OP 4.5

Copper speciation in different types of natural waters

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For copper, the predominant oxidation state in surface waters is Cu(II), since it has the highest affinity towards oxygenated ligands, namely inorganic as CO_3^{2-} and organic with carboxylic and hydroxide groups (1,2). More than 95% of Cu(II) is transported by rivers adsorbed on particles that may be coated with organic matter. On the other hand, even in aerobic conditions, the radicals formed in the photooxidation of dissolved organic matter may reduce Cu(II) to Cu(I). This can be of special importance in sea-water and estuarine conditions, where chloride stabilizes Cu(I) (3,4). Other ligands like ammonia, some types of amines and organics with soft donor atoms such as sulphur also stabilize Cu(I) (5,6,7).
In order to investigate the influence of organic matter on copper speciation in aquatic media, namely in river, estuarine and marine waters, titration of the natural sample with copper (II), while keeping the other characteristic parameters of the solution constant, has been followed by voltammetric techniques with low detection limits. The degree of lability and type of redox reaction were analysed in order to arrive at a valid interpretation of results. It was found that labile complexes, within the timescale of the technique (about 50 milliseconds), were formed during the titration of all samples. Before titration, labile complexes were also found in fresh-waters, while inert complexes were determined in the estuarine water. In some river samples, Cu(I) species were stabilized by organic matter with soft donor atoms during the redox process at the electrode, and in estuarine waters chloride ion also contributed to their stabilization. Finally, the highest complexing strength for copper was found in the estuarine water. The sea-water did not show any complexation due to the low level of dissolved organic matter. These results point to the importance of the medium, namely, type of organic / inorganic ligands present and pH in copper speciation, which can be reflected in terms of bioavailability.

1. W. Stumm, J. Morgan, Aquatic Chemistry, John Wiley & Sons (1996)
2. K.J. Wilkinson, J. Buffle, chap.10 in: IUPAC Series on Analytical and Physical Chemistry of Environmental Systems, H.P. Van Leeuwen, W. Köster, (eds), John Wiley & Sons (2004)
3. M.L.S. Conçalves, M.M.C. Santos, J. Electroanal. Chem., 143 (1983) 397
4. A. Nelson, Anal. Chim. Acta, 169 (1985) 287.
5. M.L.S. Gonçalves, L. Sigg, Electroanalysis 3 (1991) 553.
6. C.M.S. Botelho, R.A.R. Boaventura, M.L.S. Gonçalves, Electroanalysis, 14 (2002) 1713.
7. D. Buerge-Weirich, B. Sulzberger, Environ. Sci. Technol., 38 (2004) 1843.