

## Microbial volatilization of inorganic selenium sorbed by goethite, LDH and ferroselite

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Modeling radionuclide mobility for long-term risk assessment is usually based on the use of the distribution coefficient  $K_d$  as a gross estimate of the distribution of an element between the solid and aqueous phases. The uranium fission product <sup>79</sup>Se (half-life  $3.8 \times 10^5$  years) released under near field conditions of nuclear waste repositories is predicted to be scavenged in the oxoanionic form of selenite with the cement mineral hydrotalcite (Se-LDH), in the more reduced selenide form with iron as ferroselite, FeSe<sub>2</sub>, or in the more oxidized form of selenate with the Fe-hydroxide goethite. These sorption and co-precipitation processes increase the  $K_d$  and are of benefit for long-term stabilization of <sup>79</sup>Se. We will show, however, that sulfate-reducing bacteria (SRB) including the common *Desulfovibrio gigas*, as well as mycobiota including the common *Alternaria alternata* microfungi genera, are capable to volatilize the Se in presence of these solid phases. In our experiments,  $10 \text{ g L}^{-1}$  suspensions of these solids were incubated with standardized nutrient broth. For sampling the head space of the culture flasks were gently purged with nitrogen into Tedlar bags. Volatile organic selenium (VOSe) species were determined by a cryotrapping cryofocussing gaschromatographic system coupled with ICP-MS detection (CT-CF-GC-ICP-MS). Alkylated species were found by daily sampling at the tens to hundreds ng m<sup>-3</sup> level above the suspension cultures dominated by the common dimethyl selenide (DMSe) and dimethyl diselenide (DMDSe), but also ethylated forms. Species concentrations found during the FeSe<sub>2</sub> incubation were by 1-2 orders of magnitude lower, and two more but yet unknown compounds with peaks at retention times in between those of DMSe (150s) and DESe (300s) were found to occur. Microbe mediated VOSe formation decreases the dissolved Se concentrations below adsorption equilibrium levels, and therefore increases the  $K_d$  values. However, this  $K_d$  increase is concurring with a fission product mobilization which may lead to a potential onsite evapoconcentration of <sup>79</sup>Se, ultimately constituting the build-up of a radioactive contamination and radiotoxicity threat if to occur in an enclosed repository cavern.

## Adsorption energetics and structure for monorhamnolipids from *Pseudomonas aeruginosa* ATCC 9027 on solid surfaces

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### Adsorption Energetics

The adsorption energetics for a mixture of monorhamnolipids (monoRL) harvested from *P.aeruginosa* ATCC 9027 on  $\gamma\text{-Al}_2\text{O}_3$  and SiO<sub>2</sub> have been investigated as a function of pH using attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy. Adsorption isotherms are fit to a Frumkin adsorption model to determine strength of adsorption and to quantify lateral interactions between adsorbates. Values of  $\Delta G_{\text{ads}}$  generally decrease as pH increases but indicate overall strong adsorption of monoRL with positive Frumkin interaction parameters indicating net cooperative interactions across the pH 4-8 range tested. Adsorption is believed to be driven by both hydrogen bonding and hydrophobic interactions between monoRL adsorbates and hydrogen bonding and/or coordinative bonding interactions between monoRL and the surface that are sufficiently strong so as to overcome repulsion between negatively-charged head groups and between negatively charged headgroups and negatively charged surfaces. Further quantification of monoRL adsorption coverage on  $\gamma\text{-Al}_2\text{O}_3$  suggests that true planar bilayers are formed at low pH but monolayers covered with hemicylinders are formed in solutions with pH values that exceed the monoRL pK<sub>a</sub>.

### Adsorption Structure

Atomic force microscopy studies of the adsorption of this monoRL mixture on highly oriented pyrolytic graphite (HOPG), a model hydrophobic surface, indicate formation of organized hemicylindrical assemblies in which hydrophobic interactions between monoRL and HOPG and hydrogen bonding and hydrophobic interactions between monoRLs dominate the interactions. Hemicylinder spacing increases as pH increases due to repulsive interactions. This surface organizational behavior has been observed previously with conventional synthetic surfactants but not with biosurfactants. Collectively, the strong adsorptive tendencies of monoRL on all solid surfaces studied to date imply significant alteration of the apparent physicochemical characteristics of these surfaces in aqueous monoRL environments.