



Speciation of Fe adsorbed on soil and aquatic bacteria: XAS structural study

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Iron is one of the most abundant and important element in the earth and it plays a crucial role in natural environments as essential micronutrient. An important process affecting the mobility, reactivity and bioavailability of this metal in aqueous solutions is the adsorption onto microorganism surfaces. In this study, three cyanobacterial species were considered: *Synechococcus* sp., *Planktothrix* sp. and *Gloeocapsa* sp., present in natural waters as individual cells, filaments and capsules, respectively. In addition, a soil rhizospheric bacterium, *Pseudomonas aureofaciens*, grown in EPS-rich and EPS-poor media, was investigated. This study involved macroscopic characterization of bacterial surfaces using adsorption technique as a function of pH (1.7 to 3.5) and electrophoretic measurements. A Linear Programming Model was applied in order to obtain information about the functional groups and the available sites capable to bind Fe on the cell wall. The second part of this work involved X-ray absorption fine structure analysis (XANES and EXAFS) carried out for all four species studied, in order to characterize the oxidation state and local atomic environment of Fe.

Results demonstrated that the principal functional group in cyanobacteria species are phosphoryl (pKa= 6-7) and amine (pKa= 7-10). Carboxylate groups (pKa=3-5) were important in EPS-rich and EPS-poor *Pseudomonas aureofaciens* together with phosphoryl groups (1.86 and 4.19 mmol/g biomass for EPS-rich and EPS-poor strain, respectively). Electrophoretic measurements for *P. aureofaciens* demonstrated an increase of zeta-potential in the presence of added Fe³⁺, suggesting a complexation of iron(III) with negatively charged groups (carboxyl or phosphoryl-like groups) from the most external layer in the cell wall.

The X-ray absorption study demonstrated that Fe²⁺ and Fe³⁺ adsorption at pH=5-8 and 2-6, respectively, produces mostly Fe³⁺ isolated octahedral linked to carboxylate and phosphoryl groups. The polymerization of Fe(III) forming Fe oxyhydroxides was completely inhibited and iron remains in solution in the form of individual Fe(III) atoms attached to organic moieties via Fe-O-C bonds.

Overall, results of the present study allow improving our knowledge of physico-chemical factors controlling biogeochemical cycle of Fe in natural waters in the presence of aerobic microorganisms and provide a firm basis for quantitative prediction of Fe isotope fractionation in natural settings.