Biosurfactant-mediated metal behavior in soil

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It has recently been discovered that microbial surfactants (biosurfactants) strongly complex metals which brings to the fore their potential for influencing metal behavior in soil. The extent to which metal mobilization/sequestration occurs will be a function of the sorption of the biosurfactant and its metal complexes to soils. It is known that synthetic surfactants sorb as organized aggregates with structures including hemimicelles or admicelles from surfactant solutions with concentrations above the CMC (critical micelle concentration). In other words, sorption is driven by hydrophobic interactions between the surfactant molecules and less so by the surfactant-soil surface interaction. The extent to which biosurfactants and their metal complexes mimic this behavior is yet to be understood.

In this presentation, we will discuss the metal and soil interactions of a model biosurfactant, rhamnolipid, which is produced by a widespread soil bacterium, *Pseudomonas aeruginosa*, in mixtures containing primarily two forms, mono- and dirhamnolipid. Experimentally determined monorhamnolipid-metal stability constants show selectivity of rhamnolipids for metals of concern as environmental contaminants (lead, cadmium) over metals commonly found in soil solution (calcium, magnesium). Further, rhamnolipid-metal stability constants are higher than those reported for other naturally-occurring metal complexation agents, e.g., soil-derived fulvic acid-metal stability constants. Monorhamnolipid sorption to various soil constituents in the absence of metals generally followed the order: hematite (Fe_2O_3) > kaolinite > MnO_2 ≧illite ≧Ca-montmorillonite > gibbsite ($Al(OH)_3$) > humic acid-coated silica. Sorption of the monorhamnolipid form alone was found to be much higher than its sorption in a mixture containing both mono- and dirhamnolipid. Preliminary experiments using atomic force microscopy to examine the interaction of monorhamolipid with a graphite surface shows the presence of ordered surfactant aggregrates. These data will be used to develop a conceptual model of biosurfactant interactions with metals in the soil environment.

Climate change in the Black Sea region through Termination I from Sr and O isotopes

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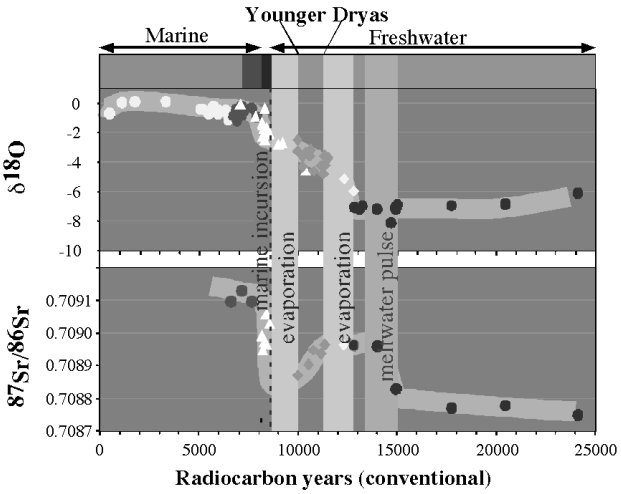
The Black Sea was an isolated, fresh to brackish water body when sea level was below the Bosporus sill. We have measured Sr and O isotopes in mollusk shell carbonate in order to investigate changes in Black Sea water composition from ~25 ka BP to the present. These changes are linked to the water balance and also are strongly influenced by the input of marine water since 8,360 y BP.

The marine input is marked by an abrupt rise in $^{87}Sr/^{86}Sr$ toward modern seawater. This also corresponds to a shift in the $\delta^{18}O$ and the appearance of brackish water mollusk fauna. Earlier variations must reflect changes in freshwater input to the basin (Sr) or evaporation (O). The Younger Dryas is seen as a shift back toward the glacial $^{87}Sr/^{86}Sr$ values, implying increased river input during this time. While melting of large ice-sheets within the Black Sea drainage could account for earlier (>14 ka) increases in freshwater delivery, the change during the Younger Dryas must either reflect an increase in precipitation or a drastic change in the drainage basin configuration.



The changes in river input inferred from the isotope records have important implications for the water balance and seasonality of moisture delivery to eastern Europe and Russia during the deglaciation interval, and for the delivery of freshwater to downstream basins (Marmara, Aegean, and Mediterranean seas). New data from the Sea of Marmara, which lies just downstream from the Black Sea on the other side of the Bosporus Strait, will test models of Black Sea outflow during this period.