A HPSEC-ICP-MS study on the affinity of trace elements (Fe, Cu, I) to dissolved organic matter in natural water samples

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The speciation of trace elements in natural waters strongly influences their mobility and geochemical behavior in the environment. Especially, the presence of dissolved organic matter (DOM) in soil and peat runoff may favor complexation of certain metals, thereby increasing the solubility. Earlier studies were focused on the concept of metal binding to organic molecules which were thought to be of considerable size (some ten to hundred thousand Da in molecular weight). The existence of large organic substances, however, has recently been challenged. It was proposed, on the basis of several different studies, that DOM may consist of much smaller molecules, probably in the size fraction of only a few hundred to thousand Da. This raises the question if these smaller fractions can be separated by analytical techniques thereby enabling a study of the metal-binding capacity of 'small' DOM.

To resolve this question we used inductively coupled plasma mass spectrometry hyphenated with gel filtration liquid chromatography. The size exclusion column used was selected to efficiently separate substances with relatively low ionic radii thus resolving predominantly smaller fractions of DOM. Samples were river waters taken from remotes sites in Patagonia, Chile as well as from the Harz mountain region, Northern Germany. All samples were filtered with 0.45 μm. Samples were initially measured in their original composition. The influence of pH was studied via the addition of nitric acid.

We found remarkable differences between the investigated metals with up to four different peaks in the chromatograms suggesting that a number of colloids/complexes of different size exist which can be separated. While some elements occurred exclusively in one or two fractions (Fe) others occur in all fractions (I, Cu) suggesting a rather non-specific binding. The addition of protons yielded the expected shift from larger to smaller fractions, possibly because metals desorb from the binding sites on the DOM or colloids/particles dissolve.

Further investigations aim to exploit the characteristic size distributions observed to create fingerprints of natural waters that help to understand the environmental distribution and cycling of these trace metals.

Microbially mediated iron reduction in the methanic zone of sediments from the Western Argentine Basin

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Variable depositional conditions in marine sediments can have a strong impact on the associated biogeochemical cycles. In areas with high sedimentation rates, including mass transport-related deposition, (highly-) reactive mineral phases can be buried rapidly. This situation leads to the availability of reactive compounds for microorganisms in deep-subsurface anoxic environments. To unravel the influence of dynamic depositional conditions on biogeochemical processes in rapidly deposited sediments we applied inorganic and organic geochemical analyses and microbiological methods on marine sediments from the western Argentine Basin collected during the RV Meteor Expedition M78/3 (May-July) 2009. Our results show that the sediments are characterized by high concentrations of highly reactive iron phases accompanied by low amounts of organic carbon throughout the sediment column. Pore water accumulations of hydrogen sulfide are restricted to a small interval at the sulfate-methane transition zone. Below this zone, methane concentrations increase strongly with depth in association with appreciable availability of highly reactive Fe (III) phases. Elevated iron concentrations in the pore water in the same depth interval indicate ongoing iron reduction. Based on preliminary results we suggest that contributions from organo-clastic Fe reduction in these sulfide-depleted sediments can be neglected. Instead, because of the abundance of methane and reactive ferric Fe in the absence of sulfide, we propose that reduction of biologically available Fe phases in the methanic zone is coupled to methanogens via hydrogen or to anaerobic oxidation of methane.