

Comparative study of organic Cd and Zn complexation in lake waters

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The complexing capacity and associated stability constants of Zn and Cd in three alpine lakes in New Zealand has been determined using Competitive Ligand Equilibration-Cathodic Stripping Voltammetry (CLE-CSV) with ammonium pyrrolidine dithiocarbamate (APDC) [1] as competing ligand for Zn and Anodic Stripping Voltammetry (ASV) was used to measure the complexing parameters for Cd [2].

We compared depth profiles, seasonal variability, pH dependence and selectivity of the natural organic ligands for both elements and took a view to similarities and differences with Cu speciation in the same lakes

Probably the most noticeable and interesting result of our study on the speciation of Cd and Zn in three freshwater lakes in southern New Zealand is the apparent difference of the Cd-binding ligand composition with depth, but also differences in summer and winter. While our data gives evidence for a rather unspecific binding affinity towards Cd in winter and in deep water, the specificity seems to be increased at the surface in summer. Both the higher stability constant and selectivity against competing elements could indicate towards a compound of recent biological origin. Ligands with a lower stability found in winter at the surface and all year around in the deep water samples are probably non-specific degradation products.

The chemistry of Zn is much more uniform throughout the depth profiles and seasons, with Zn speciation being dominated by strong organic complexes. On average 95%±5% of Zn is present as organic complex, compared to only 70% ± 22% of Cd being organically complexes. Zn binding ligands also seem to be very selective towards Zn, and thus, probably produced in response to the presence of this element on the water. The pH dependence of the complexation of both metal ions is indicating that the composition of ligands is not uniform and functional groups may consist potentially of carboxylic groups (pK_a 3-5) and groups being incompletely deprotonated at pHs as high as 8.2 (e.g. phenolic and amino groups).

Comparing the speciation of Cd and Zn with that of Cu in the same lakes, it strikes that the concentrations of all ligands for all three elements is very similar with an over all average of 6.8 nM ± 3.1 nM (SD) although the total metal concentration vary in the range of two orders of magnitude, with Cd being the least prevalent element. However, the different complex stability constants, inorganic speciation and ligand selectivities for Cd, Zn and Cu in combination with their concentration is leading to the fact, that probably the highest risk of toxicity for organisms is coming from cadmium.

References

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Interactions of uranium with Fe(III)-(hydr)oxides under sulfate reducing conditions

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Uranium (U) contamination is a global problem in water supply and related ecosystem health, and it is the primary radioactive metal contaminating subsurface environments at many sites and is of particular concern because of its carcinogenicity. The high solubility of its hexavalent form can result in U transport to sensitive receptors such as drinking water sources. One potential method of treating U contamination is by using natural dissimilatory metal reducing bacteria including sulfate reducing bacteria (SRB) to reduce soluble U(VI) to insoluble U(IV) (as uraninite, UO₂). This reduction can lead to *in situ* U immobilization; however, it is vital to understand the reactivity and stability of microbially-mediated uraninite. Our recent published HR-TEM, SAED, and EDS analysis data showed that SRB transformed U(VI) into colloidal uraninite with particle diameters of 3–5 nm. Further, we recently showed that under lactate-limited sulfate-reducing conditions, this biogenic uraninite can be oxidized by common Fe(III)-(hydr)oxides such as hematite, goethite, and ferrihydrite. In addition to the oxidation of biogenic uranium under biotic conditions, in this paper we review the oxidation of aqueous phase biogenic uraninite by Fe(III)-(hydr)oxides under abiotic conditions. These aqueous uraninite particles were separated from SRB using 0.2 μm membrane filter, and treated with hematite and ferrihydrite under strict anaerobic conditions. Our results suggest that Fe(III)-(hydr)oxides oxidized uraninite; however, the reactivity of biogenic uraninite was greater with ferrihydrite as compared to the more crystalline structure of hematite. Thermodynamic calculations also indicate congruent favorability of these reoxidation reactions. The results have strong implications for field application of *in situ* biological reduction of U(VI) since oxidation of bio-reduced uraninite by Fe(III)-(hydr)oxides *in situ* may limit U immobilization even under reducing conditions.