**Recent progress on characterizing the sorption of organic bases from aqueous solution: Lessons learnt from systematic experiments with cationic beta-blockers**

Mario Schaffer1, Susann Kutzner2, Hilmar Börnick2, Eckhard Worch2, Tobias Licha1

1 Georg-August-Universtät Göttingen, Geoscience Centre, Department of Applied Geology, Hydrochemistry Group, Goldschmidtstr. 3, D-37077 Göttingen, [Mario.Schaffer@geo.uni-goettingen.de](mailto:Mario.Schaffer@geo.uni-goettingen.de), [Tobias.Licha@geo.uni-goettingen.de](mailto:Tobias.Licha@geo.uni-goettingen.de)

2 Technische Universität Dresden, Institute of Water Chemistry, D-01062 Dresden, [Susann.Kutzner@mailbox.tu-dresden.de](mailto:Susann.Kutzner@mailbox.tu-dresden.de), [Hilmar.Boernick@tu-dresden.de](mailto:Hilmar.Boernick@tu-dresden.de), [Eckhard.Worch@tu-dresden.de](mailto:Eckhard.Worch@tu-dresden.de)

A large number of organic micropollutants detected in the aquatic environment are bases with p*Ka,base* values above the common pH range of natural waters and therefore occur as cations. In contrast to neutral and acidic compounds, the experimentally determined sorption coefficients of these organic cations are usually higher than estimated from *n*‑octanol/water partition coefficients log *KOW* or log *D*. This is because, additional, electrostatically driven sorption processes (e.g., cation exchange, hydrogen bonding) are not considered. Up to now, comprehensive models predicting the sorption behavior of organic cations are not available. Consequently, the model-based environmental risk assessment of organic bases would benefit from an improved understanding of the role of different sorption processes and the relevant influencing factors. In this context, the beta-blockers atenolol and metoprolol (secondary amines with p*Ka,base* > 9) were employed as probe compounds and have recently been investigated using different sorbents and boundary conditions in systematic batch and column experiments (Schaffer et al. 2012, Niedbala et al. 2013, Kutzner et al. 2014). Prior to the sorption experiments, all sorbents required a careful pre-treatment in order to avoid undesired effects and ensure comparable conditions for all investigated sorbent/sorbate systems (e.g., pH adjustment, initial sorbent loading).

The experiments revealed cation exchange as a relevant sorption process and confirmed that hydrophobic interactions play only a minor role for both compounds. The higher sorption of metoprolol compared to atenolol also suggests a contribution originating from further polar interaction mechanisms. However, in particular the cation exchange equilibrium shows a high sensitivity to various influencing parameters, such as the sorbent charge properties and the ionic composition of the aqueous phase. Therefore, the role of different types and concentrations of competing inorganic electrolytes in solution was subsequently studied for natural (sediments) as well as technical sorbents (silica gel). The results generally showed non-linear isotherms (Freundlich type) and clearly decreasing sorption coefficients with increasing concentrations of competing ions. The estimated regressions allow the prediction of sorption coefficients within the investigated concentration ranges. The simple transfer of the single ion contributions to systems with more than one competing ion type was only feasible at low electrolyte concentrations. Contrary to expectations, the sorption increases again at very high electrolyte concentrations (mol/L) and reaches sorption coefficients that are comparable with the lowest competition. Due to many influence factors, which are also often interconnected (e.g., pH and sorbent surface charge), a single or a defined set of efficient parameters quantitatively describing the system of interest could not be identified yet. Moreover, none of the determined sorbent parameters (e.g., cation exchange capacity, point of zero charge, surface area, OH surface density) was a meaningful descriptor for the observed sorption.

Eventually, the obtained results demonstrate the high complexity of organic cation sorption but also provide deeper insight into relevant interactions and dependences, which are crucial for a proper environmental risk assessment. The current challenges lie in the further separation of the underlying sorption processes and in the identification of suitable system parameters. For this purpose, the experimental design is permanently optimized and additional probe compounds with desired molecular properties were selected and will be investigated for sorbents with different surface functionalities.

References:

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