₂. Published tracer tests are limited to classical hydrogeological and thus commercially available tracer compounds. For example, Freifeld et al. (2005) and McCallum et al. (2005) applied several perfluorocarbons and noble gases (Kr, SF₆) for the determination of CO₂ travel times and the CO₂ saturation within the formation. Identical compounds were used from Wells et al. (2007) and Hortle et al. (2011) to detect CO₂ leakage. For the same purpose, Bachelor et al. (2008) proposed the spiking of injected CO₂ with radioactive isotopes (¹⁴C and ²²²Rn).

Due to the limitations of conventional tracers, the general applicability of molecular design for geoscientific problems is shown here with KIS tracers as an example, especially developed for CO₂ injections into deep saline aquifers.

5.3.1 Tracer requirements

A prior consideration of the KIS tracer requirements is essential for a successful target design of potential tracer substances. For describing interfacial areas between scCO₂ and brine a defined reaction of the tracer with water is required. Splitting reactions with water as nucleophilic reagent belong to hydrolysis reactions as a subgroup of solvolysis. Hydrolysable substances are alcoholic and phenolic esters, acid chlorides, acid amides, and nitriles. Due to the comparably easy synthesis, different phenol esters were suggested and used in this work. The simplified hydrolysis reaction scheme is the following:



The esters are dissolved in scCO₂ (A_{scCO_2}) and should show minimal partitioning into the polar water phase. Since scCO₂ is an excellent solvent for non-polar compounds (Luque de Castro and Tena, 1996), the applied esters should also have non-polar substructures (e.g., linear *n*-alkyl chains, aromatic rings) with corresponding high $\log K_{OW}$ values.

In contrast, at least one of the hydrolysis reaction products has to be highly polar, water soluble and mobile in order to determine it in the water phase. For this purpose, the formed acids can be exploited (B_{H_2O}). Their ability of deprotonation is very convenient, since anions are formed depending on pH. Thus, especially the esters of strong organic acids with very low logarithmic acid dissociation constants pK_a seem to be the most promising compounds.

The requirements for the second reaction product (C_{H_2O}) are not so strict. The formed alcohols or phenols can be polar or even non-polar. If the product is medium polar with suitable distribution coefficients between the brine and scCO₂ phase, it may even be used as additional partitioning tracer. However, the major task of the alcohol or phenol, respectively, is the adjustment of the KIS tracer properties during the molecular design. Beside the modification of the tracer polarity, the alcohols or phenols used for esterification have a large influence on the hydrolysis reaction rate constant k_1 . This rate constant can be modified and adapted to reservoir conditions (T , pH) as well as for experimental durations. Steric hindrance, mesomeric and inductive effects are only some reasons for different hydrolysis kinetics and can be considered during synthesis (Nottebohm et al., 2012).

Regarding the practicability for field applications, the concentrations of reaction products should preferably be measured with standard equipment in a high temporal resolution, a high selectivity, and with a low detection limit. Therefore, the synthesis of the target compounds was focused on compounds with fluorescence properties.

5.3.2 Tracer design / synthesis

As a consequence of the prior emphasized requirements, the esterification of naphthalenesulfonic acids is most promising. Because of $pK_a < 1$, these acids are deprotonated at even very low pH levels and therefore, very water soluble permanent anions are formed. Thus, no significant retardation can be expected for organic acids at $pH > pK_a + 2$ (Schaffer et al., 2012). This also applies for naphthalenesulfonates, which are established conservative, non-sorptive tracers for geothermal applications, very stable at high temperatures and anaerobic conditions

(Rose et al., 2001; Rose et al., 2002; Nottebohm et al., 2010). Furthermore, a back-partitioning of the anions into the scCO₂ phase can be excluded. For reservoirs, which are already contaminated with these compounds different constitutional isomers can be prepared to make the identification of the tracer unique. Furthermore, naphthalenesulfonates are highly fluorescent with a detection limit in the low µg L⁻¹ range. Pre-concentration and subsequent chromatographic separation lowers the detection limit by around one order of magnitude and enables the determination of different isomers even in highly saline matrices (Nottebohm and Licha, 2012).

Additional analytical problems might occur in sequestration reservoirs that contain significant residuals of hydrophobic aromatic compounds (e.g., depleted petroleum reservoirs), such as polycyclic aromatic hydrocarbons, since the dissolution of these substances in scCO₂ can be expected during the injection. The leached compounds accumulate at the scCO₂/brine interface and might cause fluorescence interferences with the tracer reaction products. Thus, online measurements would be no longer possible and chromatographic systems have to be used again for sample clean-up and compound separation prior to fluorescence analysis.

If mononaphthalenesulfonic acids are applied, the esterification of the sulfo group leads to non-polar esters. In dependence of the deployed alcohol or phenol the ester properties can further be modified. For example, the esterification with linear aliphatic alcohols leads to non-polar but also non-fluorescent esters whereby the measurement of these compounds is more complicated. For this reason, aromatic alcohols (phenols, naphthols) can be used for the esterification of the naphthalenesulfonic acids (Fig. 5.3). The resulting fluorescent esters are hydrophobic ($\log K_{OW} > 4$).

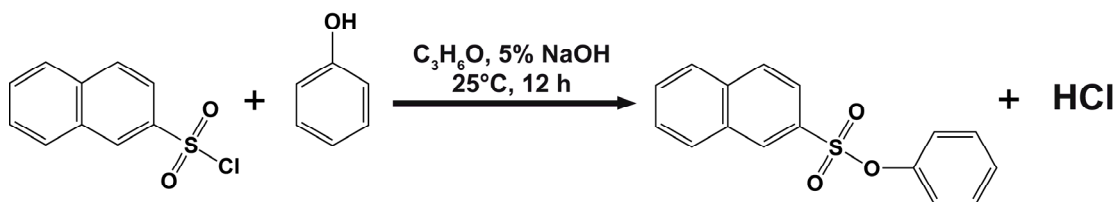


Fig. 5.3 Synthesis of phenyl naphthalene-2-sulfonate from naphthalene-2-sulfonyl chloride and phenol.

For the modification of the hydrophobic properties, different esters were synthesized by esterification of naphthalene-2-sulfonic acid (2-NSA) with different methyl

substituted phenols. The more non-polar the employed phenol, the more non-polar is the resulting ester (Table 5.1). The esterification of chlorophenols therefore leads to more hydrophobic esters. However, the higher toxicity of these compounds should be also taken into account when used in field studies.

Table 5.1 Properties of synthesized KIS tracer compounds, phenyl acetate and their respective reaction products.

Ester (Abbreviation)	→	Acid	+	Alcohol / Phenol
Phenyl naphthalene-2-sulfonate (2-NSA _{Ph}) CAS 62141-80-4	$\log K_{ow}^*$ 4.29	Naphthalene-2-sulfonic acid (2-NSA) $\log K_{ow}^* = 0.63$ $pK_a^* = 0.27$		$\log K_{ow}^*$ Phenol 1.54
<i>p</i> -tolyl naphthalene-2-sulfonate (2-NSA-4-Ph) CAS 108980-59-2	4.48			4-methylphenol (<i>p</i> -cresol) 2.07
3,5-dimethylphenyl naphthalene-2-sulfonate (2-NSA-3,5-Ph) CAS 889803-73-0	5.13			3,5-dimethylphenol (3,5-xylenol) 2.55
Phenyl acetate (PhAc) CAS 122-79-2	1.65	Acetic acid		Phenol 1.54

* SciFinder predicted values, calculated using Advanced Chemistry Development (ACD/Labs) Software (1994–2012).

The ester compounds were synthesized on the basis of naphthalene-2-sulfonyl chloride and the respective phenol under alkaline catalyzed conditions (Fig. 5.3) in a slightly modified procedure according to Vennila et al. (2008). Instead of 4 mL acetone 6 mL were used. The identity and purity of the esters were confirmed by ¹H-Nuclear Magnetic Resonance (¹H-NMR) spectroscopy. The purity was >95%. The hydrolysis reaction results in 2-NSA and the respective phenol homologues (Table 5.1). The reaction scheme and the fluorescent properties for the phenyl ester are shown in Figure 5.4.

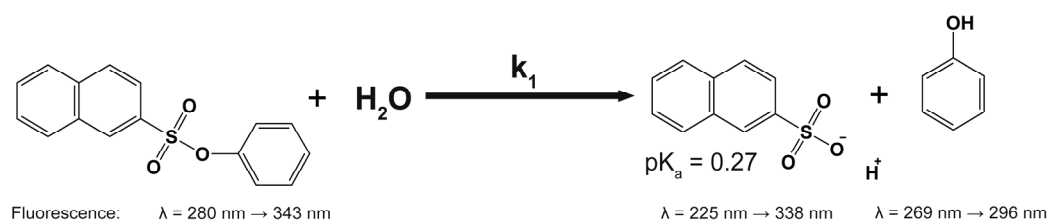


Fig. 5.4 Hydrolysis reaction of phenyl naphthalene-2-sulfonate with water and the fluorescent properties of the reagent and the reaction products.

5.4 Experiments and modeling

5.4.1 Lab experiments

5.4.1.1 Analog approach

Due to the necessity of high pressure cells to generate scCO_2 for identifying and quantifying the expected involved processes the new tracers cannot be tested easily under reservoir conditions. Available pressure cells and scCO_2 reactors are limited in size and in their setup variability. Furthermore, direct online measurements in the water phase cannot easily be employed and a sampling over time is not possible due to small cell volumes of only a few milliliters. Therefore, the use of pressure cells seems to be feasible only for a limited number of fundamental static batch experiments, such as the determination of solubilities, partitioning coefficients, further thermodynamic equilibrium parameters, and the inertness of the tracer in mixture with other compounds.

In order to overcome these limitations, to investigate and to interpret the tracer behavior in defined systems at larger scale, the scCO_2 was replaced with another solvent. Particularly, organic solvents, which are immiscible with water, are expected to show a similar behavior and allow the process identification and separation at the interface on a larger scale without special equipment. For this purpose, different non-polar solvents were selected and tested with respect to density, polarity, inertness, and solubility in water.

The alkane *n*-octane has proven most suitable as scCO_2 analog. Table 5.2 compares some selected properties of scCO_2 at reservoir conditions with *n*-octane at atmospheric conditions. Density of scCO_2 depends strongly on temperature. In contrast, the density of *n*-octane is almost constant but lies in the same range. The

solubility of scCO₂ in water under equilibrium conditions is higher than that of *n*-octane. Due to the timescale of scCO₂ dissolution (non-equilibrium), the salinity of the brine, and the presence of further dissolved gases (e.g., methane) a significantly lower water solubility can be assumed (IPCC, 2005). Therefore, *n*-octane develops analogously to scCO₂ a sharp interface to the water phase (see Section 5.1). For the comparison of the solvent polarity, which influences the tracer solubility and the partitioning between both phases, two different parameters were selected. On the one hand the log *K*_{ow} value, which depends for scCO₂ strongly on the pressure (Nakaya et al., 2001), and on the other hand the *E*_T(30) value as empirical solvent polarity indicator (Reichardt, 1994) were used. As desired, these values lie for *n*-octane in the same range as for scCO₂. Additional advantages of *n*-octane are the low cost as well as the comparable low toxicity and vapor pressure. Therefore, the handling is uncomplicated and the compound can be used in larger amounts. All obtained values for kinetic rate constants, interface adsorption parameters, mass fluxes and mass transfer coefficients in the *n*-octane/water system can be transferred and adapted later to scCO₂ based on calibrated process models.

Table 5.2 Comparison of physical and chemical properties between scCO₂ with *n*-octane as analog compound.

Parameter	scCO ₂	<i>n</i> -octane
Density [g cm ⁻³]	0.52 (150 bar, 65 °C) ^a	0.67 (1 bar, 65 °C) ^b
	0.75 (150 bar, 40 °C) ^a	0.69 (1 bar, 40 °C) ^b
<i>E</i> _T (30) [kcal mol ⁻¹]	28.5 (150 bar, 40 °C) ^c	31.1 (1 bar, 25 °C) ^d
log <i>K</i> _{ow} [-]	3.14 (150 bar, 50 °C) ^e	4.78 (1 bar, 25 °C) ^b
	4.87 (180 bar, 50 °C) ^e	
Solubility [mg L ⁻¹]	20–60E+03 ^f	1.3 ^b

^a Calculated after Stryjek and Vera (1986) (www.criticalprocesses.com).

^b SciFinder predicted values, calculated using Advanced Chemistry Development (ACD/Labs) Software (1994–2012).

^c Eberhardt et al. (1997).

^d Reichardt (1994).

^e Nakaya et al. (2001).

^f IPCC (2005).

As an analog for the aqueous brine phase (buffer) solutions with different pH values can be used. This allows investigating the effects of different hydrolysis rate

constants due to their direct relation to the pH value. The hydrolysis rate changes by about one order of magnitude per one pH unit increase (Nottebohm et al., 2012).

5.4.1.2 Experimental setup

For identifying, verifying, and separating the processes relevant for the developed novel KIS tracer application, major effort was made to simplify the experimental setup. The reason is that a profound knowledge of processes controlling the tracer interface sensitivity is fundamental to all consecutive investigations and the process modeling. Thus, an undisturbed (closed) system with fixed boundary conditions (constant interfacial area size, phase volume ratio, T , pH) and high temporal resolution measurements are necessary.

For this reason, static batch experiments were conducted directly in sealed small-volume fluorescence spectroscopy cuvettes ($V = 4$ mL). This approach has the advantage that the concentrations of the reaction products and the possibly partitioned tracer can be measured in short time intervals without mass loss and without disturbing the closed system by sampling. Furthermore, it is possible to adjust certain temperatures and stirring rates in the cells to avoid unwanted temperature changes and diffusive effects.

After providing 3 mL deionized or buffered and degassed water in the cuvette, 1 mL of *n*-octane containing the dissolved (KIS) tracer (2-NSAPh or PhAc) was carefully added above the water phase. The interfacial area was constant ($A = 1$ cm²). Consecutively, the concentration increase of the respective reaction products (2-NSA or phenol) in the water phase was recorded every minute for several thousand minutes by using fluorescence spectroscopy.

The resulting concentration curves of the measured compounds were used to determine the mass flux across the interface and to calibrate the numerical model that was developed in parallel to the experiments.

5.4.2 Numerical modeling

To understand the relationship between interface development and resulting concentration curves of the reaction products in the water phase, a numerical modeling approach using the finite element method was implemented. The problem can be described as a heterogeneous reaction of the KIS tracer at the scCO₂/water interface. The KIS tracer in the scCO₂ migrates to the interface and reacts here with the water in a hydrolysis reaction. In this study, a macroscopic model with averaged quantities was developed.

5.4.2.1 Model description

The comprehensive problem consists of the two different immiscible phases (scCO₂ or analog solvent and water) and of the allocation of the KIS tracer with its reaction products. Since the reaction at the interface is the limiting step in the mass transfer across the interface and due to high diffusion rates and the excess of tracer in the scCO₂ phase, the interface is permanently saturated. Here, a Langmuir (Langmuir, 1918) isotherm is assumed for the adsorption process onto the interface:

$$c_i = \frac{K_L \cdot c_{i,max} \cdot c_a}{1 + K_L \cdot c_a} \quad (5.3)$$

K_L is the Langmuir sorption coefficient. For high tracer concentrations c_a in the scCO₂ phase the interface concentration c_i is approximately equal to the maximum concentration of the saturated interface $c_{i,max}$. The assumption includes that the hydrolysis at the interface and the migration of the reaction products into the water phase take place within one time step. It is additionally assumed that the reacted small fraction of tracer Δc_i at the interface is instantaneously replaced from the scCO₂ bulk due to large diffusion coefficients. Consequently, due to the interface limited transfer the KIS tracer decay in the non-aqueous phase follows the linear zero order reaction kinetics of the hydrolysis reaction. The effective reaction rate constant k_a of the limiting step can be expressed as a specific constant mass flux q of the reaction products into the water phase:

$$q = k_a = \frac{\Delta c_i}{\Delta t} \quad (5.4)$$

This allows the reduction of the numerical model to a single-phase problem. The model geometry follows the cuvette used in the lab experiment (see Section 5.4.1.2) with a base area $A = 1 \text{ cm}^2$. The height depends on the volume and therefore the filling level of water. The upper model boundary is equal to the interfacial area. The constant q of tracer products into the water phase, which is represented by the model domain, is defined as boundary condition. All other boundaries are no-flow boundaries (Fig. 5.5).

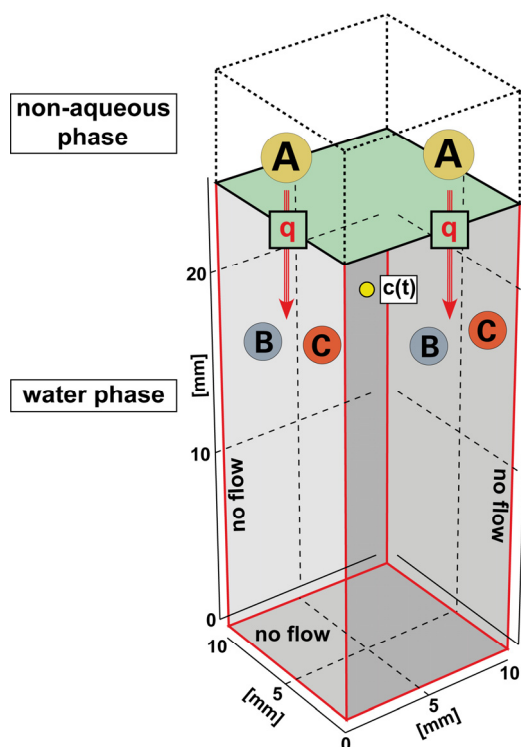


Fig. 5.5 Sketch of the numerical model domain: The yellow dot at 20 mm height represents the observation point where the fluorescence signal is measured. Red boundaries are no flow boundaries. On the upper green boundary the flux q is defined, where the reaction products flow into the water.

For the ionic tracer reaction product 2-NSA no back-partitioning into the scCO_2 phase is assumed. Hence, the concentration curve is only allowed to rise or to level at a constant value. The distribution of the product across the water volume is described through a diffusion process:

$$\frac{\partial c}{\partial t} = -D \frac{\partial^2 c}{\partial x^2} \quad (5.5)$$

Therefore, a steady-state concentration increase establishes in the model region (observation point) for a given constant interfacial area size.

5.4.2.2 Relation between concentration curve and interfacial area size

As stated above, the concentration of KIS tracer reaction product depends only on the interface size and time. The zero order kinetics of the hydrolysis reaction results for a constant interfacial area in a linear concentration curve $c(t)$:

$$c(t) = c_0 + q \frac{A}{V} t \quad (5.6)$$

Where A is the interfacial area, V the volume and c_0 the initial concentration in the water phase. From linear regression analysis the mass transfer rate q can be determined with:

$$q = m \frac{V}{A} \quad (5.7)$$

Here, m is the slope of the concentration curve. For the case of a time-dependent variable interfacial area $A(t)$ a decomposition ansatz is applied:

$$A(t) = f_A(t) \cdot A_{max} \quad (5.8)$$

A dimensionless time-dependent function $f_A(t)$ is used to scale a constant maximum area A_{max} . The function $f_A(t)$ must be equal to one when A_{max} establishes and has some additional properties:

$$f_A(t) \in [0,1] \quad \text{and} \quad \exists \hat{t} \in [0, t_{max}] \quad \text{with} \quad f_A(\hat{t}) = 1 \quad (5.9)$$

The application of the ansatz in Eq. (5.8) in Eq. (5.6) leads to:

$$\frac{dc}{dt} = \frac{A_{max}}{V} q \cdot f_A(t) \quad \text{and} \quad (5.10)$$

$$c(t) = c_0 + \frac{A_{max}}{V} q \cdot \int f_A(t) dt \quad (5.11)$$

For the determination of A_{max} a case-by-case analysis of $c(t)$ has to be carried out:

$$(1) \quad \exists \ddot{c}(\hat{t}) = 0 \quad \Rightarrow \quad f(\hat{t}) = 1 \quad \text{if} \quad c(\hat{t}) = \max \{ \dot{c}(\hat{t}) \} \quad (5.12)$$

$$(2) \quad \exists ! \dot{c}(\hat{t}) = 0 \quad \Rightarrow \quad f(\hat{t}) = 1 \quad \wedge \quad A(\hat{t}) = A_{max} \quad (5.13)$$

$$(3) \quad \neg \exists \dot{c}(\hat{t}) = 0 \quad \Rightarrow \quad f(t_{max}) = 1 \quad \vee \quad f(0) = 1 \quad \text{with} \\ A(T) = A_{max} \quad \vee \quad A(0) = A_{max} \quad (5.14)$$

Hence, A_{max} can be calculated with:

$$A_{max} = \frac{(c(\hat{t}) - c_0) \cdot V}{q} \cdot \frac{1}{\int_0^{\hat{t}} f_A(t) dt} \quad (5.15)$$

At this point it can clearly be seen that the time-dependent function $f_A(t)$ and consequently A_{max} are highly dependent on the sampling rate and detection limit of the reaction products.

5.4.3 First results from static batch experiments

Initially, the lab experiments were conducted with phenyl acetate (PhAc) as well as with the potential KIS tracer compound phenyl naphthalene-2-sulfonate (2-NSAPh) (Table 5.1). PhAc is the phenyl ester of acetic acid. Due to the significantly lower $\log K_{ow}$, the KIS tracer can be compared with a more hydrophilic compound as a reference. Thus, it is more likely that PhAc shows a stronger partitioning into the water phase than the more hydrophobic 2-NSAPh. The resulting concentration curves of the respective hydrolysis reaction products phenol (reactant: PhAc) and naphthalene-2-sulfonate (reactant: 2-NSAPh) are shown in Figure 5.6.

As expected, the desired hydrolysis reactions went on and both products could be measured online in the water phase by fluorescence spectroscopy. But obviously, both compounds developed a completely different curve shape. As mentioned above, a considerable partitioning additional to the interface sensitive part of mass transfer across the interface leads to an exponential increase of the phenol concentration curve for PhAc. Therefore, the interface sensitivity is lost and the compound is not suitable as KIS tracer. In contrast, 2-NSA showed a very promising curve shape. After an initial startup phase of around 2,000 min, a steady state condition established in the concentration change and the concentration increase became linear. The start-up phase might be caused by the initial saturation of the interface, partitioning of ester impurities (2-NSA) and the final establishment of constant diffusion gradients. Furthermore, the linear slope of the concentration curve seems to confirm the expected reduction of first order to zero order kinetics and indicates a negligible partitioning of the ester between both phases.

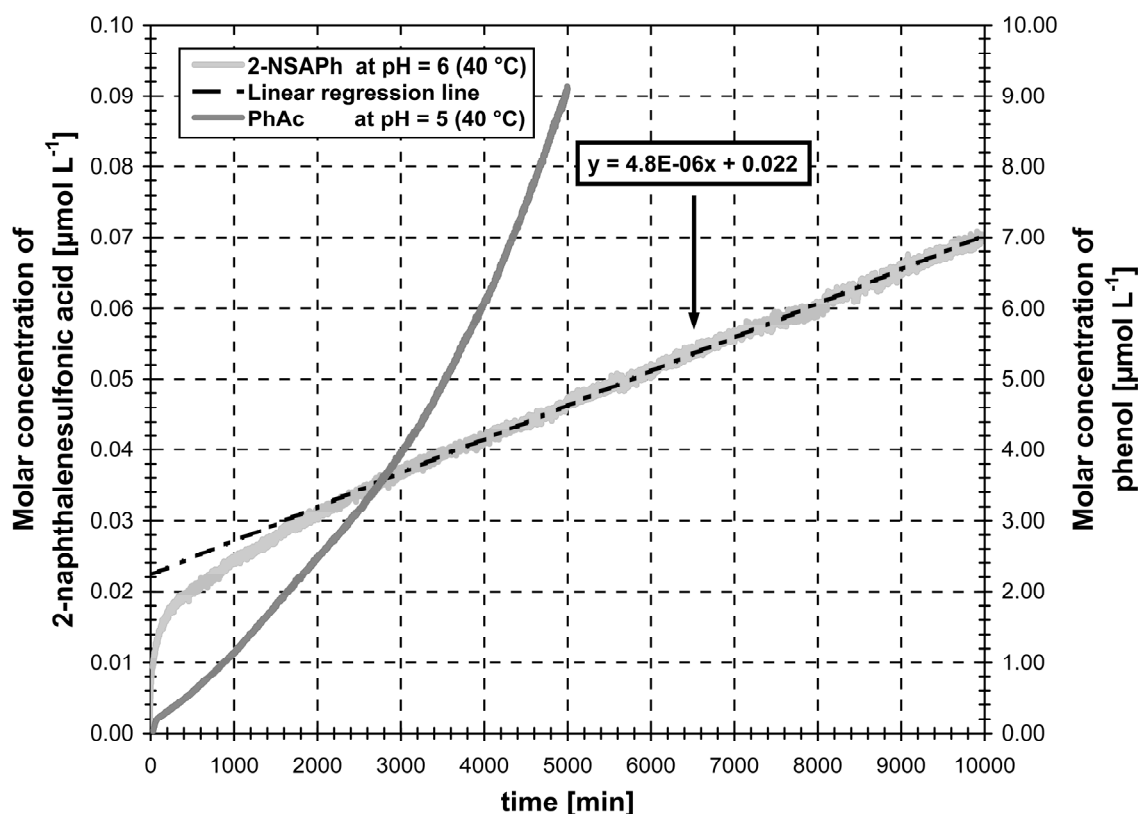


Fig. 5.6 Comparison of measured concentration curves for the hydrolysis reaction products of phenyl acetate (PhAc) and phenyl naphthalene-2-sulfonate (2-NSAPh).

For the evaluation of the interface sensitivity, a linear regression analysis was carried out for the values $t > 2,000$ min (Fig. 5.6, $R^2 = 0.99$). By applying the obtained slope $m = 4.8\text{E-}06 \mu\text{mol L}^{-1} \text{min}^{-1}$, and the given values $A = 1 \text{ cm}^2$, $V = 3 \text{ mL}$ for the cuvette in Eq. (7), q was calculated with $2.4\text{E-}06 \mu\text{mol m}^{-2} \text{s}^{-1}$. The fitted m depends directly on k_1 of the hydrolysis reaction and is only valid for the given conditions. Conceivable changes in T , pH and the molecule structure would lead to different k_1 and thus to different m and q , respectively (see Sections 5.3.1 and 5.4.1.1). During CO_2 injections, the pH is lower in the vicinity of the $\text{scCO}_2/\text{water}$ interface than for the experiments conducted in this study. Therefore, k_1 and q are also expected to be lower under field conditions.

The numerical model was calibrated using the observed m from the static batch experiment and a constant interfacial area of $A = 1 \text{ cm}^2$ (Fig. 5.7). Additionally, three different classical test functions $A(t)$ with properties according to Eq. (5.8) were applied and the resulting concentration curves were modeled to gain further insight

into the behavior of KIS tracers. The concentrations are proportional to the integrated $A(t)$ which represents an effective area A_{eff} :

$$c(t) \propto \int_0^t A(t) dt = A_{eff} \quad (5.16)$$

Furthermore, the model allows the distinction between different functions for $A(t)$ even when A_{eff} and thus also the total amount of reacted tracer is equal (Fig. 5.7). Hence, A_{eff} is one of the main target parameters for proving the effectiveness of $scCO_2$ injections.

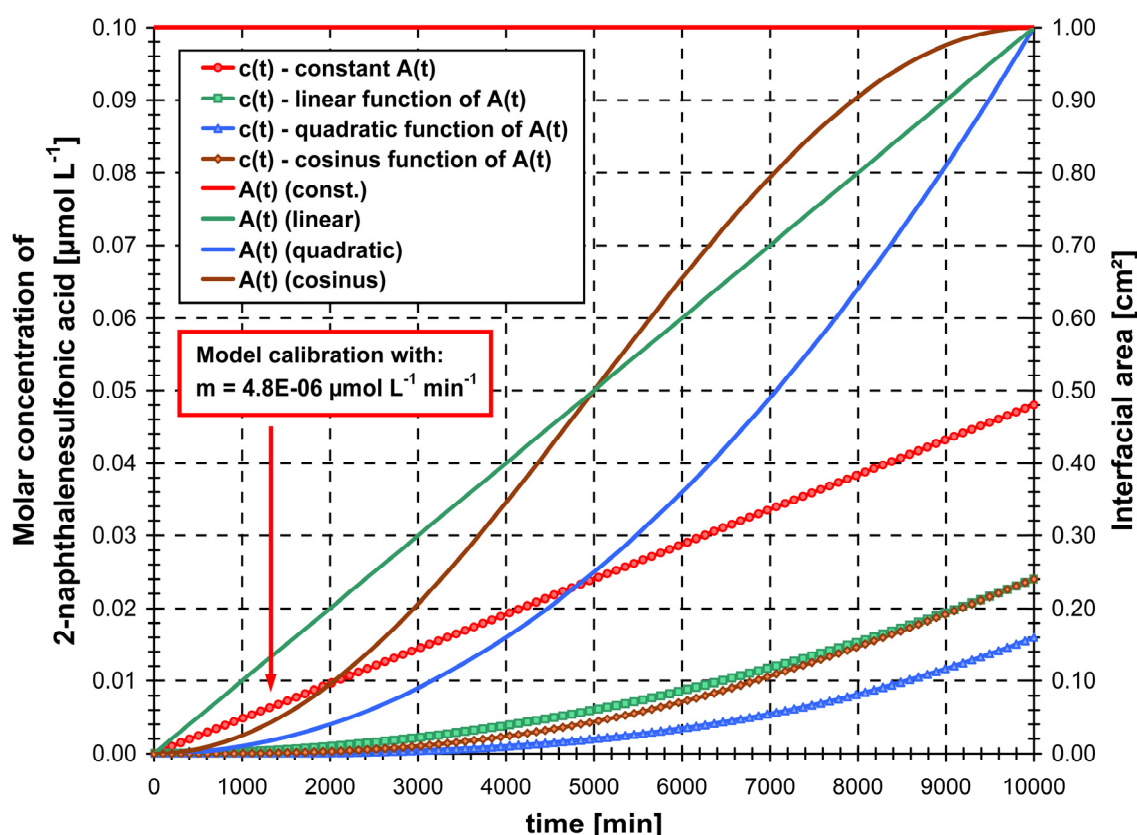


Fig. 5.7 Comparison of different modeled scenarios: Concentration curves are modeled based on different functions for $A(t)$. For the model calibration (red line) the constant A from the experiment was used.

5.5 Summary and conclusions

The interfacial area between $scCO_2$ and brine is an important parameter for the evaluation of CO_2 storage in deep saline aquifers, since numerous relevant trapping mechanisms and physicochemical processes are directly dependent on this reactive

interface. Up to now, these interfacial areas and their development during injection cannot be studied directly. In this work, a methodology for the design of kinetic-interface sensitive tracers (KIS tracers) was presented. These tracers are believed to have the potential to close the existing gaps for field experimental interpretation by implementing an interface-sensitive reaction. Here, the idea and the theoretical concept for these novel tracers were presented. After defining the tracer requirements and showing possibilities for a tailor-made molecular design, several compounds were successfully synthesized. An analog approach was proposed for testing the tracer behavior by replacing the non-aqueous scCO₂ phase with organic solvents. Additionally, a relationship between measured concentration curves and interfacial area was derived and a first model for the tracer evaluation in static batch systems was presented.

The results show, that molecular target design is a suitable method to develop these kinds of new tracers. As expected, the tested esters 2-NSAPh and PhAc confirmed the combination of mass transfer across the interface and hydrolysis reaction. The respective reaction products 2-NSA and phenol were detected in the water phase by fluorescence spectroscopy. However, in contrast to the newly synthesized potential KIS tracer compound 2-NSAPh, which demonstrated the expected linear increase of the reaction product 2-NSA in the water phase and thus interface sensitivity, PhAc showed no interface sensitivity due to a too strong partitioning behavior. The linear concentration increase of 2-NSA is very promising and supports the theoretically derived zero order reaction kinetics at the interface. Thus, a constant mass flux across the interface could be determined. Based on this flux, the new macroscopic numerical model was calibrated and different scenarios were calculated. The model demonstrated the interface sensitivity of KIS tracers and showed the possibility for evaluating the from lab experiments obtained concentration curves. In contrast to conventional equilibrium tracers (partitioning or interfacial tracers), KIS tracers are injected together with the non-aqueous phase and their reaction kinetics (non-equilibrium) is exploited to gain information on the temporal interface or plume development.

Future works will include additional process studies and modeling to describe the relevant processes, dependencies and mechanisms. Furthermore, the experiments

will be extended to dynamic systems with a variable interface as well as repeated with additional compounds with regard to their possible application as KIS tracer. The influence of a third phase (rock material) on the tracer behavior will also be investigated.

In parallel, the existing model will be extended and adapted according to the experimental progress. Hence, it is planned to use the model as forecast tool for more complex dynamic systems. Finally, when all relevant physicochemical processes are completely understood, it should be possible to implement the model in a reservoir simulator.

5.6 Acknowledgment

The research leading to these results has received funding from the European Community's 7th Framework Programme FP7/2007–2013, within the MUSTANG project (grant agreement no. 227286).

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Chapter 6

6 General conclusions and perspectives

Tracer techniques are able to provide valuable insights into aquifer systems that are not accessible with other conventional characterization methods. Due to the large number of molecules with individual properties, which can be selected or adapted to specific problems, the application of organic substances as groundwater tracers opens up the chance for gaining further information on processes influencing the tracer transport. For this purpose, however, the sufficient understanding of all involved and the awareness of potentially possible transport-relevant processes are required. Especially in the case of non-conservative compounds, which intentionally interact chemically, biochemically, or physicochemically in the aquifer, this understanding is vital. This work focused on geosorption as one of the most decisive physicochemical processes affecting the solute transport in the subsurface. Knowledge on the underlying interactions and mechanisms causing tracer retardation in a considered system is a promising key to derive process-specific information and related aquifer parameters. However, the sorption-influenced transport, especially for positively charged organic species, is rather complex and not yet fully understood. As a consequence, no resilient prognoses are possible at this time. Therefore, the identification and adequate description of relevant sorption processes including the relation to the molecular characteristics and to further influencing factors are essential in the potential use of any organic substance as hydrogeological tracer. Based on this knowledge, tailor-made tracer molecules for manifold applications could be selected or individually synthesized.

6.1 Sorption of organic molecules onto aquifer materials

Sorption onto aquifer materials is a fundamental process leading to the retardation (and/or removal) of organic compounds in natural aquatic systems. The comprehensive understanding of sorption processes is important for the successful realization and evaluation of field tracer experiments as well as for several nature-related water treatment processes, such as river bank filtration or soil aquifer treatment. Different molecular structures lead to specific properties of organic compounds. Therefore, a strong influence of the molecular character on sorption and, thus, the transport behavior can be anticipated. Evaluating the applicability of existing model approaches, identifying relevant sorption mechanisms, and studying their main influencing factors is necessary for a meaningful prediction of the subsurface transport of organic solutes.

Column experiments conducted with several ionizable pharmaceuticals and one aquifer sediment showed a strong influence of pH on sorption. Compounds with pK_a values in the considered pH range showed the strongest pH-dependence. This is because several species with different charge are formed in the aqueous phase. The comparison between measured and predicted data using a simple $\log K_{ow}$ - $\log K_{oc}$ regression gave confident results only for neutral compounds. The use of $\log D$ instead of $\log K_{ow}$ within these correlations enabled the prediction for acids and, thus, led also to acceptable results. Hence, the prediction for neutral and acidic molecules with existing classical or slightly modified concepts considering the speciation is reasonable. In contrast, the sorption of organic cations was generally underestimated, since only hydrophobic interactions are considered in these simple one-parameter correlation approaches. However, aquifer materials possess usually negative net surface charges, which induce additional electrostatic attractions between the sorbent and the positively charged sorbate. Hence, polar sorption mechanisms (e.g., cation exchange, hydrogen bonding) also have to be considered. Additionally, awareness is required that the relative role may change dramatically depending on the boundary conditions (e.g., solute speciation and variable surface charges of the sorbent are pH-dependent).

In order to predict the sorption of organic cations, the relevant sorption mechanisms have to be separated *a priori* and investigated independently. For this purpose, the

systematic study and comparison of the sorption behavior of further selected, but structurally related organic cations (e.g., homologues) under varying conditions is suggested. By using additionally defined sorbents with different surface properties, certain sorptive interactions may be excluded or emphasized and studied separately. Consecutively, it should be attempted to relate or to normalize observed sorption data with measured solution and sorbent properties.

For assessing the extent of ionic contributions to the whole sorption process of organic cations, the sorption/desorption behavior of two structurally similar cationic beta-blockers was investigated and compared for two sediments. Dramatically changing retardations due to varying concentrations of inorganic cations were observed. That means organic and inorganic cations compete for the negatively charged surface sites of the sorbent. Consequently, an important role of cation exchange processes under the applied conditions was derived. By comparing the predicted hydrophobic proportion with the observed overall sorption, the contribution of polar interactions could be quantified with more than 99%. Thus, a high relevance of non-hydrophobic sorption mechanisms for the transport of cationic beta-blocker species and most likely for the transport of further cationic compounds in aquifers can be concluded. Since the relative role and extent of all cation exchange processes generally depends on the water chemistry (e.g., pH, ionic strength, type of competing cations, dissolved organic matter) as well as the sorbent properties (e.g., cation exchange capacity, specific surface area, clay content, point of zero charge, solid organic matter), the individual influence of these factors in addition to the influence of the sorbate (molecule) properties have to be known.

As a consequence, measured sorption coefficients given in the literature cannot be directly compared for the protonated organic cation species, since the boundary conditions are most probably unequal. Therefore, a mechanistic understanding is necessary in order to compare and sufficiently predict the sorption of organic cations. For doing so, the stepwise and thorough study of relevant boundary conditions influencing polar sorbent/sorbate interactions is strongly recommended.

First systematic experiments in this context were carried out within this work. By means of batch equilibrium experiments, the influence of the background electrolyte (concentration and type of inorganic cations) on the sorption of the monovalent

organic cation metoprolol onto an aquifer sediment was studied. All competitive sorption isotherms were non-linear indicating the existence of energetically heterogeneous sorption sites. Nevertheless, constant Freundlich exponents indicated that the sorption mechanisms are not changing dramatically over a wide concentration range. Due to decreasing sorption of the organic cation with increasing concentrations of the inorganic cations Na^+ and Ca^{2+} the dominating role of cation exchange processes could be confirmed. A first simple logarithmic correlation between the sorption coefficient and the competing electrolyte concentration was found allowing the prediction of metoprolol sorption on the investigated sediment. In contrast to other authors, however, these correlations show an opposite curve shape. This difference cannot yet be explained and requires further research on the controlling influence factors. Thus, the application field of the relationships found is currently still vague.

Before general conclusions for other organic/inorganic cations and sorbents can be drawn, all sorption mechanisms and further influence factors have to be investigated and understood in more detail. The first step was done in this work. In further steps, the detected relations have to be described with effective parameters, which allow the conjunction of all system relevant factors in one model. The directly following work could include the study the sorption behavior of organic cations in mixtures of inorganic cations as well as the study of the influence of further not yet investigated competing inorganic cations under otherwise constant conditions. Subsequently, the sorbate and sorbent properties should be changed systematically.

6.2 Development of reactive organic tracers for the characterization of CO_2 plume spreading

The target synthesis of molecules with desired properties has been successfully established in many scientific disciplines. Especially in the field of life sciences (e.g., pharmacology, biochemistry, medicine) and material sciences, this methodology is used. The conscious combination of structural elements and molecular features allows the creation of novel compounds with defined properties. To date, molecular

design of hydrogeological tracers for reservoir studies, however, has not yet been considered.

The interfacial area size between supercritical CO₂ (scCO₂) and brine is an important parameter for characterizing CO₂ spreading during CO₂ sequestration into deep saline aquifers. In this work, the concept and methodology for the target design of a new reactive tracer type (KIS tracer), which may be able to detect these interfaces, were proposed. Based on the tracer concept, it is required that one of the tracer hydrolysis reaction products has to show a conservative transport behavior in the water phase. For this reason, naphthalenesulfonate was selected as base structure, because several physicochemical attributes make it convenient for the modification to a KIS tracer *via* esterification. Naphthalenesulfonic acids are strong acids with corresponding low pK_a values of <1 . Hence, these compounds are anionic over the entire pH range. Based on the previous sorption studies, a non-sorptive behavior and a high mobility in aquifer systems can be expected. Furthermore, a partitioning to the non-aqueous scCO₂ phase can be neglected due to the high affinity of these molecules to the water phase (water solubility $>1,000 \text{ g L}^{-1}$). The lab experiments confirmed that the mass transfer through the interface is limited by the hydrolysis reaction. As intended, the combined process follows zero-order kinetics. Thus, a constant mass flux through the interface could be determined. Furthermore, first modeling results demonstrated the interface sensitivity of the synthesized compound.

In the next steps, the modeling has to be extended for predicting suitable reaction rates of the hydrolysis in order to resolve the plume development. Afterwards, the hydrolysis kinetics needs to be adapted by molecular design to the required time and space scales in lab or field applications. For this purpose, the need may also arise to use other compounds than naphthalenesulfonates as base structures for the KIS tracer development. For instance, it might be suitable to use acid chlorides or acid amides instead of esters as KIS tracer, since their hydrolysis rates are very different to the aforementioned. In the case of acid amides, however, organic cations (amines) that do not have a conservative sorption behavior would also be formed during the reaction. Eventually, the findings from the previous sorption studies might be exploited for the tracer interpretation.

Appendix

Appendix A

A1 Liquid chromatography

The samples were analyzed by UV absorption using a high pressure liquid chromatograph (HPLC, Merck-Hitachi) with a diode array detector (DAD L-4500, Merck-Hitachi). A 150 × 3 mm C18-HPLC reversed phase column (Gemini-NX 3 μm C18 110A, Phenomenex) was used for chromatographic separation. The separation was operated at 29 °C, a constant flow rate of 0.5 mL min⁻¹, and an injection volume of 100 μL. Eluent A was acetonitrile (HPLC grade, Mallinckrodt Baker, Griesheim, Germany) and eluent B was a 10 mM NH₄HCO₃ (p.a., Mallinckrodt Baker, Griesheim, Germany) buffer with pH = 9.5. The elution started isocratically with 20% A and 80% B for 1 min. This step was followed by 9-minute different linear gradients to 84% of A with steps of 50% A after 4 min and 78% A after 6 min. This was held for 6 min followed by a linear gradient back to 20% of A. In the last 8 min of the procedure the system was equilibrated by holding these conditions. Thus, the measurement per sample takes 30 min. The determination limit (DIN 32645, 2008) derived from a linear calibration curve was for all compounds in the range of 5–35 μg L⁻¹ (significance level 0.05).

A2 Sediment analysis

The specific surface area of the sediment was determined with the N₂ adsorption/desorption BET method (Brunauer et al., 1938; DIN ISO 9277, 2003) by the use of Autosorb-1-C (Quantachrome) surface analyzer. Sediment pH was measured according to DIN ISO 10390, 2003 with ultrapure water as well as with a 0.01 M CaCl₂ solution. The determination of the total organic carbon TOC content was carried out by dry combustion of the priorly with 4 M HCl treated sediment at 900 °C in a total organic carbon analyzer (Dohrmann Boat Sampler 184 S / Rosemount Dohrmann DC 70). The effective (at sediment pH) and the potential (at pH = 8.1) cation exchange capacity CEC was measured in accordance with DIN ISO 11260, 1997 and DIN ISO 13536, 1997, respectively. The mineralogical constitution of the sediment was

characterized by macroscopic observation and combined X-ray diffractometry-thermoanalysis (Siemens diffractometer D5000, Netzsch STA 409 PG Luxx).

A3 Comparison of applied correlations

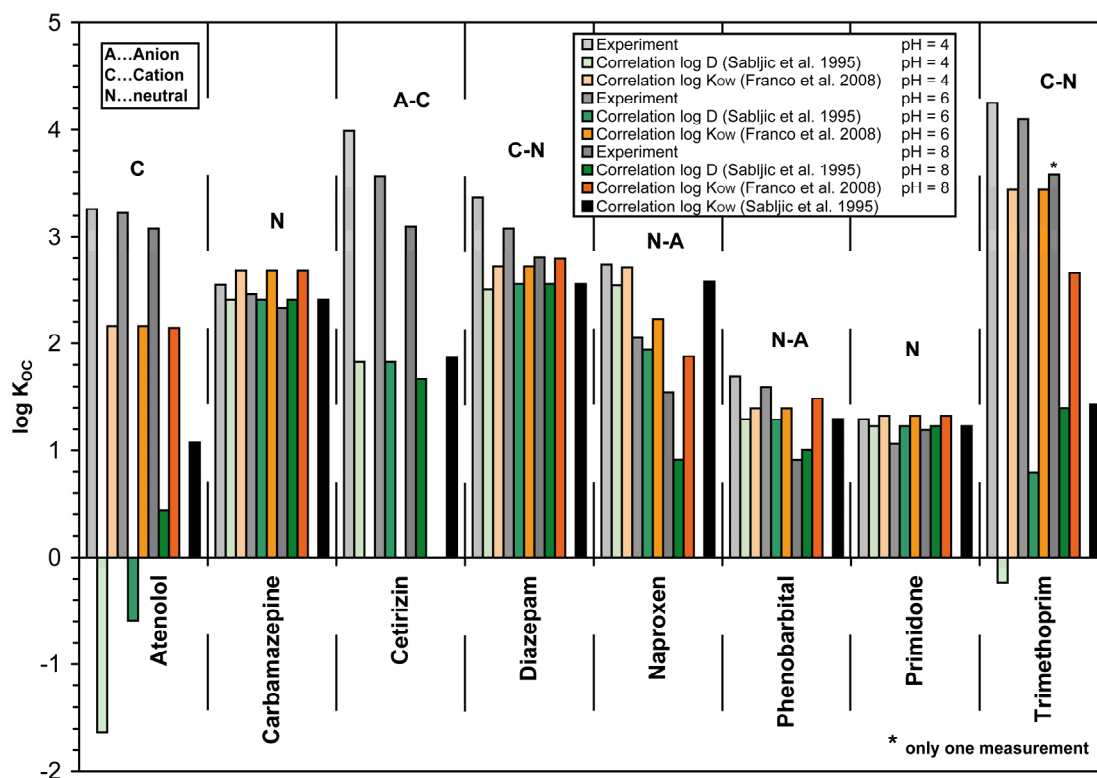


Fig. A1 Average from column experiments derived $\log K_{OC}$ values (grey columns) compared with estimated $\log K_{OC}$ values calculated with the modified $\log K_{OW}$ - $\log K_{OC}$ correlation after Sabljic et al. (1995) (green columns) and the correlations of Franco et al. (2008) (orange columns) for all compounds at pH = 4, pH = 6, and pH = 8. The correlation from Franco et al. (2008) could not be applied for the zwitter-ionic cetirizine.

A4 References

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Appendix A

DIN ISO 13536, 1997. Soil quality - Determination of the potential cation exchange capacity and exchangeable cations using barium chloride solution buffered at pH = 8.1. Deutsches Institut für Normung e. V., Beuth, Berlin, Germany.

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Appendix B

B1 Tracer tests

Table B1 Column experimental conditions and modeled parameters of the tracer tests.

Tracer test of experiment	Q [mL/min]	v_f [cm/min]	t_{id} [min]	n_e [-]	v_w [cm/min]	R [-]	λ [1/h]	α [cm]	lower α [cm]	upper α [cm]	R^2 [-]	MSE [-]
A1 & A2	0.45	0.05	178.9	0.35	0.14	1	0.000	0.301	0.250	0.326	0.99880	2.56E-04
A3 & A4	0.50	0.05	133.4	0.29	0.19	1	0.000	0.751	0.585	0.916	0.99599	8.02E-04
C1	0.50	0.05	165.6	0.36	0.15	1	0.000	0.059	0.028	0.243	0.99266	1.59E-03
C2	0.49	0.05	183.1	0.39	0.14	1	0.000	0.083	0.068	0.098	0.99879	2.59E-04
C3	0.50	0.05	184.0	0.40	0.14	1	0.000	0.233	0.167	0.299	0.99231	1.61E-03
C4	0.50	0.05	184.0	0.40	0.14	1	0.000	0.479	0.429	0.528	0.99862	2.74E-04
D1	0.50	0.05	184.0	0.40	0.14	1	0.000	0.425	0.337	0.513	0.99426	1.17E-03
<u>Replicates</u>												
C4_R	0.50	0.05	184.0	0.40	0.14	1	0.000	0.494	0.424	0.564	0.99687	5.81E-04
D1_R	0.50	0.05	188.6	0.41	0.13	1	0.000	0.205	0.159	0.251	0.99501	1.06E-03

Q = volumetric flow rate, v_f = filter velocity, t_{id} = ideal breakthrough time, n_e = effective porosity, v_w = pore water velocity, R = retardation factor, λ = first order degradation rate, α = dispersivity (including 95% confidence limits), R^2 = coefficient of determination, MSE = mean squared error

B2 Inverse modeling of the breakthrough curves

Table B2 CXTFIT modeled parameters and fit quality for all column experiments.

Experiment	Q [ml/min]	V_f [cm/min]	n_e [-]	V_w [cm/min]	λ [1/h]	lower λ [1/h]	upper λ [1/h]	a [cm]	lower a [cm]	upper a [cm]	R [-]	lower R [-]	upper R [-]	R^2 [-]	MSE [-]
A1	0.45	0.05	0.35	0.14	0.123	0.115	0.131	1.599	1.268	1.931	18.49	17.91	19.08	0.99604	3.72E-04
A2	0.45	0.05	0.35	0.14	0.100	0.095	0.104	1.548	1.262	1.835	7.42	7.23	7.60	0.99808	2.02E-04
A3	0.45	0.05	0.29	0.17	0.078	0.069	0.087	1.557	1.210	1.904	22.44	21.69	23.19	0.99673	4.58E-04
A4	0.42	0.05	0.29	0.16	0.067	0.062	0.071	1.593	1.358	1.826	12.12	11.85	12.40	0.99792	2.53E-04
B1	0.45	0.05	0.35	0.14	$c_0 = 0.73, \lambda = 0.00$		0.000	0.000	3.770	2.891	18.09	17.22	18.97	0.99169	7.70E-04
B3	0.40	0.04	0.29	0.15	$c_0 = 0.85, \lambda = 0.00$		0.000	0.000	3.112	2.701	25.14	24.60	25.68	0.99767	2.80E-04
C1	0.50	0.05	0.36	0.15	0.071	0.061	0.080	1.083	0.758	1.408	4.88	4.71	5.04	0.99478	7.79E-04
C2	0.49	0.05	0.39	0.14	0.028	0.022	0.033	0.553	0.429	0.676	4.31	4.24	4.38	0.99674	5.33E-04
C3	0.50	0.05	0.40	0.14	0.013	0.009	0.016	1.170	1.033	1.306	4.60	4.53	4.66	0.99835	3.25E-04
C4	0.50	0.05	0.40	0.14	0.013	0.008	0.017	1.660	1.445	1.877	5.36	5.27	5.46	0.99836	3.20E-04
D1_Eq	0.50	0.05	0.40	0.14	0.000	0.000	0.000	5.576	4.851	6.302	10.33	10.04	10.61	0.98683	1.83E-03
D1_nonEq	0.50	0.05	0.40	0.14	0.000	0.000	0.000	0.781	0.554	1.008	10.79	10.62	10.95	0.99767	3.32E-04
Replicates															
A1_R	0.45	0.05	0.35	0.14	0.145	0.14	0.15	1.162	0.924	1.400	17.99	17.48	18.50	0.99903	9.41E-05
C4_R	0.50	0.05	0.40	0.14	0.018	0.01	0.02	1.601	1.398	1.803	4.95	4.87	5.03	0.99809	3.24E-04
D1_R_Eq	0.50	0.05	0.41	0.13	0.000	0.00	0.00	3.448	2.506	4.391	8.54	8.14	8.95	0.97947	2.47E-03
D1_R_nonEq	0.50	0.05	0.41	0.13	0.000	0.00	0.00	0.640	0.432	0.848	9.41	9.19	9.63	0.99848	1.99E-04

Q = volumetric flow rate, V_f = filter velocity, n_e = effective porosity, V_w = pore water velocity, λ = first order degradation rate (including 95% confidence limits), a = dispersivity (including 95% confidence limits), R = retardation factor (including 95% confidence limits), R^2 = coefficient of determination, MSE = mean squared error, Eq = equilibrium model, nonEq = non-equilibrium model

B3 Exemplary replicates of the experiments

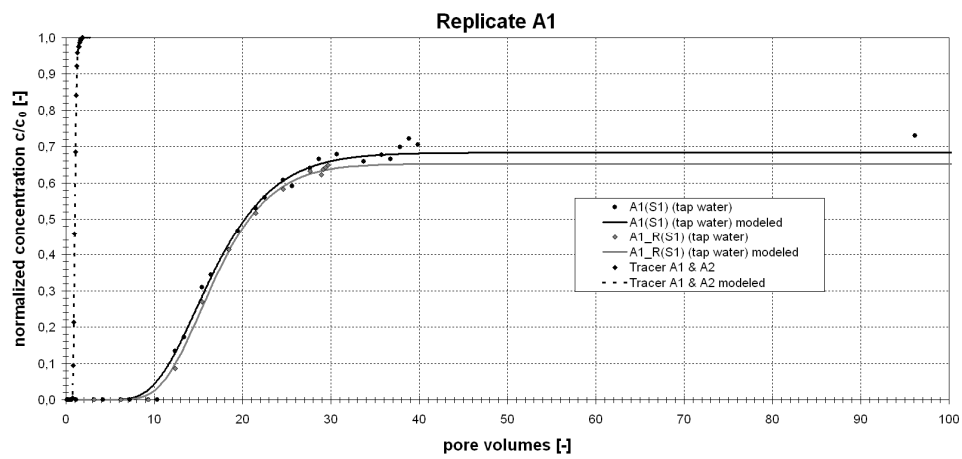


Fig. B1 Replicate of experiment A1.

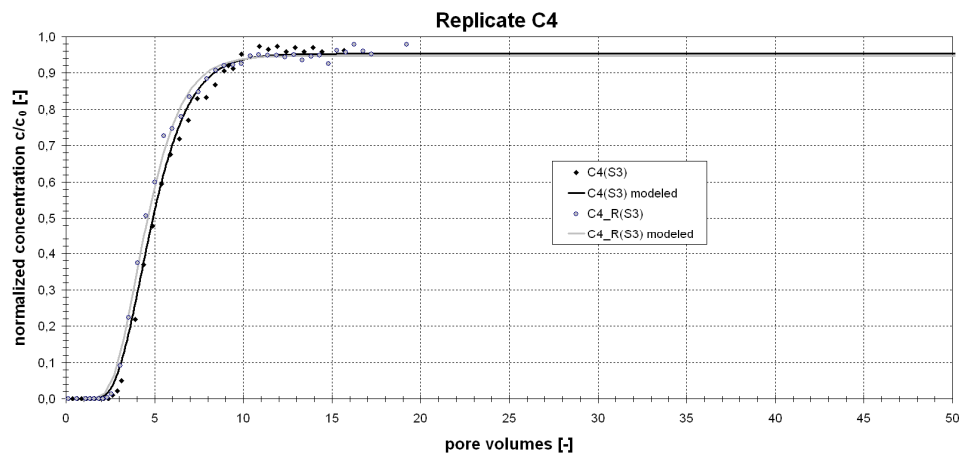


Fig. B2 Replicate of experiment C4.

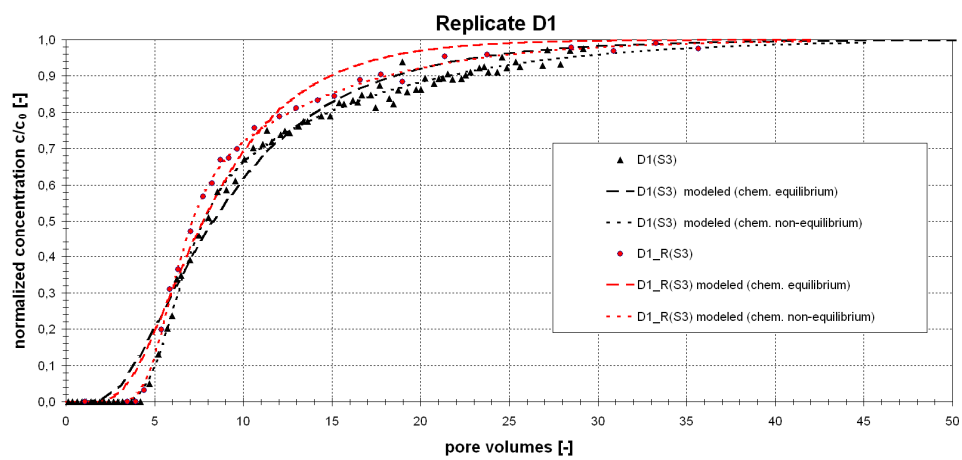


Fig. B3 Replicate of experiment D1.

Appendix C

C1 Sorption capacity of the different grain size fractions

The particle size distribution of the sediment is an important factor, which has to be considered in sorption experiments. For this reason, preliminary experiments were conducted with separated grain size fractions to prove which fractions provide the highest sorption capacities or whether the main experiments can be conducted with sediment bulk.

The particle size distribution of the sediment was analyzed with the Laser Diffraction Particle Size Analyzer LS 13320 (Beckman & Coulter Inc., Fullerton, USA), in line with the U.S.D.A. classification in a range of 0.04 μm to 2,000 μm . The sediment was divided into ten subsamples and subsequently averaged. An amount of 5–10 g of each subsample was analyzed by the ultrasonic device Sonoplus HD 2070 (Bandelin electronic, Berlin, Germany) in a suspending fluid three times. The region from 0.04 μm to 0.4 μm is covered by Polarization Intensity Differential Scattering (PIDS) technology. Afterwards, the mean was calculated.

Although the particle size distribution revealed rather well sorted sediment, different particle size fractions were tested for their sorption capacity towards metoprolol. The aquifer material was separated into five fractions representing the main size distributions. These fractions were received due to mechanical dry sieving with an even distribution over the whole particle size range. A set of five sieves in a range from 63 μm up to 1,000 μm were used. For each sieving procedure, the sieve tower was filled with 100 g of sediment and clamped on to the vibrating table for 10 min with an amplitude of 1.5 mm and a vibrating interval of 5 s. Afterwards, the different particle sizes were collected separately. Details on the sorption experiments and its chemical analysis can be found in Chapter 4.2.

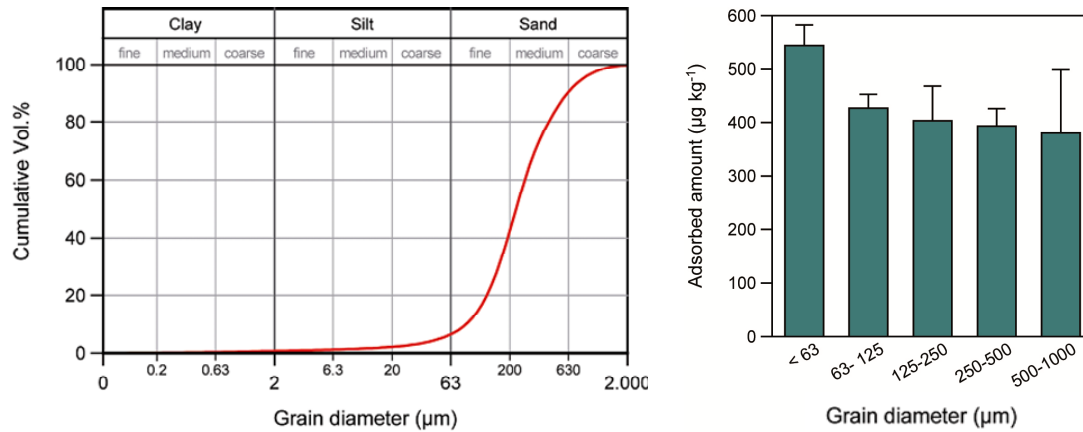


Fig. C1 left: Mean cumulative particle size distribution of the sediment; right: Distribution of sorbed metoprolol on the different particle size fractions at neutral pH and a temperature of 20 ± 1 °C. Results are presented in terms of averages of data from the duplicate batches. The error bars reported in the figure have been calculated by considering the difference between batch results.

C2 Statistical analysis of the isotherms

For evaluating the Freundlich isotherms fit quality and confidence limits, the equilibrium concentrations c_{eq} and sorbed amount q_{eq} were logarithmized and subsequently evaluated with a simple linear regression model. Assuming Student distributed (t -distribution) residuals and a two-sided significance level of $\alpha = 0.05$, the 95% confidence intervals can be calculated with:

$$n = \pm t_{n-2; 1-\alpha/2} \frac{\hat{\sigma}}{s_x \sqrt{n-1}} \quad \text{with} \quad \hat{\sigma}^2 = \frac{1}{n-2} \sum_{i=1}^n (\lg q_{eq,i} - \lg K_{Fr} - n_{Fr} \cdot \lg c_{eq,i})^2 \quad (C1)$$

where n is the number of data points, $t_{n-2; 1-\alpha/2}$ is the t -quantile, s_x is the standard deviation of $\lg c_{eq}$, $\hat{\sigma}^2$ is the variance of the residuals as estimator for the regression error, K_{Fr} is the Freundlich coefficient and n_{Fr} is the Freundlich exponent (slope of regression line). The fitted isotherms including the corresponding confidence intervals are shown in Figures C2–C8.

Further, in Table 4.2 the sum of least-square errors (SSE) is given as measure for the fit quality:

$$SSE = \sum_{i=1}^n (\lg q_{i,obs} - \lg q_{i,fit})^2 \quad (C2)$$

Appendix C

$q_{i,obs}$ is the sorbed amount observed in the experiments and $q_{i,fit}$ is the simulated sorbed amount for all c_{eq} .

C2.1 Reference Isotherm without competition

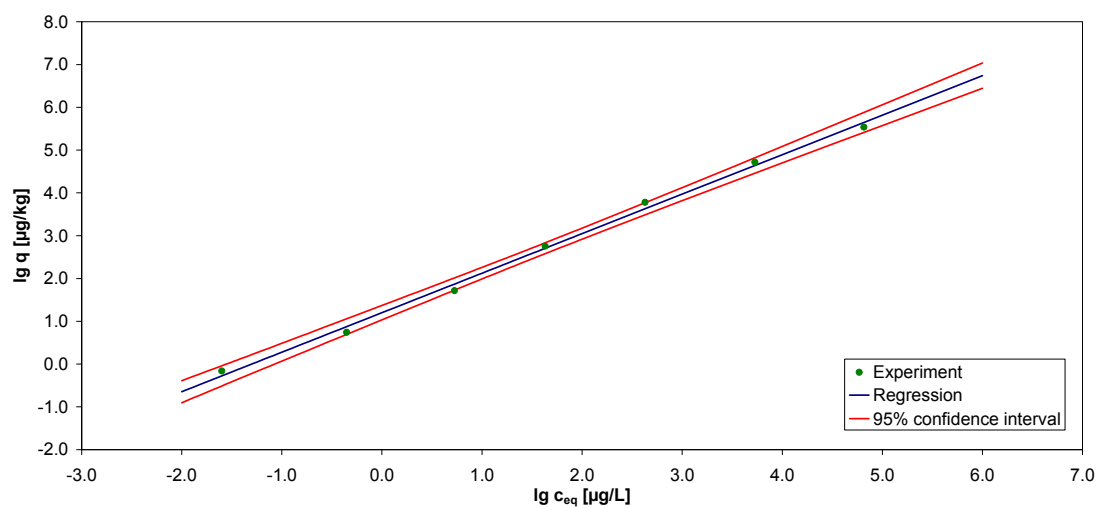
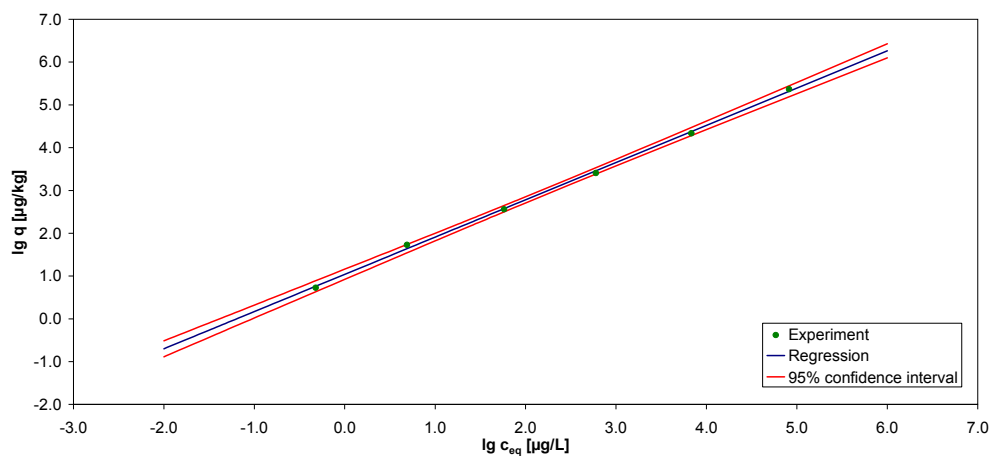
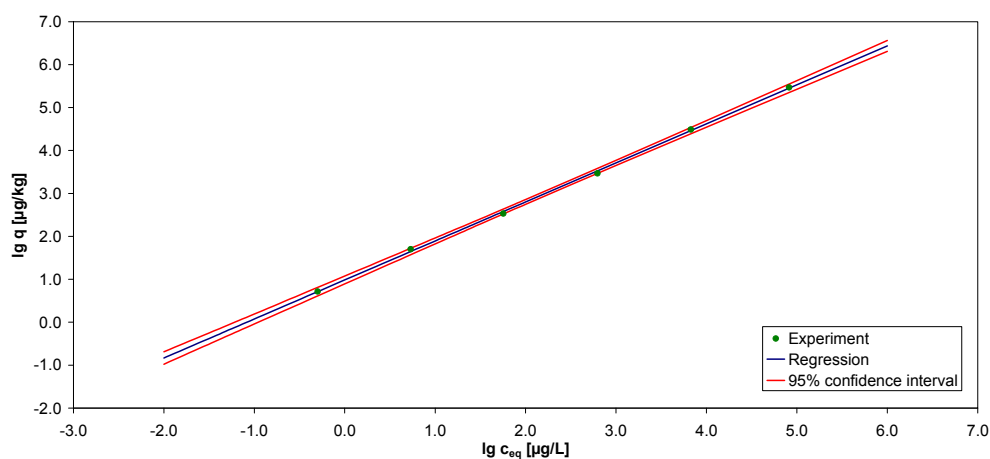
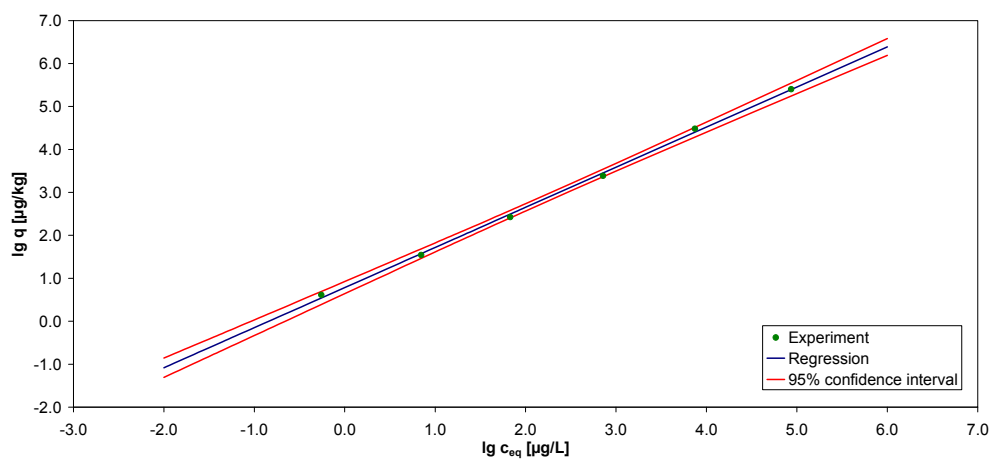


Fig. C2 Reference isotherm for metoprolol ($R^2 = 0.9962$).

C2.2 Isotherms for competition with Na^+ **Fig. C3 Isotherm of metoprolol at $0.37 \text{ mmol L}^{-1} \text{ Na}^+$ ($R^2 = 0.9989$).****Fig. C4 Isotherm of metoprolol at $3.7 \text{ mmol L}^{-1} \text{ Na}^+$ ($R^2 = 0.9994$).****Fig. C5 Isotherm of metoprolol at $37.0 \text{ mmol L}^{-1} \text{ Na}^+$ ($R^2 = 0.9986$).**

C2.3 Isotherms for competition with Ca^{2+}

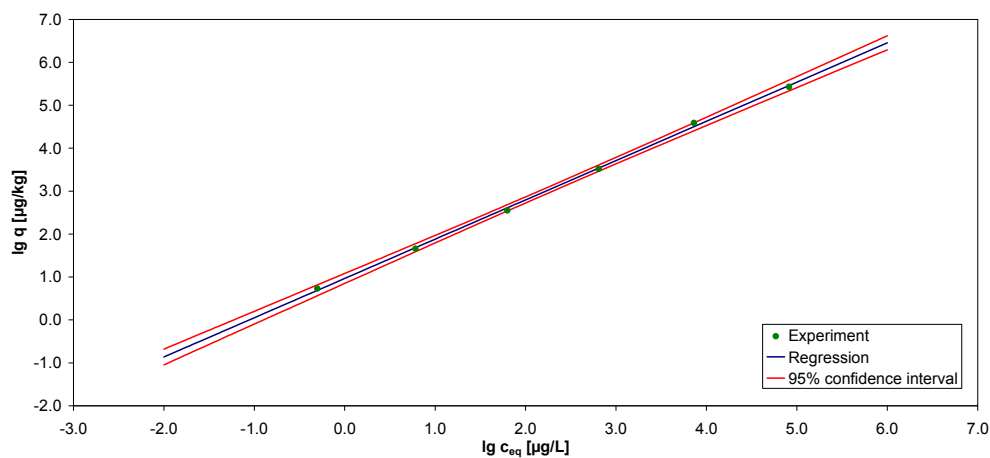


Fig. C6 Isotherm of metoprolol at 0.37 mmol L⁻¹ Ca²⁺ ($R^2 = 0.9990$).

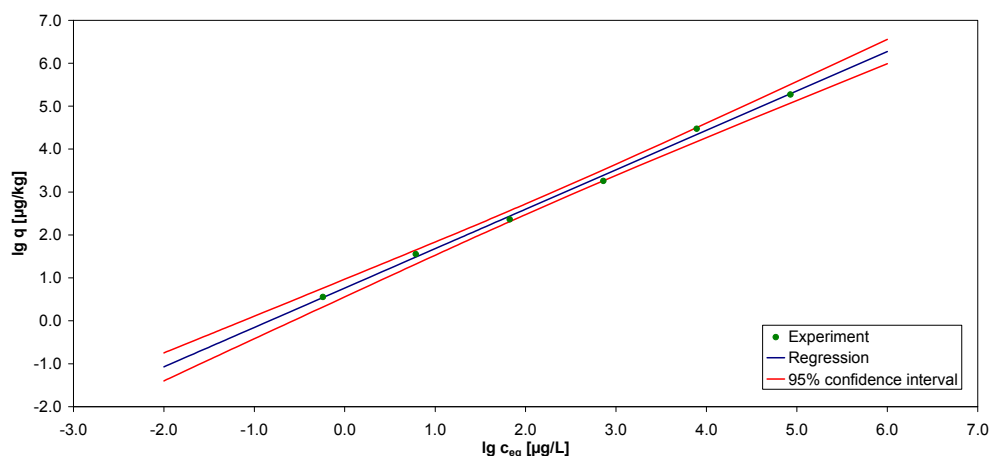


Fig. C7 Isotherm of metoprolol at 3.7 mmol L⁻¹ Ca²⁺ ($R^2 = 0.9970$).

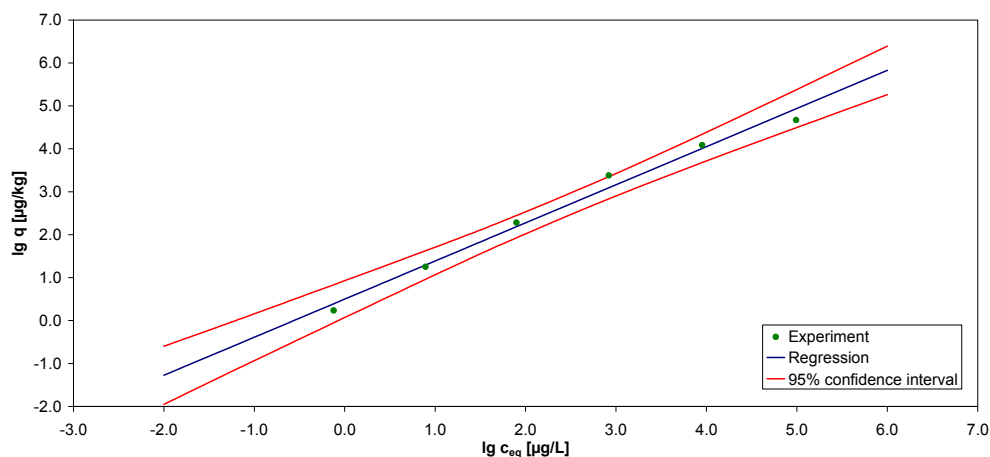


Fig. C8 Isotherm of metoprolol at 37 mmol L⁻¹ Ca²⁺ ($R^2 = 0.9869$).

Appendix D

List of all journal articles, conference abstracts, and miscellaneous publications authored or co-authored by me and related to the presented work (latest update: May 2013).

Journals (peer-reviewed)

Schaffer, M., Maier, F., Licha, T., Sauter, M., 2013. A new generation of tracers for the characterization of interfacial areas during supercritical carbon dioxide injections into deep saline aquifers: Kinetic interface-sensitive tracers (KIS tracer). *International Journal of Greenhouse Gas Control* 14, 200–208.

Niedbala, A., **Schaffer, M.**, Licha, T., Nödler, K., Börnick, H., Ruppert, H., Worch, E., 2013. Influence of competing inorganic cations on the ion exchange equilibrium of the monovalent organic cation metoprolol on natural sediment. *Chemosphere* 90 (6), 1945–1951.

Schaffer, M., Börnick, H., Nödler, K., Licha, T., Worch, E., 2012. Role of cation exchange processes on the sorption influenced transport of cationic β -blockers in aquifer sediments. *Water Research* 46 (17), 5472–5482.

Schaffer, M., Boxberger, N., Börnick, H., Licha, T., Worch, E., 2012. Sorption influenced transport of ionizable pharmaceuticals onto a natural sandy aquifer sediment at different pH. *Chemosphere* 87 (5), 513–520.

Schaffer, M., Boxberger, N., Börnick, H., Licha, T., Worch, E., 2010. Säulenversuche zur Simulation des pH-abhängigen Stofftransportes ausgewählter pharmazeutischer Wirkstoffe im Grundwasserleiter. *Vom Wasser* 108 (4), 111–130.

Conference contributions

- Tatomir, A., Maier, F., **Schaffer, M.**, Licha, T., Sauter, M., 2013. Modelling of kinetic interface sensitive tracers for two-phase systems. In: *Proceedings of the 3rd Sino-German Conference "Underground Storage of CO₂ and Energy"*, Goslar, Germany, pp. 65–74 (ISBN 978-3-642-37848-5).
- Börnack, H., Lucks, C., **Schaffer, M.**, Worch, E., Licha, T., 2012. Experimentelle Untersuchung und Modellierung des Stofftransportes von zwei UV-Filtersubstanzen unter Nichtgleichgewichtsbedingungen. In: *Tagungsband Gemeinsame Jahrestagung der SETAC GLB und der Fachgruppe Umweltchemie und Ökotoxikologie der GDCh 2012*, Leipzig, Germany, p. 156.
- Schaffer, M.**, Niedbala, A., Nödler, K., Licha, T., Börnick, H., Fona, Z., Worch, E., 2012. Untersuchungen zum Kationenaustauschverhalten des basischen β -Blockers Metoprolol an natürlichen Sorbentien. *Schriftenreihe der Deutschen Gesellschaft für Geowissenschaften* Heft 78, Tagung der Fachsektion Hydrogeologie in der DGG (FH-DGG), Dresden, Germany, p. 187 (ISSN 1860-1782).
- Schaffer, M.**, Maier, F., Licha, T., Sauter, M., 2012. Entwicklung kinetischer Tracer zur Quantifizierung von Grenzflächen bei Injektionen von überkritischem CO₂ in tiefe saline Aquifere. *Schriftenreihe der Deutschen Gesellschaft für Geowissenschaften* Heft 78, Tagung der Fachsektion Hydrogeologie in der DGG (FH-DGG), Dresden, Germany, p. 166 (ISSN 1860-1782).
- Schaffer, M.**, Niedbala, A., Nödler, K., Licha, T., Börnick, H., Worch, E., 2012. Sorptionsverhalten organischer Kationen an natürlichem Sediment am Beispiel des Beta-Blockers Metoprolol. In: *Tagungsband Jahrestagung der Wasserchemischen Gesellschaft 2012*, Neu-Ulm, Germany, pp. 410–414 (ISBN 978-3-936028-71-3).
- Schaffer, M.**, Maier, F., Licha, T., Sauter, M., 2012. Entwicklung kinetischer Grenzflächentracer für Injektionen von überkritischem CO₂ in tiefe saline Grundwasserleiter. In: *Tagungsband Jahrestagung der Wasserchemischen Gesellschaft 2012*, Neu-Ulm, Germany, pp. 387–391 (ISBN 978-3-936028-71-3).
- Ghergut, I., Behrens, H., Licha, T., Maier, F., Nottebohm, M., **Schaffer, M.**, Sauter, M., 2012. Single-well and inter-well dual-tracer test design for quantifying phase volumes and interface areas in subsurface flow and transport systems. *Geophysical Research Abstracts* 14, EGU2012-13549, EGU General Assembly 2012, Vienna, Austria.
- Schaffer, M.**, Maier, F., Licha, T., Sauter, M., 2012. Development of kinetic interface sensitive tracers (KIS-Tracer) for supercritical carbon dioxide injections into deep saline aquifers. *Geophysical Research Abstracts* 14, EGU2012-2048. EGU General Assembly 2012, Vienna, Austria.
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- Börnack, H., **Schaffer, M.**, Worch, E., Grischek, T., 2011. Characterization of the attenuation behaviour of organic micropollutants in water/sediment systems using column experiments. In: *Proceedings GEOINDO 2011*, Khon Kaen, Thailand, pp. 344–349 (ISBN 978-616-223-143-8).
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- Schaffer M.**, Börnick H., Licha, T., Worch E. (2010): Untersuchung zum Stofftransport des basischen Betablockers Atenolol in gesättigten Aquiferen unterschiedlicher Kationenaustauschkapazität. *Umweltwissenschaften und Schadstoff-Forschung* 22 (4), Gemeinsame Jahrestagung der SETAC GLB und der Fachgruppe Umweltchemie und Ökotoxikologie der GDCh 2010, Dessau-Roßlau, Germany, p. 409.
- Schaffer, M.**, Börnick, H., Boxberger, N., Licha, T., Worch, E., 2010. Investigations of the pH-dependent transport of pharmaceuticals in saturated sandy aquifers using column experiments. In: *Book of Abstracts of the 3rd EuCheMS Chemistry Congress*, Nuremberg, Germany, IIb.013.

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