Characterization of sorption processes of organic cations onto selected oxidic surfaces

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Übereinstimmungserklärung

Die Übereinstimmung dieses Exemplars mit dem Original der Dissertation zum Thema:
„Characterization of sorption processes of organic cations onto selected oxidic surfaces” wird hiermit bestätigt.

Die vorliegende Arbeit wurde im Zeitraum April 2013 bis September 2018 im Arbeitskreis von Prof. Dr. Eckhard Worch am Institut für Wasserchemie der Technischen Universität Dresden durchgeführt.

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Short Summary

Since a large number of polar and often ionizable anthropogenic organic trace compounds, such as pharmaceutical residues, can be detected in various stages of the water cycle, there is a need to elucidate the effects and behavior of such substances in the aquatic environment. Despite the fact that numerous studies on the sorption behavior of ionizable organic trace compounds have already been carried out, reliable sorption models, which allow a sufficiently accurate prediction of the sorption of organic cations, are not yet available. For this reason, the general objective of this thesis was to improve the fundamental process understanding of the interactions between dissolved cationic organic substances and solid surfaces including relevant influence parameters. The investigations were based on a differentiated process consideration in order to ultimately provide the essential prerequisites for a future reliable prediction of the sorption behavior of cationic organic compounds. Due to the complex superposition of several mechanisms, the basic relationships cannot be clearly elucidated with heterogeneous sorbents. Therefore, it was consciously worked with largely homogeneous, synthetic sorbents. The use of well-defined sorbents with different properties as well as the variation of background electrolyte concentration and the targeted use of different sorbates were the "tools" that were used to identify and to separate the underlying sorption processes.

First, the role of the already identified ion exchange mechanism has been considered in detail. For this purpose, systematic batch tests with the cationic species of metoprolol (MET), an active substance of the drug class of beta-blockers and a typical example for cationic organic trace substances occurring in surface and waste waters, on defined synthetic silica gel were carried out under variation of relevant influencing variables (e.g., nature and concentration of competing inorganic cations). All sorption data could be described well by the Freundlich isotherm model. In general, a clear reduction in the sorption of the organic cation with increasing concentration of competing inorganic cations was observed, which confirms the dominant role of cation exchange processes. Due to the higher valence of divalent cations, these ions have a substantially stronger absolute influence on the exchange equilibrium of MET than monovalent cations. However, the relative influence decreases with increasing electrolyte concentration. In the case of competing ions of the same valence, a certain

dependence of the sorption affinity on the size of the hydrated ions could be observed. For the investigated concentration range, a linear relationship between the logarithmic Freundlich sorption coefficient and the logarithmic equivalent concentration of competing inorganic cations was found. This allows the prediction of the MET sorption within the investigated range of boundary conditions. In addition, experiments with mixtures with more than one dissolved inorganic cation have shown that a prediction of the combined competitive effect by a simple addition of the contributions of individual ions can only be achieved at low electrolyte concentrations. With increasing ionic strength, the predictability decreases, and the sorption is overestimated. A possible cause might be the occupation of accessible exchange sites with competing ions reaches a maximum (cation exchange capacity). However, even at high electrolyte concentrations, a still significant sorption of the organic cation, present in substantially lower concentrations, occurred. Such pronounced sorption was observed even after a charge reversal on the silica gel surface by pH reduction. This suggests that in addition to the dominant ion exchange further interaction mechanisms are involved in sorption.

In the following, by investigating an even higher concentration level of competing inorganic cations ($c > 1$ M), the assumption of a saturation effect of exchange sites onto sorbent surface should be confirmed and the contribution of non-ionic interaction processes should be studied separately. However, the sorption of the organic cation on the two investigated silica gels (amorphous and spherical) improved significantly. The unexpected recovering in sorption was attributed to sorbate-specific, non-ionic interactions (e.g., hydrogen bonding, hydrophobic sorption), whose proportion is shifted as a function of electrolyte concentration. It is assumed that there is a link between the concentration curve of the activity coefficient and the observed sorption (expressed as sorption coefficient) or that the same cause is responsible for a similar behavior. On the basis of the achieved results, a conceptual model approach was developed, which initially distinguishes two different sorption processes: 1.) ion exchange (unspecific sorption) and 2.) non-ion exchange (specific sorption).

In the last part of the work, the main objective was to find a relation between sorbent properties and the various interactions in order to determine suitable parameters for a prediction of the sorption of organic cations. For this reason, the comprehensive and accurate determination of the sorbent properties was a special focus to better describe the dependencies and observed effects. The investigations were limited to two

fundamentally different oxidic materials (silicon dioxide and aluminum oxide). A total of five sorbents, three probe molecules and four electrolyte concentrations were used in 120 column experiments. The sorption strength of different sorbents revealed an identical sequence for all investigated factors. As expected, the sorption of probe molecules on positively charged aluminum oxide is significantly weaker in comparison to the investigated silica gels. The results show a direct relationship between the number of OH surface groups and the degree of sorption. In addition to cation exchange processes, this sorbent parameter also takes into account non-ionic interactions. Based on the found linear correlation, a sorption prediction for investigated probe molecules at different sorbents became possible. The studies with the cationic species of isopropyl-(4-methylbenzyl)-amine (iP4MBA), a substance structurally related to MET, showed similar but lower sorption compared to MET. The difference is attributed to a lower H-acceptor/donor sum. In order to quantify the contribution of non-ionic interactions to the total sorption, experiments with an uncharged compound (benzyl alcohol; BA) were carried out. Due to the lack of electrostatic interactions, a much weaker sorption was observed compared to the organic cations and an independence from ionic strength was found. In the case of very high electrolyte concentrations, however, a considerable improvement in sorption occurred, so that this effect is not specific for cationic substances and is presumably a result of the increase in non-ionic interactions.

The obtained results illustrate the high complexity of the sorption of organic cations on charged solid surfaces and provide a further step to a better process understanding, which is of crucial importance for an accurate prediction and adequate environmental risk assessment.

Kurzfassung

Da eine Vielzahl polarer und oftmals ionisierbarer anthropogener organischer Spurenstoffe, wie z. B. Pharmakarückstände, in verschiedenen Bereichen des Wasserkreislaufes nachweisbar ist, besteht die Notwendigkeit die Wirkung und das Verhalten solcher Spurenstoffe in der Umwelt näher aufzuklären. Trotz der Tatsache, dass bereits zahlreiche Untersuchungen zum Sorptionsverhalten ionisierbarer organischer Spurenstoffe bestehen, sind zuverlässige prognosefähige Sorptionsmodelle, welche eine ausreichend genaue Vorhersage der Sorption von organischen Kationen ermöglichen, zurzeit noch nicht verfügbar. Das generelle Ziel dieser Arbeit bestand daher darin, das grundlegende Prozessverständnis der Wechselwirkungen zwischen gelösten kationischen organischen Substanzen und festen Oberflächen einschließlich relevanter Einflussgrößen zu verbessern. Die Untersuchungen basierten auf einer differenzierten Prozessbetrachtung, um letztlich die wesentlichen Voraussetzungen für eine zukünftig zuverlässige Prognose des Sorptionsverhaltens kationischer organischer Verbindungen zu liefern. Aufgrund der komplexen Überlagerung mehrerer Mechanismen können die grundlegenden Zusammenhänge mit heterogen zusammengesetzten natürlichen Sorbentien nicht eindeutig aufgeklärt werden. Daher wurde bewusst mit weitgehend homogenen, synthetischen Sorbentien gearbeitet. Die Verwendung wohldefinierter Sorbentien mit unterschiedlichen Eigenschaften sowie die Variation der Elektrolytkonzentration und der gezielte Einsatz verschiedener Sorptive waren die "Werkzeuge", die verwendet wurden, um die zugrunde liegenden Sorptionsprozesse zu identifizieren und zu separieren.

Zunächst wurde die Rolle des bereits identifizierten Ionenaustauschmechanismus näher betrachtet. Hierfür wurden systematische Batchversuche mit der kationischen Spezies von Metoprolol (MET), einem Wirkstoff der Arzneimittelklasse der Beta-Blocker und ein typisches Beispiel für in Oberflächen- und Abwässern vorkommende kationische organische Spurenstoffe, an definierten synthetischen Kieselgel unter Variation relevanter Einflussgrößen (z. B. Art und Konzentration konkurrierender anorganischer Kationen) durchgeführt. Alle Sorptionsdaten konnten mit dem Freundlich-Isothermen Modell gut beschrieben werden. Generell wurde eine deutliche Verringerung der Sorption des organischen Kations mit zunehmender

Konzentration konkurrierender anorganischer Kationen beobachtet, was die dominierende Rolle von Kationenaustauschprozessen bestätigt. Aufgrund der höheren Valenz zweiwertiger Kationen besitzen diese Ionen einen wesentlich stärkeren Einfluss auf das Austauschgleichgewicht von MET als einwertige Kationen. Dieser nahm jedoch, relativ betrachtet, mit steigender Elektrolytkonzentration ab. Bei konkurrierenden Ionen gleicher Wertigkeit konnte eine gewisse Abhängigkeit der Sorptionsaffinität von der Größe der hydratisierten Ionen beobachtet werden. Für den untersuchten Konzentrationsbereich wurde ein linearer Zusammenhang zwischen dem Logarithmus des Freundlich-Sorptionskoeffizienten und dem Logarithmus der Äquivalentkonzentration konkurrierender anorganischer Kationen gefunden. Dies ermöglicht die Vorhersage der MET-Sorption innerhalb des Bereichs der untersuchten Randbedingungen. Außerdem haben Experimente mit Mischungen mit mehr als einem gelösten anorganischen Kation gezeigt, dass eine Vorausberechnung des kombinierten Konkurrenzeffektes durch einfache Addition der Beiträge einzelner Ionen nur bei niedrigen Elektrolytkonzentrationen erreicht werden kann. Mit zunehmender Ionenstärke nimmt die Vorhersagbarkeit ab und die Sorption wird überschätzt. Eine mögliche Ursache könnte sein, dass die Besetzung zugängiger Austauschstellen mit konkurrierenden Ionen ein Maximum erreicht (Kationenaustauschkapazität). Allerdings trat auch bei hohen Elektrolytkonzentrationen eine immer noch signifikante Sorption des in wesentlich geringeren Konzentrationen vorliegenden organischen Kations auf. Eine solche ausgeprägte Sorption wurde selbst nach einer Ladungsumkehr auf der Kieselgeloberfläche durch pH-Absenkung festgestellt. Dies spricht dafür, dass neben dem dominierenden Ionenaustausch noch weitere Wechselwirkungsmechanismen an der Sorption beteiligt sind.

Nachfolgend sollte durch die Untersuchung einer noch höheren Konzentrationsstufe an konkurrierenden anorganischen Kationen ($c > 1 \text{ M}$), die Vermutung einer auftretenden Sättigung des Austauschers bestätigt sowie der Beitrag von nicht-ionischen Wechselwirkungsprozessen separat studiert werden. Hierbei erhöhte sich die Sorption des organischen Kations an den beiden untersuchten Kieselgelen (amorph und sphärisch) allerdings wieder deutlich. Der unerwartete Wiederanstieg der Sorption wurde auf Sorptiv-spezifische, nicht-ionische Wechselwirkungen (z. B. Wasserstoffbrückenbindung, hydrophobe Sorption) zurückgeführt, deren Anteil sich in Abhängigkeit von der Elektrolytkonzentration verschiebt. Es wird angenommen, dass ein Zusammenhang zwischen dem Konzentrationsverlauf des Aktivitätskoeffizienten

und der beobachteten Sorption (ausgedrückt als Sorptionskoeffizient) besteht bzw. dass für ein ähnliches Verhalten die gleiche Ursache vorliegt. Anhand der erzielten Ergebnisse wurde ein konzeptioneller Modellvorschlag erarbeitet, der zunächst zwei verschiedene Sorptionsprozesse: 1.) Ionenaustausch (unspezifische Sorption) und 2.) Nicht-Ionenaustausch (spezifische Sorption) unterscheidet.

Im letzten Teil der Arbeit bestand das wesentliche Ziel darin, eine Beziehung zwischen den Sorbenseigenschaften und den verschiedenen Wechselwirkungen zu finden, um geeignete Parameter für eine Vorausberechnung der Sorption organischer Kationen zu bestimmen. Aus diesem Grund stellte zunächst die umfassende und möglichst exakte Erfassung der Sorbenseigenschaften einen besonderen Schwerpunkt dar, um die Abhängigkeiten und beobachteten Effekte besser beschreiben zu können. Die Untersuchungen wurden auf zwei grundsätzlich unterschiedliche oxidische Materialien (Siliziumdioxid bzw. Aluminiumoxid) begrenzt. In 120 Säulenversuchen kamen insgesamt fünf Sorbentien, drei Sorptive und vier Elektrolytkonzentrationen zum Einsatz. Die Sorptionsstärke der verschiedenen Sorbentien ergab für alle untersuchten Einflussgrößen eine identische Reihenfolge. Erwartungsgemäß sorbieren die Modellsubstanzen an positiv geladenem Aluminiumoxid deutlich schwächer im Vergleich zu den untersuchten Kieselgelen. Die Ergebnisse zeigen einen direkten Zusammenhang zwischen der Anzahl an OH-Oberflächengruppen und dem Sorptionsausmaß. Dieser Sorbensparameter berücksichtigt neben Kationenaustauschprozessen auch nicht-ionische Wechselwirkungen. Basierend auf der gefundenen linearen Korrelation wird die Sorptionsvorhersage für die untersuchten Modellsubstanzen an verschiedenen Sorbentien ermöglicht. Die Studien mit der kationischen Spezies von Isopropyl-(4-methylbenzyl)-amin (iP4MBA), einer strukturell mit MET verwandten Substanz, zeigten im Vergleich zu MET eine ähnliche, jedoch geringere Sorption. Dieser Unterschied wird einer geringeren H-Akzeptor-/Donorsumme zugeschrieben. Um den Beitrag nicht-ionischer Wechselwirkungen zur Gesamtsorption näher zu quantifizieren, wurden Versuche mit einer ungeladenen Substanz (Benzylalkohol; BA) durchgeführt. Aufgrund des Fehlens elektrostatischer Wechselwirkungen wurde eine deutlich schwächere Sorption im Vergleich zu den organischen Kationen beobachtet und eine Unabhängigkeit von der Ionenstärke gefunden. Bei sehr hohen Elektrolytkonzentrationen kam es jedoch zu einer erheblichen Verbesserung der Sorption, so dass dieser Effekt nicht spezifisch für

kationische Substanzen ist und vermutlich auf die Zunahme nicht-ionischer Wechselwirkungen zurückzuführen ist.

Die erhaltenen Ergebnisse verdeutlichen die hohe Komplexität der Sorption von organischen Kationen an geladenen Feststoffoberflächen und liefern einen weiteren Beitrag zum besseren Prozessverständnis, was von entscheidender Bedeutung für eine genaue Vorhersage und angemessene Umweltrisikobewertung ist.

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List of publications

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Chapter 1

1 General introduction

1.1 Motivation and background

1.1.1 Anthropogenic organic compounds in the aquatic environment

During the last decades, diverse groups of organic micropollutants, including pharmaceuticals, pesticides or surfactants have been identified in different environmental compartments, due to the continuous improvement of analytical methods and the availability of more and more sophisticated techniques (Halling-Sørensen, 1998; Daughton and Ternes, 1999; Heberer, 2002; Kolpin et al., 2002; Ternes et al., 2004; Schwarzenbach et al., 2006; Reemtsma and Jekel, 2006). These often polar and ionizable substances are often persistent and difficult removable by conventional waste water treatment technologies. Municipal waste water treatment plants are currently not designed for the elimination of anthropogenic trace compounds, so that these substances are not or only partially removed and thus can enter into the water cycle (Ternes, 1998; Heberer, 2002; Thomas et al., 2004; Reemtsma et al., 2010).

Pharmaceuticals as one important group of organic micropollutants have been highlighted and received global attentions in last decade, due to their huge quantities of production and usage (Halling-Sørensen, 1998; Richardson et al., 2005; Schulte-Oehlmann et al., 2007; Ma et al., 2017). Drug residues as well as a huge number of their transformation products are to be regarded as ubiquitous contamination, as they could be detected worldwide in various water bodies (e.g., waste water, surface water, ground water, drinking water) (Heberer, 1995, 1997, 2002; Halling-Sørensen, 1998; Ternes, 1998; Zuccato et al., 2000; Ternes et al., 2002; Kolpin et al., 2002; Thomas et al., 2004; Vieno, 2006). The full extent and consequences that pharmaceuticals pose in the environment are largely unknown. Their detected concentrations range up to the lower µg/L levels (Sacher et al., 2001; Brausch et al., 2012) and are thus generally well below their effect threshold for human use. However, there is still a dearth of information on chronic exposures and the cumulative effect of pharmaceutical mixtures. Furthermore, the interaction processes that are caused by

other water constituents and the ecosystem are only insufficiently understood (Jørgensen and Halling-Sørensen, 2000; Cleuvers et al., 2003, 2004; Sanderson et al., 2003; Schwarzenbach et al., 2006; Kümmerer, 2010). Therefore, investigations on the distribution of these substances are important in order to gain more knowledge about their fate in the environment and thus possible negative effects or consequences on ecosystems as well as for water utilization (e.g., drinking water production). The transport behavior in subsurface is of particular interest, since soils, sediments or aquifers act as natural substance sinks by sorption and degradation processes at the interfaces between water and solid.

Many of the organic micropollutants detected today in the environment have several functional groups and are often more polar and more complex in their structure as "classical pollutants" (e.g., polycyclic aromatic hydrocarbons) (Bronner and Goss, 2011). Of particular interest are especially organic bases with pK_a values above the common pH range of natural waters (pK_a of the conjugate acid), since these substances have a positive charge (= organic cation) and thus often show a considerable retardation due to cation exchange processes (Tolls, 2001; Kah and Brown, 2007; Yamamoto et al., 2009; Bäuerlein et al., 2012; Droge and Goss, 2012; Schaffer et al., 2012a, 2012b; Niedbala et al., 2013). Most models used in the context of environmental risk assessment were primarily developed for neutral organic compounds and fail for organic cations, because electrostatically driven sorption processes are not considered (Tolls, 2001; Cunningham et al., 2004; Kah and Brown, 2007; Schaffer et al., 2012a). Up to now, comprehensive models predicting the sorption behavior of organic cations are not available (MacKay and Vasudevan, 2012; Endo and Goss, 2014; Webster, 2014; Schaffer and Licha, 2015). In a study by Manallack (2007) the pK_a distribution of a test set of 582 drugs was investigated. It was found that 77.5% of the studied substances are ionizable under environmental relevant pH, hereof 55.9% had a single or bivalent base group and thus can be cationic. Consequently, investigations on the sorption behavior of ionizable organic compounds are important for the environmental assessment of a wide range of organic micropollutants.

1.1.2 Sorption processes affecting the fate of organic chemicals in natural sorbent-water systems

Sorption describes the enrichment of chemical species from a fluid phase onto the surface of a solid (or liquid) phase (=adsorption) or within the receiving phase (=absorption) (Sposito, 1998; Worch, 2012). The general term sorption is used for adsorption as well as absorption and is preferred when a clear distinction between both processes is not possible. A typical example of such complex binding mechanisms is the sorption of organic molecules by natural sorbents such as soils, sediments or aquifers (Worch, 2012). These geosorbents are of complex heterogeneous composition and consists of a mineral and an organic fraction. The mineral fraction consists mainly of various silicates and metal (hydr)oxides (e.g., of aluminum, iron and manganese). These minerals have generally OH groups on their surface, which form positive or negative charges depending on the pH value (uptake or release of protons). Accordingly, oxides/hydroxides/oxide hydrates react amphoteric and have an important function as variable ion exchangers. The sorbent-specific pH value at which the surface has the same number of positive and negative charges, i.e. at which the net charge becomes zero, is referred to as point of zero charge (pH_{PZC}). In addition to the minerals, especially the organic matter determines the properties of natural sorbents. According to Scheffer and Schachtschabel (2010), the organic matter includes all dead vegetable and animal substances in and on the mineral fraction and their organic transformation products. The organic material is characterized by a large number of hydrophobic sorption sites for non-polar organic molecules. Furthermore, the organic matter has functional groups (e.g., -OH, -SH, -COOH, -NH₂), which can be protonated or deprotonated as a function of pH value.

Due to the complex composition of natural systems, a combination of different interactions is often responsible for the sorption of organic chemicals. **Figure 1.1** illustrates, by the example of 3,4-dimethylaniline, that various sorbate-sorbent interactions can control simultaneously the association of a compound with natural solids. The sorption of neutral (non-polar) organics occurs mainly by hydrophobic sorption onto uncharged sites of sorbent organic matter (SOM) (Lambert et al., 1965, 1968; Chiou et al., 1979; Karickhoff, 1981), while the sorption of ionic species is often dominated by electrostatically (ionic) interactions, where other sorbent components such as clay minerals or oxidic surfaces are mainly relevant (Tolls, 2001; Yamamoto et al., 2009). In addition to the properties of the sorbate (e.g., molecular size, functional

Figure 1.1 Some sorbate-sorbent interactions that control the association of an organic compound (3,4-dimethylaniline) with natural solids. The figure is based on Schwarzenbach et al. (2003) and ter Laak (2005).

groups, charge state, etc.), the relative importance of one interaction mechanism compared to others depends also on the sorbent characteristics (e.g., sorbent components, surface area, cation exchange capacity, organic carbon content, clay content, etc.) as well as on the physico-chemical properties of the water (e.g., solution pH, ionic strength, water constitution, temperature, etc.) (Delle Site, 2001; Schwarzenbach et al., 2005; Schaffer et al. 2012a, 2012b; Droge and Goss, 2012, 2013a; Niedbala et al., 2013).

In Oepen et al. (1991) the possible sorbate-sorbent interactions involved in sorption are listed and described in detail. The interactions include: van der Waals interactions (dipole-dipole interactions), hydrophobic bonding, hydrogen bonding, charge transfer, ligand exchange/ion bonding, ion-dipole interactions and chemisorption. MacKay and Vasudevan (2012) only distinguish between two different categories of interaction mechanisms. *Type 1* interactions involve hydrophobic partitioning and electron donor-acceptor interactions (e.g., hydrogen bonding) and *Type 2* interactions include ion exchange and reversible reactions (surface complexation and cation bridging) at specific sites on sorbent. To some extent *Type 1* interactions occur for all organic compounds, while *Type 2* interactions play only a role for ionizable organic

compounds. An adequate prediction of the sorption behavior of non-polar organic substances is commonly possible using general or compound-class-specific correlations based on the *n*-octanol-water partition coefficient (e.g., Karickhoff et al., 1979; Sabljic et al., 1995) or the water solubility (e.g., Razzaque and Gratwohl, 2008), since the sorption is dominated by hydrophobic interactions with SOM (for more details, see **Section 1.1.4.1**). However, the relations for charged species of organic molecules are much more complex. Here, additional sorption mechanisms (e.g., ion exchange, surface complexation) must be considered. Besides the coexistence of various sorption mechanisms, it is also possible that further interactions can occur and become more important by changing the conditions of the aqueous phase. For example, pH changes may cause a shift of the species distribution of organic bases or acids, whereby a change from predominantly hydrophobic to predominantly electrostatically interactions can take place and vice versa (Tolls, 2001; Schaffer et al., 2012a; Schaffer and Licha, 2014). Using the pH-dependent *n*-octanol water partition coefficient $\log D_{ow}$ instead of $\log K_{ow}$, the species distribution at a certain pH can be taken into account (for more details see **Section 1.1.4.1**), but not the influence of the pH on sorbent surface charge. Consequently, the $\log D$ approach is not a general solution and may only lead to satisfying results if the sorbent surface and the sorbate carry identical charges (+/+, -/-) and thus no additional electrostatic interactions are expected. Therefore, meaningful predictions for the sorption coefficients of organic cations are usually very difficult with the existing concepts because most geosorbents carry a negative net surface charge in the typical pH range of natural waters (Schaffer and Licha, 2015). In addition to the pH value, the ionic composition of the water phase plays a special role, since competition effects have a considerable influence on cation exchange equilibrium of organic cations also due to the dominant concentration of inorganic ions in natural waters (Brownawell et al., 1990; Figueroa et al., 2004; ter Laak et al., 2006; Bi et al., 2006; Bäuerlein et al., 2012; Droge and Goss, 2012; Schaffer et al., 2012b; Niedbala et al., 2013). However, the relationship between the observed sorption and the influencing parameters is often unknown and thus the sorption behavior of ionizable organic compounds cannot reliably predicted (MacKay and Vasudevan, 2012; Endo and Goss, 2014; Webster, 2014; Schaffer and Licha, 2015). Therefore, extensive research is essential to allow accurate prediction of the sorption behavior.

1.1.3 Experimental methods for the determination of sorption coefficients

In solid-water systems, sorption is generally quantified by the sorption coefficient K_d [$L_{\text{solution}}/kg_{\text{solid}}$], which describes the equilibrium distribution of a given compound (sorbate) between the solid and aqueous phases. The K_d is defined as follows:

$$K_d = \frac{q_{\text{eq}}}{c_{\text{eq}}} \quad \text{Equation 1.1}$$

where q_{eq} [$mol_{\text{sorbate}}/kg_{\text{solid}}$] is the amount of sorbed solute onto sorbent surface and c_{eq} [$mol_{\text{sorbate}}/L_{\text{solution}}$] is the amount of solute retained in the aqueous phase at equilibrium.

The relationship between these two parameters (q_{eq} and c_{eq}) at a constant temperature is referred to as sorption isotherm. Sorption isotherms can be obtained from equilibrium sorption data. In the simplest case, the sorption is linear and K_d is independent of the investigated concentration range. This one-parameter equation is called Henry isotherm (**Equation 1.2**) and is identical to **Equation 1.1**. The model is often used in the case of sorption from aqueous solution with low concentrations.

$$q_{\text{eq}} = K_d \cdot c_{\text{eq}} \quad \text{Equation 1.2}$$

In natural systems or technical processes (e.g., sorption on activated carbon in drinking water treatment), linear sorption over a wide concentration range is less common and non-linear sorption is frequently observed. Due to the fact that in this case K_d is not constant when comparing different concentrations, sorption cannot be described by a single coefficient such as K_d . For non-linear sorption, different models exist to describe sorption isotherms (e.g., Freundlich, Langmuir and BET model), which are summarized in Worch (2012), for example. The most widely used non-linear sorption model is the two-parameter isotherm proposed by Freundlich (1906). This model assumes the presence of energetically heterogeneous sorption sites on sorbent surface, but does not include a maximum sorbent loading. It is applicable to the medium concentration range and the formation of multiple layers of the sorbate on sorbent surface is possible. The Freundlich isotherm has the form:

$$q_{\text{eq}} = K_F \cdot c_{\text{eq}}^{n_F} \quad \text{Equation 1.3}$$

where K_F [$(mol/kg)/(mol/L)^{n_F}$] and n_F [-] are the isotherm parameters. The Freundlich sorption coefficient K_F relates to the sorption strength and the Freundlich exponent n_F

characterizes the energetic heterogeneity of sorbent surface and determines the curvature of the isotherm. If n_F equals one, the Freundlich isotherm (**Equation 1.3**) simplifies to the Henry isotherm (**Equation 1.2**) and thus K_F and K_d are equivalent. In order to determine K_F and n_F , **Equation 1.3** is usually fitted to the logarithmic form:

$$\log q_{eq} = \log K_F + n_F \cdot \log c_{eq} \quad \text{Equation 1.4}$$

Standard methods for the determination of K_d are batch-equilibrium studies and column experiments, which are presented in the two subsections below. A more extensive summary of various methods can be found in the review article of Delle Site (2001).

1.1.3.1 Batch equilibrium studies

Batch experiments are the most frequently used method in sorption studies. A known amount of sorbent (m_{solid}) is mixed with a measured volume of solution ($V_{solution}$) containing a known concentration of the sorbate (c_0). The mixture is shaken for a time suitable to reach equilibrium, which was previously determined using kinetic data. Subsequently, the solid and liquid phases are separated. Centrifugation is generally used for this purpose. The equilibrium loading q_{eq} (mass of sorbate per unit mass of sorbent) is usually calculated by means of a simple mass balance on the basis of the difference between the initial concentration of the solute (c_0) and the concentration after equilibrium has been reached (c_{eq}) (**Equation 1.5**).

$$q_{eq} = \frac{V_{solution}}{m_{solid}} \cdot (c_0 - c_{eq}) \quad \text{Equation 1.5}$$

In order to obtain a sorption isotherm with different sorption data points, there are in principle two variants. On the one hand, different amounts of sorbent can be shaken with the same concentration of sorbate. On the other hand, it is also possible to vary the solute concentration, while the sorbent mass remains the same. The K_d value is estimated using a linear or a non-linear regression analysis (see **Equation 1.2** or **Equation 1.3**).

Batch tests are conceptually simple but relatively time consuming and there are many possible errors (Doucette, 2003). For weakly sorbing solutes a precise determination of the difference between initial and equilibrium concentration of sorbate can cause difficulties and lead to unreliable values (Bi et al., 2006). In some cases, the separation of solid and liquid phases is not fully achieved by ordinary centrifugation (Bürgisser et

al., 1993). Furthermore, often relatively long time is required until the equilibrium condition is reached, so that additional losses due to microbiological degradation or volatilization can lead to an overestimation of K_d (Doucette, 2003; Quian, 2010). Possibly, surface rub-off and particle breakup during shaking leads to an apparent higher sorption capacity due to the exposure of new sorption sites (Bürgisser et al., 1993; Doucette, 2003). Wash out effects from solids (e.g., organic sediments) lead to a change of the water composition. These difficulties of the classical batch experiments have led to the development of further techniques for the determination of sorption parameters such as the use of column experiments.

1.1.3.2 Column experiments

As an alternative to static batch tests, dynamic liquid chromatography in columns is often used for sorption studies (Bürgisser et al., 1993; Mader et al., 1997; Fesch et al., 1998). In this experimental technique, the solution containing the chemical of interest is pumped with a given flow rate through a column filled with a sorbing porous solid material under saturated, steady water flow conditions. The concentration of the solute in column effluent is monitored over the time by collecting samples with a fraction collector and subsequent concentration analysis or by a direct connection to a flow-through detector. Besides the measurement of the outlet concentration, a periodic control of the inlet concentration is also important. The columns are typically made of stainless steel and the flow direction is from the bottom to the top of the column to ensure uniform streaming and avoid channeling. Before the experiment is started, the column is equilibrated with a solution of desired pH and ionic strength and heated to a specific temperature. Subsequently, the breakthrough curve (BTC) can be recorded by continuous injection of the sorbate until the concentration of the solute in the effluent (c) equals that in influent (c_0), i.e. $c/c_0=1$. Furthermore, there is also the possibility of injecting only a sorbate pulse via an injection loop valve instead of a continuous sorbate input. In this case, the sorption data are obtained as a peak signal. Using pulse sorbate input, the complete desorption of the sorbate from the sorbent is a prerequisite. The experimental setup is shown schematically in **Figure 1.2** by the example of recording BTCs using continuous sorbate input.

In order to characterize the hydrodynamic properties of the column such as residence time and bed porosity, a tracer test with a non-sorbing substance must be performed. Furthermore, by repeated injections of the tracer during the sorption studies, the

Figure 1.2 Experimental setup for breakthrough curve determination.

stability of the column can be monitored. In literature different tracers were applied in column experiments, e.g. thiourea (Quian, 2010; Fesch et al., 1998; Bi et al., 2006), bromide (Bürgisser et al., 1993; Das et al., 2004), nitrite (Guo et al., 2004), fluorescein (Ptak et al., 2004), and tritiated water (MacIntyre et al., 1991; Culver et al., 2000). However, not every tracer is suitable for every sorbent. Therefore, studies on their suitability for a corresponding sorbent must be carried out in preliminary tests, because this affects the final calculation results. Besides the selection of a suitable tracer, the reproducible packing of columns is an important prerequisite to obtain reliable and comparable data (Bi et al., 2010; Metzelder, 2018). Practical issues for the column design, packing procedure and validation of the column have been given in detail by Relyea (1982) and Bi et al. (2010).

The retardation factor R_d [-] can be estimated by relating the retention time of the sorbing compound (t_{sorbate}) to that of the conservative tracer (t_{tracer}) using **Equation 1.6**. Therein, the travelling time through the connecting capillaries between reservoir and detector (t^*) should be subtracted from the measured retention times. t^* is obtained by determining the residence time of the tracer or the sorbate inside the system without integrated column. In Bi et al. (2010), various methods for determining retention times from BTCs are discussed, and the use of the half-mass method is recommended, where the curve is divided into two equal parts.

$$R_d = \frac{t_{\text{sorbate}} - t^*}{t_{\text{tracer}} - t^*}$$

Equation 1.6

For calculating K_d values from the obtained BTCs, a simple relationship between K_d and R_d can be used (see **Equation 1.7**), when sorption equilibrium is guaranteed in the experimental setup (i.e. independence from the flow rate of the eluent) and sorption isotherms are linear (i.e. independence from the sorbate concentration) (Mader et al., 1997; Fesch et al., 1998; Worch, 2012). In this case, R_d is constant for a given system and directly related to K_d . For non-linear equilibrium sorption, the relationship between K_d and R_d is more difficult, since R_d depends on the concentration. For example, the expression given in **Equation 1.8** is obtained assuming the Freundlich model. Here, ρ_b [kg/m³] is the bulk density of the solid and ε [-] is the porosity of the packed column.

$$R_d = 1 + \frac{\rho_b}{\varepsilon} \cdot K_d \quad \text{Equation 1.7}$$

$$R_d = 1 + \frac{\rho_b}{\varepsilon} \cdot K_F \cdot n_F \cdot c_{eq}^{n_F-1} \quad \text{Equation 1.8}$$

In addition to the injection of various sorbate concentrations (e.g., Schenzel et al., 2012), non-linear sorption isotherms can also be derived from a single column experiment with only one concentration. For the calculation, the concentration values of the desorption curve can be interpreted as equilibrium values and be assigned relative retention times $t(c_{eq})/t_{tracer}$, while neglecting dispersion. The related loadings q_{eq} can be calculated by an approach of Bürgisser et al. (1993) by integrating the tailing of the desorption front:

$$q_{eq} = \frac{1}{\rho} \int_0^c \left(\frac{t(c_{eq})}{t_{tracer}} - 1 \right) dc_{eq} \quad \text{Equation 1.9}$$

where ρ is the mass of sorbent per unit pore volume, and $t(c_{eq})$ refers to the concentration dependent retention time of the desorption curve.

Column tests have several decisive advantages compared to batch tests (Bürgisser, 1993; Doucette, 2003; Bi et al., 2006, 2010; Quian, 2010; Metzelder, 2018):

- 1.) they better simulate the transport of organic substances in solid-water systems because they more closely provide a representation of natural conditions (e.g., higher solid/water ratio, dynamic system);

- 2.) they are automatable and complex sample preparation steps can be omitted by online measurement and thus sorption data can be generated more quickly and easily for many target compounds and are less prone to errors;
- 3.) they offer the possibility to better control the essential boundary conditions (e.g., pH and ionic strength) and to change them more rapidly without the problems inherent to batch tests;
- 4.) they are particularly suitable if the sorption in the batch test is hardly detectable (e.g., low extent of sorption), since they provide higher sorbent/water ratios;
- 5.) they can be used to measure the entire sorption isotherm in a single experiment by simply integrating the tailing of the desorption curve; and
- 6.) they require a significantly lower sorbent mass, since the columns can be used several times for different concentrations, while in batch experiments sorbent is needed for each concentration point of the isotherm.

However, the equipment costs are higher and column studies can also be subject to a variety of experimental artefacts caused by non-achievement of the local equilibrium, loss of sorbent particles, wall and end effects, and column flow channeling (MacIntyre et al., 1991; Doucette, 2003). Column clogging and excessive sorption can be serious problems that result in high backpressures or cause in a long retention time. Both problems can be reduced by diluting the sorbent with an inert material, i.e. a material that does not interact with the tracer or the sorbate (Bi et al., 2006; Metzelder, 2018).

Various studies have shown that the sorption results obtained by batch experiments are comparable to those of column tests (MacIntyre et al., 1991; Bürgisser et al., 1993; Spurlock et al., 1995).

1.1.4 Predictive models for the evaluation of sorption coefficients

Since the experimental determination of sorption data is time-consuming and requires well-equipped laboratories, there is a desire for estimating the environmental fate of chemicals by prediction models. In the last decades, several relationships for the calculation of sorption coefficients based on various parameters have been published. In the following, the applicability of different models and their limitations are presented. A good overview of this topic is also given in the review articles by Goss and Schwarzenbach (2001), MacKay and Vasudevan (2012), Endo and Goss (2014), Webster (2014), and Schaffer and Licha (2015).

1.1.4.1 Single-parameter linear free energy relationships (sp-LFER)

The content of sorbent organic carbon is an important influencing factor in sorption of non-polar organic compounds, in particular when the sorption via hydrophobic mechanisms predominates (see **Section 1.1.2**). Thus, a good correlation has been found for the sorption of many non-polar substances and SOM of various sorbents, for example, by Lambert et al. (1965, 1968), Chiou et al. (1979), Karickhoff et al. (1979) and Hassett et al. (1980). Based on this, it is useful to normalize the sorption coefficient K_d to the organic carbon fraction of the sorbent, f_{OC} :

$$K_{OC} = \frac{K_d}{f_{OC}} = \frac{q_{eq}}{f_{OC} \cdot c_{eq}} \quad \text{Equation 1.10}$$

with:

$$f_{OC} = \frac{m_{OC}}{m_{solid}} \quad \text{Equation 1.11}$$

where m_{OC} is the mass of organic carbon in the solid material and m_{solid} is the total mass of the solid material. Thus, the sorption affinity of neutral (non-polar) compounds can easily be calculated when K_{OC} and f_{OC} are known. The f_{OC} can be determined from TOC analysis of the respective solid material. For the estimation of K_{OC} values, various simple relationships exist, which include a single parameter related to the hydrophobicity of the chemical such as the *n*-octanol water partition coefficient K_{OW} (e.g., Karickhoff et al., 1979; Sabljic et al., 1995) or the aqueous solubility S (e.g., Chiou et al., 1979; Razzaque and Gratwohl, 2008). Such correlations were found in numerous studies. The general forms of all these correlations are:

$$\log K_{OC} = a \cdot \log K_{OW} + b \quad \text{or} \quad \text{Equation 1.12}$$

$$\log K_{OC} = a \cdot \log S + b \quad \text{Equation 1.13}$$

An overview of compound class-specific and non-class-specific (universal) values for the empirical descriptors a and b can be found in Gawlik et al. (1997), Delle Site (2001), Doucette (2003) and Worch (2012), for example. The use of such correlations gives only an estimate of K_{OC} (varying results from different correlations), but at least the correct order of magnitude can be found for non-polar compounds.

The K_{OW} value (also referred to as P_{OW}) describes the equilibrium distribution of a substance between the two phases *n*-octanol (c_o) and water (c_w) and is a measure for the hydrophobicity of a compound (see **Equation 1.14**). This parameter is moderately temperature dependent and typically measured at 25 °C. The K_{OW} value can be experimentally determined, obtained from databases or estimated by special prediction methods. The higher K_{OW} , the more non-polar is the compound and the stronger its tendency to accumulate in the organic phase. Consequently, it can be assumed that the sorption increases with increasing hydrophobicity of the sorbate if hydrophobic interactions are the dominating sorption mechanism. In the case of ionizable compounds, the distribution of dissociated and non-dissociated species at a certain pH must be included in the calculation of K_{OW} . For this reason, the pH-dependent *n*-octanol water partition coefficient D_{OW} was introduced, which accounts for the several species as a function of pH. The D_{OW} value is calculated from the quotient of concentration sums of all species between the *n*-octanol and water phase (see **Equation 1.15**).

$$K_{OW} = \frac{c_o}{c_w} \quad \text{Equation 1.14}$$

$$D_{OW} = \frac{\sum_{i=1}^n c_{i,o}}{\sum_{i=1}^n c_{i,w}} \quad \text{Equation 1.15}$$

In general, D_{OW} can be correlated to K_{OW} and pK_a by the following relationships (Scherrer and Howard, 1977; Schaffer et al., 2012a; Schaffer and Licha, 2015):

$$\text{For acids:} \quad \log D_{OW} = \log K_{OW} + \log \left(\frac{1}{1 + 10^{pH - pK_a}} \right) \quad \text{Equation 1.16}$$

$$\text{For bases:} \quad \log D_{OW} = \log K_{OW} + \log \left(\frac{1}{1 + 10^{pK_a - pH}} \right) \quad \text{Equation 1.17}$$

However, non-hydrophobic interactions are not taken into account in these simple but commonly used single-parameter relationships ($\log K_{OW}$ - $\log K_{OC}$, $\log D_{OW}$ - $\log K_{OC}$, $\log S$ - $\log K_{OC}$). Therefore, their application for polar and especially ionizable organic compounds is limited, since, among others, ionic interactions are neglected. (Goss and Schwarzenbach, 2001; Tolls, 2001; Kah and Brown, 2007). For anionic compounds, this approach still provides meaningful results by the implementation of $\log D_{OW}$ instead of $\log K_{OW}$ into the calculation of $\log K_{OC}$ (Schaffer and Licha, 2015) or by the

use of the extended correlation after Franco and Trapp (2009) as demonstrated by Schaffer et al. (2012a). In the case of organic cations, however, the sorption is frequently considerably underestimated (Tolls, 2001; Kah and Brown, 2007; Schaffer et al. 2012a). The reason for this is that geosorbents usually have negative net surface charges and thus anionic sorbates carry identical charges and no additional electrostatic attraction forces are expected. In contrast, electrostatic attraction forces are often of particular relevance for cationic substances due to the opposite charge of sorbent surface and sorbate. Therefore, the K_{OC} approach fails particularly for cationic organics. Furthermore, in situations where sorbents have low organic carbon (<0.1%) and high clay contents the K_{OC} approach may also not be suitable, because the variability in sorbent composition is only described by the content of organic carbon (Doucette, 2003; Franco and Trapp, 2009). Thus, the predictive power of such one-parameter relationships is limited due to the fact that a single parameter is typically insufficient to describe all possible interactions that determine the sorption process (Goss and Schwarzenbach, 2001). Hence, more complex, process-based model approaches, considering additional boundary conditions, are required that allows to account for compound and sorbent variability.

1.1.4.2 Poly-parameter linear free energy relationships (pp-LFER)

In past years, multi-parameter models that incorporate other sorbent parameters or descriptors in addition to f_{OC} become more important. In contrast to sp-LFERs, these more advanced and more flexible relationships try to take into account all interactions involved in sorption by separate parameters. The concept of poly-parameter linear free energy relationships (pp-LFERs) based on Abraham predictors (Abraham et al., 1990) is currently the most robust and accurate method to determine sorption coefficients (Endo and Goss, 2014). Here, sorption coefficients K_d are derived by multiple linear regression analysis of experimental data and the following general form:

$$\log K_d = eE + sS + aA + bB + vV + c \quad \text{Equation 1.18}$$

The capital letters are the sorbate/solute descriptors (E : excess molar refraction, S : polarizability/dipolarity parameter, A : solute H-bond acidity, B : solute H-bond basicity, V : McGowan molar volume). The small letters e , s , a , b , v and c represent system-specific, (largely) solute-independent fitting coefficients (Endo and Goss, 2014; Schaffer and Licha 2015). These fitting coefficients are estimated by multiple linear

regression analysis against experimentally derived sorption coefficients. Each term of the linear combination quantitatively describes the energetic contribution of one intermolecular interaction type to $\log K_d$, where eE accounts for dispersion interactions (van der Waals interactions), sS represents the energetic contribution of interactions related to the surface polarity of the molecule (polar interactions), aA and bB describe H-bonding interactions, and vV describes cavity formation and is an additional term for dispersion interactions (Endo and Goss, 2014). The constant c is a solvent-specific coefficient depending on volume entropy effects (Ngyuyen et al., 2005). **Equation 1.18** can be extended for ions by incorporating an additional descriptor J^+ for cations or J^- for anions as indicated below (both descriptors are not included in **Equation 1.19** at the same time) (Abraham and Zhao, 2004; Abraham and Acree, 2010):

$$\log K_d = eE + sS + aA + bB + vV + j^+J^+ + j^-J^- + c \quad \text{Equation 1.19}$$

Further theoretical details on pp-LFERs and the description on solute descriptor determination can be found in the comprehensive review articles of Abraham et al. (2004), Vitha and Carr (2006), Poole et al. (2009, 2013) and Stenzel et al. (2013). A list of environmental partitioning systems for which system parameters are already available is given by Endo and Goss (2014). The same researchers reviewed how system parameters for a new partitioning system can be calibrated by using multiple linear regression analysis with experimental sorption coefficients as training data.

pp-LFERs are very powerful tools to fit the sorption data of a wide variety of compound classes by a single equation. These approaches were successful applied to hydrophobic (Goss and Schwarzenbach, 2001; Nguyen et al., 2005), polar (Ngyuyen et al., 2005; Bronner and Goss, 2011), and even some ionizable compounds (Abraham and Acree, 2010; Droge and Goss, 2013a, Sathyamoorthy and Ramsburg, 2013). Droge and Goss (2013a) and Sathyamoorthy and Ramsburg (2013) have already shown that the application of pp-LFERs for the sorption of organic cations can improve the prediction when compared with classical one-parameter-LFERs. However, the extension of pp-LFERs to ionizable organic compounds is still a subject of ongoing research (Endo and Goss, 2014).

A disadvantage of the existing pp-LFERs is the limited availability of solute descriptors for some environmentally relevant substances (Ngyuyen et al., 2005; Razzaque and Gratwohl, 2008; Tülp et al., 2008; Stenzel et al., 2013; Endo and Goss, 2014). In the

past decade, however, this situation has been greatly improved since descriptors for a wide range of important organic chemicals were calibrated by experimental data (Endo and Goss, 2014). Furthermore, a database ("UFZ-LSER database", Endo et al., 2015) with the values of descriptors published so far was established, which strongly simplifies the often time-consuming search for descriptors. Additionally, system parameters for carbonaceous sorbents (e.g., soot, char, activated carbon) are partially missing due to their strong and highly non-linear sorption (Endo and Goss, 2014). In general, pp-LFERs are not designed for non-linear sorption and thus the difficulty lies in the dependence of sorption coefficients on the concentration. Nevertheless, some efforts have been made to adapt pp-LFERs to non-linear sorption (Zhu and Pignatello, 2005; Endo et al., 2008, 2009; Hüffer et al., 2014). Another limitation of these approaches is, however, that solely sorbate parameters are explicitly considered herein, and all remaining influencing factors are incorporated in the fitted coefficients without differentiation. Thus, the derived predictors are only meaningful for very similar and homogeneous sorbents and for equal solution conditions (e.g., concentration range, pH, ionic strength) (Schaffer and Licha, 2015). The results from Sathyamoorthy and Ramsburg (2013) confirm this issue, since the predictive power of their pp-LFER approach did not improve despite the integration of further sorbate descriptors into their model. The additional consideration of sorbent-related key parameters in modeling remains essential (MacKay and Vasudevan, 2012; Sathyamoorthy and Ramsburg, 2013). Furthermore, the properties of the water phase, especially the ionic composition, must be further considered, since competitive effects strongly influence the cation exchange equilibrium of organic cations (Brownawell et al., 1990; Bilgiç, 2005; Bäuerlein et al., 2012; Schaffer et al., 2012b; Droge and Goss, 2012; Niedbala et al., 2013; Chen et al., 2013). However, these interrelations between competing organic and inorganic cations in conjunction with the sorbent characteristics are not yet well understood.

1.1.4.3 *Further concepts for predicting sorption of ionizable compounds*

Reliable predictions for sorption coefficients of organic cations (and zwitter-ions) are nontrivial and very limited to date (Schaffer and Licha, 2015). The abovementioned sp-LFERs are not suitable for such applications because they do not consider ionic interactions (see **Section 1.1.4.1**). pp-LFERs can be an alternative in certain cases (see **Section 1.1.4.2**), but cannot easily be applied to all sorbent-sorbate systems because the required descriptors are often unknown and difficult to determine

experimentally (Endo and Goss, 2014). Therefore, more general approaches are desired.

In this context, numerous studies have shown that the extent of the sorption of cationic compounds correlate with sorbent properties such as cation exchange capacity (*CEC*), clay content, pH, specific surface area (A_{BET}) and the content of Al or Fe oxides (e.g., Weber et al., 2004; Lee et al., 2005; Kah and Brown, 2007; Sassmann et al., 2007; Hu and Coats, 2009; Vasudevan et al., 2009; Kodešová et al., 2015; Ishiguro and Koopal, 2016). In contrast, f_{OC} , which is frequently used for non-polar substances, is usually not a suitable correlation parameter for organic bases (Kah and Brown, 2007; Sassmann et al., 2007). Accordingly, the identified relations can be used to determine K_d values for specific compounds by multiple regression analysis as has already been demonstrated by some authors (e.g., Weber et al., 2004; Vasudevan et al., 2009; Kodešová et al., 2015; Al-Khazarajy and Boxall, 2016). Furthermore, the normalization of K_d with *CEC* in analogy to the K_{OC} concept could represent another alternative for the prediction of K_d values because the *CEC* characterizes the sorbent negative charge density (Figueroa et al., 2004; Sassmann and Lee, 2005; Sassmann et al., 2007; Droge and Goss, 2013b, 2013c). Since these approaches consider only sorbent characteristics, a combination with the pp-LFERs is regarded as promising (Schaffer and Licha, 2015). However, the consideration of the solution conditions is still lacking.

To overcome this limitation, Droge and Goss (2013b, 2013c) developed a new sorption model for organic cations in soil wherein the sorption is composed by the summed contribution of the sorption to SOM and the sorption to clay minerals. The sub-sorption coefficients were normalized to f_{OC} and CEC_{CLAY} . The sorption affinity is assigned to a fixed media composition and varying electrolyte concentrations were taken into account by correction factors. For this purpose, however, the functional dependencies between K_d and the boundary conditions must be known. Therefore, systematic investigations are particularly important in order to obtain the corresponding correction factors. Droge and Goss (2012), Schaffer et al. (2012b) and Niedbala et al. (2013) have already started to study the role of competing inorganic cations on the cation exchange equilibrium of organic cations. It was possible to identify first mathematical relationships, which enables a prediction of K_d for different types and concentrations of inorganic cations for the studied sorbent-sorbate system. However, not all possible influencing factors were considered, which is why it is unclear whether a simple transfer to other sorbent systems, e.g., by normalization to specific sorbent parameters, is

possible at all. The determination of such compound-specific relationships is associated with a high experimental effort and thus it has to be individually assessed if this effort is worthwhile.

Another model was proposed by Tolls (2001) and Schwarzenbach et al. (2003), wherein the description of K_d results from the summed contributions of the individual mechanisms to the overall sorption in combination with sorbent characteristics:

$$K_d = \frac{q_{OC}f_{OC} + q_{min}A_{BET} + q_{iex}\sigma_{iex}A_{BET} + q_{rxn}\sigma_{rxn}A_{BET}}{c_{neutral} + c_{ion}} \quad \text{Equation 1.20}$$

where q is the concentration of sorbate in organic carbon (q_{OC} , [mol_{sorbate}/kg_{OC}]); associated with mineral surface (q_{min} , [mol_{sorbate}/m²]); sorbed by ion exchange (q_{iex} , [mol_{sorbate}/mol_{iex_sites}]) or bonded in a reversible reaction to the sorbent (q_{rxn} , [mol_{sorbate}/mol_{rxn_sites}]). f_{OC} [kg_{OC}/kg_{solid}] refers to the fraction of organic carbon, A_{BET} [m²/g] is the specific surface area of the solid, σ is the area-normalized concentration of ion exchange sites (σ_{iex} , [mol_{iex_sites}/m²]) or reactive sites (σ_{rxn} , [mol_{rxn_sites}/m²]) on the solid surface and c is the concentration of sorbate in neutral form ($c_{neutral}$, [mol_{sorbate}/L_{solution}]) or ionic form (c_{ion} , [mol_{sorbate}/L_{solution}]) in the aqueous solution. Based on **Equation 1.20**, MacKay and Vasudevan (2012) provides an advanced, mechanism-based framework for the description of K_d . The authors suggest the use of mechanism-specific probe compounds relevant to cation exchange and surface complexation/cation bridging in order to relate sorption receptor site abundances to sorption mechanisms and sorbate structure. For the transition from this "conceptual" model to a "functioning" model, however, a more extensive evaluation of the sorption of ionizable compounds under consistent experimental conditions is necessary.

1.2 Scope, objectives and further outline of the thesis

The exact knowledge of the sorption behavior of cationic organic compounds is crucial for the accurate qualitative as well as quantitative prediction. However, the underlying processes and their dependences are not fully understood and cannot yet be predicted. In order to overcome these limitations, first of all a better knowledge on the relative role of all involved processes and the impact of boundary conditions is required. However, a complete evaluation of all processes and their influencing factors is not possible within this work. For this reason, the thesis represents only a further important and useful step towards a better overall understanding of the complex

sorption behavior of organic cations in subsurface and - as a prospective extension – the transferability to other, also technical, systems and thus contributes significantly to current research. The findings can be used in future prediction models.

Due to the complexity of natural systems (e.g. heterogeneous composition of sorbent surfaces and waters), where several processes overlap simultaneously, an examination of the individual interactions is very difficult. Furthermore, the role and extent of sorption mechanisms strongly depends on the water chemistry (e.g., pH, ionic strength) and properties of the solid phase (surface area, cation exchange capacity), which leads to additional complications. For this reason, a highly-idealized model system using synthetic well-defined oxides as sorbents and synthetic model water as liquid phase was used in this work to first improve the general process understanding by a separate and systematic investigation of these relations and their interdependencies.

The most relevant sorption processes of organic cations were identified by varying the background electrolyte concentration, sorbent properties or molecule structure. A conceptual model approach is presented. The study implies a certain predictability of sorption coefficients for different competitive conditions (mono- and divalent inorganic cations) and sorbent properties. A connection between the sorption coefficient and the activity coefficient of the medium is presumed. A more detailed outline is presented in the following paragraphs. Since this thesis is a cumulative dissertation, **Chapter 2, 3 and 4** consists of published articles.

Chapter 2 demonstrates the individual as well as combined influence of competing inorganic cations (Na^+ , NH_4^+ , Ca^{2+} , and Mg^{2+}) on the sorption of the cationic species of the beta-blocker metoprolol (MET) on the oxidic sorbent silica gel. More than 400 systematic batch experiments for different electrolyte and MET concentrations were conducted and evaluated. In general, the results revealed non-linear isotherms (Freundlich type) and decreasing sorption coefficients with increasing background electrolyte concentrations. Thus, cation exchange could be identified as a relevant sorption process. Furthermore, a simple linear correlation between the logarithm of the Freundlich sorption coefficient and the logarithm of the equivalent concentration of competing inorganic cations was found, which enable a certain estimation of competitive effects for the studied sorbent within a wide concentration range. The transfer of the single ion contributions to systems with more than one competing ion

works only at low electrolyte concentrations. Finally, this work illustrates the relevance of further interactions next to the dominating cation exchange, since, despite high electrolyte concentrations, a still considerable sorption of MET was observed.

The focus of **Chapter 3** is to capture the effect of increasing competition on organic cation sorption until the point of maximum suppression for the cation exchange interactions is reached. This should allow studying the remaining non-ionic interactions separately. For this purpose, the sorption of the structurally related cationic probe molecules: MET and isopropyl-(4-methylbenzyl)-amine (iP4MBA) on two synthetic silica gels (amorphous and spherical) was studied over a wide concentration range of competing inorganic ions (Na^+ and Ca^{2+}). The study includes about 700 systematic batch experiments and 12 column tests resulting in over 40 isotherms. Compared to the sorption experiments described in Chapter 2, the background electrolyte concentration was extended by an additional concentration step. The results show again the strong impact of cation exchange process due to the decrease of organic cation sorption with increasing competition. However, at high excess concentrations of competing cations ($c > 1 \text{ M}$) the sorption recovers considerably. Due to the superposition of several processes and the shift of their relevance depending on background electrolyte concentration (opposing trends), the separation of individual sorption processes and their quantification by suppressing cation exchange was not expedient. A reduced sorption for iP4MBA compared to MET was found and attributed to a lower H-bond acceptor/donor sum. Based on these observations, a simple conceptual model is proposed, which distinguishes between two sorption processes. Furthermore, a relation between the sorption coefficient and the activity coefficient of the electrolyte is presumed and thus analogy considerations are regarded as promising. Consequently, the results improve the process understanding and help to improve predicting the sorption of organic cations.

The investigations, which are presented in **Chapter 4**, round off the previous studies, since a complete systematic data set for the sorption of three probe molecules on five synthetic sorbents (three silica gels and two aluminum oxides) at four background electrolyte concentrations was determined by a total of 120 column experiments. In addition to the compounds MET and iP4MBA used in Chapters 2 and 3, the neutral compound benzyl alcohol (BA) was used as probe molecule. In order to identify a suitable system parameter for improving the quantitative process description of organic cation sorption, the influence of the sorbent characteristics on the sorption behavior

was evaluated by linear regression analysis. For this purpose, the used sorbents were extensively characterized with regard to general solid parameters and surface properties. A direct linear correlation between the sorption results and the number of surface OH groups onto sorbent surface was found. Based on this relationship, sorption coefficients of studied probe molecules can be predicted for different oxides. Furthermore, by comparing the sorption results for different probe compounds or at different electrolyte concentrations, information on the contribution of non-ionic interactions to the overall sorption were obtained. A distinction is made between ion exchange and non-ion exchange processes, in which ion exchange depends on the background electrolyte concentration as opposed to non-ion exchange processes. Finally, this work represents an important step towards a general and systematic understanding of the relevant processes involved in the sorption of organic cations and thus contributes decisively to the development of future predictive models.

Chapter 5 summarizes the conclusions with respect to the focus of the thesis and gives an outlook for future research activities.

Chapter 6 includes a complete list of cited literature.

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 and conference contributions authored or co-authored by me and related to the presented work are listed.

Chapter 2

2 Sorption of the organic cation metoprolol on silica gel from its aqueous solution considering the competition of inorganic cations

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Abstract

Systematic batch experiments with the organic monovalent cation metoprolol (MET) as sorbate and the synthetic material silica gel as sorbent were conducted with the aim of characterizing the sorption of organic cations onto charged surfaces. Sorption isotherms for MET (>99% protonated in the tested pH of around 6) in competition with mono- and divalent inorganic cations (Na^+ , NH_4^+ , Ca^{2+} , and Mg^{2+}) were determined in order to assess their influence on cation exchange processes and to identify the role of further sorptive interactions. The obtained sorption isotherms could be described well by an exponential function (Freundlich isotherm model) with consistent exponents (about 0.8). In general, a decreasing sorption of MET with increasing concentrations in inorganic cations was observed. Competing ions of the same valence showed similar effects. A significant sorption affinity of MET with ion type dependent Freundlich coefficients $K_{F,0.77}$ between 234.42 and 426.58 $(\text{nmol/kg})/(\text{nmol/L})^{0.77}$ could still be observed even at very high concentrations of competing inorganic cations. Additional column experiments confirm this behavior, which suggests the existence of further relevant interactions beside cation exchange. In subsequent batch experiments, the influence of mixtures with more than one competing ion and the effect of a reduced negative surface charge at a pH below the point of zero charge ($\text{pH}_{\text{PZC}} \approx 2.5$) were also investigated. Finally, the study demonstrates that cation exchange is the most relevant but not the sole mechanism for the sorption of MET on silica gel.

Graphical Abstract:

2.1 Introduction

A large number of polar micropollutants, such as pharmaceuticals, biocides, surfactants, and dyes, contain ionizable nitrogen functionalities. Such basic compounds with logarithmic acid constants pK_a above the pH of the systems under investigation are predominately positively charged. The charge state of a molecule highly influences its sorption behavior onto surfaces of natural (e.g., sediments, minerals, organic matter, metal oxides) and synthetic materials (e.g., activated carbon, silica, ion exchange resins) (Parida and Mishra, 1996; Delle Site, 2001; Tolls, 2001; Kibbey et al., 2007; Schaffer et al., 2012a). The relevance of unspecific hydrophobic interactions to non-polar sorbent domains diminishes with an increasing fraction of charged species due to an increasing molecular polarity. However, a relatively strong and even increased sorption is often observed for the cationic species of organic bases (e.g., Sassman and Lee, 2005; Kah and Brown, 2007; Sibley and Pedersen, 2008; Hyland et al., 2012; Schaffer et al., 2012a). Consequently, the sorption of organic cations is dominated by electrostatic forces between the protonated nitrogen moieties of the sorbate and the negatively charged sorbent surfaces. Electrostatic forces include both, electrostatic interactions and electrostatic attractions. According to Schwarzenbach et al. (1993), a distinction is made only between ion exchange and non-ion exchange processes in this study. Previous studies identified cation exchange as the major sorption process for several organic cations onto natural and synthetic sorbents (Sassman and Lee, 2005; Bäuerlein et al., 2012; Droge and Goss, 2012; Schaffer et al., 2012b; Niedbala et al., 2013). Depending on the sorbate structure, additional polar electron donor-acceptor mechanisms, such as hydrogen bonding, may also significantly contribute to cation sorption (Senesi, 1992; MacKay and Vasudevan, 2012).

The prediction of the sorption process of organic cations is highly complex, since especially cation exchange depends on numerous influencing factors, such as the properties of the aqueous phase as well as sorbent and sorbate properties. Therefore, reliable descriptive and predictive sorption models combining all influencing variables are not yet available (MacKay and Vasudevan, 2012).

A relatively new approach is to adapt empirical poly-parameter linear free energy relationships (pp-LFERs) based on Abraham predictors (Abraham et al., 1990) for estimating sorption to condensed phases (Goss and Schwarzenbach, 2001). Here, a

distribution coefficient is expressed as a linear combination of known sorbate descriptors with sorbent- and system-specific coefficients, respectively. The coefficients are estimated by multiple regression analysis of experimentally derived calibration data sets. These relationships were applied to hydrophobic (e.g., Nguyen et al., 2005), polar (Bronner and Goss, 2011), and even ionizable compounds (Abraham and Acree, 2010; Droge and Goss, 2013a). Generally, the disadvantage of the pp-LFER approaches is, however, that solely sorbate parameters are explicitly considered herein, and all remaining influencing factors are incorporated into the fitted coefficients without differentiation. Thus, the derived predictors are only meaningful for similar sorbents and aqueous media conditions. The results from Sathyamoorthy and Ramsburg (2013) confirm this issue, since the predictive power of their pp-LFER approach did not further improve despite the integration of further sorbate descriptors into their model. Hence, the additional consideration of sorbent-related key parameters in modeling remains essential (MacKay and Vasudevan, 2012; Sathyamoorthy and Ramsburg, 2013). Furthermore, the properties of the water phase, especially its ionic composition, must be further considered, since competitive effects strongly influence the cation exchange equilibrium of organic cations (Brownawell et al., 1990; Bilgiç, 2005; Bäuerlein et al., 2012; Schaffer et al., 2012b; Droge and Goss, 2012; Niedbala et al., 2013; Chen et al., 2013). However, these interrelations between competing organic and inorganic cations in conjunction with the sorbent characteristics are not yet well understood.

The key for a better understanding of organic cation sorption is in the separate quantification of these relations and their interdependencies. This is highly complex due to the heterogeneous composition of natural sorbent surfaces and waters. Therefore, this study focuses on the systematic investigation of competitive effects that govern the cation exchange equilibrium of organic cations under defined boundary conditions and on a largely homogenous, synthetic material. For this purpose, the experiments were conducted with synthetic water and the oxidic, negatively charged material silica gel was selected as sorbent. Batch experiments were carried out with the basic beta-blocker metoprolol ($pK_a(\text{MET})=9.63$) under the influence of systematically varied electrolyte concentrations. Isotherms for MET were determined for the competitive sorption under the influence of single inorganic cations (Na^+ , NH_4^+ , Ca^{2+} , Mg^{2+}) as well as for the combined effect of two cation types. Furthermore, the contribution of oxidic surfaces (amorphous SiO_2) for further potentially occurring

sorption processes (e.g., hydrogen bonding, hydrophobic interactions) can be elucidated. As a result, sorption on silica surfaces can be studied separately and valuable implications for more complex natural or technical systems may be derived. This is because many silanol-bearing materials, such as quartz and further minerals (Nyfeler and Armbruster, 1998), are essential components of natural sorbents. Thus, the experiments provide a deeper understanding of relevant sorption mechanisms for organic cations. Eventually, these findings give further implications for future model developments and can be used to assess the sorption behavior of organic cations in more complex systems.

2.2 Material and methods

2.2.1 Chemicals

The beta-blocker metoprolol (MET) as tartrate salt with a minimum content of 98% was purchased from Sigma-Aldrich (Steinheim, Germany). Its structure and its physicochemical properties are given in **Table 2.1**. Due to its high pK_a value, MET is positively charged at neutral pH. Since the pH of the used aqueous solutions was always lower than 7, the secondary amine moiety is readily protonated (Schaffer and Licha, 2014) and, thus, MET was cationic in all experiments. Stock solutions of MET with a concentration of 10 g/L were prepared in methanol (HPLC grade, VWR, Leuven, Belgium). All other used chemicals were of high purity (analytical grade). NH_4Cl was purchased from Laborchemie Apolda (Apolda, Germany), $NaCl$ from Th. Geyer (Renningen, Germany), $CaCl_2 \cdot 2 H_2O$ and $MgCl_2 \cdot 6 H_2O$ from Merck (Darmstadt, Germany), and 1 M HCl from KMF (Lohmar, Germany). Ultrapure water for the preparation of all solutions was obtained from the water purification system GenPure from TKA (Niederelbert, Germany). The eluents for liquid chromatography were of HPLC grade. Acetonitrile was purchased from Sigma-Aldrich (Steinheim, Germany), formic acid from Carl Roth (Karlsruhe, Germany), and water from VWR (Leuven, Belgium).

2.2.2 Sorbent

To investigate the sorption of MET on oxidic surfaces, experiments were carried out with the technical sorbent Silica gel 60 (0.2–0.5 mm, amorphous), which was purchased from Merck (Darmstadt, Germany). Due to the expected low point of zero charge ($pH_{PZC} < 4.5$, if any; Kosmulski, 2002) the amphoteric silanol groups are mostly

deprotonated and the net surface charge of silica gel is negative over a wide pH range. Therefore, it acts as a weak cation exchanger.

Measured properties of the used sorbent are listed in **Table 2.1**. The specific surface area of the sorbent (A_{BET}) was analyzed by experimental nitrogen adsorption- and desorption-data with the BET-analyzer Autosorb-1 (Quantachrome, Odelzhausen, Germany). The pH value of the sorbent was measured in a suspension of ultrapure water with a solid to liquid ratio of 1:10 (m:V). The total organic carbon (TOC) was determined with a TOC-L analyzer (Shimadzu, Duisburg, Germany) by catalytic oxidation at 680 °C. The determination of the potential cation exchange capacity (CEC_{pot}) was carried out following DIN ISO 13536. The point of zero charge (pH_{PZC}) was measured using the pH drift method after Khan and Sarwar (2007). Silanol surface functional groups were determined by a standardized modification (Goertzen et al., 2010) of Boehm's titration method (Boehm, 1966, 2002).

Since silica gel contains soluble inorganic ions, a washing step was required afore experiments. For this, the material was washed twice with ultrapure water with a solid to liquid ratio of 1:10 (m:V). Subsequently, the washed silica gel was dried in a compartment drier at 45 °C for more than 24 h until weight constancy. The concentrations of inorganic ions released from silica gel were measured using ion chromatography (see **Section 2.2.6.2**). The washing resulted in a sufficient removal of inorganic ions from the silica gel (see **Table A.1** in **Appendix A**).

Table 2.1 Physicochemical properties of sorbate and sorbent.

Compound	Structure	CAS number	^{a, b} pK _a	^{a, c} log K _{OW}	^d log D
Metoprolol (MET)		51384-51-1	9.63	1.95	−0.81

Sorbent	A _{BET} [m ² /g]	pH (H ₂ O, 100 g/L) [-]	TOC [mg/g]	CEC _{pot} [cmol _c /kg]	pH _{PZC} [-]	n _{Si-OH} [mmol/g]
Silica gel 60	518	6.97	0.32	8.2	≈2.5	1.03

A_{BET} =specific surface area, TOC=total organic carbon, CEC_{pot} =potential cation exchange capacity at pH=8.1, pH_{PZC} =point of zero charge, $n_{\text{Si-OH}}$ =density of silanol groups.

^a Caron et al. (1999).

^b $\text{p}K_{\text{a}}$ value refers to $\text{p}K_{\text{a}}$ value for the conjugate acid (protonated species).

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

^d $\log D$ value refers to all species at pH=7. SciFinder Scholar predicted values, calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (1994–2013 ACD/Labs).

2.2.3 Model water

A synthetic water was used for studying the effects of competing inorganic cations on the sorption equilibrium of MET due to ion exchange. This synthetic water is hereafter referred to as model water. The ionic composition of the model water was adjusted by adding different types and amounts of inorganic salts (NaCl, NH₄Cl, CaCl₂·2 H₂O, and MgCl₂·6 H₂O) to the MET containing aqueous solutions. The target concentrations for each cation were 0.37, 3.7, 37 and 370 mM. For measuring the competitive MET isotherms, aqueous solutions with six different MET concentrations between 1.87E-04 and 3.74E-01 mM (50–100,000 µg/L) were prepared. The pH of the solutions varied in the range of 5.5 to 7. In this pH range, MET is completely cationic and the impact of pH on the surface charge (characterized by the zeta potential) of silica gel is very small (Park and Lee, 2012). For one isotherm, the pH of the model water was adjusted with 1 M HCl to pH=1.8±0.2 (below the pHPZC of ≈2.5) to study the influence of a reduced negative surface charge.

Furthermore, the influence of competing inorganic cations on the transport of MET was exemplarily studied in column experiments with Na⁺. Breakthrough curves of MET were determined in pure water without competition (experiment A) as well as for a Na⁺ concentration of 370 mM (experiment B). The experiments were carried out with an initial MET concentration of $c_0=600$ µg/L.

2.2.4 Batch experiments

Isotherms were determined in batch tests according to the bottle-point method (Worch, 2012). All experiments were repeated three times (triplicates). Preliminary tests on the sorption kinetics of MET on silica gel revealed that the equilibrium was certainly achieved within two days under shaking conditions. Therefore, samples were shaken for at least 48 h with 120 rpm using a universal shaker (SM 30 B control, Edmund Bühler, Hechingen, Germany). All experiments were conducted at 8±1 °C under thermostated conditions in order to reduce biological degradation of MET and to simulate natural groundwater temperatures. The batch vessels were prepared by accurately weighing (±0.5 mg) the washed and dried silica gel in 100 mL Erlenmeyer flasks. Afterward, MET solutions containing the respective electrolytes were added. Batch tests were carried out with a constant solid to liquid ratio of 1 g/L and 10 g/L (m:V) for the highest investigated concentrations (370 mM) of competing inorganic

cations, respectively. The sorbed amount at equilibrium was calculated based on the concentration decrease of MET in solution with:

$$q_{eq} = \frac{V_0(c_0 - c_{eq})}{m_A} \quad \text{Equation 2.1}$$

where q_{eq} [nmol/kg] refers to the sorbed amount at equilibrium, V_0 [L] is the volume of the aqueous phase, c_0 [nmol/L] is the initial concentration in the aqueous phase, c_{eq} [nmol/L] is the equilibrium concentration, and m_A [kg] is the mass of the sorbent.

2.2.5 Column experiments

For the two column experiments, a stainless-steel HPLC column with dimensions of 250×10 mm was filled with silica gel and closed with stainless-steel frits. As in the batch experiments, the tests were conducted at a constant temperature of 8 °C. A flow rate of 0.5 mL/min was achieved with a Merck-Hitachi L-6000 HPLC pump. The water was pumped in up-flow direction to ensure saturated column conditions. The column was equilibrated with model water (MET-free) until equal electrical conductivities and pH values were reached at inlet and outlet. Consecutively, MET was added to the reservoir before starting the experiment. Samples were collected at the outlet every 45 min using a fraction collector (Retriever II, Teledyne Isco). Only a limited number of samples were used for the reconstruction of the breakthrough curves. During the experiments, no degradation of MET or pH changes were observed in the reservoir. After each main experiment, the effective porosity ε was calculated according to Schaffer et al. (2012b) from the conductivity breakthrough curves $\kappa(t)$ of a conservative tracer (NaCl) recorded by a microprocessor conductivity meter LF 537 with a flow through cell LDM/S, WTW. All experimentally obtained breakthrough curves were evaluated based on the analytical solution of the advection-dispersion-equation under the assumption of local equilibrium with the CXTFIT code (Toride et al., 1995) within the software STANMOD (Version 2.07).

2.2.6 Chemical analysis

2.2.6.1 *Analysis of MET*

MET concentrations from the batch equilibrium tests and column experiments were analyzed using HPLC with UV detection. Prior to HPLC analysis, all samples were filtered with a 0.45 µm cellulose nitrate membrane filter (Satorius Stedim Biotech, Göttingen, Germany) to remove all suspended particles. Samples with initial

concentrations $c_0 > 1000 \mu\text{g/L}$ were diluted with ultrapure water to fit into the concentration range of the linear calibration curve (20–1000 $\mu\text{g/L}$). For the external calibration, eight concentration levels were used. The HPLC system consists of a Merck-Hitachi L-6200 A pump and a Merck-Hitachi L-7200 autosampler. For chromatographic separation, a Polaris C18-Ether column (150×3 mm, 3 μm) from Agilent was used. The separation was operated at 26 °C in a Merck-Hitachi L-5025 column oven with an injection volume of 100 μL . MET was detected with a diode-array detector (DAD L-4500, Merck-Hitachi). The samples were analyzed at a detection wavelength of 225 nm and a constant flow rate of 0.5 mL/min.

2.2.6.2 Analysis of inorganic ions

The quantification and confirmation of the intended inorganic cation concentrations (Na^+ , NH_4^+ , Ca^{2+} , and Mg^{2+}) were performed by ion exchange chromatography (IC) as described in Niedbala et al. (2013). In addition, inorganic anion concentrations (Cl^- , NO_3^- , SO_4^{2-} , and PO_4^{3-}) were analyzed by means of an IC system with conductometric detection and electrochemical suppression (Dionex, Sunnyvale, USA) using 10 mM KOH as eluent. The AS 19 IonPac column system (250×4 mm, 5 μm ; Dionex) was employed for separation. The flow rate of the eluent was 0.25 mL/min. Samples with high electrolyte concentrations were diluted into the operating range of their individual calibration curves.

2.3 Results and discussion

2.3.1 Estimation of isotherm data

The sorption data of all experiments were fitted by linear least-square regression of the linearized Freundlich equation (**Equation 2.2**, for more details see **Section A.2** and **Section A.5** in **Appendix A**). Furthermore, a non-linear least-square optimization procedure (see **Section A.2** in **Appendix A**) was applied for fitting the data with the Langmuir sorption model (**Equation A.2** and **Equation A.3** in **Appendix A**). In general, the evaluation of the fit quality by means of Chi-square analysis in **Equation A.4** in **Appendix A** (Ho, 2004) led to similar results for both models. Due to the fact that the Freundlich fits are slightly better for the majority of the experiments (**Table A.2** in **Appendix A**), the main discussion of the results is based on Freundlich parameters (**Equation 2.2**):

$$\log q_{\text{eq}} = \log K_F + n_F \cdot \log c_{\text{eq}} \quad \text{Equation 2.2}$$

where K_F [(nmol/kg)/(nmol/L) ^{n_F}] is the Freundlich coefficient, n_F is the Freundlich exponent. The n_F values describe the degree of deviation from a linear behavior. The Freundlich model was also applied by Brownawell et al. (1990), ter Laak et al. (2006), Bäuerlein et al. (2012), Droge and Goss (2012) and Niedbala et al. (2013) to describe the sorption behavior of organic cations.

The obtained n_F for all averaged isotherms are in the range between 0.71 and 0.86 with an average of $n_F=0.77$. The isotherm's non-linearity may indicate the existence of energetically heterogeneous sorption sites (Calvet, 1989). Additionally, the comparable n_F values suggest no significant changes of the relevant sorption mechanisms at various conditions. To enable the direct comparison of the Freundlich coefficients, the $\log K_F$ values were recalculated using **Equation 2.2** and a consistent n_F of 0.77 ($\log K_{F,0.77}$ in **Table 2.2**) for each isotherm point based on the obtained q_{eq} [nmol/kg] and the measured c_{eq} [nM] in the batch tests. Subsequently, the average $\log K_{F,0.77}$ was calculated and used. As reported earlier by Niedbala et al. (2013), the use of activities a_{eq} (using Davies activity coefficients) instead of concentrations c_{eq} resulted in no significant differences for the Freundlich parameters. This is confirmed exemplarily for Mg^{2+} in **Figure A.1** in **Appendix A**. In conclusion, solely concentrations and $\log K_{F,0.77}$ values were used in the following to simplify the data evaluation.

2.3.2 *Influence of competing inorganic cations on MET sorption*

2.3.2.1 *Influence of single ion competition*

Competitive MET isotherms for different types and concentrations of competing inorganic cations are presented in **Figure 2.1**. The respective isotherm parameters can be found in **Table 2.2**. The results show a general decrease of the MET sorption (lower $\log K_F$ values) with increasing concentration of inorganic cations compared to the reference isotherm using pure water. This decrease of sorption can be attributed to cation exchange processes, where inorganic and organic cations compete for the negatively charged sorption sites on the sorbent. The relevance of cation exchange processes for the cationic species of MET (Schaffer et al., 2012b; Niedbala et al., 2013, Droge and Goss, 2013a) and further organic cations (e.g., Brownawell et al., 1990; Bilgiç, 2005; Bi et al., 2006; ter Laak et al., 2006; Droge and Goss, 2012) was also reported in earlier studies.

Figure 2.1 Linearized Freundlich sorption isotherms of MET on silica gel in pure water and with different concentrations of competing inorganic cations: Na^+ (A), NH_4^+ (B), Ca^{2+} (C), and Mg^{2+} (D). The pH of the model water was between 5.5 and 7 for all experiments. Each isotherm point represents the average of a triplicate. Error bars indicate the range of the experimentally derived $\log q_{eq}$.

Table 2.2 Freundlich regression parameters of all batch tests.

Water matrix	Added electrolyte		Freundlich regression parameters								
	c [mM]	log c [-]	log K _F [-]	lower log K _F [-]	upper log K _F [-]	n _F [-]	lower n _F [-]	upper n _F [-]	R ² [-]	SSE [-]	* log K _{F,0.77} [-]
Pure water	0	-	3.45	3.02	3.88	0.83	0.70	0.95	0.9885	5.94E-02	3.65
Pure water + NaCl	0.37	-0.43	3.64	3.31	3.97	0.75	0.65	0.84	0.9915	4.06E-02	3.55
	3.7	0.57	3.55	3.34	3.76	0.74	0.68	0.80	0.9966	1.62E-02	3.46
	37	1.57	2.88	2.24	3.53	0.78	0.60	0.96	0.9733	1.26E-01	2.91
	370	2.57	2.56	2.27	2.85	0.72	0.64	0.80	0.9934	2.80E-02	2.37
Pure water + NH ₄ Cl	0.37	-0.43	3.70	3.37	4.03	0.76	0.66	0.85	0.9916	4.35E-02	3.66
	3.7	0.57	3.35	3.15	3.55	0.75	0.70	0.81	0.9971	1.39E-02	3.29
	37	1.57	2.91	2.47	3.36	0.74	0.62	0.86	0.9862	5.77E-02	2.79
	370	2.57	2.18	1.98	2.38	0.86	0.81	1.00	0.9977	1.41E-02	2.51
Pure water + CaCl ₂	0.37	-0.43	3.01	2.90	3.12	0.84	0.81	0.88	0.9993	3.79E-03	3.28
	3.7	0.57	2.90	2.56	3.24	0.76	0.66	0.85	0.9921	3.36E-02	2.85
	37	1.57	2.68	2.39	2.96	0.78	0.70	0.86	0.9941	3.26E-02	2.71
	370	2.57	2.66	2.40	2.92	0.75	0.67	0.82	0.9948	2.61E-02	2.58
Pure water + MgCl ₂	0.37	-0.43	3.41	2.82	4.00	0.75	0.59	0.92	0.9756	1.14E-01	3.36
	3.7	0.57	2.93	2.43	3.42	0.77	0.63	0.90	0.9838	7.49E-02	2.92
	37	1.57	2.75	2.31	3.19	0.79	0.67	0.91	0.9881	5.83E-02	2.84
	370	2.57	2.67	2.51	.83	0.76	0.71	0.80	0.9981	1.05E-02	2.63
Pure water + NaCl + NH ₄ Cl	3.7 + 3.7	0.57 + 0.57	3.40	3.06	3.73	0.71	0.62	0.80	0.9910	3.66E-02	3.18
Pure water + CaCl ₂ + MgCl ₂	3.7 + 3.7	0.57 + 0.57	2.95	2.54	3.36	0.75	0.63	0.88	0.9861	7.66E-02	2.90
Pure water + NaCl + CaCl ₂	3.7 + 3.7	0.57 + 0.57	2.79	2.13	3.46	0.77	0.58	0.95	0.9712	1.33E-01	2.78
	37 + 3.7	1.57 + 0.57	2.54	1.91	3.17	0.83	0.65	1.00	0.9781	1.16E-01	2.74
	3.7 + 0.37	0.57 + (-0.43)	3.31	2.79	3.82	0.74	0.59	0.88	0.9803	8.91E-02	3.19
Pure water + HCl (pH ≈ 2)	-	-	2.53	2.18	2.88	0.81	0.71	0.90	0.9928	3.61E-02	2.66

K_F =Freundlich sorption coefficient $\left[\frac{(\text{mmol/kg})}{(\text{mmol/L})^{0.77}} \right]$ (including 95% confidence limits), n_F =Freundlich exponent (including 95% confidence limits), R^2 =coefficient of determination, SSE=sum of squared errors (see Equation A.3 in Appendix A).

* Recalculated log K_F for constant $n_F=0.77$.

At low to moderate background concentrations of inorganic cations ($c=0.37\text{--}37\text{ mM}$), lower sorption of MET was found in the presence of divalent (Ca^{2+} , Mg^{2+}) compared to monovalent inorganic cations (Na^+ , NH_4^+). For instance, the comparison of the $\log K_F$ values at a competing ion concentration of 3.7 mM with the reference isotherm ($\log K_{F,0.77}=3.65$) illustrates that the (absolute) influence of Ca^{2+} ($\log K_{F,0.77}=2.85$) and Mg^{2+} ($\log K_{F,0.77}=2.92$) on the exchange equilibrium of MET is substantially stronger than for Na^+ ($\log K_{F,0.77}=3.46$) or NH_4^+ ($\log K_{F,0.77}=3.29$). Hence, a higher fraction of the exchange sites is initially occupied with Ca^{2+} and Mg^{2+} cations at equal molar concentrations. This higher affinity of divalent cations to exchange sites in comparison to monovalent cations can be attributed to their higher valence and, thus, the charge density of the hydrated cation (Scheffer and Schachtschabel, 2010). The consideration of cations with the same valence ($\text{Na}^+/\text{NH}_4^+$ and $\text{Ca}^{2+}/\text{Mg}^{2+}$, respectively) shows that their competitive effects are in the same order of magnitude. Slight differences might be attributed to different space requirements according to their hydrated ion radii (Volkov et al., 1997): 331 pm (NH_4^+), 358 pm (Na^+), 412 pm (Ca^{2+}), and 428 pm (Mg^{2+}).

At high electrolyte concentrations ($c=370\text{ mM}$), the difference between mono- and divalent cation competition vanishes due to their large excess. The resulting $\log K_F$ values of MET are comparable for all competing cations (**Table 2.2** and **Figure A.3** in **Appendix A**) suggesting a maximal sorbent loading of accessible exchange sites with competing ions (saturation effect). The remaining sorption of MET may be mainly attributed to non-ion exchange processes (e.g., hydrogen bonding, hydrophobic interactions, etc.). Column experiments also demonstrated a still considerable retardation with $R_d=85.74$ at high concentrations of competing ions ($c(\text{Na}^+)=370\text{ mM}$) (see **Section 2.3.4**).

In order to consider the different valence z of the competing ions, the charge-corrected equivalent concentration $z \cdot c_{\text{ion}}$ is introduced. **Figure 2.2** shows the relationship between the $\log K_{F,0.77}$ values and the logarithmized equivalent concentrations $\log(z \cdot c_{\text{ion}})$ of added inorganic cations, respectively. This allows the comparison and quantification of the relative change in MET sorption affinity caused by varying concentrations of competing inorganic cations. For the considered concentration range, a linear regression for the logarithmized variables may be performed (**Table 2.3**). A consideration of the ionic strength expressed as activity of the electrolyte solutions instead of $z \cdot c_{\text{ion}}$ slightly affects the slopes of the regression lines (**Figure A.2** in **Appendix A**). Therefore, to simplify the data evaluation the use of equivalent

concentrations $z \cdot c_{\text{ion}}$ was preferred. The slopes of the regression lines for di- and monovalent cations differ by a factor of around two (slope ($\text{Na}^+/\text{NH}_4^+$) = $-0.41/-0.40$; slope ($\text{Ca}^{2+}/\text{Mg}^{2+}$) = $-0.22/-0.23$). Thus, the overall relative change with increasing equivalent concentrations of monovalent cations is around twice as high as for divalent cations. Consequently, the absolute differences of the sorbed amount of MET become smaller with increasing equivalent concentrations of the background electrolyte (**Figure 2.1** and **Figure 2.2**). Similar trends between competing electrolyte concentrations and the K_F were also found by Niedbala et al. (2013) for MET on natural sediment, by Bäuerlein et al. (2012) for diverse charged organic species on exchange polymers, and by Droge and Goss (2012) for amines on soil organic matter. Differences in the slopes for $\log K_F$ vs. $\log (z \cdot c_{\text{ion}})$ relationships can be attributed to the varying sorbent properties in these studies (Chen et al., 2013). This general tendency between the relative effects of competing monovalent and divalent cations can be explained qualitatively by a simple mass action law considering ion exchange equilibrium (Droge and Goss, 2012). However, mass action laws are most likely too simple to quantitatively describe the sorption of organic cations on charged surfaces.

Figure 2.2 Relationship between the logarithmized Freundlich coefficient $\log K_{F,0.77}$ and the logarithmized equivalent concentration $\log (z \cdot c_{\text{ion}})$ considering the valence z of each added competing inorganic ion. The $\log K_F$ values were refitted with a constant value for the Freundlich exponent of $n_F=0.77$.

Table 2.3 Parameters for the linear regression lines ($\log K_{F,0.77}=m \cdot \log (z \cdot c_{ion})+n$) in **Figure 2.2**.

Competing ion	m(slope)	n(intercept)	R^2
Na ⁺	-0.4090	5.9634	0.9313
NH ₄ ⁺	-0.3950	5.8544	0.9897
Ca ²⁺	-0.2240	4.5057	0.9047
Mg ²⁺	-0.2270	4.6103	0.9108

R^2 =coefficient of determination.

The direct comparison of the regression lines slopes for Na⁺ and Ca²⁺ competition from the current study (slope -0.41 for Na⁺ and -0.22 for Ca²⁺, **Table 2.3**) with the reported results from Niedbala et al. (2013) (slope -0.13 for Na⁺ and -0.23 for Ca²⁺), obtained by a very similar methodology for a natural sediment, shows that the relationship for Ca²⁺ is in the same order of magnitude. In contrast to the presented study, however, their reported slope was greater for Ca²⁺ than for Na⁺ by a factor of approximately two. The data for the synthetic material silica gel confirm this behavior only for low concentrations of inorganic cations ($c=0.37\text{--}3.7$ mM) where the relative impact of divalent cations is higher than for monovalent ions (**Figure 2.2**). At moderate to high background concentrations of competing ions ($c=3.7\text{--}370$ mM), a stronger relative influence of monovalent compared to divalent cations was found. Therefore, the overall slope of the regression line for Ca²⁺ is smaller than for Na⁺. Thus, the assumption of a linear relationship between $\log K_F$ and equivalent concentration of inorganic cations does not apply for the whole investigated concentration range ($c=0.37\text{--}370$ mM). On the one hand, the sorption capacity of ion exchange sites seems to be asymptotically reached at higher concentrations of inorganic ions ($c=37\text{--}370$ mM, **Figure A.3** in **Appendix A**). On the other hand, the point where competition has a minimal effect on the sorption of MET was measured with $\log K_{F,0.77}=3.65$ in pure water without adding competing inorganic ions (**Figure 2.2** and **Table 2.2**). Furthermore, the maximum capacity of silica gel calculated from the Langmuir fit of the pure water isotherm ($q_{\max}=0.1$ mol/kg, **Table A.2** in **Appendix A**) is in the same order of magnitude than the measured potential cation exchange capacity of the used silica gel ($CEC_{\text{pot}}=0.082$ mol/kg).

2.3.2.2 Influence of dual ion competition

Sorption experiments with MET in competition with two inorganic cations were carried out to study the combined effects of mixtures with more than one dissolved inorganic cation. This study is vital in order to transfer the results to environmental conditions

(natural waters) where always more than one relevant inorganic cation can be found. The resulting sorption isotherms are given in **Figure 2.3**. The experimentally determined sorption isotherms of the mixtures (red dashed lines) are compared with the pure water isotherm at minimal competitive influence and with the respective single competition isotherms (black and grey solid lines). To predict the isotherms of MET in the presence of two competing ions, the combined competition on the sorption equilibrium of MET was calculated by cumulating the competitive effects of the added inorganic single ions relative to pure water (red dotted lines). The Freundlich exponent n_F was set again to 0.77.

As expected, the combined competitive effect of two inorganic cations in a mixture is greater when compared to the individual effect of only one competing ion at the same concentration. In **Figure 2.3A**, for example, the sorbed amount of MET ($\log K_F$) under combined Na^+ and NH_4^+ competition ($\log K_F=3.18$) is smaller than for their respective single influence (Na^+ : $\log K_F=3.46$, NH_4^+ : $\log K_F=3.29$). The expected difference to the reference isotherm ($\log K_F=3.65$) was $\Delta \log K_F=0.55$ and fits very well with the measured data ($\Delta \log K_F=0.47$). While in **Figure 2.3B**, as another example, the sorption of MET in the mixture shows only a slight change compared to single competition isotherms. A $\log K_F$ value of 2.12 was predicted, however, the experiment resulted in a $\log K_F$ value of 2.90.

As it can be seen from the investigated mixtures, the predicted and measured sorption isotherms are in relatively good agreement (**Figure 2.3A**, **Figure 2.3C** and **Figure 2.3E**) only for low electrolyte concentrations. In contrast, the combined competitive impact was overestimated for higher concentrations (**Figure 2.3D**) and for the co-existence of two divalent inorganic cations (**Figure 2.3B**). A possible reason for these deviations might be an increasing saturation of the exchange sites at the silica gel surface (compare with **Figure 2.2**). Therefore, the prediction of the combined effects in mixtures with more than one competing cation by simply cumulating the single ion effects is limited. The additional consideration of increasing ionic strength by means of activities does also not considerably reduce the remaining deviations.

Figure 2.3 Linearized Freundlich sorption isotherms of MET on silica gel in competition with two inorganic cations and the comparison with the refitted MET sorption isotherms ($n_F=0.77$) in pure water and under the influence of individually competing ions. Error bars indicate the range of the experimentally derived $\log q_{eq}$. The expected influence of the combined competition on the sorption of MET was predicted by cumulating the contributions of individual ion competition effects (for $n_F=0.77$) with respect to the isotherm in pure water.

2.3.3 *Role of the surface charge (point of zero charge)*

For studying the influence of a reduced sorbent surface charge, the sorption of MET at pH values below the pH_{PZC} of ≈ 2.5 was investigated. At the studied $pH \approx 2$, the number of negatively charged surface sites is much lower than at neutral pH, because the majority of the silanolate groups is protonated by H^+ . It is known that H^+ have a high covalent proportion in their bonds (Zumdahl and Zumdahl, 2007). Consequently, the probability for cation exchange processes is strongly reduced. By decreasing the pH, however, the concentration of competing free H^+ ions in solution also increases to $c(H^+) = 10$ mM.

The pH reduction below the pH_{PZC} resulted in a significant decrease in the MET sorption compared to the experiments with pure water at $pH \approx 6$ (**Figure 2.4**). Assuming a similar competitive effect for the monovalent Na^+ and H^+ ions on the sorption of MET (at equimolar concentrations), the additional comparison with the isotherm at 37 mM Na^+ shows that the reduced sorption of MET in acidified water at $pH \approx 2$ (10 mM H^+) cannot solely be explained by competition effects of the H^+ ions alone. Eventually, the sorbed amount of MET and thus $\log K_F$ at $pH \approx 2$ ($\log K_{F,0.77} = 2.66$) is in the same order

Figure 2.4 Linearized Freundlich sorption isotherms of MET on silica gel for pure water at $pH \approx 6$ and $pH \approx 2$ (10 mM H^+). Additionally, the comparison with the MET isotherms with 37 mM and 370 mM Na^+ is shown. Each isotherm point represents the average of a triplicate. Error bars indicate the range of the experimentally derived $\log q_{eq}$.

of magnitude when compared with high concentrations (370 mM) of competing inorganic cations ($\log K_{F,0.77} \approx 2.5$). As a consequence, the conclusion may be derived that beside the contingent cation exchange processes further interactions, such as hydrogen bonding and hydrophobic interactions, are responsible for the remaining sorption of MET.

2.3.4 *Column experiments to verify batch results*

The influence of inorganic ions on the sorption behavior of MET was also studied using column experiments. For this purpose, breakthrough curves with and without NaCl addition ($c(\text{Na}^+) = 370 \text{ mM}$) were recorded. The obtained breakthrough curves are shown in **Figure 2.5**. The fitted parameters are listed in **Table 2.4**.

The results show a dramatically decreased retardation after Na^+ addition when compared to the reference breakthrough curve using pure water. The retardation factor R_d decreases from 1202 for pure water with minimal competition (experiment A) to 86 with addition of Na^+ (experiment B). In analogy to the batch experiments, this effect can be explained by the shift of the cation exchange equilibrium (see **Section 2.3.2.1**). Thus, the addition of Na^+ leads to a significantly weaker sorption of MET on the sorbent.

Figure 2.5 Experimental and modeled breakthrough curves (including tracer tests) of MET for silica gel with and without NaCl addition ($c(\text{Na}^+) = 370 \text{ mM}$). 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 tracer (NaCl).

Table 2.4 Modeled parameters and fit quality of the column experiments.

Experiment	Q [mL/min]	ε [-]	v_w [cm/min]	R_d [-]	lower R_d [-]	upper R_d [-]	R^2 [-]	MSE [-]
A (pure water)	0.49	0.39	1.81	1202	1200	1205	0.9899	1.5E-03
Tracer A	0.49	0.39	1.61	1	-	-	0.9995	7.9E-05
B (370 mM Na⁺)	0.50	0.34	1.87	85.74	84.08	87.40	0.9931	1.3E-03
Tracer B	0.54	0.34	1.98	1	-	-	0.9987	2.0E-04

Q =volumetric flow rate, ε =effective porosity, v_w =pore water velocity, R_d =retardation factor (including 95% confidence limits), R^2 =coefficient of determination, MSE =mean squared error.

For comparing the sorption coefficients of the column experiments with the results of the batch tests, the $\log K_{F,0.77}$ values were calculated from R_d :

$$R_d = 1 + \frac{\rho_b}{\varepsilon} \cdot n_F \cdot K_F \cdot c^{n_F-1} \quad \text{Equation 2.3}$$

where ρ_b denotes the bulk density [kg/m³] and ε [-] the effective column porosity.

The $\log K_{F,0.77}$ values of MET on silica gel obtained from column and batch experiments are compared in **Table 2.5**. Despite some differences between the two applied determination methods, the obtained sorption coefficients are in the same order of magnitude and therefore consistent.

The column experiments confirm the results of the batch tests and show that cation exchange is the dominating sorption process. However, a significant sorption with the resulting retardation of MET could still be observed by adding an extremely high concentration of Na⁺ ($c=370$ mM). Due to the excess of inorganic cations added to the solution, it can be assumed that the relevance of MET sorbed onto ion exchange sites reaches a minimum. In addition to the potentially still occurring ion exchange processes, the remaining sorption of MET can be attributed again to other interaction processes (e.g., hydrogen bonding, hydrophobic interactions, etc.).

Table 2.5 Comparison of Freundlich sorption coefficients for column and batch experiments.

Experiment	Column experiments		Batch experiments
	ρ_b [kg/m ³]	$\log K_{F,0.77}$ [-]	$\log K_{F,0.77}$ [-]
A (pure water)	372.8	3.98	3.65
B (370 mM Na⁺)	360.1	2.79	2.37

ρ_b =bulk density, K_F =Freundlich sorption coefficient $\left[\frac{(\text{nmol/kg})}{(\text{nmol/L})^{0.77}} \right]$.

2.4 Conclusions

Systematic batch sorption experiments with the cationic species of the basic beta-blocker MET onto the synthetic material silica gel were performed. For detecting and evaluating competitive effects, the sorption was systematically investigated in the absence as well as in the presence of Na^+ , NH_4^+ , Ca^{2+} and Mg^{2+} , respectively. Furthermore, the effect of reducing the pH below pH_{PZC} was investigated. Based on these results, the following conclusion can be drawn:

- Cation exchange was identified as a relevant sorption mechanism, due to a decreased sorption with increasing concentrations of competing cations (Na^+ , NH_4^+ , Ca^{2+} and Mg^{2+}) and also by a reduced sorbent surface charge ($\text{pH} < \text{pH}_{\text{PZC}}$).
- Divalent cations show a stronger absolute effect on the sorbed amount of MET at low and moderate equimolar concentrations ($c = 0.37\text{--}37\text{ mmol/L}$) than monovalent cations, which may be attributed to their higher charge densities. However, the relative influence of divalent cations compared to monovalent inorganic cations on MET sorption decreases with increasing concentrations.
- At high concentrations of competing cations ($c = 370\text{ mM}$), the sorption of MET via ion exchange is suppressed to a minimum (saturation effect). However, the remaining sorption coefficients are still relatively high (e.g., $K_{\text{F},0.77} = 380.19\text{ (nmol/kg)/(nmol/L)}^{0.77}$ at $c(\text{Ca}^{2+}) = 370\text{ mM}$) indicating the existence of further sorptive interactions.
- Only small differences in sorption were observed for competing cations of the same valence.
- At lower total equivalent concentrations of added inorganic cations (sum of $z \cdot c_{\text{ion}} \leq 10\text{ mM}$), a reduced sorption for the organic cation MET caused by the presence of several competing inorganic cations (mixtures of two inorganic cations) can be predicted by simply cumulating their individual influences relative to pure water.

In addition to the systematic batch studies, column experiments were performed, which have shown that:

- The calculated sorption coefficients ($\log K_{\text{F}}$ values) from the obtained breakthrough curves are comparable with the batch test results.

- A retardation factor of about $R_d=86$ for MET could still be observed even for a large excess of competing inorganic cations ($c(\text{Na}^+)=370$ mM) confirming the relevance of further sorption mechanisms (e.g., hydrogen bonding) additional to cation exchange.

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Chapter 3

3 Sorption of organic cations onto silica surfaces over a wide concentration range of competing electrolytes

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Abstract:

The fundamental understanding of organic cation-solid phase interactions is essential for improved predictions of the transport and ultimate environmental fates of widely used substances (e.g., pharmaceutical compounds) in the aquatic environment. We report sorption experiments of two cationic model compounds using two silica gels and a natural aquifer sediment. The sorbents were extensively characterized and the results of surface titrations under various background electrolyte concentrations were discussed. The salt dependency of sorption was systematically studied in batch experiments over a wide concentration range (five orders of magnitude) of inorganic ions in order to examine the influence of increasing competition on the sorption of organic cations. The organic cation uptake followed the Freundlich isotherm model and the sorption capacity decreases with an increase in the electrolyte concentration due to the underlying cation exchange processes. However, the sorption recovers considerably at high ionic strength ($I > 1$ M). To our knowledge, this effect has not been observed before and appears to be independent from the sorbent characteristics and sorbate structure. Furthermore, the recovery of sorption was attributed to specific, non-ionic interactions and a connection between the sorption coefficient and activity coefficient of the medium is presumed. Eventually, the reasons for the differing sorption affinities of both sorbates are discussed.

Graphical Abstract:

3.1 Introduction

3.1.1 *Motivation and objectives*

A large number of polar organic contaminants detected in the aquatic environment are bases containing nitrogen moieties which are positively charged at environmentally relevant pH values ($pK_a > 7$). These compounds are released into different parts of the water cycle due to their extensive use in industry, agriculture and pharmacy (Halling-Sørensen et al., 1998; Daughton and Ternes, 1999; Tolls, 2001; Heberer, 2002; Franco et al., 2010; Samaraweera et al., 2014). Therefore, comprehensive knowledge about their sorption on different sorbents is crucial in order to assess their ultimate environmental fate and bioavailability.

Numerous studies have shown that organic cations, in spite of their high polarity, sorb considerably onto negatively charged surfaces of many natural (e.g., sediments, clays, organic matter) (Tolls, 2001; Kah and Brown, 2007; Kibbey et al., 2007; Sibley and Pedersen, 2008; Droge and Goss, 2012, 2013a, 2013b; Schaffer et al., 2012a, 2012b; Niedbala et al., 2013; Li et al., 2015) and technical sorbents (e.g., activated carbon, silica, ion exchange resins) (Parida and Mishra, 1996; Bäuerlein et al., 2012; Kutzner et al., 2014). Here, cation exchange processes are of major importance (Droge and Goss, 2012, 2013a, 2013b; Schaffer et al., 2012b; Niedbala et al., 2013). Depending on the sorbate structure (presence of functional groups with electronegative atoms), additional polar electron donor-acceptor mechanisms (e.g. hydrogen bonding) may also significantly contribute to the overall cation sorption (Senesi, 1992; MacKay and Vasudevan, 2012; Li et al., 2015; Yu and Bi, 2015). The identification and separation of these potential sorptive interactions is very challenging due to the complex interrelation of many influencing factors such as compound structure (e.g., molecular size, functional groups), sorbent characteristics (e.g., surface area, ion exchange capacity, mineral composition) and the properties of the water phase (e.g., pH, ionic strength, dissolved organic matter). For example, decreasing sorption coefficients with increasing concentrations of competing inorganic ions, and thus a simultaneous shift of the exchange equilibrium in favor of the added cations, was observed in previous studies for natural as well as technical sorbents (Bäuerlein et al., 2012; Droge and Goss, 2012, 2013a, 2013b; Schaffer et al., 2012b; Niedbala et al., 2013; Kutzner et al., 2014). A considerable sorption of organic cations, even at very high background electrolyte concentrations (>1 g/L), was still determined (Kutzner et al., 2014). This

observation suggests that additional sorptive interactions (e.g., hydrogen bonding, surface complexation) besides cation exchange play a crucial role. The identification and separation of these potential sorption processes has stimulated this research.

Despite the fact that a number of studies on the sorption of organic cations were already carried out, there are still knowledge gaps regarding the fundamental understanding of the individual sorption mechanisms, their quantitative contribution to the total sorption, as well as the impact of boundary conditions. This is, however, a prerequisite for accurate quantitative predictions. For example, the interrelations between competing organic and inorganic cations in combination with sorbent-related key parameters are not yet well understood. Therefore, a series of systematic experiments was conducted focusing on the characterization of organic cation sorption on silica surfaces as a function of competing electrolyte concentrations. For doing so, a wide concentration range of competition was covered (five orders of magnitude). The initial aim of this study was to capture the effect of increasing competition on organic cation sorption until the point of maximum suppression for the cation exchange interactions is reached, thus enabling the separate study of the remaining non-ionic interactions. In order to decrease the complexity and to avoid ambiguities, defined model solutions with a known constitution, two different sorbate molecules, and largely homogenous and well determined sorbents were used in the experiments. Eventually, several comparative experiments were carried out with a natural sorbent to study the transferability of the findings to heterogeneous sorbents.

3.1.2 General aspects of the physical chemistry of dissolved ions in solution

Since very high electrolyte concentrations were applied, it is initially important to understand the physical chemistry of electrolyte solutions. Different theoretical approaches for the calculation of activity coefficients are described in the literature (e.g., Debye and Hückel, 1923; Güntelberg, 1926; Davies, 1938, 1962; Bromley 1973; Pitzer, 1973, 1991). The majority of them are limited to low ionic strengths and fail for concentrated electrolyte solutions, as only long-range Coulomb attraction interactions of cations and anions are considered (Luckas and Krissmann, 2001). This interaction, however, is only relevant for highly diluted solutions where the interionic distances are large. Generally, every ion is preferably surrounded by a hydration shell and oppositely charged ions, which hinder its reactivity (activity coefficient is smaller than one). In concentrated solutions, short-range forces (ion/molecule, and molecule/molecule

interactions) predominate, which are mostly of repulsive nature (Chen et al., 1982; Luckas and Krissmann, 2001). Moreover, Coulomb repulsion interactions of equally charged ions dominate at high electrolyte concentrations and an increasing proportion of water molecules are bound in ionic hydration shells. The concentration of free water molecules is thus considerably reduced. At very high concentrations, it is even possible that the number of available solvent molecules is insufficient to complete the formation of a hydration shell (Chen et al., 1982; Schmidt, 2003; Ferse, 2013). Consequently, the ions are more polarized and susceptible to chemical processes (e.g., surface reactions, ionic association of both ions and solvent molecules, formation of ion-pairs) resulting in a higher effective concentration (activity) than the real concentration of the ions (Chen et al., 1982; Schmidt, 2003; Moggia and Bianco, 2007; Ferse, 2013). Hence, in highly concentrated solutions the activity coefficients are considerably greater than one. This phenomenon is considered, for example, in the model approach of Pitzer (1973, 1991).

3.2 Material and methods

3.2.1 Chemicals

The beta-blocker metoprolol (MET) as tartrate salt with a minimum content of 98% was purchased from Sigma-Aldrich (Steinheim, Germany). The internal reference standard metoprolol-D₇ as hydrochloride was purchased from EQ Laboratories (Augsburg, Germany). Isopropyl-(4-methylbenzyl)-amine (iP4MBA) and the used internal reference standard isopropyl-(2,4-dimethylbenzyl)-amine as hydrochloride with a minimum content of 95% were obtained from Evo Blocks (Budapest, Hungary). Stock solutions of MET and iP4MBA with a concentration of 37.4 mM (10 g/L and 6.04 g/L) were prepared in methanol. The pH was adjusted by adding 1 M HCl solution until a pH of 5.6 was reached. The internal standards were prepared in methanol with a concentration of 100 mg/L. All reference standard solutions were stored at –18 °C. MET and iP4MBA are positively charged at the experimental pH of 5.6, as the secondary amine moiety is readily protonated due to its $pK_a > 9$ (Schaffer and Licha, 2014). MET and iP4MBA were selected as sorbates in this study because both compounds have a partially similar structure (secondary amine, para-substituted benzene ring) and therefore similar physicochemical properties (polarity, acidity constant, see **Table 3.1**). Since iP4MBA has no additional functional groups such as

Table 3.1 Physicochemical properties of the used sorbates.

Compound	Metoprolol (MET)	Isopropyl-(4-methylbenzyl)-amine (iP4MBA)
Structure
CAS number	51384-51-1	70894-75-6
H acceptors	4	1
H donors	2	1
^{a,b,c} pK _a	9.92 (9.43±0.10)	10.14 (10.00±0.19)
^{c,d} log K _{OW}	1.63	2.82
^{c,e} log D	-1.33	-0.23

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

^b Experimentally determined by acid-base titration.

^c SciFinder Scholar predicted values, calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (1994–2016).

^d log K_{OW} values refers to the neutral species.

^e log D values refers to all species at pH=6.

ether or hydroxyl groups, conclusions on the type and proportion of other relevant interactions, e.g., H-donor/acceptor mechanisms such as hydrogen bonds, can be drawn. All other used inorganic chemicals were of high purity (>99%, analytical grade). Ultrapure water for the preparation of all solutions was obtained from the water purification system GenPure from TKA (Niederelbert, Germany).

3.2.2 Sorbents

Two silica gel materials with different surface properties and one sediment were used as sorbents (**Table 3.2**). Silica gel-1 (Silica gel 60, 200–500 µm, amorphous) was purchased from Merck (Darmstadt, Germany). The second synthetic sorbent material silica gel-2 (Nucleodur 100-50, 50 µm, spherical, ultrapure) was obtained from Macherey-Nagel (Düren, Germany). The aquifer sediment, which was already used in other studies (Schaffer et al., 2012b; Niedbala et al., 2013), was selected for an exemplary comparison of the results of the synthetic sorbents with natural sorbents. Due to the expected low point of zero charge of the silica gels (pH_{PZC}<4.5) (Kosmulski, 2002), the surfaces are net negatively charged at the experimental pH and both sorbents act as cation exchangers. The same applies for many mineral surfaces of the sediment, which consists mainly of quartz, feldspars and layered silicate minerals with pH_{PZC} values <5 (Niedbala et al., 2013). Silica gel-2 was conditioned (preloaded) with Na⁺ and Ca²⁺ solutions having the same concentrations as in the subsequent

Table 3.2 Physicochemical properties of the used sorbents (for more detail see **Section B.1** in **Appendix B**).

Sorbent properties	Silica gel-1	Silica gel-2	Sediment
A_{BET} [m ² /g]	487	327	3.17
d_{pore} [nm]	6.56	13.9	5.09
V_{pore} [cm ³ /g]	0.76	1.00	0.01
d_{particle} [μm]	302	52.7	193
pH (H ₂ O) [-]	7.04	4.26	8.56
CEC_{pot} [μmol _c /g]	279	170	44.0
CEC_{eff} [μmol _c /g]	24.4	11.2	9.23
α_{OH} [mmol/g]	4.23	4.40	1.81

A_{BET} =specific surface area, d_{pore} =mean pore diameter, V_{pore} =pore volume, d_{particle} =mean particle diameter, CEC_{pot} =potential cation exchange capacity at pH=8.1, CEC_{eff} =effective cation exchange capacity at pH=5.6, α_{OH} =density of OH groups.

experiments. For this, the sorbent was flushed in a stainless-steel column until the pH and electrical conductivity values from the inlet matched the values observed at the outlet of the column. The other sorbents were either pre-treated as described in Kutzner et al. (2014) (silica gel-1) or in Niedbala et al. (2013) (sediment). Measured properties of the used sorbents are listed in **Table 3.2** and further information on sorbent characterization methods and data are available in **Appendix B** (see **Section B.1**).

3.2.3 *Potentiometric surface titration*

The determination of the surface charge density of sorbents was carried out by potentiometric titration in pure water containing different concentrations of NaCl (0.37, 3.7, 37, 370, and 3700 mM). An aliquot of 30 mL salt solution was filled into an Erlenmeyer flask. To the solution 0.2 g of the solid material was added and equilibrated at room temperature for 10 min under stirring. Before the experiments, the sorbents were washed several times with ultrapure water with a solid to liquid ratio of 1:10 until an electrical conductivity of <5 μs/cm was reached and then dried at 40 °C until a constant weight. Afterwards, 2 mL of 0.1 M HCl was added to the suspension and stirred for 10 min while purging it with nitrogen to remove CO₂. After recording the initial pH, the sample was titrated with 0.1 M NaOH solution using 0.2 mL or 0.05 mL (close to the transition point) portions under a continuous nitrogen stream and stirring. Each corresponding pH value was recorded after 2 min. The titrations for silica gel-1 and silica gel-2 were performed until pH=8, since silica gel dissolves at higher pH values. The pH measurements were carried out using a WTW pH electrode (SenTix 41) at a temperature of 25 °C.

Finally, a correction curve was obtained by repeating the titration only with the electrolyte solution (blank) using the same volume and concentration as in the sorbent suspensions in order to account for salt effects on the pH measurement (e.g., alkaline error, potential drift, etc.). The difference between the amounts of H^+/OH^- in the blank sample and sorbent suspension (calculated from the measured pH) gives the amount of H^+/OH^- sorbed on the sorbent surface. For each point of the titration curve, the surface charge density, σ_s [C/m²], was calculated from the general mass/charge balance with:

$$\sigma_s = \frac{V_L}{m_A} \cdot \frac{(c_0(H^+) - c_{eq}(H^+)) - (c_0(OH^-) - c_{eq}(OH^-))}{A_{BET}} F \quad \text{Equation 3.1}$$

where:

$$c_0(H^+) = \frac{a_0(H^+)}{\gamma(H^+)} \quad c_{eq}(H^+) = \frac{a_{eq}(H^+)}{\gamma(H^+)} \quad \text{Equation 3.2}$$

$$a_0(H^+) = 10^{-pH} \quad a_{eq}(H^+) = 10^{-pH} \quad \text{Equation 3.3}$$

$$c_0(OH^-) = \frac{K_w(c)}{c_0(H^+)} \quad c_{eq}(OH^-) = \frac{K_w(c)}{c_{eq}(H^+)} \quad \text{Equation 3.4}$$

and $c_0(H^+)$ or $c_0(OH^-)$ is the molar concentration of respective ions [mol/L] in the blank sample, $c_{eq}(H^+)$ or $c_{eq}(OH^-)$ is the molar concentration of respective ions [mol/L] in the sorbent suspension, F is the Faraday constant [C/mol], V_L is the total volume of the solution [L], m_A is the sorbent mass [kg], A_{BET} is the specific surface area of the sorbent [m²/kg], $a_0(H^+)$ or $a_{eq}(H^+)$ is the activity of H^+ in the blank sample or sorbent suspension (directly derived from the measured pH), $\gamma(H^+)$ is the activity coefficient of H^+ , and $K_w(c)$ is the ionic product of water that includes $\gamma(H^+)$ and $\gamma(OH^-)$. The $\gamma(H^+)$ and $K_w(c)$ values for the respective NaCl concentrations were determined with the PHREEQC software (Interactive Version 2.18.3.5570 implements PHREEQC 2.18.3, 16/08/2011) using the *pitzer.dat* database. The data is available in **Appendix B** (see **Section B.1.4: Table B.1 and Table B.2**).

3.2.4 *Batch experiments*

The already published experiments on the sorption of MET on silica gel-1 under the influence of inorganic ions (Kutzner et al., 2014), were extended by an additional concentration step of competing ions ($c(\text{Na}^+, \text{Ca}^{2+})=3700 \text{ mM}$). Experiments with silica gel-2 were carried out in order to directly compare the results between different silica gel materials. Isotherms were determined using batch experiments as described in Kutzner et al. (2014). All tests were conducted as triplicates at a constant temperature of 8 °C in order to simulate natural groundwater conditions. Preliminary tests on sorption kinetics of MET and iP4MBA on silica gel-2 revealed that equilibrium was certainly achieved within 24 h under shaking conditions at 120 rpm without any mass loss due to transformation. The competitive impact was studied over a concentration range of five orders of magnitude. The final concentrations of each inorganic cation were 0.37, 3.7, 37, 370, and 3700 mM. For the determination of the competitive sorption isotherms, the sorbate concentration was also varied over six orders of magnitude ($3.7\text{E-}09$ – $3.7\text{E-}04 \text{ M}$). The batch experiments were carried out with a constant solid to liquid ratio $m_A/V_L=5 \text{ g/L}$. The sorbed amount at equilibrium was calculated based on the concentration decrease of the organic cation in the solution with:

$$q_{\text{eq}} = \frac{V_L(c_0 - c_{\text{eq}})}{m_A} \quad \text{Equation 3.5}$$

where q_{eq} is the sorbed amount at equilibrium [nmol/kg], V_L is the volume of the solution [L], c_0 and c_{eq} refer to the initial and equilibrium concentration of sorbate [nM], respectively, and m_A is the mass of sorbent [kg]. The concentrations of MET and iP4MBA were measured by HPLC-ESI(+)-MS/MS. All samples were spiked with the same concentration of internal standard (100 µg/L). Samples with initial concentrations of $c_0 > 3.7 \text{ µM}$ were diluted with pure water to fit into the concentration range of the linear calibration curve. Prior to analysis, all samples were centrifuged at 15000 rpm ($16602 \times g$) with a Sigma 1-14K device for 10 min. The HPLC system (Agilent 1100) was coupled with a mass selective detector (Applied Biosystems 3200 QTrap). For the chromatographic separation, a Gemini-NX C18 column (150x2 mm, 3 µm) from Phenomenex was used. Four calibration ranges (0.37–3.7 nM, 3.7–37 nM, 37 nM–0.37 µM, and 0.37–3.7 µM) with ten calibration points were determined. The detection and quantitation limit for MET is 0.26 nM (0.07 µg/L) and 0.97 nM (0.26 µg/L) and for

iP4MBA 0.18 nM (0.03 µg/L) and 0.61 nM (0.10 µg/L). Due to the low detection and quantitation limits, a pre-concentration of the samples was not necessary. To compare the results with a natural sorbent, an experimental series using MET and Na⁺ as competing ions was conducted using the sediment from Niedbala et al. (2013). The applied Na⁺ concentrations cover the whole concentration range between pure water and 3700 mM.

3.2.5 Estimation of isotherm data

All sorption data was fitted using the Freundlich sorption model. This is in accordance with numerous publications on the sorption of organic cations (Kah and Brown, 2007; Kibbey et al., 2007; Sibley and Pedersen, 2008; Droge and Goss, 2012, 2013a, 2013b; Niedbala et al., 2013; Li et al., 2015). Due to the wide concentration range (five orders of magnitude), the following discussion is primarily based on the linearized Freundlich isotherm:

$$\log q_{\text{eq}} = \log K_{\text{F}} + n_{\text{F}} \cdot \log c_{\text{eq}} \quad \text{Equation 3.6}$$

where K_{F} [(nmol/kg)/(nmol/L) ^{n_{F}}] is the Freundlich coefficient, and n_{F} [-] the Freundlich exponent. All obtained isotherms and Freundlich parameters can be found in **Appendix B** (see **Section B.2: Figure B.9–Figure B.12 and Table B.3**).

In order to enable the direct comparison of sorption isotherms for different sorbents with different n_{F} values, the equilibrium loading q_{eq} [nmol/kg] of MET or iP4MBA was calculated by the linearized Freundlich equation (**Equation 3.6**) using the determined Freundlich parameters for a medium equilibrium concentration c_{eq} of 370 nM. The values obtained are given in **Table B.3** in **Appendix B**.

3.3 Results and discussion

3.3.1 Potentiometric surface titration

Figure 3.1 (silica gel-1 and 2) and **Figure B.7** in **Appendix B** (sediment) illustrate the influence of the pH on σ_{s} for different electrolyte concentrations. The pH_{PZC} determined at $\sigma_{\text{s}}=0$ is around 6 (silica gel-1), 3 (silica gel-2) and 11 (sediment), respectively. The concentration of the background electrolyte shows a very weak effect on the position of pH_{PZC} (see **Figure B.8** in **Appendix B**), and therefore a common intersection point

Figure 3.1 Surface titration curves for silica gel-1 (A) and silica gel-2 (B) at different electrolyte concentrations of NaCl.

at different salinities can be assumed. Accordingly, the point of zero salt effect and pH_{PZC} would be identical and NaCl may be identified as being indifferent or as inert electrolyte (Tadros and Lyklema, 1968; Lyklema, 1995). However, a precise determination of pH_{PZC} is difficult because the surface charge of silica is close to zero over a wide pH range and thus instead of one sharp pH_{PZC} there is rather a pH range over which σ_s equals zero as discussed in Kosmulski (2006). In the literature, a range of 1.6 to 4.5 (if any) is specified for the pH_{PZC} of various silica gels (Kosmulski, 2002). The pH_{PZC} of the ultrapure silica gel-2 lies within this range. The higher pH_{PZC} of silica gel-1 suggests admixtures or impurities (Lyklema, 1995). The same applies for the sediment, which also consists of mineral phases having higher pH_{PZC} values, e.g., iron oxides.

In general, the $\sigma_s(\text{pH})$ curves show the characteristic shape for silica gels that is different from that of other oxides (Tadros and Lyklema, 1968; Lyklema, 1995; Sonnefeld et al., 1995; Goloub et al., 1996; Lagaly et al., 1997; Dove and Craven, 2005; Kosmulski, 2006; Salis et al., 2010). The negative σ_s increases with increasing pH, because the hydroxide ions react with protons of the sorbent surface, and thus an increasing number of surface OH groups dissociate. This becomes more apparent at $\text{pH} > 6$ for both silica gels or $\text{pH} > 11$ for the sediment. For $\text{pH} < \text{pH}_{\text{PZC}}$, the surface charge is weakly positively charged, suggesting the sorption of protons. At lower pH values,

however, the observed differences between blank sample and sorbent suspension ($C_0 - C_{eq}$, see **Equation 3.1**) are prone to errors and have to be considered with caution due to the fact that the measured pH values of both were almost equal and partially differ only in the second decimal place (Kosmulski, 2006). Generally, it is expected that $|\sigma_s|$ increases with increasing ionic strength (Tadros and Lyklema, 1968; Goloub et al. 1996; Kosmulski, 2006). This was confirmed by the titration results for both silica gels and partially for the sediment.

Since the following experiments were carried out at an experimental pH of 5.6, the discussion below refers to weakly negatively charged silica surfaces. At this pH, the change in σ_s as a function of background electrolyte concentration is very small (e.g., silica gel-2: $\sigma_s(0.37 \text{ mM NaCl}) = -4.3 \text{ mC/m}^2$ vs. $\sigma_s(3700 \text{ mM NaCl}) = -11.9 \text{ mC/m}^2$) and can therefore be neglected.

3.3.2 *Influence of the concentration of competing cations*

The sorption results of MET for different concentrations and types of added inorganic cations are compared for different sorbents in **Figure 3.2**. In general, sorption decreased with increasing electrolyte concentrations. This is expected and can be explained by the occurrence of cation exchange processes as already discussed in Schaffer et al. (2012), Droge and Goss (2012, 2013a), Niedbala et al. (2013) or Kutzner et al. (2014). For further increasing concentrations, however, sorption recovered for all three studied sorbents. This independence from the sorbent type is probably linked to strong ionic interactions in the highly saline waters. This is also reflected by an increase in the activity coefficient (see **Section 3.1.2**). At the experimental pH of 5.6, the change of surface charge caused by varying electrolyte concentrations is very low and cannot explain the considerable recovering of sorption at very high background electrolyte concentrations (see **Figure 3.1** and **Section 3.3.1**).

Based on these observations, a simple conceptual model may be developed including two different types of sorption sites a) deprotonated ($\equiv\text{Si-O}^-$); and b) not deprotonated sorption sites ($\equiv\text{Si-OH}$). The deprotonated sorption sites are accessible to all cations in the solution, such as H^+ , MET^+ , Na^+ or Ca^{2+} . In the following, this unspecific sorption process is referred to as cation exchange and can be described, for example with MET^+ and Na^+ as competing ions, with the following exchange equilibrium formulation:

Using the law of mass action for **Equation 3.7** the following dependency can be derived (assuming $\gamma=1$ for the solid phase):

$$q_{\text{MET}^+} = c_{\text{Si-O}^- \cdot \text{MET}^+} = \frac{K_{\text{MET}^+, \text{Na}^+} \cdot c_{\text{MET}^+} \cdot \gamma_{\text{MET}^+} \cdot q_{\text{Na}^+}}{c_{\text{Na}^+} \cdot \gamma_{\text{Na}^+}} \quad \text{Equation 3.8}$$

Consequently, q_{MET^+} at a constant c_{MET^+} is a function of $\frac{1}{c_{\text{Na}^+} \cdot \gamma_{\text{Na}^+}}$ and the sorption therefore decreases with increasing electrolyte concentrations and activities, respectively ($c(\text{NaCl}, \text{CaCl}_2) = 0.37\text{--}370 \text{ mM}$).

In addition, uncharged sorption sites are assumed, which show a not further specified surface reaction with MET^+ :

$$q_{\text{MET}^+} = c_{\text{Si-OH} \cdot \text{MET}^+} = c_{\text{MET}^+} \cdot \gamma_{\text{MET}^+} \cdot K_{\text{Si-OH} \cdot \text{MET}^+} \quad \text{Equation 3.10}$$

Here, other ions do not have access to these sorption sites (specific sorption), thus the extent of sorption is controlled by the activity of the sorbate and competition plays no role. Therefore, q_{MET^+} at constant c_{MET^+} depends only on γ_{MET^+} and thus indirectly on the electrolyte concentration.

This dependency may explain the sorption recovery at very high electrolyte concentrations ($c(\text{NaCl}, \text{CaCl}_2) = 3700 \text{ mM}$), as γ strongly increases with ionic strength (**Figure 3.2** by the example of γ_{H^+}). γ_{H^+} for the investigated systems were calculated as a function of the NaCl or CaCl₂ concentration based on the Pitzer theory (Pitzer, 1973, 1991) using PHREEQC (pitzer.dat). According to **Equation 3.10**, the use of γ_{MET^+} instead of γ_{H^+} would be more meaningful, however, due to the lack of the required Pitzer parameters for MET^+ , the calculation was not possible. Nevertheless, the general tendency in $\gamma(c)$ is expected to be very similar for all monovalent ions and therefore the calculated function of H^+ is expected to be also a suitable estimate for MET^+ . The lowest sorption of the organic cations was observed at $c(\text{NaCl}, \text{CaCl}_2) = 370 \text{ mM}$. A detailed discussion on the sorption minimum can be found in **Section 3.3.5** using additional column experiments.

In conclusion, specific sorption of organic molecules via all other mechanisms except cation exchange (e.g., hydrogen bonding, surface complexation or π -interactions; Sensesi, 1992; Li et al., 2015; Yu and Bi, 2015) accompanied with the change of γ and resulting activity, respectively, may be an explanation for the enhanced sorption of MET at very high concentrations of NaCl or CaCl₂. In the case of lower electrolyte concentrations ($c(\text{NaCl}, \text{CaCl}_2) \leq 370 \text{ mM}$) this effect plays a minor role as $\gamma < 1$ and does not change considerably. Therefore, (unspecific) cation exchange processes are very likely to dominate the sorption in this concentration range.

Figure 3.2 Influence of background electrolyte concentration of Na⁺ (A) or Ca²⁺ (B) on the sorption of MET onto different silica surfaces. The horizontal dashed lines show the $\log q_{\text{eq}}$ values without competition in pure water of respective sorbent (q_0).

3.3.3 *Influence of sorbent*

The studied organic cation MET showed a higher absolute sorption affinity on silica gel-1 compared to silica gel-2. For example, in pure water (horizontal dashed lines in **Figure 3.2**), under the lowest competition, q_{eq} of MET on silica gel-1 was higher by a factor of 2.1 ± 0.45 at $c_{eq}=370$ nM (**Figure 3.2**). This was likely a result of the 1.5 times larger A_{BET} and the 1.6 times higher CEC_{eff} (see **Table 3.2**). Accordingly, due to the substantially lower A_{BET} (factor 154 and 103), V_{pore} (factor 76 and 100) and CEC_{eff} (factor 2.6 and 1.2) of the natural sorbent, q_{eq} of MET on the natural sandy aquifer was two orders of magnitude lower compared to the mesoporous synthetic silica materials.

The relative change of MET sorption (q_{eq}/q_0) caused by varying electrolyte concentrations is shown in **Figure B.13** in **Appendix B**. Here, the q_{eq} values were normalized to sorption without competition using pure water (q_0). For the majority of the experiments, the relative impact of competing Na^+ and Ca^{2+} ions was stronger for silica gel-1 than for silica gel-2. However, at very high electrolyte concentrations ($c(NaCl, CaCl_2)=3700$ mM) the sorption of MET recovered more strongly on silica gel-2 (factor 3.5 (Na^+) or 10.4 (Ca^{2+})) than on silica gel-1 (factor 2.6 (Na^+) or 4.1 (Ca^{2+})), based on the lowest observed sorption at 370 mM NaCl or $CaCl_2$.

The comparative study of the sediment as sorbent showed a similar relative influence of Na^+ competition on the sorption of MET as compared to silica gel-2. At the sorption minimum ($c(NaCl)=370$ mM), q_{eq} values of the sediment and silica gel-2 were reduced to 18% or 19% with respect to sorption in pure water, whereas $q_{eq}/q_0=7\%$ for silica gel-1. Furthermore, the extent of the improved sorption at high ionic strength is more comparable to that of silica gel-2, since with 65% (sediment) or 90% (silica gel-2) more than half of the sorption capacity in pure water without competition was reached. In contrast, the sorption of MET on silica gel-1 achieved only 17% of the highest sorption, in spite of an increase by a factor of 2.6 with respect to the sorption minimum.

A simple connection between the surface characteristics and the extent of sorption was not identified. Thus, none of the determined sorbent parameters seem to be a meaningful single descriptor for the observed sorption due to the intersection of the curves for different sorbents (see **Figure 3.2** and **Figure B.13** in **Appendix B**). The results, however, indicate that the relative increase in sorption at very high electrolyte concentrations depends on the sorbent's CEC , as surfaces with less cation exchange sites showed an enhanced effect (see **Figure B.13** in **Appendix B** and **Table 3.2**).

This finding also agrees well with the proposed model, where the relevance of specific sorption mechanisms for organic compounds increase when cation exchange is reduced to a very low limit (see **Section 3.3.2**).

3.3.4 *Influence of sorbate*

The absolute sorption affinity of MET and iP4MBA on silica gel-2 is compared in **Figure 3.3**. The studies with iP4MBA as the sorbate showed a similar, but slightly lower, sorption compared to MET. The sorption recovery at high background electrolyte concentrations and the potential connection between q_{eq} and γ_{H^+} were also found for iP4MBA. Accordingly, the observed behavior is not limited to MET. In contrast to MET, iP4MBA contains no hydroxyl or ether groups (see **Table 3.1**). The number of potentially available H-bond acceptor/donor sites for MET (4/2) is therefore higher than for iP4MBA (1/1). Consequently, the probability for the formation of hydrogen bonds is markedly higher for MET. Due to the protonation of the secondary amine moiety (sole H-acceptor/donor functionality of iP4MBA) at experimental pH, iP4MBA is virtually unable to form additional hydrogen bonds. Electrostatic interactions as well as steric effects should play a similar role because of the structural similarity between MET and iP4MBA. Thus, conclusions on the role of cation exchange processes and hydrogen bonds can be drawn by comparing the sorption results of both compounds.

In most cases, especially under Ca^{2+} competition, q_{eq} of MET is higher than for iP4MBA. For example, a difference of 30.3% was determined in pure water and 29.7% at $c(CaCl_2)=370$ mM (see q_{eq} values in Table B.3 in Appendix B). However, it seems likely that in addition to the dominant cation exchange processes, hydrogen bonds also play a crucial role. Similar results were found by Li et al. (2015) for the uptake of MET and atenolol (ATE) on kaolinite. In their study, a reduced sorption for MET compared to ATE was found and attributed to a lower H-bond acceptor/donor sum.

Nevertheless, the sorption of iP4MBA cannot only be explained by cation exchange processes due to the considerable sorption under highly competitive conditions. An alternative explanation may be the specific sorption, as discussed in Section 3.3.2.

Figure 3.3 Comparison of the sorbed amount of MET and iP4MBA on silica gel-2 considering the background electrolyte concentration of Na^+ (A) or Ca^{2+} (B). The horizontal dashed lines show the $\log q_{eq}$ values without competition in pure water of respective sorbate (q_0).

3.3.5 *Influence of valence of competing inorganic cations*

The influence of monovalent and divalent cations on MET and iP4MBA sorption are compared in **Figure 3.4**. At low background electrolyte concentrations ($c=0.37$ – 37 mM), lower sorption of MET or iP4MBA was found in the presence of Ca^{2+} compared to Na^+ . Therefore, a higher proportion of exchange sites is occupied with Ca^{2+} ions at equimolar concentrations. This fact can be attributed to the higher valence, and thus higher charge density. Similar trends were also found by Bäuerlein et al. (2012), Droge and Goss (2012), Niedbala et al. (2013), and Kutzner et al. (2014). With

increasing electrolyte concentrations, however, the difference between Na^+ and Ca^{2+} competition vanished. At a competing ion concentration of 370 mM, $\log K_F$ values were in the same order of magnitude (e.g., silica gel-1: $\log K_F=2.56$ vs. $\log K_F=2.66$). This indicates an almost complete reduction of cation exchange processes. At very high electrolyte concentrations ($c=3700$ mM), the recovery in sorption of MET and iP4MBA is stronger for equimolar concentrations of Ca^{2+} compared to Na^+ . As previously mentioned, a connection between the increase in q_{eq} and γ_{MET^+} (here represented by γ_{H^+}) is expected (see **Section 3.3.2**). When comparing the competitive impact of Na^+ and Ca^{2+} by using the charge-corrected equivalent concentration $c_{\text{equivalent}} (z \cdot c)$ instead of equimolar concentrations, the influence of mono- and divalent cations is comparable and lies on a common curve (see **Figure B.14** in **Appendix B**).

For each sorbent-sorbate combination, the lowest sorption was observed at a competitive ion concentration of 370 mM Na^+ or Ca^{2+} . Here, the sorption compared to the sorption in pure water without competition was reduced by at least 70% (silica gel-2 + iP4MBA + Ca^{2+}) with an average value of $80.4 \pm 9.1\%$ for all studied sorbent-sorbate combinations and Na^+ or Ca^{2+} competition. At $c(\text{NaCl}, \text{CaCl}_2) > 370$ mM, the relative proportion of other interactions becomes more relevant, while cation exchange processes were reduced to a very low level. Due to the superposition and the shift in the relevance of different interactions (opposing trends), the exact minimum is still unknown.

To detect this limiting region more accurately, two more concentrations ($c(\text{NaCl}, \text{CaCl}_2)=740$ and 1850 mM) were investigated for the sorption of MET on silica gel-2 using additional column experiments. Details for the experimental procedure and results of these additional experiments are available in **Appendix B** (see **Section B.3: Figure B.15–Figure B.17** and **Table B.4–Table B.7**). The minimum is located at a molar electrolyte concentration of $c(\text{Na}^+)=740$ mM and $c(\text{Ca}^{2+})=370$ mM. Thus, using $c_{\text{equivalent}}$ of competing ions, the position of sorption minimum is identical. The transferability of the data derived from the column experiments to the batch tests was confirmed by identical results for equal concentrations (see **Section B.3.3** in **Appendix B: Figure B.17** and **Table B.7**). As expected from the batch experiments, the retardation recovers at very high salinities, supporting the found relationship between q_{eq} and γ_{H^+} (see **Figure B.17** in **Appendix B**).

Figure 3.4 Comparison of the competitive impact of Na⁺ and Ca²⁺ cations on the sorption of MET on silica gel-1 (A) and silica gel-2 (B) and of iP4MBA on silica gel-2 (C). The q_{eq} values were normalized to the sorption without competition effect using pure water (q_0).

3.4 Conclusions

In order to improve the knowledge about relevant sorption processes of organic cations onto solid surfaces, the sorption of two selected organic cations (secondary amines with and without oxygen containing moieties) were studied by batch equilibrium tests with three different silica materials (two silica gels and one sediment). Here, the cation exchange processes, which strongly depend on the characteristics of the aqueous phase, were systematically investigated by considering a wide concentration range of competitive inorganic ions. At very high background electrolyte concentrations, the influence of additionally occurring interactions was investigated. Based on the results, the following conclusions can be drawn:

- In accordance with the literature, the experiments identified cation exchange as the dominating sorption process due to the decrease in organic cation sorption with increasing concentration of competitive inorganic cations ($I < 1$ M).
- The competitive impact of Na^+ and Ca^{2+} is comparable, using charge-corrected equivalent concentrations instead of equimolar concentrations.
- Contrary to expectations, sorption recovers considerably at very high ionic strengths and reaches sorption coefficients that are comparable or even higher than for pure water with minimum competition. This was explained by additional sorbent-sorbate interactions, such as hydrogen bonding, specific surface complexation and π -interactions, which cannot be neglected for very high ionic strengths ($I > 1$ M).
- The sorption at high background electrolyte concentrations seems to be indirectly affected by Na^+ or Ca^{2+} concentration through changes in activity coefficients of the sorbing compound as a function of ionic strength of the medium, due to the incomplete hydration and thus higher activity of the ions.
- At the experimental pH of 5.6, changes in background electrolyte concentrations do not or only very slightly influence the surface charge density of sorbents.
- The number of potentially available H-bond acceptor/donor functionalities in the molecule seems to play a crucial role, as the compound with a lower H-bond acceptor/donor sum showed a weaker sorption.
- Independent exemplary column experiments confirmed the results of batch tests as they revealed nearly similar sorption coefficients. Thus, the transferability of static to dynamic systems was shown.

Eventually, the separation of different sorption processes by suppressing cation exchange interactions was not expedient due to the superposition of several processes and the shift of the relevance of occurring processes depending on salinity. Nevertheless, this study provides an important step for improved future predictions of the sorption behaviors of cationic trace organics. Analogy considerations to the course activity coefficients are regarded as promising in order to obtain a better understanding of the complex processes. In addition, this work illustrates the relevance of further interactions next to the dominating cation exchange and enable a certain estimation of competitive effects for the same sorbent within a wide concentration range.

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Chapter 4

4 Sorption of cationic organic substances onto synthetic oxides: Evaluation of sorbent parameters as possible predictors

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Abstract:

Knowledge on the sorption behavior of cationic organic substances in aquatic systems is vital for their risk assessment due to the increasing detection of such chemicals in the hydrosphere. Their sorption behavior is strongly influenced by sorption processes onto mineral surfaces (e.g., oxides, clays). To contribute to the development of prediction tools, the impact of sorbent characteristics on the sorption strength was studied in a highly-idealized model system. In addition to the properties of the solid phase, the concentration of other ions in direct competition for sorption sites and the molecular structure of the sorbate were changed to separate ion exchange and non-ion exchange processes. The study includes in total 120 systematic column experiments using five extensively characterized synthetic oxides (three silica gels, two aluminum oxides), three probe molecules (two structurally related cationic substances, one neutral compound), and four distinctively different NaCl concentrations. The results show that the concentration of OH groups on the sorbent surface is a meaningful descriptor for the observed variations in sorption capacity onto different oxides. Compound-specific linear correlations were obtained, enabling the prediction of sorption coefficients. In addition, a more complex sorption behavior of organic cations compared to uncharged molecules were observed as demonstrated by the sorption results at different electrolyte concentrations. Thus, the study provides an important step towards a better principal mechanistic understanding of organic cation sorption. However, further work using other sorbents including natural ones and other probe molecules is needed to verify the identified relationships within the scope of developing reliable prediction models for cation sorption.

Graphical Abstract:

4.1 Introduction

In the last years, numerous studies on the prediction of (linear) sorption coefficients (K_d values) for organic cations on geosorbents have been published (e.g., Kah and Brown, 2007; Bronner and Goss, 2011; MacKay and Vasudevan, 2012; Droge and Goss, 2013a, 2013b; Sathyamoorthy and Ramsburg, 2013; Samaraweera et al., 2014). However, no generally accepted and universally applicable model is available until now. Recent comprehensive reviews (Endo and Goss, 2014; Webster, 2014; Schaffer and Licha, 2015) give an overview on proposed models and their limitations. The demand for developing improved sorption models for ionizable organic compounds was enforced in various studies that documented a significant number of chemicals being present in the aquatic environment (e.g., pharmaceuticals, personal care products, pesticides) which are either partially or completely ionized (Manallack, 2009; Franco et al., 2010).

The commonly applied standard method for predicting sorption coefficients of organic chemicals (e.g., $\log K_{oc} - \log K_{ow}$ correlations) (e.g., Chiou et al., 1979; Karickhoff, 1981; Sabljic et al., 1995) is generally based on the assumption of interactions between neutral organic compounds and solid organic carbon, but does not consider the electrostatic interactions of a charged molecule with the charged solid surface nor any relationships between polar compounds and polar surfaces (Tolls, 2001; Cunningham et al., 2004; Kah and Brown, 2007; Schaffer et al., 2012a; ECETOC, 2013). Since a large proportion of soils and sediments have a negative net surface charge, these model concepts fail for organic cations (Tolls, 2001; Kah and Brown, 2007). Here, the sorption is dominated by cation exchange processes and is, thus, clearly underestimated (Brownawell et al., 1990; Bi et al., 2006; Bäuerlein et al., 2012; Droge and Goss, 2012, 2013a, 2013b; Schaffer et al., 2012b; Niedbala et al., 2013; Kutzner et al. 2014, 2016).

In recent years, it became apparent that sorption processes of organic cations onto environmental surfaces are more complex than a simple partitioning between the aqueous phase and the organic matter of a solid. Depending on the sorbate properties and the boundary conditions of the aqueous solution, other sorbent constituents such as oxides or clay minerals are of increasing relevance (Brownawell, 1990; Tolls, 2001; Figueroa et al., 2004; Gao and Pedersen, 2005; Martinez-Hernandez et al., 2014). Consequently, knowledge of the relationships between sorption strength and

characteristic properties of inorganic sorbents (e.g., oxides) is vital to generate improved predictions.

Currently, the most robust and accurate method for predicting sorption coefficients is the concept of poly-parameter linear free energy relationships (pp-LFERs) (Endo and Goss, 2014). The sorption coefficients are determined herein by multiple linear regression of selected sorbate parameters, which are representative of different interaction types. All remaining influencing factors (properties of sorbent and water phase) are described by the regression parameters adapted to experimental data. Consequently, the obtained predictors are valid only for the considered system (similar sorbents and solution conditions) and the transfer to other (heterogeneous) systems and conditions is limited (Schaffer and Licha, 2015). However, the additional consideration of sorbent-related key parameters is of importance in particular to predict cation exchange processes. Therefore, this study focuses on the possibility to relate evaluated sorption coefficients to sorbent properties for identifying system parameters that are meaningful for predictions. For this purpose, a highly-idealized model system was used to evaluate the parameters of the solid that correlate with experimentally determined K_d . Accordingly, largely monophasic synthetic solids of high purity were used in the sorption studies. In contrast to natural surfaces (e.g., soils, sediments, organic matter) these do not contain a complex mixture of heterogeneous phases with a number of overlapping interactions and thus allow a more simplified inspection of the individual processes. The sorption of three probe compounds (two structurally related cationic substances with and without oxygen containing moieties, one neutral compound) on five synthetic oxides (3 silica gels, 2 aluminum oxides) were evaluated under comparable experimental conditions. As reported in earlier studies of the authors (Kutzner et al., 2014, 2016; Schaffer et al., 2017), cation exchange is the most relevant but not the sole mechanism for the sorption of organic cations in aquatic systems. To separate ion exchange from the remaining other processes, the sorption of probe molecules was investigated over a wide concentration range of a background electrolyte (NaCl) and onto sorbents with different properties. The selected oxides have either a predominately negatively (silica) or positively charged (alumina) surface at the selected pH and thus cation exchange should play either a significant or minor role. Silica and alumina were selected as sorbents as they represent best natural mineral surfaces and belong to the most abundant minerals in the earth's crust. Furthermore, they can be purchased with high purity from chromatography material

suppliers. However, the initially aim of this study was not to directly transfer the results to real field scenarios, but rather focuses on principal research as a contribution to a better understanding of the mechanisms and being an element for the development of more sophisticated models for complex systems.

4.2 Material and methods

4.2.1 Chemicals

Two cationic and one neutral compound were selected as model sorbates in the presented study. The experiments were carried out at a constant pH of 5.6. This pH is the pH of pure water in equilibrium with the atmospheric CO₂. It was selected because it lies between the pH_{PZC} values of the different sorbent types and no additional buffer is required in the experiments (a buffer would add undesired competing cations). At this pH, the silica gels are negatively charged whereas the aluminum oxides are positively charged. Comparing the results for both sorbents allows to differentiate between the different types of interaction. All probe molecules along with their physico-chemical properties are given in **Table 4.1**. Metoprolol (MET) and isopropyl-(4-methylbenzyl)-amine (iP4MBA) have already been used in own previous research (Schaffer et al., 2012b; Niedbala et al., 2013; Kutzner et al., 2014, 2016). MET as

Table 4.1 Physico-chemical properties of selected probe compounds.

Compound	Molecular structure H-acceptors/H-donors	CAS number	pK _a ^{a, b}	log K _{ow} ^b	log D _{ow} ^{b, c}
Metoprolol (MET)	 4/2	51384-51-1	9.43	1.63	-1.33 (-1.45)
Isopropyl-(4-methylbenzyl)-amine (iP4MBA)	 1/1	70894-75-6	10.00	2.82	-0.23 (-0.27)
Benzyl alcohol (BA)	 1/1	100-51-6	-	1.06	1.06 (1.06)

^a pK_a values refers to the conjugate acid (protonated species).

^b SciFinder Scholar predicted values, calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (1994–2016).

^c log D_{ow} values refer to all species at pH=6 (or pH=5).

tartrate salt with a minimum content of 98% was purchased from Sigma-Aldrich (Steinheim, Germany) and iP4MBA with a minimum content of 95% was obtained from Evo Blocks (Budapest, Hungary). Benzyl alcohol (BA) with a minimum content of 99% was purchased by Alfa Aesar (Karlsruhe, Germany). MET is a typical example for organic cationic pollutants occurring in surface and waste waters (e.g., Ternes, 1998; Heberer, 2002; Huggett et al., 2003; Vieno, 2006). MET and iP4MBA are structurally related (secondary amine, para-substituted benzene ring) and due to their high pK_a values positively charged in all experiments. However, in comparison to iP4MBA, the molecular structure of MET is larger and more complex due to the additional oxygen-containing ether and hydroxyl group. Consequently, these substructures provide considerably more H-acceptor/donor functionalities for MET (4/2) than for iP4MBA (1/1) and thus enable further interactions additional to cation exchange. In contrast, BA is uncharged at pH=5.6 but hydrophilic due to the hydroxyl group contained in the molecule, so that the contribution of non-ionic interactions to the total sorption (e.g., hydrogen bonds, hydrophobic sorption) can be examined. All other used inorganic chemicals were of high purity (>99%, analytical grade). Ultrapure water for the preparation of all solutions was obtained from the water purification system GenPure from TKA (Niederelbert, Germany).

4.2.2 Sorbents and sorbent characterization

Silica gel-1 (Silica gel 60, 200–500 μm , amorphous) was purchased from Merck (Darmstadt, Germany). Silica gel-2 (Nucleodur 100-50, 50 μm , spherical), silica gel-3 (Nucleodur 300-5, 5 μm , spherical) and aluminum oxide-1 (Aluminum oxide 90, neutral, 50–200 μm) were obtained from Macherey-Nagel (Düren, Germany). Aluminum oxide-2 (Aluminum oxide 150, basic, 63–200 μm) was received from Merck (Darmstadt, Germany). Silica gel-1 and silica gel-2 have also already been used in other studies of Kutzner et al. (2014, 2016). The net surface charge of silica gels is negative at a consistent experimental pH of 5.6, based on the literature value of the point of zero charge of the amphoteric silanol groups ($\text{pH}_{\text{PZC}}=1\text{--}4.5$ (if any), Kosmulski, 2016). Thus, organic cations should preferentially sorb on these materials by means of electrostatic attraction forces. In contrast, alumina has a much higher pH_{PZC} ($\text{pH}_{\text{PZC}}=8.5\text{--}9.5$, Kosmulski, 2016) and, thus, has a positive net surface charge at the investigated pH. Consequently, the probability for cation exchange processes is strongly reduced and, thus, the relevance of non-ion exchange processes could be studied.

All sorbents were extensively characterized with state-of-the-art methods. Scanning electron microscope (SEM) image analysis and the determination of particle size distribution d_{particle} , specific surface area A_{BET} , pore size d_{pore} , pore volume V_{pore} , potential cation exchange capacity CEC_{pot} , point of zero charge pH_{PZC} were carried out as described in Kutzner et al. (2016). The concentration of surface OH groups α_{OH} [mmol/g] was analyzed by thermogravimetric analysis - TGA (STA 409, Netzsch). The thermal analysis was carried out in the temperature range from 30 to 1400 °C at a heating rate of 5 °C/min under argon atmosphere. The resulting TGA signal allows calculating of α_{OH} based on the weight loss due to the removal of chemically bound water (dehydroxylation of surface OH groups). The material density ρ_{m} was determined with the Ultrapycnometer 1000 from Quantachrome. The bed density ρ_{b} in the column experiments was calculated from the dry mass of a packed column and the column volume. The effective porosity ε was determined using a column experiment with a conservative tracer showing no retardation (see **Section 4.2.3**).

4.2.3 *Column experiments*

The presented study focuses on column experiments since they have some advantages over the classical batch equilibrium technique (e.g., Bürgisser, 1993; Doucette, 2003; Bi et al., 2006, 2010; Metzelder and Schmidt, 2017). Further, the data obtained by both methods are comparable (e.g., MacIntyre et al., 1991; Bürgisser et al., 1993; Spurlock et al., 1995; Kutzner et al., 2016). For column experiments, a stainless-steel chromatography column was packed with the sorbent, closed with stainless steel frits (0.5 μm) and equilibrated with the respective eluent until equal electrical conductivities and pH values were reached at the outlet relative to the inlet. To achieve reproducible column packings, the columns were first filled with the dry sorbent and subsequently connected to the HPLC pump and rinsed with pure water to compress the sorbent phase inside the column. Then the column was opened again and the void space further filled with the dry sorbent. This procedure was repeated several times until the column packing has stabilized and resulted in good reproducibility of the column packing. Due to widely differing sorption strength for the different sorbent-sorbate combinations, two different columns sizes (12.5×0.4 cm or 25×1 cm, see **Table C.1** in **Appendix C**) had to be used to keep the experimental time as low as possible but also to separate the breakthrough curves of the respective probe compounds and non-sorbing reference compound (conservative tracer) clearly from each other. A synthetic water was used as eluent for studying the breakthrough

behavior of the probe compounds under different competitive conditions. The ionic composition of the eluent was adjusted by adding different amounts of NaCl to pure water. In total, the competitive impact was tested at four NaCl background concentrations: at none ($c=0$ mM), medium ($c=37$ mM) and extreme competition ($c=3700$ mM) and at the previously determined sorption minimum ($c=740$ mM, Kutzner et al., 2016). The investigations were limited to the monovalent cation Na^+ , since inorganic ions of the same charge show similar effects (Kutzner et al., 2014) and the influence of monovalent and divalent cations is comparable if the charge-corrected equivalent concentration is used instead of equimolar concentrations (Kutzner et al., 2016). The pH was adjusted by adding 1 M HCl solution until a pH of 5.6 was reached, which corresponds to the (unbuffered) pH of ultrapure water in CO_2 equilibrium. The whole experimental setup including eluents was placed in a thermostat cabinet to perform all experiments under constant temperature conditions. A temperature of 8 °C was selected in order to simulate natural groundwater conditions and to minimize biotransformation of the probe compounds. All tests were repeated twice. The eluents were permanently pumped in up-flow direction to ensure saturated column conditions. In preliminary investigations two different flow rates were tested (0.25 and 0.5 mL/min) to check possible sorption non-equilibrium. The measurements show that the flow rate has no or little effect on the retardation factor and thus the sorption was at or very close to equilibrium (data not shown). Since the deviations were negligible, the highest tested flow rate of 0.5 mL/min was used in all experiments (HPLC pump, Merck-Hitachi L-6000).

Before starting the experiments, a tracer test was conducted in order to determine the hydraulic parameters of the column and to normalize the breakthrough times of the probe compounds. Furthermore, the stability of the column was tested by repeated injections of the conservative tracer. There was no significant change in the retention times of the tracer from the beginning to the end of an experimental series. Deuterium oxide (99.9%, Deutero) was selected as a conservative tracer due to its similarity to normal water and non-reactive properties. The use of chloride as a conservative tracer like in previous works (e.g., Schaffer et al., 2012a, 2012b, Kutzner et al., 2014) was not possible due to ion exchange on the positively charged aluminum oxides with a point of zero charge in the range of 7.9–8.9 (see **Figure C.12** in **Appendix C**). Since deuterium oxide is not UV detectable, the breakthrough curves were measured at the column outlet using a differential refractometer (GAT-LCD 202, Gamma

Analysentechnik GmbH). For each probe molecule, the same column was used and only the NaCl concentrations were varied. An irreversible sorption of probe molecules was excluded by determining the desorption curve in each sorption experiment using the same eluent without addition of probe molecules (data not shown). There were no significant variations in the mass balance between sorbed and desorbed amount so that sorption seems to be fully reversible. The sorption behavior of the different probe compounds as well as the duplicates were studied in separate (independent) column experiments.

After an equilibration phase for each new electrolyte concentration, the probe compound was added to the eluent ($c_0(\text{MET}) = 5 \text{ mg/L} = 18.7 \text{ } \mu\text{M}$, $c_0(\text{iP4MBA}) = 3.05 \text{ mg/L} = 18.7 \text{ } \mu\text{M}$, $c_0(\text{BA}) = 100 \text{ mg/L} = 0.92 \text{ mM}$). The column experiments were carried out with continuous injection and the breakthrough curves $c(t)$ were detected by UV-VIS spectrophotometry (photoLab 6600 UV-VIS, WTW) at 223 nm (MET), 216 nm (iP4MBA) or 257 nm (BA) with a flow cuvette (10 mm, 390 μL , Hellma). The detection and quantitation limit for MET is 0.13 mg/L (0.48 μM) and 0.40 mg/L (1.49 μM), for iP4MBA 0.05 mg/L (0.32 μM) and 0.18 mg/L (1.09 μM) and for BA 0.40 mg/L (3.67 μM) and 1.37 mg/L (12.6 μM). Due to the higher detection and quantitation limit for BA, a different molar concentration was chosen for this probe molecule. During the experiments, no degradation (mass loss) of the probe compounds or pH changes were observed within a period of maximal 24 h. The experimental conditions of the column studies are summarized in **Table C.1** in **Appendix C**.

In order to compare sorption results for different sorbents and sorbates, linear equilibrium sorption (Henry isotherm) is assumed and the sorption coefficients (K_d values) were calculated using **Equation 4.1** by evaluating the breakthrough curves of the probe compound and the conservative reference tracer.

$$K_d = \frac{q}{c} = \frac{Q \cdot (t_{\text{id,sorbate}} - t_{\text{id,tracer}})}{m_{\text{sorbent}}} \quad \text{Equation 4.1}$$

$$\text{with} \quad t_{\text{id}} = t_{\text{max}} - \frac{\int_0^{t_{\text{max}}} c(t) dt}{c_0} \quad \text{Equation 4.2}$$

where q [mol/kg] is the sorbed amount, c is the solute concentration [mol/L], Q [L/h] is the flow rate, $t_{\text{id,sorbate}}$ [h] is the ideal breakthrough time of the sorbing compound, $t_{\text{id,tracer}}$ [h] is the breakthrough time of the non-sorbing conservative reference tracer and

m_{sorbent} [kg] is the sorbent mass. The ideal breakthrough time $t_{\text{id,sorbate}}$ or $t_{\text{id,tracer}}$ (center of gravity) was calculated after a cubic spline interpolation of measured data points and integrating with the trapezoidal rule. Here, t_{max} denotes the duration of the experiment and c_0 is the initial concentration of the sorbate or tracer.

4.2.4 Statistical analysis

The statistical analyses were performed by using OriginPro 2016. The aim was to identify the best parameter(s) to describe the variation in sorption results on different sorbents. Therefore, the Pearson product-moment correlation coefficient R was used, which is a measure of the strength and direction of the linear relationship between two variables. For regression equations, the following statistical data are given: correlation coefficients R and R^2 and 95% confidence limits. The statistical significance of variables was evaluated with the p value which should be less than 0.10.

4.3 Results and discussion

4.3.1 Sorbent characterization

The measured properties of sorbents applied in this study are listed in **Table 4.2**. In order to get more information about the structure of the studied sorbents, SEM analysis were conducted for two magnifications (200× and 20,000×). The microscopic images

Table 4.2 Experimental determined properties of selected synthetic sorbents.

Sorbent properties	Silica gel-1	Silica gel-2	Silica gel-3	Aluminum oxide-1	Aluminum oxide-2
d_{particle} [μm]	302	52.7	5.81	105	101
A_{BET} [m ² /g]	487	327	115	152	101
$d_{\text{pore(BJH)}}$ [nm]	6.20	10.8	29.3	4.76	6.31
$d_{\text{pore(DFT)}}$ [nm]	6.56	13.9	35.0	6.56	11.7
V_{pore} [cm ³ /g]	0.76	1.00	1.07	0.27	0.24
CEC_{pot} [μmol/g]	279	170	48.4	50.2	32.1
α_{OH} [mmol/g]	4.23	4.40	2.91	2.17	2.19
ρ_{m} [g/cm ³]	2.11	2.20	2.43	3.26	3.34
ρ_{b} [g/cm ³]	0.48	0.45	0.41	1.13	1.04
ε [-]	0.82	0.87	0.93	0.68	0.65
pH _{PZC} [-]	5.7–6.4*	2.3–3.3	2.3–4.3	7.9–8.5	8.3–8.9

d_{particle} = mean particle diameter, A_{BET} = specific surface area, d_{pore} = mean pore diameter, V_{pore} = pore volume, CEC_{pot} = potential cation exchange capacity at pH = 8.1, α_{OH} = concentration of surface OH groups per unit mass of sorbent, ρ_{m} = material density, ρ_{b} = bed density, ε = effective porosity, pH_{PZC} = point of zero charge at background electrolyte concentrations of 0.37 mM to 3.7 M NaCl.

* The experimental value is significantly higher than the literature value and is therefore uncertain (possibly due to trace contamination, see also Kutzner et al. (2016)).

Table 4.3: Correlation coefficients R to describe relationships between sorbent properties. Statistical significant correlations were highlighted in bold (** $p < 0.01$, * $p < 0.05$, $p < 0.10$).

	d_{particle}	A_{BET}	d_{pore} (BJH)	d_{pore} (DFT)	V_{pore}	CEC_{pot}	α_{OH}	ρ_{b}	ε
d_{particle}	1								
A_{BET}	0.76	1							
$d_{\text{pore}}(\text{BJH})$	-0.60	-0.33	1						
$d_{\text{pore}}(\text{DFT})$	-0.67	-0.44	0.99***	1					
V_{pore}	-0.21	0.36	0.70	0.63	1				
CEC_{pot}	0.75	1.00***	-0.28	-0.39	0.40	1			
α_{OH}	0.36	0.87*	0.02	-0.07	0.72	0.88**	1		
ρ_{b}	-0.02	-0.52	-0.61	-0.52	-0.97***	-0.56	-0.80	1	
ε	-0.21	0.32	0.76	0.68	0.99***	0.36	0.65	-0.96***	1

are shown in **Appendix C** (see **Figure C.1–Figure C.5**). The experimental data of particle size analysis, BET area/pore size analysis and thermogravimetric analysis are available in **Appendix C** (see **Figure C.6–Figure C.11**). All studied sorbents are highly porous, with the silica gels generally having larger pore diameters and/or larger pore volumes than the aluminum oxides. At the adjusted experimental pH of 5.6, the net surface charge of silica gels is weakly negative whereas the surface of aluminum oxide is positively charged as can be seen from the potentiometric surface titration results (see **Figure C.12** in **Appendix C**). The determined points of zero charge (pH_{PZC}) are in good agreement with literature data (Tadros and Lyklema, 1968; Leyva-Ramos et al., 2008; Kosmulski, 2016).

Table 4.3 shows the relationships between the different sorbent properties expressed by the Pearson correlation coefficient R . Statistically significant correlations ($p < 0.10$) are highlighted in bold and are presented graphically in **Figure C.19** in **Appendix C**. The parameters of the linear regression are listed in **Appendix C** (see **Table C.3**). Positive correlations are found for A_{BET} and CEC_{pot} , A_{BET} and α_{OH} , CEC_{pot} and α_{OH} as well as for V_{pore} and ε whereas ρ_{b} is negatively correlated to V_{pore} and ε . These correlations are plausible (physically correct) and have partly been reported in the literature (Banin and Amiel, 1970; Tanaka and Locat, 1999; Tamura et al., 1999). Furthermore, a positive correlation between the different methods for calculating pore size distributions (BJH and DFT) was found. The values for DFT are generally higher, but comparable with BJH (slope regression line 1.14). Accordingly, both approaches are suitable for the used materials.

4.3.2 *Sorption of probe compounds on different sorbents*

Plots of K_d values for MET, iP4MBA or BA on different sorbents depending on background electrolyte concentrations are compared in **Figure 4.1**. The BTCs of all tests are illustrated in **Appendix C** (see **Figure C.13–Figure C.17**) and the K_d values together with their standard deviations are given in **Table C.2**.

General observations

In general, the sorption of all probe compounds follows the order silica gel-2 > silica gel-1 > silica gel-3 >> aluminum oxide-2 > aluminum oxide-1, which applies to the whole investigated concentration range of NaCl ($c=0$ –3700 mM). The only deviation from this order was observed during the sorption of MET and iP4MBA under minimal competition in pure water (see **Figure 4.1A** and **Figure 4.1B**). Here, the sorption on silica gel-1 was slightly stronger than on silica gel-2. However, this deviation of K_d is only within a factor of 2 to 3 and can presumably be attributed to slightly different boundary conditions (dissolution of competing ions from the sorbent), since even very low background electrolyte concentrations already have a considerable influence on the sorbed amount of organic cations. Results shown in **Figure 4.1** are used for the visualization in **Figure C.18** in **Appendix C**, where different probe compounds instead of sorbents are compared. In general, the sorption strength (K_d values) increases in the following order BA << iP4MBA < MET for the studied sorbents (see **Appendix C: Figure C.18** and **Table C.2**). Due to the weak sorption of all probe compounds on aluminum oxide and the overlapping error bars, these results are not suitable for a quantitative evaluation. In the case of silica gels, however, there are clear differences between different probe compounds, which may be attributed to a different strength or number of relevant interactions. Since the sorption of organic cations is dominated by cation exchange, the tests show a high sensitivity, especially with respect to the surface properties of the sorbents and the ionic composition of the solution.

Sorption of the organic cations: MET and iP4MBA

Generally, the sorption of organic cations onto negatively charged silica gel surfaces decreased with increasing electrolyte concentrations (see **Figure 4.1A** and **Figure 4.1B**). This finding is expected and can be explained by the occurrence of cation exchange processes, where the organic cations and the inorganic electrolyte cations compete for the sorption sites (Schaffer et al., 2012b, 2017; Droge and Goss, 2012, 2013a; Niedbala et al., 2013; Kutzner et al. 2014, 2016). However, at the highest

tested electrolyte concentration ($c(\text{NaCl})=3700 \text{ mM}$) the sorption on the three silica gels recovered considerably. This effect has already been described in Kutzner et al. (2016) for silica gel-1 and -2 as well as for a natural aquifer sediment and seems to be independent from the structure of probe molecule and sorbent characteristics. A possible explanation for the improved sorption might be the increased activity coefficient γ of the probe compound at highly concentrated electrolyte solutions ($\gamma \gg 1$) due to the incomplete hydration and thus higher activity resulting in an increase of sorbate-specific sorption processes (hydrophobic partitioning, electron donor-acceptor interactions). This phenomenon is considered, e.g., in the model approach of Pitzer (1973, 1991). For more details see also Kutzner et al. (2016).

Similar trends were also observed for the sorption results on aluminum oxide, but the sorption is almost zero and the absolute effect is therefore much weaker. Due to the positive net surface charge of aluminum oxide at experimental pH of 5.6 (see **Section 4.3.1**), anion sorption is favored, and cation exchange processes play only a minor role. In addition, other interactions are probably impaired by electrostatic repulsion forces due to the same charge of sorbent and probe compound. Accordingly, MET and iP4MBA sorb considerably weaker or sorption is negligible on aluminum oxides than on the negatively charged silica gels (e.g., K_d differs in pure water up to 4 orders of magnitude).

Both organic cations have a similar sorption behavior, but as expected, MET sorbed more strongly than iP4MBA. For example, a difference of approximately 35% (pure water), 12% (37 mM NaCl), 39% (740 mM NaCl) and 52% (3700 mM NaCl) were determined for silica gel-1 depending on the background electrolyte concentration (see **Figure C18A** in **Appendix C**). The higher absolute sorption of MET compared to iP4MBA is likely due to the larger and more complex molecular structure (additional oxygen-containing ether and hydroxyl group). These functionalities lead to a higher H-bond acceptor/donor sum for MET (4/2) than for iP4MBA (1/1), which facilitates further interactions additional to cation exchange as already discussed in Kutzner et al. (2016). Since iP4MBA is practically unable to form hydrogen bonds (protonation of sole H-acceptor/donor functionality), a further process (e.g., hydrophobic partitioning) is likely to be responsible for the considerable sorption under strong competition conditions, where cation exchange processes are suppressed to a minimum.

Figure 4.1 Comparison of the sorption of MET (**A**), iP4MBA (**B**) and BA (**C**) on different sorbents over a wide concentration range of NaCl. To represent the results in the logarithmic scale the NaCl concentrations of the experiments in pure water was set to 0.1 mM.

Hydrophobic partitioning is primarily important for interactions of non-polar compound with organic matter or poorly solvated mineral surfaces, but occur to some extent for all organic molecules (MacKay and Vasudevan, 2012). A reduced hydration of the sorbent surface due to the reduced number of available solvent molecules at very high electrolyte concentrations (Chen et al., 1982; Ferse, 2013) in combination with an enhanced hydrophobic sorption caused by the displacement of probe compounds from the aqueous phase to hydrophobic domains of the sorbent surface is conceivable (salting-out effect). Besides hydrophilic ($\equiv\text{Si-OH}$) groups, the surface structure of silica contains also stronger hydrophobic sites ($\equiv\text{Si-O-Si}\equiv$) (Chen, 1976; Zhuravlev, 2000; Isaenko and Borguet, 2013; Ishiguro and Koopal, 2016). The thinner hydration layer around the particles is likely the cause that the molecules are able to get closer to the surface and establish short-range hydrophobic interactions. In the literature, this has already been reported for the hydrophobic sorption of peptides on siloxane bridges (Puddu and Perry, 2012).

Sorption of the uncharged compound: BA

The neutral compound BA shows the weakest sorption of the investigated probe compounds. The sorption is considerably lower compared to MET and iP4MBA, since only non-ionic interactions (e.g., electron donor-acceptor interactions, hydrophobic sorption) are possible. In contrast to organic cation sorption (see **Figure 4.1A** and **Figure 4.1B**), the sorption of the neutral compound (see **Figure 4.1C**) remained approximately constant over a wide concentration range of NaCl for all studied sorbents due to the lack of electrostatic interactions (no competition). At $c(\text{NaCl})=0$ –740 mM, the K_d values vary only slightly between 1.13 and 1.46 L/kg for silica gel-1, 1.54 and 1.89 L/kg for silica gel-2, 0.40 and 0.42 L/kg for silica gel-3, 0.06 and 0.12 L/kg for aluminum oxide-1, and 0.06 and 0.07 L/kg for aluminum oxide-2. This leads to the conclusion that the sorption of BA is independent of the electrolyte concentration and only sorbate-specific sorption processes, where competition with inorganic ions plays no role, are relevant. However, an increase in sorption also occurs at high ionic strengths, which is comparable in its relative extent with the improved sorption of MET or iP4MBA. As mentioned before, this effect is not specific for cationic substances and is probably the result of an increase in non-ionic (polar and hydrophobic) interactions. Comparing the courses of the functions, $\gamma(c)$ derived from the Pitzer theory (see Kutzner et al., 2016 for the example of γ_{H^+}) appears to be similar to $K_d(c)$ of BA (see **Figure 4.1C**). Consequently, a relationship between both variables

may be derived and it can be concluded that the same effects are responsible for the observed, very similar behavior. Zhao et al. (1994) indicates that hydrogen bonding is mainly responsible for the sorption of BA on silica. Furthermore, aromatic compounds are found to involve the π -electrons of the benzene ring in hydrogen bonding with surface OH group during sorption (Parida et al., 2006).

4.3.3 *Correlations between sorbent parameters and sorption strength*

The K_d values of MET, iP4MBA, and BA on the studied sorbents were correlated with the sorbent properties. The results are shown in **Table 4.4**. Statistically significant correlations ($p < 0.10$) are highlighted in bold and presented graphically in **Appendix C** (see **Figure C.20–Figure C.22**). The parameters for the linear regression are listed in **Appendix C** (see **Table C.4–Table C.6**). Multiple linear regressions with more than one sorbent parameter were not applied, because many of the variables are self-correlative (not independent, e.g., A_{BET} , CEC_{pot} and α_{OH}). Furthermore, the obtained single-parameter regressions with $R^2 \geq 0.87$ are already very good. It has to be noted that, due to the weak sorption of all probe compounds on both aluminum oxides, the regressions are largely driven by the three silica gels.

For all probe compounds and concentrations of NaCl, the K_d values were positively related with α_{OH} and the correlation coefficients are close to 1 (see **Table 4.4**). In some cases, also a correlation between K_d and A_{BET} or K_d and CEC_{pot} exist. However, the three parameters (α_{OH} , A_{BET} , CEC_{pot}) are statistically not independent (see **Section 4.3.1**). The other investigated sorbent properties show no statistically significant correlation with K_d . A positive correlation between organic cation sorption and the soil CEC has already been reported in literature (e.g., Kodešová et al., 2015), because the CEC characterizes the sorbent negative charge density and is, thus, a measure for the electrostatic attraction with cationic substances. However, common methods apply inorganic cations for the determination of the CEC and, therefore, bear a relatively high risk to miscalculate the sorption, especially of larger organic cations. This is because inorganic cations represent point charges and the organic cation sorption may consequently be influenced by steric constraints (MacKay and Vasudevan, 2012). Furthermore, relationships between K_d and soil properties such as pH, clay content, specific surface area and content of Al or Fe oxides were observed by several authors (Weber et al., 2004; Lee et al., 2005; Kah and Brown, 2007; Sassmann et al., 2007; Hu and Coats, 2009; Vasudevan et al., 2009; Kodešová et al.,

2015; Ishiguro and Koopal, 2016; Vitoratos et al., 2016). However, none of the above cited studies could propose a general equation applicable to a range of compounds, probably due to the complexity of sorption onto environmental surfaces (e.g., heterogeneous sorbent phases, several parallel occurring sorption mechanisms, a number of different influencing factors). Consequently, a universal sorbent parameter that accounts for all heterogeneities and boundary conditions cannot be derived from the existing studies.

The fact that the best-fit K_d equations were determined with α_{OH} can probably be explained by the fact that at least two sorption mechanisms are logically related to this parameter (see **Section 4.3.2**). This applies on the one hand for ion exchange processes (at deprotonated surface OH groups) and on the other hand for hydrophilic

Table 4.4 Correlation coefficients R to describe relationships between K_d values for MET, iP4MBA or BA on studied sorbents and sorbent properties. Statistical significant correlations were highlighted in bold (** $p < 0.01$, * $p < 0.05$, $p < 0.10$).

	K_d , pure water	K_d , 37 mM NaCl	K_d , 740 mM NaCl	K_d , 3700 mM NaCl
MET				
$d_{particle}$	0.80	0.17	0.17	0.26
A_{BET}	0.97***	0.76	0.76	0.81*
$d_{pore(BJH)}$	-0.23	0.01	0.03	-0.09
$d_{pore(DFT)}$	-0.33	-0.06	-0.04	-0.17
V_{pore}	0.39	0.71	0.72	0.63
CEC_{pot}	0.99***	0.76	0.76	0.81*
α_{OH}	0.83*	0.97***	0.97***	0.97***
ρ_b	-0.57	-0.75	-0.76	-0.69
ε	0.36	0.63	0.64	0.55
iP4MBA				
$d_{particle}$	0.68	0.17	0.13	0.22
A_{BET}	0.99***	0.74	0.73	0.79
$d_{pore(BJH)}$	-0.23	-0.11	0.03	-0.03
$d_{pore(DFT)}$	-0.33	-0.17	-0.04	-0.11
V_{pore}	0.48	0.61	0.71	0.68
CEC_{pot}	0.99***	0.73	0.73	0.79
α_{OH}	0.93**	0.93**	0.96**	0.97***
ρ_b	-0.62	-0.64	-0.74	-0.72
ε	0.43	0.51	0.63	0.6
BA				
$d_{particle}$	0.19	0.28	0.30	0.32
A_{BET}	0.77	0.83*	0.84*	0.85*
$d_{pore(BJH)}$	-0.03	-0.04	-0.07	-0.06
$d_{pore(DFT)}$	-0.1	-0.12	-0.15	-0.14
V_{pore}	0.68	0.68	0.66	0.66
CEC_{pot}	0.77	0.83*	0.84*	0.85*
α_{OH}	0.97***	0.99***	0.99***	0.99***
ρ_b	-0.72	-0.74	-0.72	-0.73
ε	0.6	0.6	0.58	0.58

non-ionic interactions (e.g., hydrogen bonding at neutral surface OH groups). The reason for the generally weaker correlation with CEC_{pot} is that this parameter only considers the sorption on negatively charged groups and thus accounts only for one sorption mechanisms (cation exchange). Eventually, the use of α_{OH} is recommended for predicting the sorption of organic cations in future modeling. Moreover, it seems that this parameter also shows a relationship for the sorption of neutral aromatic compounds due to the interaction of π -electrons with surface OH groups.

4.4 Conclusions

Systematic column experiments with three probe molecules as sorbate and five synthetic oxides as sorbent were conducted at four varying background electrolyte concentrations in order to improve the fundamental process understanding of organic cation sorption onto charged solid surfaces. The use of well-defined sorbents with different (specific) properties as well as the variation of background electrolyte concentrations and the systematic use of certain sorbates are the "tools" in the presented study to separate ion exchange from further (remaining) sorption processes. The influence of the sorbent properties on the sorption behavior was evaluated by linear regression analysis for identifying a suitable system parameter allowing for improved predictions.

The presented study implies a certain predictability of K_d for different oxides with known α_{OH} for investigated probe molecules. However, the one-parameter linear regressions presented in this work needs to be tested on further sorption data, to verify whether they are appropriate for a wider range of sorbents. Furthermore, α_{OH} is a suitable parameter for predicting the sorption onto synthetic and well-defined oxides, but the transferability from homogeneous phases to heterogeneous phases, especially geosorbents in natural systems, is probably difficult and a challenging task for further research. In addition, the study allows an estimation of the competitive sorption equilibrium of organic cations within a wide concentration range, however, only for the investigated sorbent-sorbate systems. Nevertheless, the obtained results provide an important step towards a better understanding of the mechanisms and dependencies that determine the sorption behavior of organic cations in the environment. The results confirm the assumption of Kutzner et al. (2016) that the sorption of organic cations onto oxide surfaces involves at least two main types of interactions: 1.) ion exchange and 2.) non-ion exchange processes (e.g., hydrogen bonding, hydrophobic sorption). If ion

exchange predominates, the sorbed amount decreases with increasing ionic strength. In contrast, the second group of interactions is insensitive to ionic strength and considerably weaker as shown by the results with BA. However, at very high electrolyte concentrations, where cation exchange processes are suppressed to a minimum, the role of non-ion exchange sorption mechanisms increases regardless of the nature of the probe compound (neutral or cationic) and generally results in an enhanced sorption.

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Chapter 5

5 General conclusions and outlook

Due to the increasing number of organic micropollutants that are cationic at environmental relevant pH and the poor predictability of their sorption behavior to various environmental matrices, there is a high need to get a better fundamental process understanding as basis for environmental risk assessment. Therefore, the current mechanistic understanding, which is largely based on interactions between neutral organic compounds and sorbent organic matter, needs to be extended to account for the electrostatic interactions of a charged molecule to charged solid surfaces. The thesis presented within this work focused on the separation of ion exchange and non-ion exchange processes by studying the influence of selected boundary conditions (e.g., the type and the concentration of other ions in direct competition for sorption sites, the properties of the solid surface, the molecular structure of the sorbate) on the observed sorption. Within the scope of these investigations, it was of particular interest to determine the extent and relevance of further interactions (e.g., hydrogen bonding, hydrophobic sorption) in comparison with the dominating cation exchange.

The obtained results help to identify the most relevant sorption processes and to get a better understanding of the effect of increasing competition on sorption equilibrium as well as the variations in sorption depending on the sorbent characteristics. Based on the results of this work, the main conclusions can be summarized as follows:

- Cation exchange processes play a dominating role for the sorption of organic cations onto negatively charged solid surfaces, since the sorbed amount was considerably affected by competing inorganic cations. The sorption coefficients decrease with increasing background electrolyte concentration.
- The absolute competitive influence of divalent inorganic cations is greater in comparison to monovalent inorganic cations. However, in relative terms, this difference vanishes with increasing background electrolyte concentration due to their large excess and a saturation of the exchange capacity of the sorbent.

- Competing cations having the same valence, show a dependence of the sorption affinity on the size of the hydrated ions, but their competitive effects are in the same order of magnitude and only slight differences are detectable.
- A simple one-parameter logarithmic correlation between the sorption coefficient of organic cations and the equivalent concentration of competing inorganic cations is suitable for the prediction of sorption coefficients from low to moderate background electrolyte concentrations. However, this functional relationship is specific for each sorbent-sorbate system and must be determined separately.
- The prediction of the combined competitive effect of mixtures with more than one dissolved competing cation species by a simple addition of the contributions of the individual ions is limited to low background electrolyte concentrations. With increasing ionic strength, the predictability decreases since a saturation of accessible exchange sites on the sorbent surface with competing ions is achieved. Consequently, a reliable prediction of the competitive sorption equilibrium of organic cations is possible only with high experimental effort and in limited concentration ranges.
- The sorption of organic cations cannot be completely prevented even with a strong excess of competing inorganic cations due to the simultaneous occurrence of additional, non-ion exchange processes (e.g., hydrogen bonding, hydrophobic sorption).
- In strongly concentrated electrolyte solutions (mol/L), the sorption of organic cations recovers considerably and sorption coefficients that are comparable or even higher than in pure water with the lowest competition are reached. This effect seems to be independent from sorbent characteristics and sorbate structure. A possible explanation for the improved sorption might be the increased activity coefficient γ of the probe compound at highly concentrated electrolyte solutions ($\gamma \gg 1$) due to the incomplete hydration and thus higher activity resulting in an increase of non-ion exchange processes (hydrophobic partitioning, electron donor acceptor interactions), which cannot be neglected for very high ionic strengths.
- The separation of ion exchange and non-ion exchange processes is difficult due to the superposition and the shift in their relevance depending on the electrolyte concentration. Thus, the exact quantitative contribution of the individual mechanisms cannot easily be specified.

- In general, the Freundlich sorption model seems to be most suitable for the description of the sorption of organic cations, which is probably due to the superposition of different sub-processes. In addition, the Freundlich exponents (i.e. the non-linearity of the sorption isotherms) change depending on the used sorbents, which is an indication of the presence of energetically heterogeneous sorption sites.
- The number of potentially available H-bond acceptor/donor functionalities in the sorbate molecule plays an important role for the sorption strength, since a stronger sorption can be observed for compounds with a higher H-bond acceptor/donor sum.
- The sorption of equally charged sorbent-sorbate systems is very low, since it is dominated by electrostatic repulsion forces, so that non-ionic interactions are difficult to establish.
- The use of well-defined sorbents with different surface properties is a promising key to derive related parameters for predicting sorption.
- The concentration of OH groups on sorbent surface (α_{OH}) is a meaningful descriptor for the variations in sorption onto different oxides. Compound-specific one-parameter linear regressions with high correlation coefficients are obtained, which enable the prediction of sorption coefficients when α_{OH} is known. However, the equations presented in this work will have to be tested on further sorption data, to see whether they are appropriate for a wider range of sorbents.
- In general, sorption of neutral (polar) compound onto oxidic surfaces appears to be weak compared to cationic compounds. The sorption of organic cations tends to be stronger at low electrolyte concentrations and in sorbents containing a higher number of surface OH groups. However, approaches specific to each compound are required.
- Reliable sorption results can be obtained by batch experiments as well as column studies. Thus, the transferability of static to dynamic systems is given. Comparing both methods, column tests provide some crucial advantages over batch tests. For example, column experiments can be automated and time-consuming sample preparation steps can be eliminated by online measurement. In addition, substantial boundary conditions, such as the pH, can be better controlled in a dynamic column system and thus the comparability of the results can be improved. As a result, column tests are a suitable alternative

to the more time-consuming batch tests. The results can be better interpreted, and the sorption isotherm can be derived by simple numerical integration. In contrast to batch experiments, the method can be used to measure the isotherm in a single experiment.

Finally, this study reports new information on the sorption behavior of cationic compounds and thus contributes significantly to current research on the development of advanced prediction models. However, an improved system understanding, in particular with regard to the basic mechanisms and all relevant influencing parameters, requires further systematic investigations under consistent and comparable experimental conditions and setups. By knowing the individual relationships, it may be possible to obtain reliable information on the sorption of organic cations from some basic parameters (e.g., by recording a reference isotherm) for unknown systems. Due to the variety of influencing factors and their complex interplay, a single or a set of efficient parameters quantitatively describing various environmental systems cannot be currently identified. The same applies for comparing different sorbents. Although the concentration of OH groups on sorbent surface could be regarded as meaningful descriptor for the sorption onto synthetic, well-defined oxides, the transferability from homogeneous phases to natural real-world systems is probably difficult, also due to the lack of experimental methods for the determination of sorbent parameters for such complex systems.

For future research, a mechanism-based approach, which distinguishes only the following three basic types of interactions: 1.) ion exchange, 2.) polar non-ionic interactions and 3.) hydrophobic sorption, is considered to be useful. This model should incorporate relevant properties of the sorbate and key characteristics of the system. The sorbent properties should be taken into account not by measured parameters, but by reference tests with a strongly limited number of selected mechanism-specific probe molecules, which are representative for certain interactions. As a result, the specific characterization of sorbent with probe molecules can be used to quantify the relative contributions from different interactions for a particular sorbent. The identification of universal probes and the construction of explicit structure-based scaling factors, in order to ensure the application of mechanism-specific probe sorption measures to other organic compounds, are essential for the successful development. A gradual and thorough investigation of relevant influencing factors is strongly recommended. The first phase of this was done by this work. In further steps the

detected relations have to be linked with effective parameters, which allow the conjunction of all parameters in one model. Therefore, further probe molecules and sorbents should be studied systematically. In addition, the more extensive application of powerful spectroscopic techniques (e.g, ATR-FTIR) can provide further information about the actual binding mechanisms. Finally, the approaches and findings may be transferred to real (i.e. more complex) systems.

Chapter 6

6 References

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Appendix

Appendix A

Supplementary material for

Sorption of the organic cation metoprolol on silica gel from its aqueous solution considering the competition of inorganic cations

A.1 Inorganic ion concentrations released from silica gel

Table A.1 Analysis of inorganic ions in pure water and wash water after washing the silica gel with pure water in a solid to liquid ratio of 100 g/L.

Inorganic ions	c [mg/L]		
	Pure water	First wash water	Second wash water
NH_4^+	<0.1	<0.1	<0.1
Na^+	<0.1	100	7.5
K^+	<0.1	3.3	0.3
Mg^{2+}	<0.1	1.3	<0.1
Ca^{2+}	<0.1	8.9	<0.1
Cl^-	<0.1	12.8	1.2
NO_3^-	<0.1	0.7	0.4
SO_4^{2-}	<0.1	233	<0.1
PO_4^{3-}	<0.1	0.1	1.8
κ [$\mu\text{S}/\text{cm}$]	1.1	552	33

A.2 Comparison of Freundlich with Langmuir isotherm data

All sorption data were evaluated with the Freundlich as well as with the Langmuir sorption model. The decision, which sorption isotherm fits best, was done by non-linear Chi-square analysis (Ho, 2004).

Freundlich equation:

$$q_{eq} = K_F \cdot c_{eq}^{n_F} \quad \text{Equation A.1}$$

Langmuir equation:

$$q_{eq} = \frac{K_L \cdot q_{max} \cdot c_{eq}}{1 + K_L \cdot c_{eq}} \quad \text{Equation A.2}$$

The Langmuir isotherm parameters were fitted with the non-linear Generalized Reduced Gradient 2 (GRG 2) optimization algorithm implemented in the Microsoft Excel 2003 Add-In "Solver" using the least-square error (SSE) of the vertical differences as objective function:

$$SSE = \sum_{i=1}^n (\log q_e - \log q_{e,m})^2 \quad \text{Equation A.3}$$

where q_e is the sorbed amount observed from the experimental data and $q_{e,m}$ is the fitted sorbed amount for all c_{eq} .

For the non-linear Chi-square analysis, the squared errors were normalized to $q_{e,m}$ and summarized (**Table A.2**):

$$Chi^2 = \sum_{i=1}^n \frac{(\log q_e - \log q_{e,m})^2}{\log q_{e,m}} \quad \text{Equation A.4}$$

Table A.2 Comparison of Freundlich and Langmuir sorption model for all experiments.

Water matrix	Added electrolyte c [mM]	Freundlich regression parameters				Langmuir regression parameters				Best-fitting model
		$\log K_F$ $\left[\frac{(\text{nmol/kg})}{(K_F \text{ in } (\text{nmol/L})^{n_F})} \right]$	n_F [-]	SSE [-]	χ^2 [-]	$\log q_{\max}$ [$q_{\max}$ in nmol/kg]	$\log K_L$ [K_L in L/nmol]	SSE [-]	χ^2 [-]	
Pure water	-	3.45	0.83	5.94E-02	9.84E-03	8.00	-5.03	3.14E-02	4.75E-03	Langmuir
Pure water + NaCl	0.37	3.64	0.75	4.06E-02	6.18E-03	7.62	-4.68	6.11E-02	1.87E-02	Freundlich
	3.7	3.55	0.74	1.62E-02	2.68E-03	7.81	-5.02	2.10E-01	1.03E-02	Freundlich
	37	2.88	0.78	1.26E-01	2.55E-02	7.14	-4.92	1.24E-01	2.32E-02	Langmuir
	370	2.56	0.72	2.80E-02	5.68E-03	6.42	-4.68	9.54E-02	1.74E-02	Freundlich
Pure water + NH ₄ Cl	0.37	3.70	0.76	4.35E-02	7.60E-03	7.80	-4.76	1.17E-01	1.71E-02	Freundlich
	3.7	3.35	0.75	1.39E-02	2.45E-03	7.48	-4.84	1.10E-01	1.72E-02	Freundlich
	37	2.91	0.74	5.77E-02	1.09E-02	6.92	-4.78	5.39E-02	9.99E-03	Langmuir
	370	2.18	0.86	1.41E-02	2.97E-03	7.16	-5.38	7.56E-02	1.43E-02	Freundlich
Pure water + CaCl ₂	0.37	3.01	0.84	3.79E-03	6.84E-04	7.86	-5.32	5.71E-02	9.54E-03	Freundlich
	3.7	2.90	0.76	3.36E-02	6.43E-03	7.07	-4.89	7.89E-02	1.25E-02	Freundlich
	37	2.68	0.78	3.26E-02	6.95E-03	6.91	-4.83	7.54E-02	1.39E-02	Freundlich
	370	2.66	0.75	2.61E-02	5.28E-03	6.72	-4.76	8.76E-02	1.71E-02	Freundlich
Pure water + MgCl ₂	0.37	3.41	0.75	1.14E-01	1.82E-02	7.47	-4.75	1.86E-02	3.35E-03	Langmuir
	3.7	2.93	0.77	7.49E-02	1.37E-02	7.10	-4.85	3.13E-02	5.06E-03	Langmuir
	37	2.75	0.79	5.83E-02	9.46E-03	7.41	-5.33	2.55E-01	4.58E-02	Freundlich
	370	2.67	0.76	1.05E-02	2.30E-03	6.84	-4.85	1.57E-01	3.15E-02	Freundlich
Pure water + NaCl + NH ₄ Cl	3.7 + 3.7	3.40	0.71	3.66E-02	6.26E-03	7.21	-4.64	6.19E-02	9.74E-03	Freundlich
Pure water + CaCl ₂ + MgCl ₂	3.7 + 3.7	2.95	0.75	7.66E-02	1.48E-02	6.95	-4.61	5.02E-02	8.22E-03	Langmuir
Pure water + NaCl + CaCl ₂	3.7 + 3.7	2.79	0.77	1.33E-01	2.66E-02	6.96	-4.84	8.27E-02	1.54E-02	Langmuir
	37 + 3.7	2.54	0.83	1.16E-01	2.17E-02	7.51	-5.54	2.79E-01	5.53E-02	Freundlich
	3.7 + 0.37	3.31	0.74	8.91E-02	1.55E-02	7.27	-4.70	3.51E-02	6.04E-03	Langmuir
Pure water + HCl (pH ≈ 2)	10	2.53	0.81	3.61E-02	6.69E-03	8.95	-7.12	3.17E-01	6.20E-02	Freundlich

A.3 Use of activities instead of concentrations

Figure A.1 Comparison of MET sorption isotherms on silica gel at different concentrations of Mg^{2+} at pH=5.5–7: (A) plotted against equilibrium concentration c_{eq} of MET; and (B) plotted against equilibrium activity a_{eq} of MET.

Figure A.2 Relationship between the logarithmized Freundlich coefficient $\log K_{F,0.77}$ and the logarithmized activity of the medium. The $\log K_F$ values were refitted with a constant value for the Freundlich exponent ($n_F=0.77$).

A.4 Semi-logarithmic relationship

Figure A.3 Relation between the logarithmized Freundlich coefficient $\log K_{F,0.77}$ and the equivalent concentration $z \cdot c_{ion}$ of competing inorganic ions. The $\log K_F$ values were refitted with a constant value for the Freundlich exponent ($n_F=0.77$).

A.5 Statistical analysis of the isotherms

For evaluating the Freundlich isotherm's fit quality and confidence limits, the equilibrium concentrations c_{eq} and surface coverages 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:

$$n = \pm t_{n-2; 1-\frac{\alpha}{2}} \frac{\hat{\sigma}}{s_x \sqrt{n-1}} \quad \text{Equation A.5}$$

$$\hat{\sigma}^2 = \frac{1}{n-2} \sum_{i=1}^n (\log q_i - \log K_F - n_F \cdot \log c_{eq_i}) \quad \text{Equation A.6}$$

where $t_{n-2; 1-\alpha/2}$ is the t -quantile, s_x is the standard deviation of $\log c_{eq}$, $\hat{\sigma}^2$ is the variance of the residuals as estimator for the regression error, K_F is the Freundlich coefficient and n_F is the Freundlich exponent (slope of regression line). The fitted isotherms including the corresponding confidence intervals are shown in **Figure A.4–Figure A.26**

A.5.1 Reference isotherm without competition

Figure A.4 Reference isotherm of MET in pure water without competition.

A.5.2 Isotherms for competition with Na^+

Figure A.5 Isotherm of MET at 0.37 mM Na^+ .

Figure A.6 Isotherm of MET at 3.7 mM Na⁺.

Figure A.7 Isotherm of MET at 37 mM Na⁺.

Figure A.8 Isotherm of MET at 370 mM Na⁺.

A.5.3 Isotherms for competition with NH₄⁺

Figure A.9 Isotherm of MET at 0.37 mM NH₄⁺.

Figure A.10 Isotherm of MET at 3.7 mM NH_4^+ .

Figure A.11 Isotherm of MET at 37 mM NH_4^+ .

Figure A.12 Isotherm of MET at 370 mM NH_4^+ .

A.5.4 Isotherms for competition with Ca^{2+}

Figure A.13 Isotherm of MET at 0.37 mM Ca^{2+} .

Figure A.14 Isotherm of MET at 3.7 mM Ca^{2+} .

Figure A.15 Isotherm of MET at 37 mM Ca^{2+} .

Figure A.16 Isotherm of MET at 370 mM Ca^{2+} .

A.5.5 Isotherms for competition with Mg^{2+}

Figure A.17 Isotherm of MET at 0.37 mM Mg^{2+} .

Figure A.18 Isotherm of MET at 3.7 mM Mg^{2+} .

Figure A.19 Isotherm of MET at 37 mM Mg^{2+} .

Figure A.20 Isotherm of MET at 370 mM Mg^{2+} .

A.5.6 Isotherm for competition with Na^+ and NH_4^+

Figure A.21 Isotherm of MET at 3.7 mM Na^+ and 3.7 mM NH_4^+ .

A.5.7 Isotherm for competition with Ca^{2+} and Mg^{2+}

Figure A.22 Isotherm of MET at 3.7 mM Ca^{2+} and 3.7 mM Mg^{2+} .

A.5.8 Isotherms for competition with Na^+ and Ca^{2+}

Figure A.23 Isotherm of MET at 3.7 mM Na^+ and 3.7 mM Ca^{2+} .

Figure A.24 Isotherm of MET at 37 mM Na⁺ and 3.7 mM Ca²⁺.

Figure A.25 Isotherm of MET at 3.7 mM Na⁺ and 0.37 mM Ca²⁺.

A.5.9 Isotherm at $pH \approx 2$

Figure A.26 Isotherm of MET at $pH \approx 2$.

Appendix B

Supplementary material for

Sorption of organic cations onto silica surfaces over a wide concentration range of competing electrolytes

B.1 Sorbent characterization

SEM image analysis was conducted on a Zeiss DSM 982 Gemini to characterize the shape of sorbents (see **Section B1.1**). The specific surface areas A_{BET} [m^2/g] of the sorbents were determined with the BET method (nitrogen adsorption and desorption) according to DIN ISO 9277 by using the Autosorb-iQ surface analyzer (Quantachrome). In addition, the pore size d_{pore} [nm] and pore volume V_{pore} [cm^3/g] of the materials were also measured with this instrument. The pore size distribution curves were obtained by using the density functional theory (DFT) method. The particle size distribution was determined by sieve analysis (AS200digit, Retzsch) or laser diffraction spectroscopy (HELOS/KR-H2487, Sympatec). Sorbent pH values were obtained in a suspension of ultrapure water with a solid liquid ratio of 100 g/L. The potential cation exchange capacity (CEC_{pot}) was determined based on DIN ISO 13536 after Handbuch Forstliche Analytik - A3.2.1.2. For this purpose, 1 g of the sorbent sample was percolated in a column with a large excess of Ba^{2+} ions to achieve a complete exchange of all cations. The exchange was carried out with a 0.1 M barium chloride solution that was buffered at pH=8.1 using triethanolamine. Subsequently, the remaining BaCl_2 was rinsed from the column with pure water and, thereafter, the exchanged Ba^{2+} ions were exchanged back with a MgCl_2 solution. The determination was always carried out in triplicate. The CEC_{pot} [$\mu\text{mol}/\text{g}$] was calculated by measuring the Ba^{2+} concentration in Mg-percolate using ICP-MS (4500 Series, Hewlett Packard). The determination of the effective cation exchange capacity (CEC_{eff}) was carried out as described for CEC_{pot} . In contrast, the pH of BaCl_2 and CaCl_2 was adjusted to 5.6 using 0.1 M HCl and no buffer was used. The samples were percolated with BaCl_2 until equal pH values and electrical conductivities at the inlet and outlet of the column were reached. Afterwards, the second percolation was performed using MgCl_2 . The surface hydroxyl site density was analyzed by thermogravimetric analysis - TGA (STA 409,

Netzsch). The thermal analysis was carried out in the temperature range 30–1400 °C at a heating rate of 5 °C/min under Ar atmosphere. The number of surface hydroxyl groups on sorbents [mmol/g] can be calculated based on the weight loss from 190 to 1400 °C.

B.1.1 SEM image analysis

Figure B.1 SEM-images of silica gel-1 with 200-fold and 20,000-fold magnification.

Figure B.2 SEM-images of silica gel-2 with 200-fold and 20,000-fold magnification.

Figure B.3 SEM-images of sediment with 200-fold and 20,000-fold magnification.

B.1.2 BET area and pore size analysis

Figure B.4 N₂ adsorption/desorption isotherm (A) and DFT pore size distribution (B) of silica gel-1 and silica gel-2.

Figure B.5 N_2 adsorption/desorption isotherm (A) and DFT pore size distribution (B) of sediment.

B.1.3 Thermogravimetric analysis

Figure B.6 TG (A) and DTG curves (B) of silica gel-1, silica gel-2, and sediment.

B.1.4 Potentiometric surface titration

Table B.1 Calculated $pK_w(c)$ and $K_w(c)$ values at 25 °C for varying NaCl concentrations using PHREEQC-software (*pitzer.dat*).

$c(\text{NaCl})$ [mM]	$pK_w(c)$	$K_w(c)$
0	14.00	1.00E-14
0.37	13.98	1.05E-14
3.7	13.94	1.15E-14
37	13.85	1.42E-14
370	13.72	1.91E-14
3700	14.09	8.05E-15

Table B.2 Calculated $\gamma(\text{H}^+)$ values for varying NaCl concentrations using PHREEQC-software (*pitzer.dat*).

$c(\text{NaCl})$ [mM]	$\gamma(\text{H}^+)$		
	pH=2	pH=3	pH=4–12
0.37	0.9268	0.9683	0.9772
3.7	0.9099	0.9333	0.9376
37	0.8472	0.8511	0.8511
370	0.8054	0.8054	0.8054
3700	2.6730	2.6669	2.6669

Figure B.7 Surface titration curves for the sediment at different electrolyte concentrations of NaCl.

Figure B.8 Influence of NaCl electrolyte concentration on pH_{PZC} of studied sorbents.

B.2 Batch experiments

B.2.1 MET sorption on silica gel-1

Figure B.9 Linearized Freundlich sorption isotherms of MET on silica gel-1 ($T=8\text{ }^{\circ}\text{C}$) in pure water and with five different concentrations of Na^+ (A) and Ca^{2+} (B) between 0.37 and 3700 mM. Each isotherm point represents the average of a triplicate. Error bars indicate the range of the experimentally derived $\log q_{\text{eq}}$. The results marked with * were already published in Kutzner et al. (2014). The concentration range of competition with Na^+ and Ca^{2+} was extended by one order of magnitude.

B.2.2 MET sorption on silica gel-2

Figure B.10 Linearized Freundlich sorption isotherms of MET on silica gel-2 ($T=8^{\circ}\text{C}$) in pure water and with five different concentrations of Na⁺ (A) and Ca²⁺ (B) between 0.37 and 3700 mM. Each isotherm point represents the average of a triplicate. Error bars indicate the range of the experimentally derived $\log q_{eq}$.

B.2.3 MET sorption on sediment

Figure B.11 Linearized Freundlich sorption isotherms of MET on sediment ($T=8^{\circ}\text{C}$) in pure water and with four different concentrations of Na⁺ between 3.7 and 3700 mM. Each isotherm point represents the average of a triplicate. Error bars indicate the range of the experimentally derived $\log q_{eq}$.

B.2.4 iP4MBA sorption on silica gel-2

Figure B.12 Linearized Freundlich sorption isotherms of iP4MBA on silica gel-2 ($T=8\text{ }^{\circ}\text{C}$) in pure water and with five different concentrations of Na^+ (**A**) and Ca^{2+} (**B**) between 0.37 and 3700 mM. Each isotherm point represents the average of a triplicate. Error bars indicate the range of the experimentally derived $\log q_{eq}$.

B.2.5 Results of all batch tests**Table B.3** Freundlich regression parameters of all batch experiments.

Sorbent	Sorbate	Water matrix	Added electrolyte c [mM]	log c	Freundlich regression parameters				
					log $K_F \pm \log SD$	$n_F \pm SD$	R^2	SSE	$^a q_{eq} \pm SD$ [nmol/kg]
Silica gel-1	MET	Pure water	0*	-	3.45 ± 0.18	0.83 ± 0.06	0.9885	5.97E-02	3.81E+05 ± 2.67E+04
		Pure water + NaCl	0.37*	-0.43	3.64 ± 0.07	0.75 ± 0.03	0.9915	4.06E-02	3.59E+05 ± 1.25E+04
			3.7*	0.57	3.55 ± 0.13	0.74 ± 0.05	0.9966	1.62E-02	2.90E+05 ± 2.62E+04
			37*	1.57	2.88 ± 0.23	0.78 ± 0.08	0.9733	1.26E-01	7.60E+04 ± 7.82E+03
			370*	2.57	2.56 ± 0.14	0.72 ± 0.04	0.9934	2.80E-02	2.52E+04 ± 3.68E+03
			3700	3.57	2.88 ± 0.12	0.75 ± 0.03	0.9974	3.13E-02	6.48E+04 ± 6.58E+03
		Pure water + CaCl ₂	0.37*	-0.43	3.01 ± 0.14	0.84 ± 0.06	0.9993	3.79E-03	1.53E+05 ± 2.74E+03
			3.7*	0.57	2.90 ± 0.32	0.76 ± 0.11	0.9921	3.36E-02	7.05E+04 ± 7.57E+03
			37*	1.57	2.68 ± 0.06	0.78 ± 0.02	0.9941	3.26E-02	4.85E+04 ± 2.75E+03
			370*	2.57	2.66 ± 0.14	0.75 ± 0.03	0.9948	2.61E-02	3.82E+04 ± 5.18E+03
Silica gel-2	MET	Pure water	0	-	3.09 ± 0.11	0.79 ± 0.01	0.9957	5.69E-02	1.33E+05 ± 2.46E+04
		Pure water + NaCl	0	-	3.44 ± 0.09	0.71 ± 0.03	0.9784	2.84E-01	1.79E+05 ± 1.28E+04
			0.37	-0.43	3.34 ± 0.02	0.70 ± 0.01	0.9726	3.45E-01	1.39E+05 ± 2.73E+03
			3.7	0.57	3.17 ± 0.03	0.70 ± 0.00	0.9949	6.09E-02	9.32E+04 ± 6.24E+03
			37	1.57	2.84 ± 0.08	0.72 ± 0.03	0.9939	6.77E-02	4.86E+04 ± 4.19E+03
			370	2.57	2.56 ± 0.04	0.77 ± 0.02	0.9936	7.17E-02	3.38E+04 ± 4.77E+02
			3700	3.57	3.20 ± 0.03	0.73 ± 0.01	0.9915	1.01E-01	1.17E+05 ± 1.84E+03
		Pure water + CaCl ₂	0.37	-0.43	3.02 ± 0.07	0.73 ± 0.03	0.9831	2.02E-01	7.74E+04 ± 4.25E+03
			3.7	0.57	2.91 ± 0.06	0.74 ± 0.02	0.9932	8.20E-02	6.49E+04 ± 8.72E+02
			37	1.57	3.06 ± 0.02	0.69 ± 0.00	0.9991	8.60E-03	6.78E+04 ± 1.52E+03
			370	2.57	2.86 ± 0.03	0.73 ± 0.01	0.9997	3.24E-03	5.35E+04 ± 3.04E+03
Sediment	MET	Pure water	0	-	3.93 ± 0.10	0.71 ± 0.03	0.9880	1.91E-01	5.57E+05 ± 4.76E+04
		Pure water + NaCl	0	-	1.66 ± 0.19	0.85 ± 0.05	0.9864	2.05E-01	7.03E+03 ± 1.28E+03
			3.7	0.57	1.38 ± 0.02	0.92 ± 0.01	0.9928	3.77E-02	5.59E+03 ± 2.11E+02
			37	1.57	1.31 ± 0.03	0.87 ± 0.01	0.9982	7.47E-03	3.54E+03 ± 2.18E+02
			370	2.57	0.76 ± 0.30	0.91 ± 0.07	0.9785	8.33E-02	1.26E+03 ± 3.68E+02
			3700	3.57	1.59 ± 0.13	0.86 ± 0.03	0.9805	9.02E-02	6.35E+03 ± 7.56E+02

Sorbent	Sorbate	Water matrix	Added electrolyte c [mM]	log c	log $K_F \pm \log SD$	$n_F \pm SD$	R^2	SSE	^a $q_{eq} \pm SD$ [nmol/kg]
Silica gel-2	iP4MBA	Pure water	0	-	3.47 ± 0.22	0.63 ± 0.06	0.9728	3.01E-01	1.25E+05 ± 2.03E+04
		Pure water + NaCl	0.37	-0.43	3.35 ± 0.07	0.70 ± 0.02	0.9929	9.87E-02	1.40E+05 ± 2.29E+03
			3.7	0.57	3.06 ± 0.09	0.64 ± 0.01	0.9924	7.81E-02	5.20E+04 ± 1.16E+04
			37	1.57	2.90 ± 0.09	0.71 ± 0.03	0.9947	6.43E-02	5.11E+04 ± 3.54E+03
			370	2.57	2.74 ± 0.08	0.68 ± 0.05	0.996	3.99E-02	2.96E+04 ± 4.66E+03
			3700	3.57	3.07 ± 0.15	0.70 ± 0.03	0.9969	3.80E-02	7.54E+04 ± 1.31E+04
		Pure water + CaCl ₂	0.37	-0.43	3.24 ± 0.12	0.66 ± 0.02	0.9870	9.70E-02	8.57E+04 ± 1.43E+04
			3.7	0.57	3.11 ± 0.08	0.61 ± 0.04	0.9889	1.81E-02	4.84E+04 ± 4.49E+03
			37	1.57	2.86 ± 0.05	0.69 ± 0.01	0.9983	1.02E-01	4.37E+04 ± 2.26E+03
			370	2.57	2.75 ± 0.07	0.71 ± 0.02	0.9909	8.79E-02	3.76E+04 ± 2.66E+03
			3700	3.57	3.46 ± 0.12	0.68 ± 0.03	0.9935	3.01E-01	1.60E+05 ± 3.24E+04

K_F =Freundlich sorption coefficient in (nmol/kg)/(nmol/L) ^{n_F} , n_F =Freundlich exponent, R^2 =coefficient of determination.

$$SD = \sqrt{\frac{1}{N-1} \cdot \sum_{i=1}^N (x_i - \bar{x})^2}$$

where ($x_1, x_2, \dots, x_N$)=observed values of the sample item, $\bar{x}$ =mean value, and N=sample size.

$$SSE = \sum_{i=1}^n (\log q_{eq, \text{experiment}} - \log q_{eq, \text{fitted}})^2$$

with $\log q_{eq, \text{experiment}} = \log \left(\frac{V_L (c_{eq} - c_0)}{m_A} \right)$ and $\log q_{eq, \text{fitted}} = \log K_F + (n_F \cdot \log c_{eq})$.

^a equilibrium loading q_{eq} at the equilibrium concentration c_{eq} =370 nM.

* Results were compiled from Kutzner et al. (2014).

B.2.6 Influence of sorbent (relative sorption affinity of MET)

Figure B.13 Comparison of relative sorption affinities of MET on various sorbents considering the background electrolyte concentration of Na^+ (**A**) or Ca^{2+} (**B**). Relationship between the equilibrium loadings q_{eq} at an equilibrium concentration of $c_{\text{eq}}=370$ nM and the applied molar concentration $c(\text{Na}^+)$ or $c(\text{Ca}^{2+})$ of competing ions. The q_{eq} values were normalized to the sorption without competition effect using pure water (q_0).

B.2.7 Use of equivalent concentration instead of molar concentration

Figure B.14 Comparison of the competitive impact of Na^+ and Ca^{2+} cations on the sorption of MET or iP4MBA on silica gel-1 or silica gel-2 ($T=8^\circ\text{C}$). The q_{eq} values at an equilibrium concentration $c_{eq}=374$ nM were normalized to the sorption without competition effect using pure water (q_0) and were plotted against the applied molar concentration c (A, C, E) or against the charge-corrected equivalent concentration $c_{equivalent}$ (B, D, F) of the electrolyte solution.

B.3 Additional column experiments

Additional column tests for the sorption of MET on silica gel-2 were performed to verify the results of static batch experiments with a dynamic column system and to determine the point of almost complete suppression of cation exchange interactions (minimal sorption) more accurately. For column experiments, a stainless-steel column (125×4 mm) was filled with the sorbent, closed with stainless-steel frits and equilibrated with the respective electrolyte solutions until equal electrical conductivities and pH values were reached at inlet and outlet. Before starting the experiment, MET ($c_0=5.5$ mg/L) was added to the eluent. As in the batch tests, the experiments were conducted at a constant temperature of 8 °C. A flow rate of 0.5 mL/min was achieved with a Metrohm 709 IC pump. The water was pumped in an up-flow direction to ensure saturated column conditions. The concentration change of MET as a function of time was detected by UV-VIS spectrophotometry (photoLab 6600 UV-VIS, WTW) at 220 nm with a flow cuvette. After the sorption experiment, the desorption curve in each case was recorded by changing the eluent without addition of MET. During the experiments, no degradation of MET or pH changes were observed. Before sorption experiments, a tracer test was conducted in order to determine the hydraulic parameters of the column and to normalize the breakthrough times of the sorbing substances. Deuterium oxide was used as conservative tracer. The breakthrough curves were measured at the column outlet using a differential refractometer (GAT-LCD 202, Gamma Analysentechnik GmbH)

For the calculation of sorption isotherms from column experiments the concentration values of the desorption curve can be interpreted as equilibrium values and be assigned relative retention times $t(c_{eq})/t_{Tracer}$, while neglecting dispersion. The related loadings q_{eq} can be calculated by an approach of Bürgisser et al. (1993) by integrating the tailing of the desorption front:

$$q_{eq} = \frac{1}{\rho} \int_0^c \left(\frac{t(c_{eq})}{t_{Tracer}} - 1 \right) dc_{eq} \quad \text{Equation B.1}$$

where q_{eq} is the equilibrium loading, ρ is the mass of sorbent per unit pore volume, $t(c_{eq})$ refers to the concentration dependent breakthrough time of the desorption curve, t_{Tracer} is the breakthrough time of the tracer, and c_{eq} is the equilibrium concentration. Thus, the isotherms are determined and directly compared with those from the batch experiments. Due to the relatively large Peclet number in the experiments ($Pe > 100$),

the influence of the dispersion on the isotherm is small and can be neglected. The experimental conditions of the column studies are summarized in **Table B.4**.

Table B.4 Column conditions for all runs.

L [cm]	12.5	L =column length, A =cross sectional area of column, Q =volumetric flow rate, ε =effective porosity, v_f =filter velocity, v_w =pore water velocity, c_0 =initial concentration of MET, ρ_b =bulk density.
A [cm ²]	0.13	
Q [cm ³ /min]	0.49 ± 0.02	
ε [-]	0.89 ± 0.02	
v_f [cm/min]	3.88 ± 0.13	
v_w [cm/min]	5.23 ± 0.18	
c_0 [mg/L]	5.30 ± 0.28	
ρ_b [kg/m ³]	446 ± 18.5	

B.3.1 Breakthrough curves

Figure B.15 Sorption and desorption breakthrough curves of MET on silica gel-2 ($T=8\text{ }^{\circ}\text{C}$) at different concentrations of Na^+ . Every breakthrough curve represents the average breakthrough curve of a double determination. 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 tracer.

Figure B.16 Sorption and desorption breakthrough curves of MET on silica gel-2 ($T=8\text{ }^{\circ}\text{C}$) at different concentrations of Ca^{2+} . Every breakthrough curve represents the average breakthrough curve of a double determination. 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 tracer.

Table B.5 Experimental and modeled parameters of the column experiments ($T=8\text{ }^{\circ}\text{C}$).

Water matrix	Q [mL/min]	v_f [cm/min]	v_w [cm/min]	c_0 [mg/L]	ρ_b [kg/m ³]	$R_d \pm SD$ [-]
3.7 mM NaCl	0.47	3.74	5.04	5.32	477.05	49.31 ± 1.77
37 mM NaCl	0.48	3.82	5.15	5.41	455.12	33.77 ± 4.99
370 mM NaCl	0.48	3.78	5.10	5.16	458.78	24.94 ± 4.67
740 mM NaCl	0.48	3.90	5.26	5.36	452.57	24.77 ± 1.44
1850 mM NaCl	0.51	4.02	5.42	5.06	441.62	33.10 ± 0.57
3700 mM NaCl	0.47	3.74	5.04	5.26	455.66	69.93 ± 3.30
3.7 mM CaCl_2	0.48	3.82	5.15	5.36	445.95	40.75 ± 4.77
37 mM CaCl_2	0.51	4.06	5.47	5.12	445.07	26.00 ± 0.55
370 mM CaCl_2	0.52	4.14	5.58	6.10	450.92	24.60 ± 0.01
740 mM CaCl_2	0.49	3.90	5.26	5.35	432.81	33.47 ± 0.71
1850 mM CaCl_2	0.49	3.90	5.26	5.10	437.33	58.64 ± 3.93
3700 mM CaCl_2	0.47	3.74	5.04	5.04	399.92	257.69 ± 14.07

Q =volumetric flow rate, v_f =filter velocity, v_w =pore water velocity, c_0 =initial concentration of metoprolol, ρ_b =bulk density, R_d =retardation factor.

SD =standard deviation: $SD = \sqrt{\frac{1}{N-1} \cdot \sum_{i=1}^N (x_i - \bar{x})^2}$ where $(x_1, x_2, \dots, x_N)$ =observed values of the sample item, $\bar{x}$ =mean value, and N =sample size.

B.3.2 Calculation of sorption isotherms**Table B.6** Freundlich regression parameters of column experiments (T=8 °C).

Water matrix	Added electrolyte		Freundlich regression parameters			
	c [mM]	log c	log K_F	n_F	R^2	^a log $K_{F,0.72}$
Pure water + NaCl	3.7	0.57	3.10	0.71	0.9898	3.07
	37	1.57	2.71	0.76	0.9951	2.89
	370	2.57	2.43	0.79	0.9826	2.73
	740	2.87	1.96	0.87	0.9839	2.57
	1850	3.27	3.00	0.69	0.9934	2.88
	3700	3.57	3.33	0.69	0.9891	3.22
Pure water + CaCl ₂	3.7	0.57	2.91	0.73	0.9979	2.96
	37	1.57	2.72	0.74	0.9976	2.78
	370	2.57	2.36	0.82	0.9950	2.77
	740	2.87	3.02	0.69	0.9961	2.89
	1850	3.27	3.35	0.67	0.9965	3.14
	3700	3.57	3.83	0.67	0.9532	3.62

K_F =Freundlich sorption coefficient, n_F =Freundlich exponent, R^2 =coefficient of determination.

^a Recalculated log K_F for a constant n_F .

B.3.3 Comparison of batch with column data**Table B.7** Comparison of Freundlich sorption coefficients for batch and column experiments (T=8 °C).

Water matrix	Added electrolyte		Batch experiments	Column experiments
	c [mM]	log c	^a log $K_{F,0.72}$	^a log $K_{F,0.72}$
Pure water + NaCl	3.7	0.57	3.12	3.07
	37	1.57	2.83	2.89
	370	2.57	2.68	2.73
	3700	3.57	3.22	3.22
Pure water + CaCl ₂	3.7	0.57	2.96	2.96
	37	1.57	2.98	2.78
	370	2.57	2.88	2.77
	3700	3.57	3.90	3.62

K_F =Freundlich sorption coefficient.

^a Recalculated log K_F for a constant n_F .

Figure B.17 Comparison of Freundlich sorption coefficients for batch and column experiments ($T=8^\circ\text{C}$). The $\log K_F$ values were refitted with a constant value for the Freundlich exponent of $n_F=0.72$. Relationship between the logarithmized Freundlich sorption coefficient ($\log K_{F,0.72}$) of MET on the molar concentration $c(\text{Na}^+)$ (**A**) or $c(\text{Ca}^{2+})$ (**B**) of competing ions. The activity coefficient $\gamma(\text{H}^+)$ depending on NaCl and CaCl_2 concentration was calculated by PhreeqC (*pitzer.dat*).

Appendix C

Supplementary material for

Sorption of organic cations onto oxides: Are there suitable parameters to predict sorption coefficients based on sorbent properties?

C.1 Sorbent characterization

C.1.1 SEM image analysis

Figure C.1 SEM-images of silica gel-1 with 200-fold and 20,000-fold magnification.

Figure C.2 SEM-images of silica gel-2 with 200-fold and 20,000-fold magnification.

Figure C.3 SEM-images of silica gel-3 with 200-fold and 20,000-fold magnification.

Figure C.4 SEM-images of aluminum oxide-1 with 200-fold and 20,000-fold magnification.

Figure C.5 SEM-images of aluminum oxide-2 with 200-fold and 20,000-fold magnification.

C.1.2 Particle size distribution

Figure C.6 Frequency distribution of particle size of silica gel-1, aluminum oxide-1 and aluminum oxide-2 determined by sieve analysis.

Figure C.7 Frequency distribution of particle size of silica gel-2 (A) and silica gel-3 (B) determined by laser diffraction spectrometry.

Figure C.8 Cumulative distribution curve of studied sorbent (S: sieve analysis, L: laser diffraction spectrometry).

C1.3 BET area and pore size analysis

Figure C.9 N₂ adsorption/desorption isotherm (at 77 K) of studied sorbents.

Figure C.10 BJH (A) and DFT (B) pore size distribution of studied sorbents.

C1.4 Thermogravimetric analysis

Figure C.11 TG (A) and DTG (B) curves of studied sorbents.

C1.5 Potentiometric surface titration

Figure C.12 Surface titration curves of silica gel-1 (A), silica gel-2 (B), silica gel-3 (C), aluminum oxide-1 (D) and aluminum oxide-2 (E) at different background electrolyte concentrations of NaCl.

C2. Column experiments

C2.1 Column conditions

Table C.1 Column conditions of all tests.

Sorbent	Sorbate	L [cm]	A [cm ²]	V [cm ³]	Q [mL/min]	ε [-]	c_0 [mg/L]	ρ_b [g/cm ³]	pH [-]
Silica gel-1	MET	12.5	0.13	1.58	0.45 ±0.08	0.84 ±0.02	4.71 ±0.48	0.46 ±0.02	5.59 ±0.10
	iP4MBA	12.5	0.13	1.58	0.46 ±0.14	0.82 ±0.06	2.51 ±0.28	0.45 ±0.03	5.66 ±0.11
	BA	25.0	3.14	78.5	0.49 ±0.01	0.79 ±0.05	97.89 ±4.86	0.54 ±0.01	5.64 ±0.08
	MET	12.5	0.13	1.58	0.47 ±0.04	0.89 ±0.02	5.34 ±0.20	0.45 ±0.01	5.61 ±0.09
	iP4MBA	12.5	0.13	1.58	0.43 ±0.09	0.84 ±0.09	2.85 ±0.21	0.42 ±0.04	5.66 ±0.09
	BA	25.0	3.14	78.5	0.49 ±0.01	0.89 ±0.02	97.42 ±2.25	0.47 ±0.01	5.61 ±0.10
Silica gel-3	MET	12.5	0.13	1.58	0.39 ±0.10	0.93 ±0.09	5.00 ±0.42	0.38 ±0.02	5.68 ±0.09
	iP4MBA	12.5	0.13	1.58	0.47 ±0.09	0.93 ±0.02	2.78 ±0.10	0.39 ±0.02	5.64 ±0.07
	BA	25.0	3.14	78.5	0.47 ±0.07	0.92 ±0.02	96.25 ±2.17	0.43 ±0.01	5.60 ±0.10
	MET	25.0	3.14	78.5	0.48 ±0.06	0.69 ±0.08	4.54 ±0.31	1.12 ±0.01	5.64 ±0.10
	iP4MBA	25.0	3.14	78.5	0.43 ±0.11	0.69 ±0.05	2.72 ±0.17	1.16 ±0.04	5.67 ±0.08
	BA	25.0	3.14	78.5	0.49 ±0.29	0.67 ±0.04	96.72 ±3.95	1.11 ±0.01	5.67 ±0.08
Aluminum oxide-1	MET	25.0	3.14	78.5	0.49 ±0.01	0.65 ±0.04	4.56 ±0.19	1.04 ±0.00	6.47 ±0.33
	iP4MBA	25.0	3.14	78.5	0.49 ±0.01	0.66 ±0.04	2.70 ±0.38	1.05 ±0.01	6.33 ±0.15
	BA	25.0	3.14	78.5	0.50 ±0.01	0.65 ±0.02	92.81 ±6.05	1.04 ±0.03	6.42 ±0.26
	MET	25.0	3.14	78.5	0.49 ±0.01	0.65 ±0.04	4.56 ±0.19	1.04 ±0.00	6.47 ±0.33
	iP4MBA	25.0	3.14	78.5	0.49 ±0.01	0.66 ±0.04	2.70 ±0.38	1.05 ±0.01	6.33 ±0.15
	BA	25.0	3.14	78.5	0.50 ±0.01	0.65 ±0.02	92.81 ±6.05	1.04 ±0.03	6.42 ±0.26
Aluminum oxide-2	MET	25.0	3.14	78.5	0.49 ±0.01	0.65 ±0.04	4.56 ±0.19	1.04 ±0.00	6.47 ±0.33
	iP4MBA	25.0	3.14	78.5	0.49 ±0.01	0.66 ±0.04	2.70 ±0.38	1.05 ±0.01	6.33 ±0.15
	BA	25.0	3.14	78.5	0.50 ±0.01	0.65 ±0.02	92.81 ±6.05	1.04 ±0.03	6.42 ±0.26
	MET	25.0	3.14	78.5	0.49 ±0.01	0.65 ±0.04	4.56 ±0.19	1.04 ±0.00	6.47 ±0.33
	iP4MBA	25.0	3.14	78.5	0.49 ±0.01	0.66 ±0.04	2.70 ±0.38	1.05 ±0.01	6.33 ±0.15
	BA	25.0	3.14	78.5	0.50 ±0.01	0.65 ±0.02	92.81 ±6.05	1.04 ±0.03	6.42 ±0.26

C2.2 Breakthrough curves

C2.2.1 Silica gel-1

Figure C.13 Breakthrough curves of MET (A), iP4MBA (B) and BA (C) on silica gel-1 at different NaCl concentrations. Every breakthrough curve represents the average breakthrough curve of a double determination. Pore volumes were calculated by normalizing the experiment duration to the ideal breakthrough time of the tracer.

C2.2.2 Silica gel-2

Figure C.14 Breakthrough curves of MET (A), iP4MBA (B) and BA (C) on silica gel-2 at different NaCl concentrations. Every breakthrough curve represents the average breakthrough curve of a double determination. Pore volumes were calculated by normalizing the experiment duration to the ideal breakthrough time of the tracer.

C2.2.3 Silica gel-3

Figure C.15 Breakthrough curves of MET (A), iP4MBA (B) and BA (C) on silica gel-3 at different NaCl concentrations. Every breakthrough curve represents the average breakthrough curve of a double determination. Pore volumes were calculated by normalizing the experiment duration to the ideal breakthrough time of the tracer.

C2.2.4 Aluminum oxide-1

Figure C.16 Breakthrough curves of MET (A), iP4MBA (B) and BA (C) on aluminum oxide-1 at different NaCl concentrations. Every breakthrough curve represents the average breakthrough curve of a double determination. Pore volumes were calculated by normalizing the experiment duration to the ideal breakthrough time of the tracer.

C2.2.5 Aluminum oxide-2

Figure C.17 Breakthrough curves of MET (A), iP4MBA (B) and BA (C) on aluminum oxide-2 at different NaCl concentrations. Every breakthrough curve represents the average breakthrough curve of a double determination. Pore volumes were calculated by normalizing the experiment duration to the ideal breakthrough time of the tracer.

C2.3 Sorption coefficients

Table C.2 Sorption coefficients of all column experiments.

Sorbate	Water matrix	Silica gel-1	Silica gel-2	Silica gel-3	Aluminum oxide-1	Aluminum oxide-2
	c(NaCl) [mM]	$K_d=Q^*(t_{\text{sorbate}}-t_{\text{tracer}})/m_{\text{sorbent}}$ [L/kg]				
MET	0	611 ±13.2	246 ±27.2	55.3 ±1.99	0.06 ±0.08	1.40 ±0.40
	37	40.3 ±2.47	63.3 ±7.53	15.3 ±0.53	0.12 ±0.05	0.18 ±0.07
	740	27.6 ±3.58	42.8 ±4.77	11.2 ±1.61	0.07 ±0.05	0.23 ±0.14
	3700	93.4 ±3.75	135 ±7.72	19.9 ±3.87	0.31 ±0.06	0.32 ±0.18
iP4MBA	0	398 ±5.99	259 ±54.4	34.3 ±0.09	0.06 ±0.05	2.11 ±0.11
	37	35.5 ±2.13	64.7 ±7.79	5.93 ±1.57	0.03 ±0.07	0.04 ±0.15
	740	16.8 ±6.29	28.4 ±2.25	6.99 ±0.07	0.15 ±0.10	0.20 ±0.15
	3700	45.1 ±2.59	67.7 ±2.94	13.7 ±0.80	0.21 ±0.14	0.27 ±0.17
BA	0	1.13 ±0.01	1.74 ±0.32	0.41 ±0.08	0.12 ±0.01	0.06 ±0.05
	37	1.18 ±0.08	1.54 ±0.02	0.40 ±0.09	0.06 ±0.01	0.07 ±0.06
	740	1.46 ±0.01	1.89 ±0.00	0.42 ±0.00	0.07 ±0.03	0.06 ±0.11
	3700	4.07 ±0.28	5.10 ±0.29	1.17 ±0.03	0.09 ±0.02	0.23 ±0.06

C2.4 Sorption of different probe compounds

Figure C.18 Comparison of the sorption of studied probe molecules on silica gel-1 (A), silica gel-2 (B), silica gel-3 (C), aluminum oxide-1 (D) and aluminum oxide-2 (E) over a wide concentration range of NaCl. To represent the results in the logarithmic scale the NaCl concentrations of the experiments in pure water was set to 0.1 mM.

C3. Statistical analysis/correlations

C3.1 Sorbent parameters

Figure C.19 Statistical significant correlations ($p < 0.10$) between experimental determined sorbent parameters with 95% confidence limits.

Table C.3 Results of the linear regression ($y = mx + n$) from **Figure C.19**.

y	x	m(slope)	n(intercept)	R^2
CEC_{pot}	A_{BET}	0.64	-34.7	0.9941
α_{OH}	A_{BET}	0.01	1.85	0.7549
d_{pore} (DFT)	d_{pore} (BJH)	1.14	1.69	0.9764
ρ_B	V_{pore}	-0.84	1.27	0.9466
ϵ	V_{pore}	0.30	0.59	0.9833
α_{OH}	CEC_{pot}	0.01	2.15	0.7735
ϵ	ρ_B	-0.34	1.03	0.9213

C3.2 Sorption relative to sorbent properties

C3.2.1 MET

Figure C.20 Statistical significant correlations ($p < 0.10$) between experimental determined sorption coefficients for MET on studied sorbents and sorbent parameters with 95% confidence limits.

Table C.4 Results of the linear regression ($y = mx + n$) from **Figure C.20**.

y	x	m(slope)	n(intercept)	R^2
K_d , pure water	A_{BET}	1.51	-175	0.9462
K_d , pure water	CEC_{pot}	2.40	-95.5	0.9706
K_d , pure water	α_{OH}	198	-448	0.6809
K_d , 37 mM NaCl	α_{OH}	24.7	-54.6	0.9394
K_d , 740 mM NaCl	α_{OH}	16.7	-36.7	0.9436
K_d , 3700 mM NaCl	A_{BET}	0.30	-20.7	0.6592
K_d , 3700 mM NaCl	CEC_{pot}	0.47	-4.13	0.6559
K_d , 3700 mM NaCl	α_{OH}	55.2	-126	0.9446

C3.2.2 *iP4MBA*

Figure C.21 Statistical significant correlations ($p < 0.10$) between experimental determined sorption coefficients for iP4MBA on studied sorbents and sorbent parameters with 95% confidence limits.

Table C.5 Results of the linear regression ($y=mx+n$) from **Figure C.21**.

y	x	m(slope)	n(intercept)	R^2
A_{BET}	K_{d} , pure water	1.07	-114	0.9718
CEC_{pot}	K_{d} , pure water	1.68	-56.2	0.9848
α_{OH}	K_{d} , pure water	155	-354	0.8577
α_{OH}	K_{d} , 37 mM NaCl	24.5	-56.8	0.8719
α_{OH}	K_{d} , 740 mM NaCl	10.7	-23.6	0.9171
α_{OH}	K_{d} , 3700 mM NaCl	27.0	-60.4	0.9473

C3.2.3 BA

Figure C.22 Statistical significant correlations ($p < 0.10$) between experimental determined sorption coefficients for BA on studied sorbents and sorbent parameters with 95% confidence limits.

Table C.6 Results of the linear regression ($y = mx + n$) from **Figure C.22**.

y	x	m(slope)	n(intercept)	R^2
$K_{d, \text{pure water}}$	α_{OH}	0.6466	-1.3666	0.9322
$K_{d, 37 \text{ mM NaCl}}$	A_{BET}	0.0034	-0.1426	0.6873
$K_{d, 37 \text{ mM NaCl}}$	CEC_{pot}	0.0053	0.0392	0.6929
$K_{d, 37 \text{ mM NaCl}}$	α_{OH}	0.6169	-1.3123	0.9772
$K_{d, 740 \text{ mM NaCl}}$	A_{BET}	0.0043	-0.2262	0.7061
$K_{d, 740 \text{ mM NaCl}}$	CEC_{pot}	0.0067	0.0067	0.7086
$K_{d, 740 \text{ mM NaCl}}$	α_{OH}	0.7724	-1.6756	0.9740
$K_{d, 3700 \text{ mM NaCl}}$	A_{BET}	0.0117	-0.6299	0.7146
$K_{d, 3700 \text{ mM NaCl}}$	CEC_{pot}	0.0184	0.0039	0.7206
$K_{d, 3700 \text{ mM NaCl}}$	α_{OH}	2.1125	-4.5852	0.9796

Appendix D

List of all journal articles and conference abstracts authored or co-authored by me and related to the presented work (latest update: May 2019).

Journals

Kutzner, S., Schaffer, M., Licha, T., Worch, E., Börnick, H., **2018**. Sorption of cationic organic substances onto synthetic oxides: Evaluation of sorbent parameters as possible predictors. *Science of the Total Environment* 643, 632-639.

Schaffer, M., Warner, W., **Kutzner, S.**, Börnick, H., Worch, E., Licha, T., **2017**. Organic molecules as sorbing tracers for the assessment of fracture surfaces in consolidated aquifer systems. *Journal of Hydrology* 546, 370-379.

Kutzner, S., Schaffer, M., Licha, T., Worch, E., Börnick, H., **2016**. Sorption of organic cations onto silica surfaces over a wide concentration range of competing electrolytes. *Journal of Colloid and Interface Science* 484, 229-236.

Schaffer, M., **Kutzner, S.**, Börnick, H., Nödler, K., Worch, E., Licha, T., **2016**. Charakterisierung der Sorption organischer Basen aus wässrigen Lösungen: Aktuelle Ergebnisse und Limitierungen bei der Prognose des Umweltverhaltens. *Mitteilungen der Fachgruppe Umweltchemie und Ökotoxikologie* 22. Jahrgang 2016/ Nr. 3 (ISSN 1618-3258), 67-70.

Kutzner, S., Schaffer, M., Schulz, J., Börnick, H., Licha, T., Worch, E., **2015**. Bestimmung von nicht-linearen Sorptionsisothermen aus Säulenversuchen am Beispiel von Metoprolol und Kieselgel. *Vom Wasser* 113(3), 93-96.

Kutzner, S., Schaffer, M., Niedbala, A., Börnick, H., Nödler, K., Licha, T., Worch, E., **2014**. Untersuchungen zum gemeinsamen Einfluss von Na⁺- und Ca²⁺-Ionen auf die Sorption von organischen Kationen am Beispiel des Beta-Blockers Metoprolol. *Vom Wasser* 112(3), 90-93.

Kutzner, S., Schaffer, M., Börnick, H., Licha, T., Worch, E., **2014**. Sorption of the organic cation metoprolol on silica gel from its aqueous solution considering the competition of inorganic cations. *Water Research* 54, 273-283.

Conference contributions

Kutzner, S., Schaffer, M., Licha, T., Worch, E., Börnick, H., **2016**. Säulenversuche zur Sorption organischer Kationen über einen breiten Konzentrationsbereich an konkurrierenden anorganischen Kationen. Jahrestagung der Wasserchemischen Gesellschaft, *Wasser 2016*, Tagungsband (ISBN 978-3-936028-94-2), 310-314.

Kutzner, S., Schaffer, M., Schulz, J., Börnick, H., Licha, T., Worch, E., **2015**. Bestimmung von nicht-linearen Sorptionsisothermen aus Säulenversuchen am Beispiel von Metoprolol und Kieselgel. Jahrestagung der Wasserchemischen Gesellschaft, *Wasser 2015*, Tagungsband (ISBN 978-3-936028-90-4), 310-314.

Kutzner, S., Börnick, H., Schaffer, M., Licha, T., Worch, E., **2015**. Sorption organischer Kationen an synthetischen oxidischen Materialien. GDCh-Wissenschaftsforum, *Chemie 2015*, Dresden, Germany, 30.08-02.09.2015.

Schaffer, M., **Kutzner, S.**, Börnick, H., Worch, E., Licha, T., **2015**. Recent progress on characterizing the sorption of organic bases from aqueous solution: Lessons learnt from systematic experiments with cationic beta-blockers. 15th EuCheMS International Conference on Chemistry and the Environment, *ICCE 2015*, Leipzig, Germany, 20.09-24.09.2015.

Kutzner, S., Schaffer, M., Börnick, H., Nödler, K., Niedbala, A., Licha, T., Worch, E., **2014**. Untersuchungen zum gemeinsamen Einfluss von Na⁺- und Ca²⁺-Ionen auf die Sorption von organischen Kationen am Beispiel des Beta-Blockers Metoprolol. Jahrestagung der Wasserchemischen Gesellschaft, *Wasser 2014*, Tagungsband (ISBN 978-3-936028-83-6), 295-299.

Kutzner, S., Börnick, H., Schaffer, M., Licha, T., Worch, E., **2013**. Untersuchung der Sorption organischer Kationen an oxidische Oberflächen am Beispiel von Metoprolol und Kieselgel. Jahrestagung der Wasserchemischen Gesellschaft, *Wasser 2013*, Tagungsband (ISBN 978-3-936028-71-3), 399-403.

Eidesstattliche Erklärung

Hiermit versichere ich eidesstattlich, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe; die aus fremden Quellen direkt oder indirekt übernommenen Gedanken sind als solche kenntlich gemacht. Die Arbeit wurde bisher weder im Inland noch im Ausland in gleicher oder ähnlicher Form einer anderen Prüfungsbehörde zum Zwecke der Promotion vorgelegt.

Dresden, 01. Mai 2019

Susann Kutzner