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Copper (Cu) and zinc (Zn) isotope fractionation during their interaction with phototrophic biofilm

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The understanding of the mechanisms that control the transfer of trace metals (TM) in natural waters is essential due to their potential toxicity for the environment and for humans. In geochemistry, the study of the interactions between TM and aquatic microorganisms is limited essentially by the characterisation of surface's interactions for short exposure time and for uptake experiments for selected monospecific groups of algae and bacteria. The originality of our work is to combine stable isotopic approach with biological characterisation of monospecific or complex natural biofilms during long incubation times in order to allow for the integration of an ecological dimension. Our specific aim is to study the stable isotopic fractionation of copper (Cu) and zinc (Zn) during their interaction with river phototrophic biofilm. The choice of two important transition metals is dictated, first, by their essential role in the lifecycle of aquatic microorganisms and, second, by the difference in their solution structure and the need versus toxicity for live cells. Two biological models are selected: a biofilm of microcosm composed essentially by cyanobacteria belonging of the genus *Leptolyngbia sp* and a monospecific non-axenic biofilm composed of cyanobacteria *Phormidium automnale.*

The experiment was conducted by exposing the biofilm biomass to different Cu or Zn concentrations (incubation time of 96 hrs, temperature of 18 $\pm$ 1°C, pH of 6.5 to 8.5, total concentration of TM = 3.10^{-3} to $1.6.10^{-1}$ mmol/L, and fresh biomass concentration of 10 to 16 g_{humid}/L). Copper and zinc stable isotopic ratios were measured using Neptune multicollector ICP-MS for the samples of solution and for acid-digested biomass sampled during different exposure time (t_0, 1 hr, 48 hrs and 96 hrs). Moreover, eco-toxicity of Cu and Zn at their total concentration from 0.5 to 1.57 mmol/L was studied for the planktonic form of *P. automnale.*

Upon exposure of metal-bearing solution to the live biofilm, there is an abrupt decrease of metal concentration followed by a slower uptake/efflux phenomenon, depending on solution conditions and metal concentration level. Generally similar pattern of TM isotopic fractionation is observed in both biofilm models. For Zn, the following features were observed: (i) the short-term (1 hr) adsorption from solution onto the biomass surface induces an enrichment of the cell surface in heavy isotopes ($\Delta^{66}Zn_{(solid-solution)}$ = 1.61 $\pm$ 0.04 ‰ for the biofilm from microcosm and $\Delta^{66}Zn_{(solid-solution)}$ = 0.60 $\pm$ 0.02 ‰ for the monospecific biofilm) and (ii) Zn accumulation into the cell during 48 hrs leads to an enrichment of light isotopes ($\Delta^{66}Zn_{(solid-solution)}$ = 0.29 $\pm$ 0.14‰ and 0.26 $\pm$ 0.09 ‰ for the biofilm from microcosm and for the monospecific biofilm, *respectively*). The adsorption features can be explained by the change of complex structure from solution ($Zn(H_2O)_6^{2+}$) to the algal surface ($>$R-$Zn(H_2O)_5COO^-$). The incorporation features of Zn fractionation may be linked to the efflux phenomenon of preferentially heavy isotope into the bulk solution whereas the light isotope remains partially linked to sulhydryl group (-SH) in proteins in the interior of the cell induced by a mechanism of active detoxification.

For Cu, only an accumulation of the light isotope inside the biomass is observed during all exposure times ($\Delta^{65}Cu_{(solid-solution)}$ increase from -0.85 $\pm$ 0.13‰ to 0.44 $\pm$ 0.10‰ between 1 hr and 48 hrs exposure for both biofilm models). This can be explained by higher toxicity of Cu compared to cells and thus more efficient efflux mechanism for this metal. Our results provide firm basis for establishing the link between metal complexes structure and

toxicity and the degree of stable isotope fractionation that can be used for tracing biological processes in natural waters.