Abstract

Sediments are a highly dynamic compartment of the aquatic system. Contaminants such as trace metals, which can accumulate in sediments, are, therefore, not necessarily isolated from the aquatic system, but may be solubilized and can diffuse back to the water column. Numerous biogeochemical transformations take place at and below the sediment water interface (SWI) changing the distribution of trace metals between solid and liquid phases. In this study, suitable sampling tools, Diffusive Equilibrium in Thin Films (DET) and Diffusive Gradients in Thin Films (DGT) are used to assess high resolution profiles of trace metals, respecting the initial in situ conditions in aquatic sediments (riverine and marine sediments).

In order to validate the DET and DGT techniques, intra- (VUB) and inter-laboratory (VUB and USTL) comparisons were carried out. For the intra-laboratory comparison, two couples of DET and DGT probes arranged back to back were inserted into two sediment cores, taken close to each other. DET (Fe, Mn, Co and As) as well as many DGT trace metal profiles were very similar in magnitude and shape. For the inter-laboratory comparison, a similar procedure was adopted. Again a good agreement between the metal profiles obtained by VUB and USTL with the DET and also the DGT samplers was observed.

In riverine sediments of Spierre, Helkijn and Wervik (Belgium), trace metal behavior has been studied during early diagenesis. Furthermore, sulfidization processes have been examined; they revealed a production of pyrite near the water-sediment interface at Helkijn and Wervik sampling sites, probably due to a partial re-oxidation of reduced sulphur species. In Spierre sediments, where Eh values are the most negative, pyrite production should be mainly due to strict anaerobic processes. Values of Cd, Cu and Pb DGT concentrations remain low in pore waters whatever the site, due to their strong affinity with the reduced sulphur pool. It has also been demonstrated that the labile fractions of Pb and Cd are the lowest and do not exceed 0.5, while Co and Ni are the most available metals. In marine sediments of Belgian coastal station 130, trace metal profiles were assessed by DET and DGT techniques as well as sulphide by DGT. Most trace elements show subsurface maxima and low concentrations beneath 8 cm of depth. The main physicochemical parameters controlling the vertical concentration profiles are dissolved oxygen and redox potential in the surface sediment and sulfide in the deeper sediment layers. Thermodynamic equilibrium calculations have been carried out verifying which solid phases can explain the dissolved trace metal concentrations. Seasonal variations of trace elements have been observed during the sampling period and sedimentation of fresh particulate organic matter (POM) derived from phytoplankton blooms appear to be the main cause of this temporal variability.

In Flanders, manufacturers of phosphate fertilizers increased the natural radioactivity levels in 2 small rivers, the Laak and Winterbeek, as well as surrounding flooding zones (hundreds of hectares). Typical concentrations of $^{226}$Ra found in the soils of the flooding zones around the Winterbeek in
Flanders amount to 2,000 Bq per kg or 0.055 ng $^{226}$Ra g$^{-1}$. This implies that a large fraction of the discharged $^{226}$Ra in the Winterbeek ends up in the sediments. Unfortunately, little is known about the mobility of the $^{226}$Ra stored in those sediments. A DGT probe containing a functional resin will satisfy two conditions: it allows high resolution profiles and preconcentration. Besides the classical resin-chelex 100, three other resins Ln, Actinide and MnO$_2$ resin gel were selected to test Ra$^{226}$ in water column and sediments in the Winterbeek (Belgium). A DGT probe containing MnO$_2$ resin appeared to be the best choice to capture Ra$^{226}$ comparing to the three other ones. The exchange flux of Ra$^{226}$ between sediments and overlying water was then assessed via Fick’s law, using the DGT concentration gradients and an appropriate diffusion coefficient.