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Chemical status of Cu adsorbed on and incorporated into aquatic microorganisms: insights from EXAFS and macroscopic interaction studies

O.S. Pokrovsky (1), G.S. Pokrovski (1), L.S. Shirokova (2) and E.E. Emnova (3)

(1) Géochimie et Biogéochimie Expérimentale, LMTG, CNRS, Université de Toulouse, 14 Avenue Edouard Belin 31400, Toulouse, France (oleg@lmtg.obs-mip.fr), (2) Institute of Ecological Problems of the North, Russian Academy of Science, Arkhangelsk, Russia; (3) Institute of Genetics and Plant Physiology, Moldavian Academy of Science, Kishinev, Moldova

Compared to other essential oligoelements, copper is particularly interesting as it combines versatile chemical properties and molecular structures with multiple oxidation states (+1 and +2) both in solution and in solid. It is very toxic for all aquatic photosynthetic micro-organisms. This toxicity is usually explained by blocking and reducing the thiol sites on proteins. Although a significant amount of work has been devoted to Cu(II) ion binding to algal and bacterial surfaces, provision of its limitation versus toxicity for biota remains largely unknown.

This work is aimed at quantifying the main structural factors controlling Cu interaction with various aquatic microorganisms. Photosynthetic eukaryotes (diatoms), cyanobacteria and anoxygenic phototrophic bacteria were selected as three most representative and contrasting taxons of photosynthesizing microorganisms exhibiting very low tolerance to Cu. In addition, soil rhizospheric aerobes grown in Cu-rich media were used as an example of non-synthesizing, highly resistant to Cu microbes.

Reversible adsorption and irreversible uptake of Cu on the surface and inside the cells of aerobic rhizospheric (*Pseudomonas aureofaciens* CNMN PsB-03) and phototrophic anaerobic aquatic (*Rhodovulum*. sp. A-20s, *Gloeocapsa* sp. f-6gl) bacteria, uptake of Cu by marine (*Skeletonema costatum, Thalasssiosira weisfloggi*) diatoms, uptake by

and adsorption onto freshwater (*Navicula minima*) diatoms were studied using a batch reaction as a function of pH, copper concentration in solution and time of exposure.

To gain structural information on Cu status in microorganisms, *in-situ* Cu K-edge X-ray absorption fine structure (XAFS) spectroscopic study was conducted at the FAME (ESRF, Grenoble). Upon short- and long-term adsorption at the freshwater diatom and cyanobacteria cell surface from inert electrolyte, Cu remains octahedrally coordinated with oxygen and binds (presumably bidentatly) to one or two carboxylate groups as also follows from surface complexation modeling based on macroscopic adsorption experiments. The similarities in Cu molecular structures of both Cu adsorbed and incorporated into freshwater diatoms and cyanobacteria species strongly suggest that the mechanism of Cu interaction with aerobic photosynthetic organisms is essentially the same, and no significant change in Cu environment in cells occurs as a function of level, duration of exposure and solution pH (from 4 to 7).

In contrast, long-term interaction of Cu with anoxygenic phototrophic bacteria (*Rhodovulum sp.*) brings about the appearance of sulfur atoms in Cu 1^{st} coordination shell, suggesting Cu scavenging in the form of sulfhydryl complexes. Similar environment has been detected for Cu incorporated into soil aerobic bacteria (*Pseudomonas aurefaciens*). Since EXAFS did not detected sulfur atom in the first shell of aqueous Cu^{2+} in the growth media, detoxification mechanisms are likely to be linked to inner-cellular enzymes or proteins Indeed, reversible (passive) adsorption of Cu on the surface of these microorganisms at pH 4 to 6 is essentially governed by carboxylate and/or phosphoryl complexes.

These new structural data demonstrate, for the first time, essentially carboxylate binding of Cu on the surface of aquatic microorganisms and non-specific storage in the form of carboxylate/phosphate groups inside the cells of cyanobacteria and freshwater diatoms. Highly specific Cu binding in the form of sulfhydryl groups in anoxygenic phototrophic bacteria and soil *Pseudomonas aurefaciens* is another new feature, which is certainly intimately linked to the bioavailability of this metal.