[OP 1.2]

Metal Speciation in Natural Waters – Measurements and Modelling

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Providing the complete quantitative description of the chemical species present in natural waters has been a major goal for many environmental chemists for decades. Geochemists need speciation information to understand mineral formation and dissolution processes and the role of solution speciation in biological uptake is a preoccupation of both biologists and regulators concerned with environmental risk. A simple procedure that can provide an accurate description of the solution speciation is required. The new technique of diffusive gradients in thin-films (DGT) (Davison and Zhang, 1994; Zhang and Davison, 1995) has been developed to fulfil this requirement.
The DGT technique is based on a simple device (Figure 1) which accumulates solutes on a binding agent after passing through a well defined diffusion layer of hydrogel. It relies on the establishment of a steady-state concentration gradient from solution to the binding agent. For measurement of trace metal species, a layer of gel impregnated with Chelex-100 resin was used. It was separated from the solution by an ion-permeable hydrogel of thickness Δg as shown in Figure 2. Concentration in bulk solution (C_b) can be calculated from the mass of metal (M) accumulated in the resin layer after a known deployment time (t) using Fick's first law of diffusion:

$$C_b = M \bullet \Delta g / (D \cdot A \cdot t)$$

Where D is the diffusion coefficient of metal ion in the gel (Zhang and Davison 1999) and A is the exposure area of the DGT device. The mass of metal ions accumulated in the resin layer can be measured using atomic absorption spectroscopy (AAS) or ICP-MS after acid elution.
Speciation capabilities of DGT are demonstrated in two ways: (1) lability distinctions and (2) size discrimination between inorganic and organic species. The resin is assumed to bind exclusively with the free metal ion so that measurement of a metal complex, ML, only occurs if it can dissociate during the time that it passes through the diffusive gel layer. Another discriminator is the pore size of the diffusive gel layer which can be varied by changing the gel composition. In this way DGT can be use to distinguish between small and large species, which we have ascribed to inorganic and organic species present in natural waters. This operational definition is based on their mobility, calibrated by simple inorganic solutions or by fulvic or humic acids. Only labile species are measured, which is appropriate for speciation calculations based on equilibrium models.
DGT devices were deployed in situ in an organic rich stream water. The concentrations of labile inorganic and organic species were obtained from the mass of metal accumulated on each device. The speciation model WHAM was also used to predict the labile inorganic and organic concentrations for the same water. The comparison between DGT measurements and modelling has demonstrated the difficulties of using speciation models to obtain accurate speciation prediction. For example, DGT in situ measurements of Cu show that there were 0.75 $\mu g\ l^{-1}$ labile inorganic and 1.20 $\mu g\ l^{-1}$ labile organic species in the stream water. The speciation model WHAM predicted labile inorganic Cu concentration of from 0.08 to 1.6 $\mu g\ l^{-1}$ depending on (1) whether Fe^{3+} data was included in the input parameters, (2) how much DOC was assumed to be humic material and (3) the ratio of humic acid to fulvic acid.
Like other speciation techniques, DGT can not measure all individual species, so reliance has to be placed on measuring single or sets of species and using calculations to estimate the remaining species. The DGT measurement is appropriate for speciation calculations based on equilibrium models as it only measures labile species. The measured total labile inorganic species can therefore be used as an input parameter, along with major ions and cations, in a speciation program, allowing the calculation of the concentration of all species. The free ion activities of metal ions measured using DGT with an appropriate speciation calculation are compared with independent measurements using adsorptive cathodic stripping voltammetry. The implications of these results are then discussed.
Other advantages of DGT have made it an unique speciation tool for natural waters. DGT can measure a suite of up to 10 trace metals simultaneously and it can be deployed in situ in natural waters. Moreover, it is simple, robust, easy to use and can be used in diverse matrixes without any special precautions. It therefore provides a breakthrough in the routine quantification of labile species and free ion activities for both regulatory monitoring and studies of biological uptake.

Reference

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