

Physico-chemical and structural controls on copper isotope fractionation during its sorption by benthic algae and a phototrophic biofilm

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The interaction of one of the most phyto-toxic but also essential metals, copper, with different phototrophic microorganisms as a function of exposure time was studied via physico-chemical characterization of metal adsorption and incorporation into cells under controlled laboratory conditions. The novelty of the present study is to combine two different approaches, the “macroscopic” stable-isotope techniques with the “microscopic” molecular-level observations using X-ray absorption spectroscopy (XAS) of the complexes formed on the surface and inside the cells. The isotopic study included batch and flow-through experiments which allowed to distinguish among assimilation, excretion and adsorption processes within the mature biofilm dominated by cyanobacteria. Moreover, relationships between the fractionation of Cu stable isotopes and the biofilm growth cycle in a Taylor Couette flow-through reactor was quantified. To investigate the local atomic environment of Cu in periphytic biofilms and benthic algae, freeze-dried samples with 1 to 5000 ppm Cu were examined by XAS at beamline ID26 (ESRF). The high-resolution mode, for the first time used for Cu in biological matrices, allowed establishing specific features of the Cu pre-edge and quantifying the oxidation state, the nature and the number of neighbours around Cu. Results show that the degree of isotope fractionation depends on the metal concentration in the biomass, the degree of Cu reduction and the structural environment of Cu. For instance, heavy Cu isotopes are preferentially adsorbed on the surface whereas the intracellular incorporation favours light Cu isotopes. These trends may be linked to the drastic changes in the local chemical environment of copper occurred upon its adsorption onto or incorporation in the cells, similarly to Zn and Cd [1-3]. However, in contrast to other heavy metals, Cu undergoes Cu(II) to Cu(I) reduction during its uptake by our biomodels. Thus, low-concentrated samples (1-20 ppm), demonstrate the presence of sulfur in the nearest atomic shell of Cu(I), whereas in concentrated samples, the carboxylic complexes of Cu(II) predominate. These findings help to establish the interaction mechanism of autotrophic photosynthetic microorganisms with copper both at trace and toxic level of metal concentration. The results of this integrated study can be useful for tracing the environmental effects of copper - biofilm interactions, and allow to identify the factors exerting the direct control on the mechanisms of Cu stable isotope fractionation in biological systems.

[1] Guiné *et al.* (2006) *Environ. Sci. Technol.* **40**, 1806-1813. [2] Pokrovsky *et al.* (2005) *Environ. Sci. Technol.* **39**, 4490-4498. [3] Pokrovsky *et al.* (2008) *Geochim. Cosmochim. Acta* **72**, 1742-1757.

Arsenic sequestration during early diagenetic sulfur redistribution

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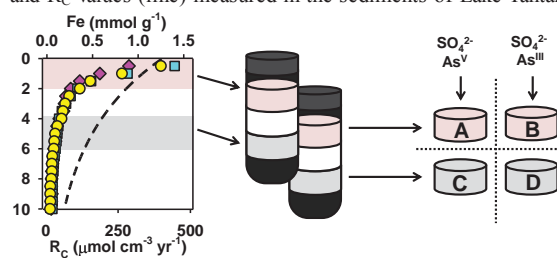
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Despite accumulating evidence that thiolated arsenic (As) species play a major role As cycling, the pathways leading to the formation of these elusive species in freshwater environments, as well as their sorption affinity in redox-active sediments, remain poorly studied. We used flow-through reactors (FTRs) to look at the fate of As species during the degradation of sedimentary organic carbon (C_{org}) and iron (Fe) oxyhydroxides under sulfate (SO_4^{2-}) reducing conditions. Sediment samples from Lake Tantaré, a well studied oligotrophic lake whose surface sediments are supplied with both labile C_{org} (C_{org} oxidation rates, R_c , up to $400 \mu\text{mol cm}^{-3} \text{yr}^{-1}$) and reactive ferric Fe ($Fe \geq 1 \text{ mmol g}^{-1}$), were incubated for 8 weeks in reactors supplied with SO_4^{2-} and soluble As (Fig. 1). Lactate was added to the inflowing solutions after depletion of the labile sedimentary C_{org} pool, which occurred after 21 days. As and sulfur (S) solid phase speciation was investigated using X-ray absorption spectroscopy (XAS), and aqueous speciation using a combination of ion chromatography, voltammetry, spectro-photometry.

Figure 1. Sample selection based on the Fe (symbols, triplicate) and R_c values (line) measured in the sediments of Lake Tantaré [1].



Aqueous S speciation throughout the experiment was dominated by (poly)sulfides, while As speciation was dominated first by arsenite and then, in FTR A (Figure 1), by mono-thioarsenate. The availability of labile C_{org} exerted the following dual control on the fate of S during the incubations: i) higher SO_4^{2-} reduction rates were observed in FTRs A-B than in FTRs C-D, and ii) evolving sulfides were sequestered as organic-S^{-II} in FTRs A-B and as FeS_2 and $\alpha S_{8(s)}$ in FTRs C-D. Similarly, As removal proceeded through either realgar (FTR A-B) or orpiment (FTR C-D) formation, confirming the key influence of free S^{-II} on the mechanisms of As sequestration [2]. XAS data also show that solid-phase tetra-thioarsenate was present, probably as a sorbed complex, representing up to 35% of total As in FTR C. While current geochemical models are able to reasonably predict As speciation in the aqueous phase, they fail to predict the prevalent form of As in the solid phase.

[1] Couture *et al.* (2010) *ES&T* **44**, 197-203.

[2] O'Day *et al.* (2004) *PNAS* **101**, 13703-13708.