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## **Bioavailability of Cationic Surfactants**

### **Understanding bioavailability of cationic surfactants – [BCS]**

Cationic surfactants can strongly adsorb to natural particular and dissolved sorbents, which reduces the bioavailability of these chemicals to exposed organisms in contaminated environments. Solid-phase microextraction [SPME] was developed and validated to measure bioavailable concentrations, a soil sorption model was developed and validated to predict the adsorption affinity of organic cations to soil and soil components under variable medium conditions.

### **Project Description**

The BCS project, performed at the Institute for Risk Assessment Sciences [IRAS] at Utrecht University, was part of a larger project lead by the Helmholtz Centre for Environmental Research – UFZ, in Leipzig, funded by the European Oleochemicals & Allied Products Group (APAG) sector group of CEFIC. The project is directly complementary to the 2004-2008 ERASM PhD project “Bioavailability of surfactants in marine sediments”.

Whereas IRAS focused on a top-down approach, developing tools to measure and validate bioavailability of cationic surfactants, UFZ focused on a bottom-up approach, developing and validating sorption models for all kinds of environmentally relevant organic cations.

### **Setup**

The SPME-technique was optimized to work for quaternary ammonium compounds<sup>1</sup> and lauryldiethanolamine<sup>2</sup>. SPME was used to determine humic acid/water partition coefficients under different medium compositions<sup>3</sup>. SPME was applied to determine the freely dissolved concentrations in a variety of toxicity tests with a pure benzalkonium surfactant, in the presence and absence of different natural sorbents or protein enrichment<sup>4</sup>.

To define all relevant parameters that influence the sorption of organic cations to soil, a customized HPLC column technique was applied, with both reference soil components<sup>5-7</sup> and natural soils<sup>8</sup> as column packing material, to create a consistent high quality sorption data set for more than 50 different organic cation structures.

### **Results**

SPME was identified in the IRAS project as a simple technique to analyse the freely dissolved concentrations of cationic surfactants<sup>1,2</sup>, which opens up many possibilities to perform environmental studies more accurately. For C12-benzalkonium, the log  $K_{OC}$  ranged 5.6-6.8 depending on pH and salinity<sup>3</sup>. This high affinity significantly reduced freely dissolved, bioavailable concentrations of cationic surfactants in the presence of natural levels of dissolved organic matter, which reduced acute toxicity to daphnids<sup>4</sup> as experimentally determined. Also other eco-toxicity test assays and in *in-vitro* cytotoxicity assays with cultured fish gill cells in the presence of serum were

shown to be best related to bioavailable concentrations, rather than nominal or total dissolved concentrations<sup>4</sup>.

A soil sorption model for organic cations was developed based on two standard soil parameters -  $f_{OC}$  and CEC -, and sorption data on two reference soil components - Illite clay and Pahokee peat<sup>8</sup>. Sorption affinities to natural soils were predicted within a factor of  $\pm 3$ . A suite of empirical rules were defined to facilitate detailed predictions of soil sorption affinities for strongly ionized bases and quaternary ammonium compounds. These modelling results, and column experiment findings, corresponded closely to the batch sorption tests on cationic surfactants performed with SPME.

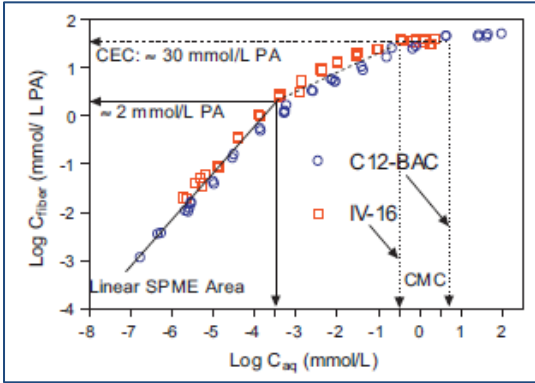
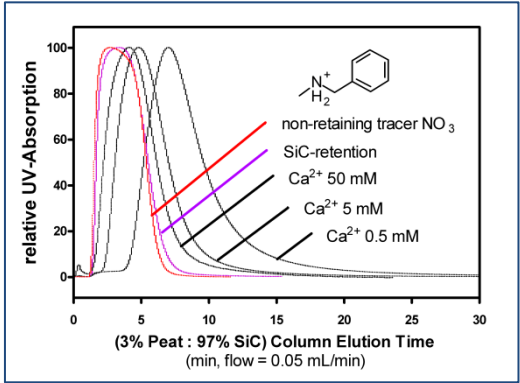
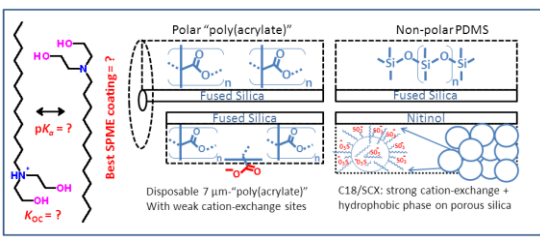
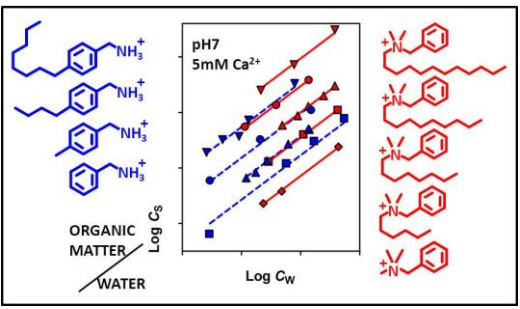
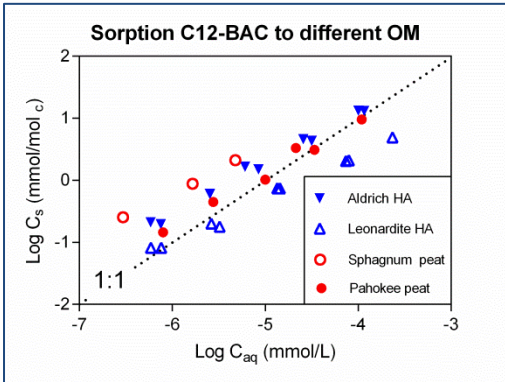
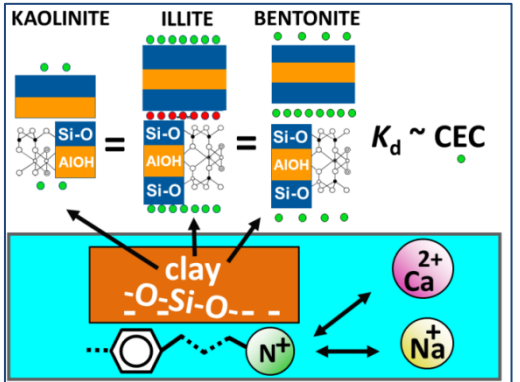
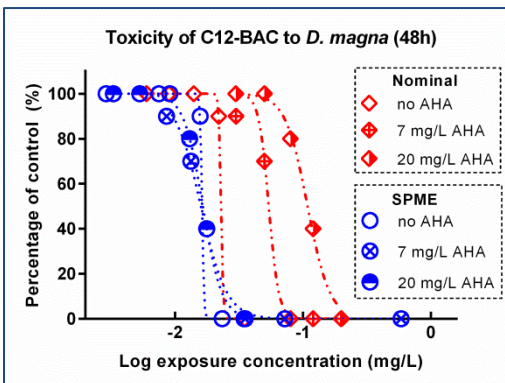
### Conclusions

The strong adsorptive properties of cationic surfactants are due to combined hydrophobic and electrostatic interactions, and may reduce the bioavailability of these compounds in natural systems compared to total concentrations in sample extracts. In soils, cationic surfactants are not only strongly adsorbed to organic matter, but also to clay minerals. This influences the derived  $K_{OC}$  value from batch sorption studies with natural soils, and may result in lower bioavailable concentrations in natural (or artificial) soils than calculated based on  $K_{OC}$  values derived with e.g. humic acid.

### References

1. Chen, Y.; Droge, S.T.J.; Hermens, J.L.M. Analyzing freely dissolved concentrations of cationic surfactant utilizing ion-exchange capability of polyacrylate coated solid-phase microextraction fibers. *J. Chromatogr. A* 2012, 1252, 15-22.
2. Wang, F.; Chen, Y.; Hermens, J.L.M.; Droge, S.T.J. Evaluation of passive samplers with neutral or ion-exchange polymer coatings to determine freely dissolved concentrations of the basic surfactant lauryl diethanolamine: Measurements of acid dissociation constant and organic carbon-water sorption coefficient. *Journal of Chromatography A* 2013, 1315, 8-14.
3. Chen, Y.; Hermens, J.L.M.; Droge, S.T.J. Influence of organic matter type and medium composition on the sorption affinity of C12-benzalkonium cation. *Environ. Pollut.* 2013, 179, 153-159.
4. Chen, Y.; Geurts, M.; Sjollema, S.B.; Kramer, N.I.; Hermens, J.L.M.; Droge, S.T.J. Acute toxicity of the cationic surfactant C12-benzalkonium in different bioassays: How test design affects bioavailability and effect concentrations. *Environ. Toxicol. Chem.* 2014, 33, 606-615.
5. Droge, S.T.J. and Goss, K.U. Sorption of organic cations to phyllosilicate clay minerals: CEC-normalization, salt dependency, and the role of electrostatic and hydrophobic effects. *Environ. Sci. Technol.* 2013, 47, 14224-14232.
6. Droge, S.T.J. and Goss, K.U. Effect of sodium and calcium cations on the ion-exchange affinity of organic cations for soil organic matter. *Environ. Sci. Technol.* 2012, 46, 5894-5901.
7. Droge, S.T.J. and Goss, K.U. Ion-exchange affinity of organic cations to natural organic matter: influence of amine type and nonionic interactions at two different pHs. *Environ. Sci. Technol.* 2013, 47, 798-806.
8. Droge, S.T.J. and Goss, K.U. Development and evaluation of a new sorption model for organic cations in soil: Contributions from organic matter and clay minerals. *Environ. Sci. Technol.* 2013, 47, 14233-14241.

## External publication links and visuals

IRAS/ERASM-BSC	UFZ/APAG-BSC
<p>ref 1. <a href="http://dx.doi.org/10.1016/j.chroma.2012.06.080">http://dx.doi.org/10.1016/j.chroma.2012.06.080</a></p> 	<p>ref 5. <a href="http://dx.doi.org/10.1021/es204449r">http://dx.doi.org/10.1021/es204449r</a></p> 
<p>ref 2. <a href="http://dx.doi.org/10.1016/j.chroma.2013.09.041">http://dx.doi.org/10.1016/j.chroma.2013.09.041</a></p> 	<p>ref 6. <a href="http://dx.doi.org/10.1021/es3033499">http://dx.doi.org/10.1021/es3033499</a></p> 
<p>ref 3. <a href="http://dx.doi.org/10.1016/j.envpol.2013.04.017">http://dx.doi.org/10.1016/j.envpol.2013.04.017</a></p> 	<p>ref 7. <a href="http://dx.doi.org/10.1021/es403187w">http://dx.doi.org/10.1021/es403187w</a></p> 
<p>ref 4. <a href="http://dx.doi.org/10.1002/etc.2465">http://dx.doi.org/10.1002/etc.2465</a></p> 	<p>ref 8. <a href="http://dx.doi.org/10.1021/es4031886">http://dx.doi.org/10.1021/es4031886</a></p> 