SUPPORTING INFORMATION

Properties governing the transport of trace organic contaminants through ion-exchange membranes

Marjolein Vanoppen*[,a], Annelise F.A.M. Bakelants[a], Dorien Gaublomme[a], Klaas V.K.M. Schoutteten[a], Julie Vanden Bussche[b], Lynn Vanhaecke[b], Arne R.D. Verliefde[a]

[a] Particle and Interfacial Technology Group, Department of Applied Analytical and Physical Chemistry, Faculty of Bioscience Engineering, Ghent University, Ghent, Belgium
[b] Laboratory of Chemical Analysis, Department of Veterinary Public Health and Food Safety, Faculty of Veterinary Medicine, Ghent University, Merelbeke, Belgium
Corresponding author email: marjolein.vanoppen@ugent.be, tel. +32 (0)9 264 99 11

Number of pages: 11

Number of figures: 10

Number of tables: 0

Resistance measurement. The clamp has platinum electrodes fitted in each leg, with a surface area of 1 cm². A picture of the clamp is shown in Figure S1. When screwing both sides of the clamp together, the electrodes are exactly 1 cm apart. The electrodes were connected to a multimeter (LCR-3500, Monacor, Germany). The resistance was measured in AC mode by measuring the resistance of a 0.5M NaCl solution with and without a membrane placed between the electrodes. The membranes and resistance clamp were pre-equilibrated in the 0.5M NaCl bath at a constant temperature of 25°C for at least 30 minutes.

Figure S1. Picutre of the constructed resistance clamp showing the two legs and the electrodes

UHPLC-HR-Orbitrap™-MS analysis. Prior to the TOrC analyses, a sample clean-up was required to remove all salts. An internal standard mixture, consisting of metoprolol-d_7, atrazine-d_5, diuron-d_6, paracetamol-d_4, sulfamethoxazole $^{13}C_6$ and ketoprofen-d_3 was added to all samples to ensure proper quantification.

For desalination, an SPE procedure with Oasis HLB SPE cartridges (6cc, 200 mg of sorbent, Waters Corporation, Ireland) was employed. First, the cartridges were conditioned with 2 ml LC-MS grade methanol (VWR, Belgium) and equilibrated with 2 ml ultrapure water. Next, 16 ml of sample was diluted to 50 ml with ultrapure water and loaded onto the cartridge. After this, the cartridge was washed with two times 5 ml of ultrapure water for desalination and afterwards dried by a forced airflow. This volume was shown to be effective in removing all the salts from the adsorbent while avoiding any washing out of the adsorbed TOrCs. Finally, the TOrCs were eluted with two times 4 ml of LC-MS grade methanol, effectively doubling the concentrations in all eluted samples. To eliminate any possible effect of the sorbents, the standards used for the calibration curve underwent the same SPE treatment as the samples, which results in an automatic correction for any potential TOrC losses.

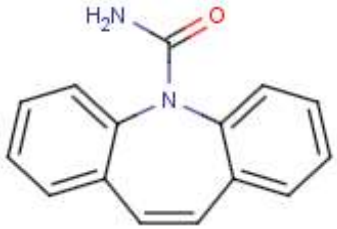
Furthermore, the internal standards added ensured a further correction in case of any alterations in the concentration. All of these steps ensured a reliable results was obtained after treatment and analysis, as shown for example by the correlation coefficient of the standard curves, which was > 0.99 for all elements.

The UHPLC-HR-Orbitrap™-MS was coupled to an Accela autosampler, maintained at 15°C, an Accela degasser and an Accela 1250 pump. The solvents (0.08% HCOOH in ultrapure water (A) and MeOH (B)) and samples were pumped over a Nucleodur C_{18} pyramid (100 mm x 2.1 mm, 1.8 µm) column (Machery-nagel, USA) at a temperature of 25°C. The flow rate was set to 300 µl/min and the injection volume was equal to 10 µl. For ensuring proper chromatographic separation, gradient elution was applied. The solvent gradient applied started with 1 minute 98% solvent A and 2% solvent B, then the fraction of solvent B was increased to 90% in 3.5 minutes. In the end, the fraction of solvent B was increased to 100% in 2 minutes. After separation of the mixture on the column, the compounds were ionized with an HESI-II (Heated ElectroSpray Ionization) interface, which measured in positive and negative scan mode. The spray voltage was set to 4000 V, the capillary temperature to 250°C and the capillary voltage to 82.50 V. The sheath gas flow rate was set to 30 arbitrary units and no auxiliary gas nor sweep gas was used. The tube lens voltage and skimmer voltages were set to 120 and 20 V respectively and the vaporizer heater temperature to 350°C. Detection was performed with an Orbitrap™ HRMS from Thermo Fisher Scientific (USA) that operated in a full scan range from 100.0-700.0 *m/z*, measuring all precursor ions with a maximum mass deviation of 5 ppm. A resolution of 50 000 was used, and the AGC target was set to $5E10^5$, with a maximum injection time of 500 ms. The in-source CID was disabled. Analysis of the UHPLC-HR-Oritrap™-MS output was performed with the Thermo Xcalibur 2.1.0.1140 software (Thermo-Scientific, USA).

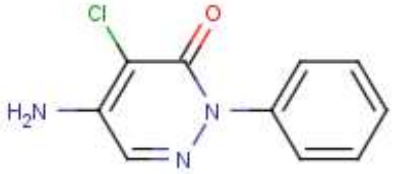
Chemical structure of the used TOrCs.

Atrazine

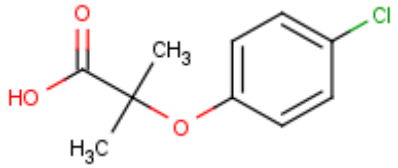
Carbamazepine



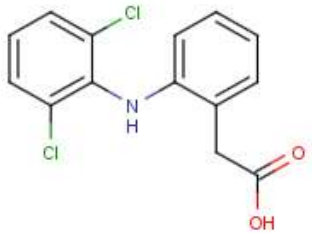
Chloridazon



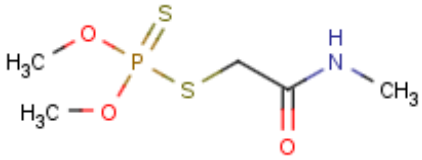
Clofibric acid



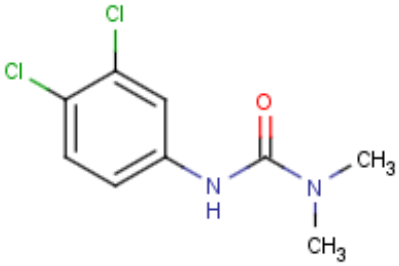
Diclofenac



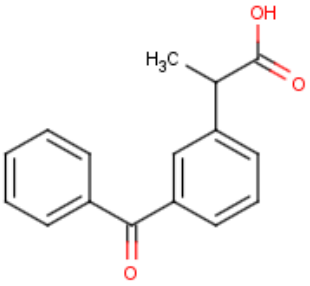
Dimethoate



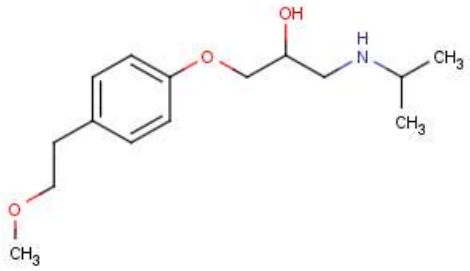
Diuron



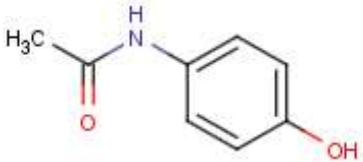
Ketoprofen



Metoprolol

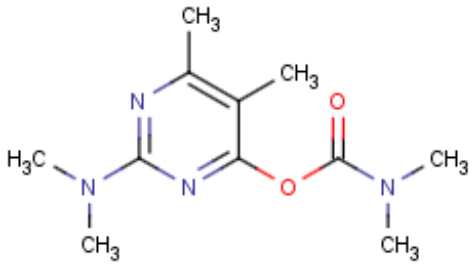


Paracetamol



Phenazone

Pirimicarb



Simazine **Sulfamethoxazole** **Theophylline** **Triclopyr**

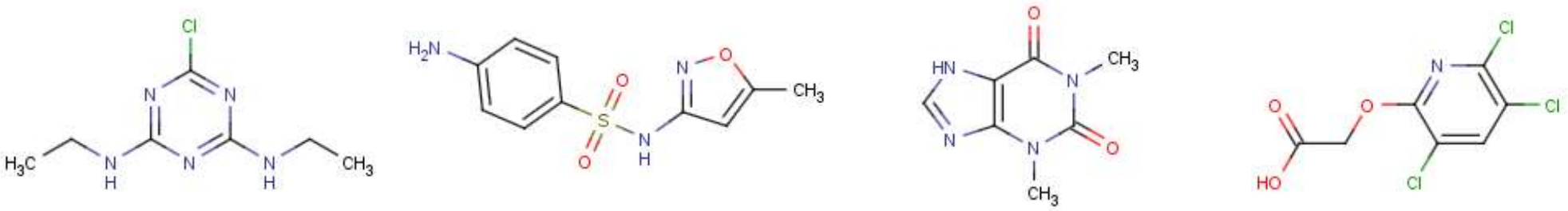


Figure S2. Chemical structure of the used TOrCs

Adsorption of TOrCs onto spacer material, stack and tubing.

The adsorption of TOrCs onto the ED-equipment was investigated by recirculating 5 litres of a 100 µg/l TOrC-solution with 100 g/l NaCl through the stack without membranes (but with spacers inside) for 24 hours. The total organic carbon (TOC) concentration was monitored as a substitute for the TOrC-concentration by a total organic carbon analyser (TOC-Vcpn, Shimadzu Benelux B.V., Belgium) as shown in Figure S3.

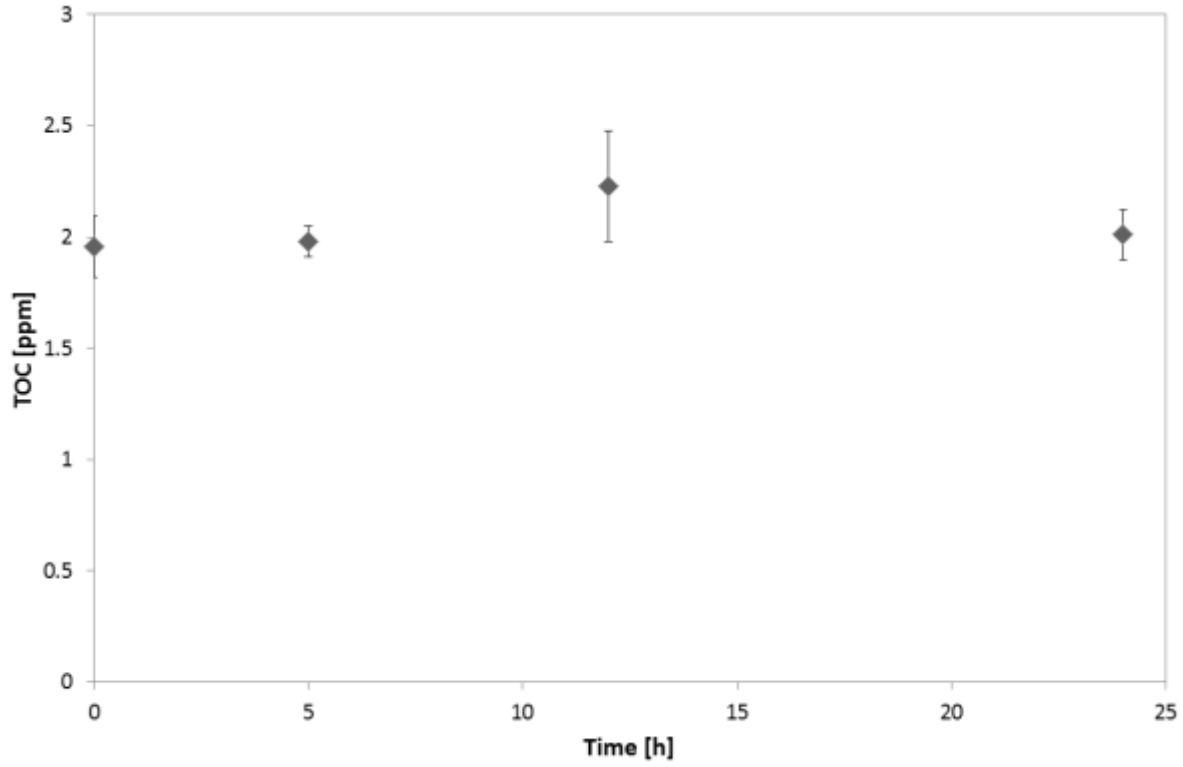


Figure S3. TOC concentration over time.

Adsorption of TOrCs onto the membranes during adsorption experiments

The equilibrium adsorption time for TOrCs onto the membranes was determined, to determine the flushing time needed before the ED experiments. By ensuring the saturation of the membranes with TOrCs prior to the ED experiments, underestimation of the transport at the beginning of the experiments is avoided. The results for all TOrCs during the three adsorption experiments with 100 g/l NaCl in both diluate and concentrate in the concentrate is shown in. Figure S4 and S5 clearly show

that adsorption equilibrium sets in at around 24-36 hours. In the absence of salt however, no equilibrium is reached after 48 hours, as shown in Figure S6.

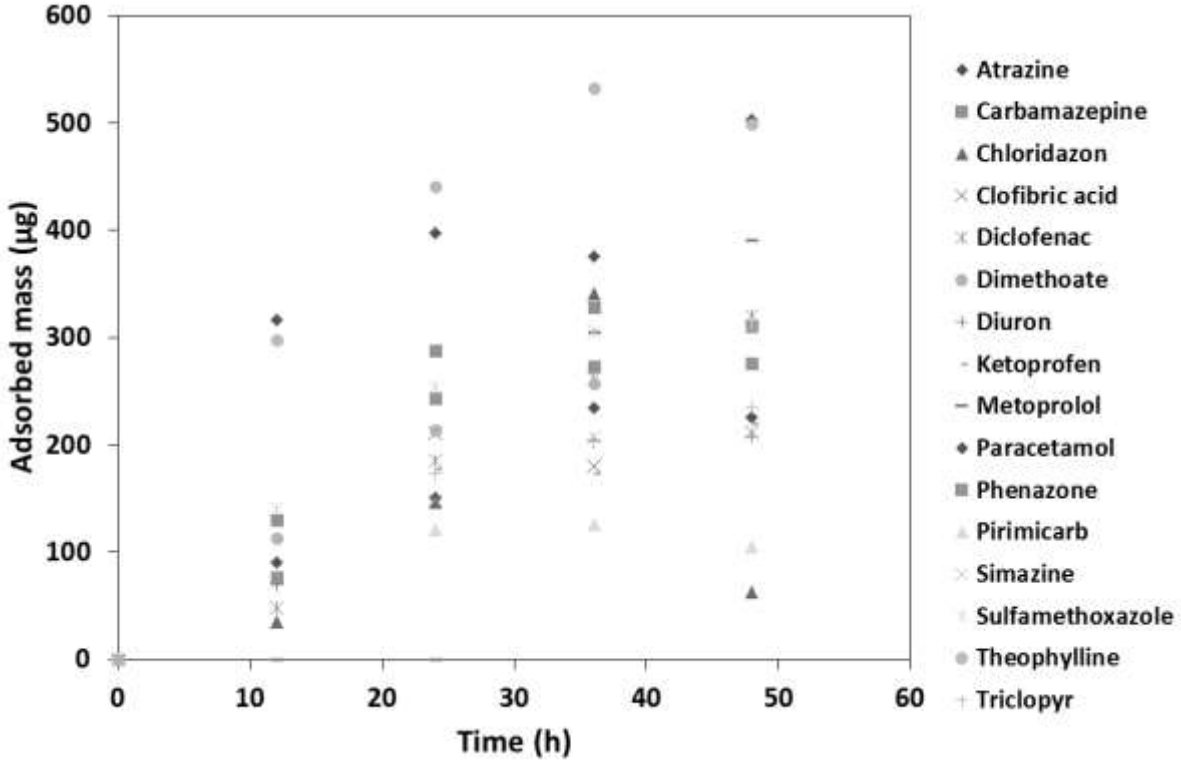


Figure S4. Diluate TOrC concentration over time for the 100 g/l NaCl + TOrCs|10 g/l NaCl diluate|concentrate diffusion experiment

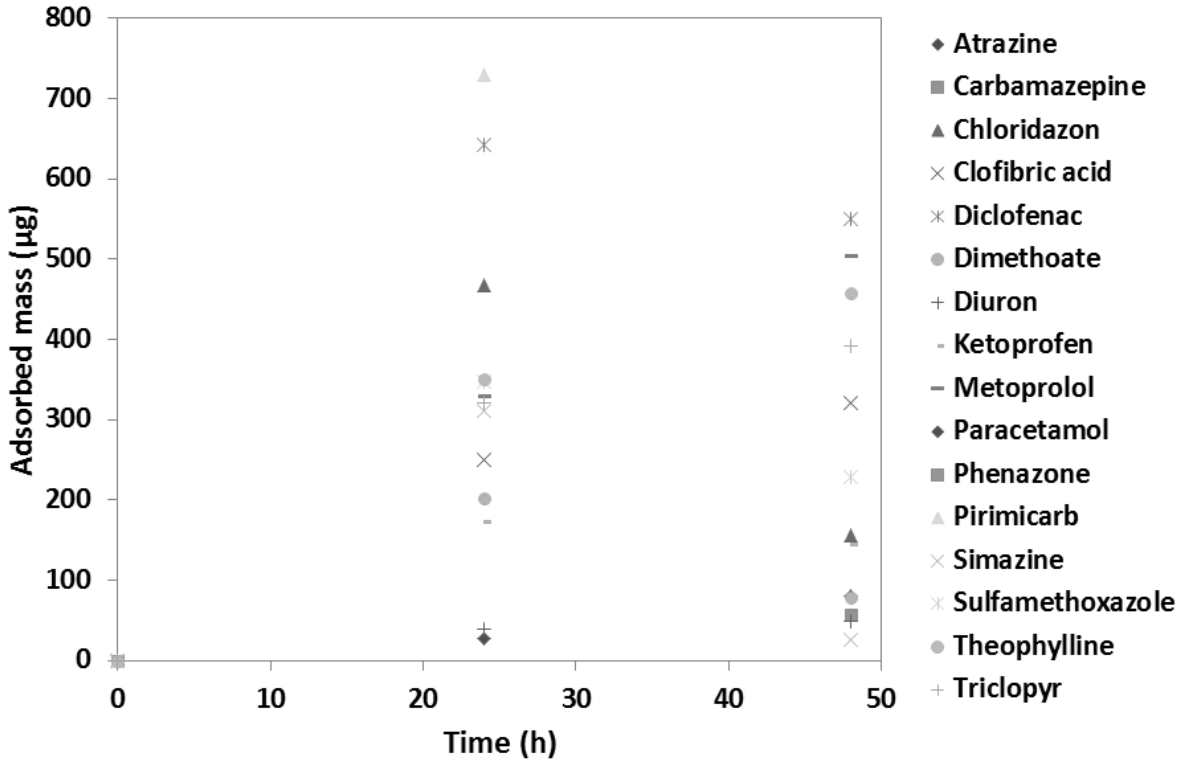


Figure S5. Diluate TOrC concentration over time for the 100 g/l NaCl + TOrCs|100 g/l NaCl diluate|concentrate diffusion experiment

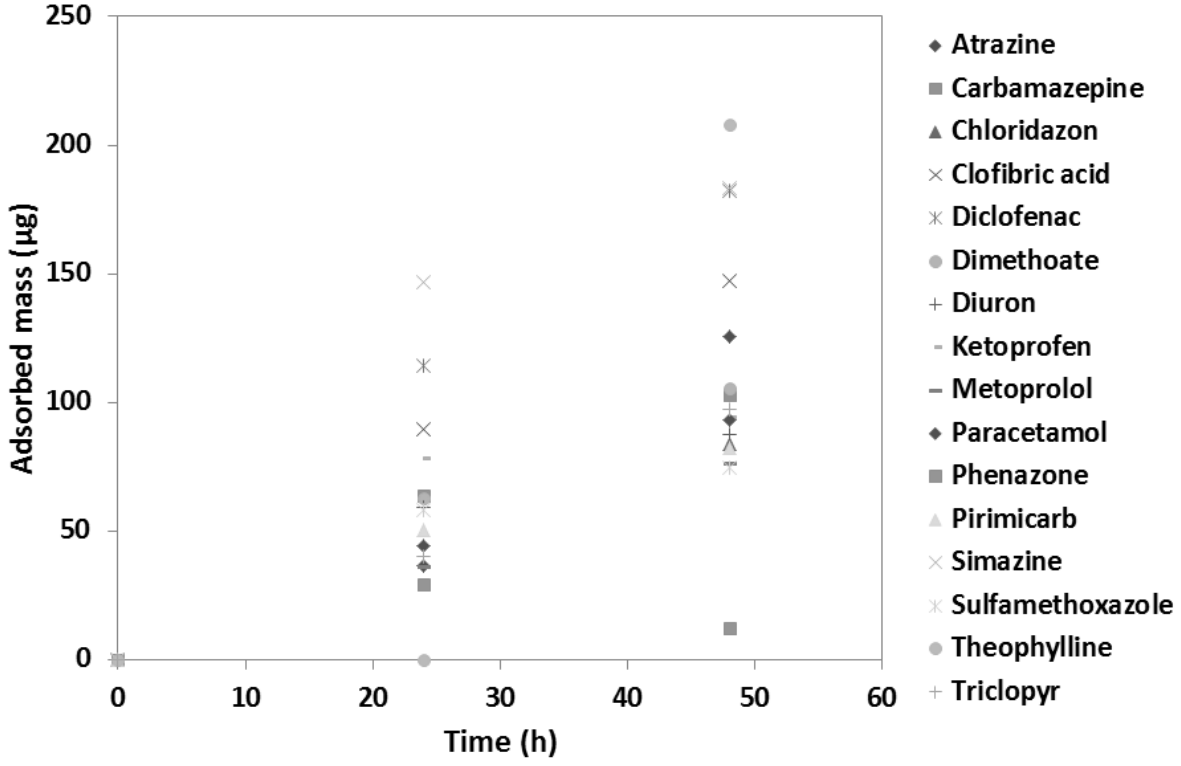


Figure S6. Diluate TOrC concentration over time for the 0 g/l NaCl + TOrCs|0 g/l NaCl diluate|concentrate diffusion experiment

Influence of salt concentration on TOrC diffusion coefficient.

The diffusion coefficient of atenolol was determined in the presence of different salt concentrations by PFG-NMR with a convection compensated double-stimulated-echo experiment[1] using monopolar smoothened square shaped gradient pulses and a modified phase cycle[2]. A detailed description of the PFG-NMR method and the sequences mentioned above is given by Johnson et al.[3] The measured diffusion coefficient shows a good correlation with the salt concentration (R^2 = 0.9978) as shown in Figure S7.

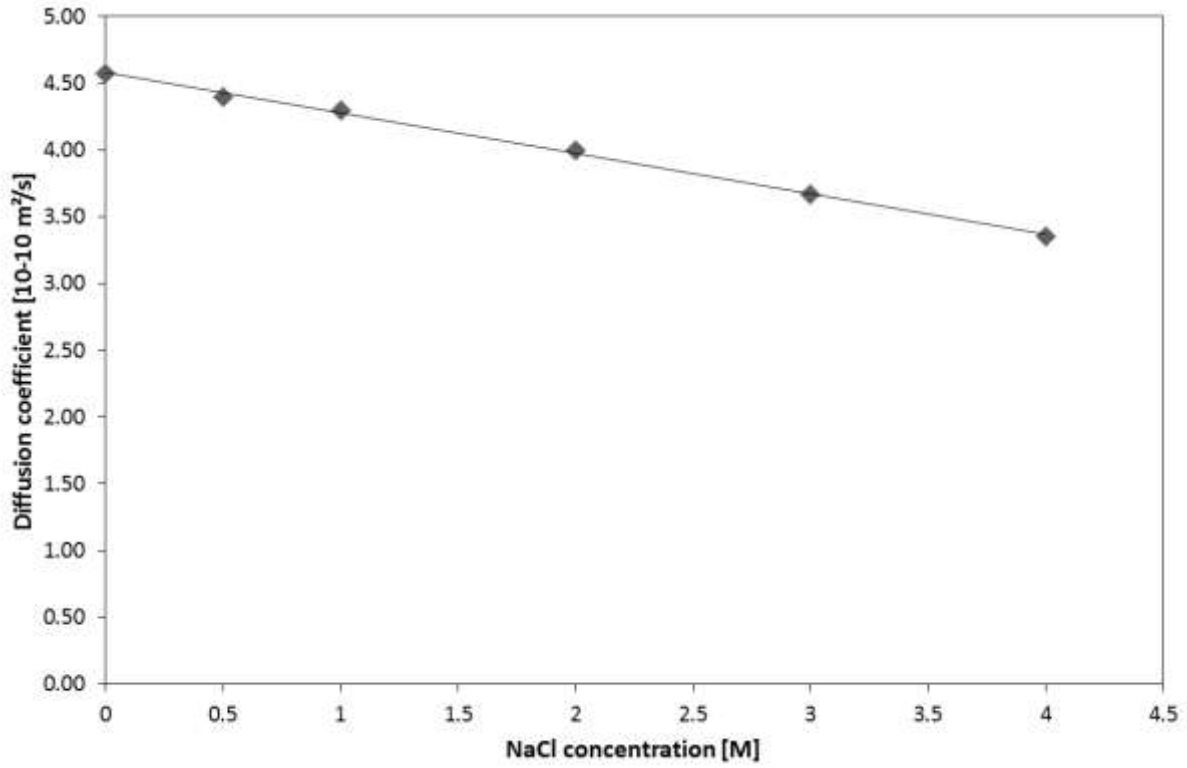


Figure S7. Diffusion coefficient of atenolol versus NaCl concentration

Course of the TOrC concentration over time in the electrodialysis experiments

In the figures below, the TOrC concentration over time for the three different ED experiments (100, 150 and 200 A/m²) is given. These show a linear transport when correlated to the desalination extent with an R^2 value of 0.94 ± 0.06.

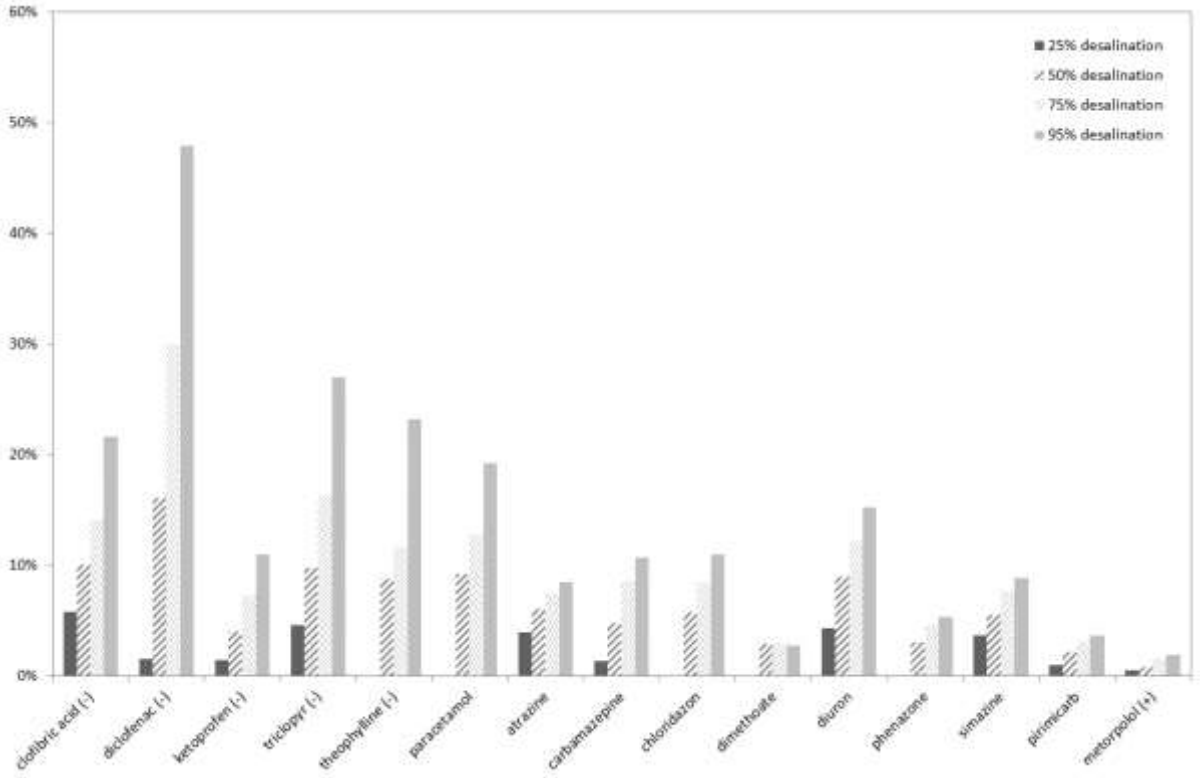


Figure S8. TOrC concentration at different desalination extents at 100 A/m². Based on quantitative analysis with a calibration curve with an $R^2 > 0.99$.

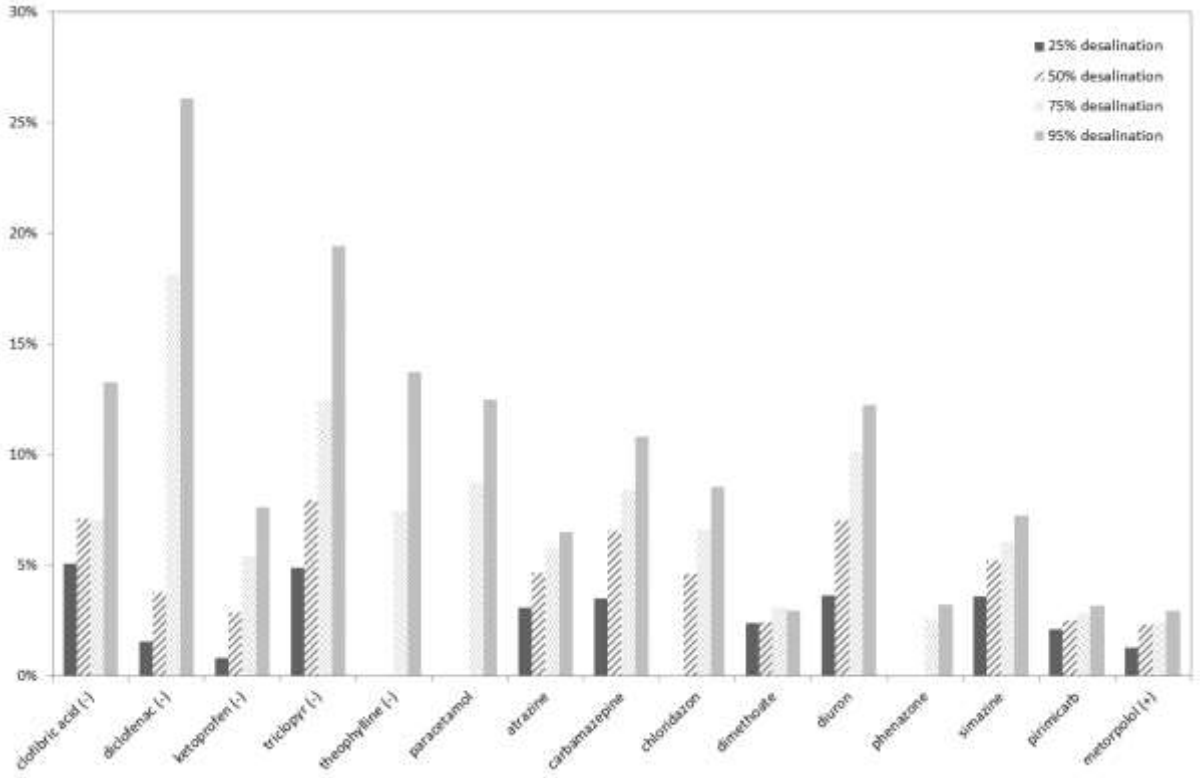


Figure S9. TOrC concentration at different desalination extents at 150 A/m². Based on quantitative analysis with a calibration curve with an $R^2 > 0.99$.

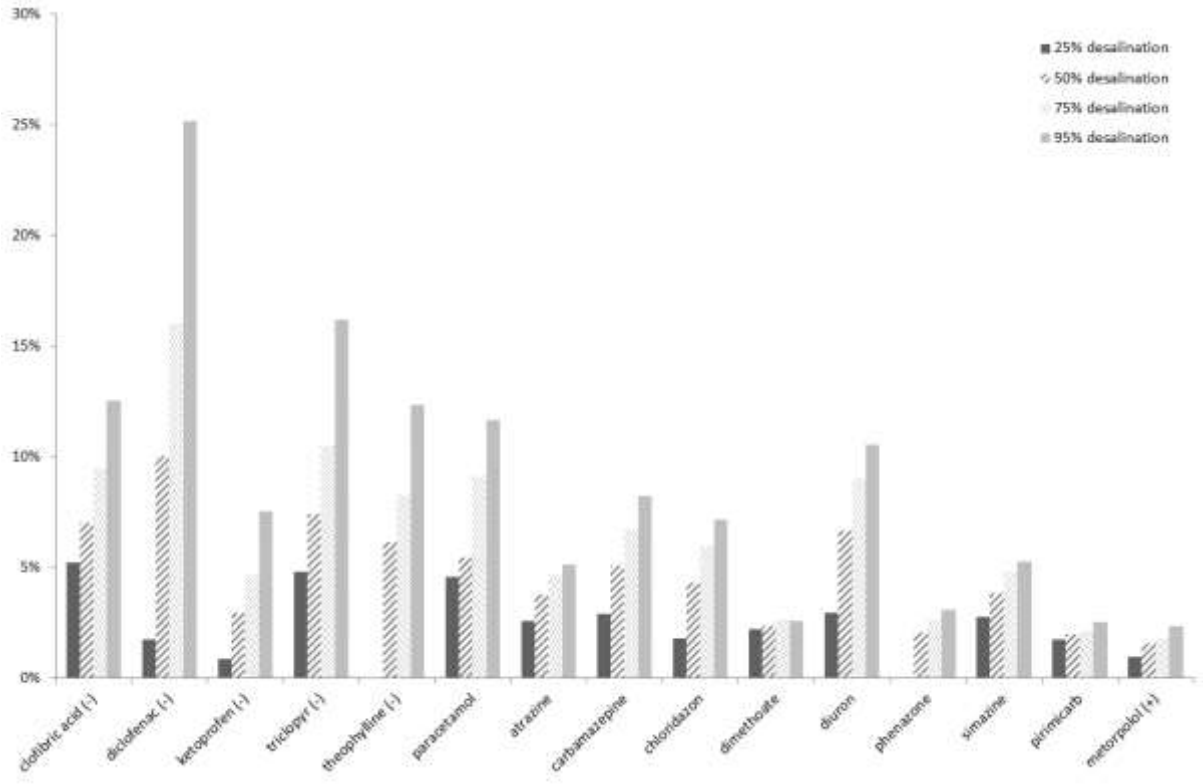


Figure S10. TOrC concentration at different desalination extents at 200 A/m². Based on quantitative analysis with a calibration curve with an $R^2 > 0.99$.

LITERATURE CITED

(1) Jerschow, A.; Müller, N. *J. Magn. Reson.* **1997**, *375*, 372–375.

(2) Connell, M. a; Bowyer, P. J.; Adam Bone, P.; Davis, A. L.; Swanson, A. G.; Nilsson, M.; Morris, G. a. *J. Magn. Reson.* **2009**, *198*, 121–131.

(3) Johnson Jr., C. S. *Prog. Nucl. Magn. Reson. Spectrosc.* **1999**, *34*, 203–256.