[OP 1.10

In-situ and High Spatial Resolution Measurement of Trace Metals Concentration Profiles in Sediment Pore Waters with Diffusive Gradients in Thin-Films (DGT) and LA-ICP-MS

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The sediment-water interface is chemically and microbially the most active site in natural waters, with steep gradients in physical, chemical and biological properties. Biogenic, authigenic and mineral particles which settle at the sediment surface accumulate to relatively high concentrations and, compared to their time in the water column, have a long residence time in which to react. The microbially mediated oxidation of natural organic carbon and the subsequent reduction of electron acceptors such as O_2, NO_3^-, Mn(IV), Fe(III) and SO_4^{2-} results in sharp gradients of pH, redox potential and ionic composition across the interface. Trace metals may be liberated directly from the decomposing organic material or from associated reactions such as the reduction of oxyhydroxides. Understanding of trace metal remobilization in lakes and calculating fluxes to and from sediments, requires precise and simultaneous measurements of concentration gradients in pore waters together with key-parameters (oxygen, redox potential etc.).

The novel technique of diffusive gradients in thin-films (DGT) uses a credit card size probe inserted into the sediment. Metal ions bind to a chelating resin after diffusion through a layer of polyacrylamide hydrogel (1). This device allows minimum disturbance of the sampled medium. DGT probes has proved to determine concentration-depth profiles of metals in surface sediment with fine scale features (2). However when using conventional methods for trace elements analysis based on spectrochemical techniques, the spatial resolution was limited to the millimeter scale as it is necessary to slice the gel and then back-elute it. Alternatively, beam techniques can be used for the direct micro and profile analysis of the DGT devices. High spatially resolved profiles could be obtained with Proton Induced X-Ray Spectrometry but for major and minor elements only (3). In fact solid state analytical methods often lack the sensitivity to perform trace elements analysis and are not adequate for measurement of DGT deployed in pristine environments.

Recent hyphenated techniques with sensitive spectrochemical methods are challenging tools for solid state spectrometry. Laser ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) has the unique potential for multi-elementary analysis at trace levels but also to perform micro-analysis down to a few microns (4). The aim of this study was, therefore, to exploit this new technology together with DGT to determine in-situ ultra-high resolution (100 µm) vertical profiles of trace metals at the sediment-water interface of lakes. DGT devices were deployed in sediments cores taken from a seasonal anoxic lake. LA-ICP-MS was then used to analyze the resin but also the diffusive gel layers of the DGT. Both fluxes to the resin and concentration in pore waters could be therefore calculated. Multi-elementary profiles for trace metals together with Fe, Mn and S(-II) could then be established and used to provide mechanistic information about the remobilization processes of metals at the water-sediment interface.

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