

## Surface Complexes: Copper (II) and Glyphosate on Boehmite and Goethite Surfaces

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Interactions of copper (II) and glyphosate (N-(phosphonomethyl)glycine) with mineral surfaces were investigated with both macroscopic and spectroscopic techniques. Conclusions concerning the surface complexes formed were drawn from the results of quantitative adsorption experiments and the complementary structural evidence provided by EXAFS (Extended X-ray Absorption Fine Structure) and IR (Infrared) spectroscopies. The surfaces of commercially available boehmite (AlOOH) and synthesised goethite (FeOOH) were chosen as they represent naturally occurring mineral surfaces present in soils and sediments. Glyphosate, an organic ligand also known as PMG, is a component of organo-phosphorus herbicides widely used in agriculture, which is why interactions both with mineral surfaces and trace metal ions, such as copper (II), are of great interest. Glyphosate has three donor groups that are able to partake in complexation reactions, a phosphonate group, an amine group and a carboxylate group. A major motive for the choice of adsorbates is the hard/soft chemical nature of glyphosate. The hard phosphonate donor group has the potential to bind to the hard acceptor atoms at the mineral surface (Al (III), Fe (III)), while the softer amine and carboxylate groups have a greater affinity for copper (II).

Initially, EXAFS and IR spectra of aqueous copper (II)-N-(phosphonomethyl)glycine complexes were analysed in order to provide suitable references for the subsequent investigation of adsorbate behaviour at the surface. Conclusions drawn from the spectral information partly confirmed, but also even contradicted some of the structures previously suggested in the literature (Motekaitis et al., 1985; Daniele et al., 1997; McBride, 1991; Clarke et al., 1989). Structures of the 1:1 complexes, CuL and CuHL were found to be very similar, the main difference being deprotonation/protonation of the phosphonate group. The 1:2 complex, CuL<sub>2</sub><sup>4-</sup>, probably exists as a mixture of different isomers in solution. The EXAFS and IR results for CuL<sub>2</sub><sup>4-</sup> showed evidence of phosphonate and carboxylate binding at both equatorial and axial positions.

Following characterisation of the aqueous Cu-PMG complexes, glyphosate and copper, both in the absence of and in the presence of each other, were adsorbed onto the boehmite and goethite surfaces as functions of pH and ligand/surface ratio. A <sup>14</sup>C radioisotope labelling technique and AAS (Atomic Absorption Spectroscopy) were used to quantify the adsorbed glyphosate and copper, respectively. The resulting adsorption curves show that the adsorption of copper is greatly influenced by the presence of glyphosate and vice versa.

EXAFS and IR measurements indicate a difference in the structure of a ternary surface complex depending on pH. A closer interpretation of the spectra suggests that Type B ternary surface complexes (surface-ligand-metal ion) predominate over the greater part of the pH range studied (4 < pH < 9.5), while a Type A ternary surface complex (surface-metal-ligand) is formed at higher pH. Also, compared to the reference EXAFS spectra of the Cu-PMG aqueous complexes, there is a marked change in the spectral contribution of the phosphonate and possibly carboxylate groups of the glyphosate ligand. This provides evidence that these groups are no longer bound to a central copper atom in the same manner as in the aqueous Cu-PMG chelates but are indeed involved in surface complexation.

In summary, the intended conference poster will present both quantitative and structural information concerning the surface complexes formed from the adsorption of copper and glyphosate onto goethite and boehmite, as determined from adsorption experiments and EXAFS and IR spectroscopies.

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