

Root-metal stability constants: comparing toxicity and accumulation endpoints

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Very few root-metal stability constants ($\log K_{\text{Root-Me}}$) for higher plants are available in the literature. Those that are available have been derived mainly from two different endpoints: toxicity and accumulation. The interchangeability of $\log K$ values has not been investigated. Do they generate like-values? Or do the data collected from each of these endpoints represent fundamentally different aspects of root-metal binding? The answer to this question is important because modelers faced with a shortage of root-metal binding data are likely to merge all available resources into a single database. The potential consequence is erroneous model output if the $\log K_{\text{Root-Me}}$ values derived from different endpoints are not statistically equal. In this work, conditional stability constants for durum wheat (*Triticum turgidum*) were derived from both toxicity and accumulation data and compared. Hydroponically grown plants exposed to a range of $\{\text{Cu}^{2+}\}$ ($10^{-9.03}$ to $10^{-4.38}$ M) were analyzed with respect to % reduction in root mass, % reduction in transpiration, and root-tissue Cu concentration, constituting the toxicological and accumulation endpoints, respectively. Our results indicate that conditional stability constants determined from the toxicological endpoints ($\log K_{\text{Root-Cu}} = 4.95 \pm 0.16$ SE and 4.53 ± 0.40 SE for root mass and transpiration, respectively) are statistically equal to each other. However, only the $\log K_{\text{Root-Cu}}$ calculated from transpiration data was statistically equal to the $\log K_{\text{Root-Cu}}$ determined for the accumulation endpoint ($\leq 4.10 \pm 0.18$ SE). This equality was further conditional upon the accuracy of the $\log K_{\text{Root-Cu}}$ estimate for accumulation, since the reported $\log K_{\text{Root-Cu}}$ is a less-than or equal-to value. Based on this statistical analysis of the data, and further qualitative analysis, it is recommended that root-Cu stability constants determined from toxicity and accumulation endpoints not be used interchangeably in aqueous speciation modeling, since they likely represent fundamentally different aspects of root-Cu binding.

Aqueous speciation models have become an important tool for the assessment of metal bioavailability in the environment. As models for higher plants become increasingly refined in their approach, it is critical that the science used to acquire the fundamental data necessary for input be conducted in a systematic manner for which the implications are well understood.

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Domain: Processes

Metal-sulfide species in oxic waters: Complexes, clusters, or colloids?

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Sulfide is well known to control the speciation of many metals of environmental concern in anoxic, sulfidic waters. Less well known is that metal-sulfide species can also be present in oxic surface waters, despite of the instability of the free sulfide in such oxic environments.

Several analytical techniques were employed to characterize oxidation-resistant metal-sulfide species that have recently been suggested to be present in oxic waters. Sulfide in synthetic Cd-, Zn-, Pb-, Cu-sulfide solutions was found to persist in oxic waters for a prolonged period of time (2 to more than 10 weeks) whereas it was oxidized rapidly in Fe-, Mn- and Ni-sulfide solutions. Multi-lines of evidence from UV-visible absorption spectroscopy, mass spectrometry (MS), and transmission electron microscopy (TEM) did not support for the presence of soluble molecular metal-sulfide clusters in these solutions as suggested previously. Instead, the metal-sulfide species resistant to oxidation in oxic waters were more likely a mixture of truly dissolved metal-sulfide complexes and dynamic metal-sulfide colloids. The morphology and size of the colloids changed significantly with time.

Nanomolar to sub-micromolar levels of acid-volatile sulfide (AVS) and chromous-volatile sulfide (CVS) were measured in oxic surface waters of 6 lakes located on the Canadian Shield and nearby areas. Thermodynamic calculations indicated that at the AVS levels measured, the dissolved metal-sulfide complexes play a minor role in the speciation of Class B metal ions such as Pb, Cd, Cu, Hg. The relative importance of metal-sulfide colloids in these natural oxic waters remains unknown.

The above findings from this research are highly significant with respect to ecological risk assessment of metals in surface waters, as the speciation of metals represents one of the most challenging issues in conducting ERA of metals. This research suggests that, despite the presence of certain metal-sulfide complexes in surface waters, they play a minor role in metal speciation when compared with metal complexes with other ligands such as dissolved organic carbon (DOC). Further studies are, however, warranted to study the relative importance and bioavailability of metal-sulfide colloids.

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Chemical speciation techniques: what have they achieved for metal speciation and bioavailability in the freshwater environment?

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Atmospheric deposition from smelting operations in the Rouyn-Noranda area has resulted in metal contamination from to the surrounding areas. Mechanistic biogeochemical models such as the Biotic Ligand Model (BLM) show promise for providing direct, quantitative estimates of metal bioavailability across a wide range of water quality parameters, e.g. pH, hardness, Dissolved Organic Matter (DOM). However, most current approaches for chemical speciation only provide results that are operationally-defined. The objective of this research project was to investigate the impact of metal contamination on chemical speciation (which influences metal bioavailability) in lake water samples collected from the Rouyn-Noranda area. A variety of electrochemical speciation techniques and competing ligand exchange methods were used in this investigation.

Kinetic, equilibrium and electrochemical studies revealed a general increase in dissolved metal concentration and lability (and hence, bioavailability) with decreasing distance from the source. Any exceptions were attributed to additional factors such as high concentrations of dissolved organic matter and competition by major cations (e.g. Ca^{2+} and Mg^{2+}). In addition, the kinetics of the trace metal competition was found to be influence by three factors: 1) metal-to-ligand ratio, 2) ionic potential (z^2/r), and 3) Ligand Field Stabilization Energy. Our results suggest that for transition metals with slow coordination equilibrium (e.g. Cu(II) and Ni(II)), the equilibrium assumption of the BLM may not be valid. Hence, an improved BLM should take into account the kinetics of metal complexation.

The analytical timescale of measurement was identified as the critical parameter for defining the chemical species. For competing ligand exchange methods, the measurement timescale is simply the time required to complete the experiment (e.g. equilibration time for equilibrium studies and total run time for kinetic investigations). However, for both Anodic Stripping Voltammetry (ASV) and BLM, the measurement timescale is defined by the thickness of the Nernstian diffusion layer which is a function of the shape and size of the electrochemical or biological surface. These findings have important consequences for interpreting experimental results from conventional ASV (and other speciation techniques) and may explain some of the reported exceptions to the BLM.

Financial support: Metals In The Environment-Research Network (MITE-RN), NSERC, Ontario Power Generation, Mining Association of Canada, Nickel Producers Environmental Research Association, USA.

Development of rational models for relating metal accumulation by aquatic organisms to metal concentrations in their environment.

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The overall goal of our MITE-RN funded research was to develop and test under natural conditions mechanistic models that relate metal concentrations in aquatic organisms to those in their surroundings. To develop such models we needed to better understand the chemical and biological processes involved in metal bioaccumulation. Thus we attempted to refine the idea of exposure, as used in ecological risk assessments, by moving from metal measurements in bulk sediment or water to considering the manner in which animals are exposed to metals in specific phases.

In the case of benthic animals, we recorded their behaviour using infrared video and radiographic images to understand their exposure to metals above and below the sediment-water interface. Various types of invertebrates differed in their burrowing and irrigation behaviours (as shown by C. Gallon, A. Gosselin and F. Wang), which influenced their exposure to metals in anoxic interstitial waters. Furthermore, we showed that Cd present in sediment at concentrations measured in lakes near the Rouyn-Noranda metal smelter did not influence the behaviour of the burrowing mayfly *Hexagenia* (as shown by A. Gosselin); these observations could explain in part the wide distribution of this insect in metal-contaminated circum-neutral lakes.

We conducted experiments to determine the relative importance of food and water as metal sources for aquatic insects. The results of several experiments indicate that larvae of the phantom midge *Chaoborus* take up Cd solely from their planktonic prey and that prey community structure likely influences Cd concentrations in this predator (as shown by M.N. Croteau). We also showed that benthic prey are the source of the great majority of the Cd, Cu and Pb accumulated by larvae of the predatory alderfly *Sialis* (as shown by L. Croisetière). Thus food choice, the rate at which prey are ingested and the efficiency with which metals are assimilated can all influence metal uptake by predators. Our results underline the importance of considering trophic structure when predicting animal metal exposure in nature.

We used our experimental data to develop and test mechanistic models that would allow organisms such as *Chaoborus*, *Sialis*, and the aquatic moss *Fontinalis* to be used as metal biomonitors in lakes and streams. We tested the mechanistic basis of such models by determining the trophic level(s) at which cadmium and hydrogen ions compete for Cd uptake sites on organisms. For the food chain leading to *Chaoborus*, we determined that Cd²⁺-H⁺ competition does not take place at the level of *Chaoborus* and that although some competition takes place on the copepods consumed by *Chaoborus*, competitive interactions on algal cell walls best explain the reduced bioaccumulation measured in these planktonic invertebrates in acidic lakes (as shown by J. Orvoine). Overall, environmental regulations springing from ecological risk assessments resting on a sound understanding of metals and their interactions with living organisms are more likely to be defensible scientifically than are other more empirical approaches.

Post-depositional mobility of trace elements in northern forest ecosystems: root soil interactions

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Predicting the amount of metal that will be transferred from soils to plants is a critical part of risk assessment for metals in the environment. The recent USEPA SAB report on metals recommends that metal effects and accumulation (thus risk) be studied in the context of bioavailability. Failure to include bioavailability or bioaccessibility often results in very conservative estimates of risk, and very low environmental criteria for metals in soils. On occasion, these criteria are lower than background concentrations, or those that are readily achievable by remediation technology. However, these relationships between the properties of environmental media, and metal bioavailability, are complex, as they are influenced by other ions, organic and inorganic ligands, and the biota themselves.

A review of the literature a few years ago indicated that there was no scientifically defensible way of evaluating the risk that was posed by metals (Cu, Ni, Pb and Zn) deposited from smelter emissions to the boreal forest. We established study sites downwind from the smelters at Sudbury and Rouyn-Noranda so that we would be able to establish the amounts of metal deposited to the terrestrial ecosystem, the mobility of the metals in the soils and their uptake by plants. From this modelling was used to develop predictive equations that would be useful to those responsible for risk assessment and the regulation of the metals industry. Hydroponic studies were used in parallel, to validate these equations.

The key findings were:

- Plant species that dominate plant community biomass control trace metal dynamics;
- Fine root decomposition dominates annual plant trace metal cycling relative to foliar litter;
- Fine roots contribute to sequestration/cycling of trace metals disproportionately to their mass, except for Zn, for which these processes are proportional to biomass;
- Metal binding to soil particles can be predicted using a simplified NICA-Donnan model;
- Bioaccumulation factors (BAFs) for metals in the whole plant, expressed relative to free metal ion concentration in the soil, were more similar among study sites than BAFs calculated using total soil metal concentrations;
- Buffered Cu solution results in enhanced Cu accumulation in roots, at lower $\{Cu^{2+}\}$, thus, a BLM for plants needs conditional stability constants for metal binding that have been determined in the presence of a metal buffer, as soil solutions would be similarly buffered;
- Conditional stability constants for accumulation of Cu by roots were similar for multiple situations, and concentrations of root binding sites; thus, there is potential to predict the accumulation of Cu by plants from soil solution using metal speciation modelling software;
- Predictions for metal rhizotoxicity given by BLM, Gouy-Chapman-Stern model and Freundlich equation modes were compared with predictions based on free metal ion activities in solution, including variation in Ca and H. The BLM best predicted rhizotoxicity.

The key findings were that the movement of metals within the soils and from the soils to the biota could be predicted with reasonable accuracy. Different estimates of bioavailable metals were used and in general the biotic ligand approach appears to be a promising avenue for future development. The database that was developed and the development and calibration of predictive models provides regulators with a tool to evaluate the effects of smelter emissions on the boreal terrestrial ecosystem.

TRANSPEC a Coupled Speciation–Fate Model: Lake and Model Comparisons

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A coupled TRANsport and SPECiation/ complexation (TRANSPEC) model has been developed to quantify the fate of multiple, interconverting metal species in aquatic systems. The model was applied to estimate movement of Zn species in Ross Lake, Manitoba, Canada (Bhavsar et al. 2004, Bhavsar et al. accepted, Diamond et al. In press.). The main aim of this project was to investigate the generality of TRANSPEC by applying it to a range of lakes and a range of cationic metals. We applied the model to estimate movements of Cu in Ross Lake, Cd, Co, Cu, Ni, Pb and Zn in Kelley Lake (Ontario) and Cd, Pb and Zn in Lake Tantare (Quebec). We selected these lakes based on the range of metal and nutrient loadings, limnological characteristics, as well as availability of measured data to parameterize the model and evaluate model estimates. A secondary aim was to assess the importance of metal speciation/complexation estimates on fate results which is relevant when linking loadings to resultant concentrations. We developed two versions of the model that were coupled with different speciation/complexation models – WHAM (Tipping 1994, 1998) and MINEQL+ (Schecher and McAvoy 2001). A third aim was to assess estimates of truly dissolved species concentrations, which is useful in the context of metal hazard assessment.

TRANSPEC faithfully estimates ambient concentrations of cationic metals (Cd, Cu, Ni, Pb, Zn) in all three lakes that ranged from eutrophic status with high concentrations of metal loadings from mining and mineral processing activities (Ross Lake), to oligotrophic lake with low metal concentrations from weathering and atmospheric deposition (Lake Tantare). MINEQL+ and WHAM provide different estimates of speciation within the soluble phase but similar estimates of the distribution of metals between soluble to particle phases. As such, both versions of the model provide similar estimates of metal fate which is highly dependent on the particle-phase metal in these lakes. Subtle differences in transport processes were evident between the models in terms of the diffusive exchange between sediment and water that can be attributed to differences in estimated colloidal versus truly dissolved speciation. WHAM estimates a higher fraction of the soluble phase is in the colloidal phase (sorbed to DOM) whereas MINEQL+ estimates a higher fraction of the soluble phase is in the free ion form. These differences are significant in terms of hazard and risk assessment.

Trace metal speciation and mineral weathering at the soil-root interface of forest soils

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Due to its proximity to the site of elemental uptake by plants, the rhizosphere is viewed as a biogeochemical hotspot characterized by massive fluxes of matter and energy. Of particular interest to scientists is the response of the rhizosphere to perturbations of natural or anthropogenic origin. The long-term objective of this project is to establish the contribution of rhizospheric processes to the cycling of trace metals in terrestrial ecosystems. The specific objectives are a) to contrast the fractionation of trace metals (Cd, Cu, Ni, Pb, Zn) and mineralogical assemblages between the rhizosphere and bulk components of forest soils exposed to different levels of contamination by metals and b) to determine the links between soil organic matter, microbial activity and the speciation of metals in the rhizosphere. The study sites are located along transects of metal deposition in the Sudbury (under *Betula papyrifera* and *Pinus resinosa*) and Rouyn-Noranda (under *Populus tremuloïdes*) areas, and under different forest canopies (*Abies balsamea*, *Acer saccharum*, *Betula papyrifera*) at St-Hippolyte in the Lower Laurentians. The separation of 'inner' and 'outer' rhizosphere fractions from bulk soil materials is performed in the laboratory by shaking in a Teflon container. Trace metals are extracted (H_2O , $BaCl_2$, Na-pyrophosphate, ammonium oxalate and HNO_3-HCl) from the rhizosphere and bulk soil materials of the B horizon and analyzed by GFAAS, ICP-AES or ICP-MS. The activity of free Cu^{++} in H_2O extracts is measured using the ion selective electrode (ISE) method whereas labile Zn is estimated by differential pulse anodic stripping voltammetry (DPASV). The mineralogy of the clay fraction is determined by x-ray diffraction (XRD).

Our studies have clearly established that the rhizosphere is more acidic than the soil matrix and that it is enriched in organic substances (dissolved and solid phases), nutrient cations (Ca, Mg) and trace metals. Indeed, the rhizosphere systematically acts as a sink for Cd, Cu, Ni, Pb and Zn, notably under bioavailable (water-soluble and salt-extractable) forms. However, the activity of free Cu^{++} ions is lower in the rhizosphere than in the bulk soil mostly because of the strong complexation of Cu by soluble organic compounds. As for labile Zn, its concentration decreases with distance from roots and is strongly associated to total dissolved Zn concentrations. XRD results show differences in the mineralogical abundance that are interpreted as an increase in mineral weathering in the rhizosphere as compared to the bulk soil, particularly for easily weathered minerals such as amphibole, chlorite and plagioclases. The corrosive environment forming in the rhizosphere also impacts on the accumulation of weathering products such as Fe, Mn and Al oxides. The acquisition of new knowledge on the rhizosphere is crucial to increase our capacity to understand, manage and model soil-plants systems. Moreover, results from rhizosphere research help define new approaches designed either to restrict the entrance of potentially toxic elements in crops and, hence, in the food chain or, contrarily, to increase the uptake of trace elements by plants in contaminated environments to be bioremediated.

This study was supported by Metals in the Environment Research Network (MITE-RN) and the National Sciences and Engineering Research Council of Canada (NSERC).

Chemical speciation techniques: what have they achieved for metal speciation and bioavailability in the freshwater environment?

Murimboh, John, I.I. Fafous, T. Yapici, C.L. Chakrabarti and D.C. Grégoire

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Atmospheric deposition from smelting operations in the Rouyn-Noranda area has resulted in metal contamination from to the surrounding areas. Mechanistic biogeochemical models such as the Biotic Ligand Model (BLM) show promise for providing direct, quantitative estimates of metal bioavailability across a wide range of water quality parameters, e.g. pH, hardness, Dissolved Organic Matter (DOM). However, most current approaches for chemical speciation only provide results that are operationally-defined. The objective of this research project was to investigate the impact of metal contamination on chemical speciation (which influences metal bioavailability) in lake water samples collected from the Rouyn-Noranda area. A variety of electrochemical speciation techniques and competing ligand exchange methods were used in this investigation.

Kinetic, equilibrium and electrochemical studies revealed a general increase in dissolved metal concentration and lability (and hence, bioavailability) with decreasing distance from the source. Any exceptions were attributed to additional factors such as high concentrations of dissolved organic matter and competition by major cations (e.g. Ca^{2+} and Mg^{2+}). In addition, the kinetics of the trace metal competition was found to be influence by three factors: 1) metal-to-ligand ratio, 2) ionic potential (z^2/r), and 3) Ligand Field Stabilization Energy. Our results suggest that for transition metals with slow coordination equilibrium (e.g. Cu(II) and Ni(II)), the equilibrium assumption of the BLM may not be valid. Hence, an improved BLM should take into account the kinetics of metal complexation.

The analytical timescale of measurement was identified as the critical parameter for defining the chemical species. For competing ligand exchange methods, the measurement timescale is simply the time required to complete the experiment (e.g. equilibration time for equilibrium studies and total run time for kinetic investigations). However, for both Anodic Stripping Voltammetry (ASV) and BLM, the measurement timescale is defined by the thickness of the Nernstian diffusion layer which is a function of the shape and size of the electrochemical or biological surface. These findings have important consequences for interpreting experimental results from conventional ASV (and other speciation techniques) and may explain some of the reported exceptions to the BLM.

Financial support: Metals In The Environment-Research Network (MITE-RN), NSERC, Ontario Power Generation, Mining Association of Canada, Nickel Producers Environmental Research Association, USA.

Metal speciation, challenges, and prospects for the freshwater environment

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Abstract

Environmental regulators and water resources managers require science-based answers about the maximum permissible loading of toxic metal species in effluents that may be discharged to freshwaters while protecting aquatic ecosystems. Mechanistic biogeochemical models such as the Biotic Ligand Model (BLM) are beginning to be applied for setting site-specific acute water quality criteria. The current implementation of the BLM does not account for the impacts of multiple metal exposure systems. Expanding the BLM approach to account for trace metal competition is highly desirable from an effluent discharge point of view, but presents significant challenges in chemistry, toxicology and modelling. We have sought to answer this challenge by developing metal speciation models that are applicable to the freshwater environment. The objective of this research project was to investigate the impact of metal contamination on chemical speciation (which determines bioavailability) in lake water samples collected from the Rouyn-Noranda (Quebec) and Sudbury (Ontario) areas.

Three factors were found to influence the dissociation kinetics of the trace metal competition:

- 1) Metal-to-ligand ratio
- 2) Charge-to-radius ratio
- 3) Ligand Field Stabilization Energy

Our results suggest that for transition metals with slow coordination equilibrium (e.g. Cu(II) and Ni(II)), the equilibrium assumption of the BLM may not be valid. Hence, an improved BLM should take into account the kinetics of metal complexation. The results suggest that freshwaters are dynamic systems that are often far removed from equilibrium.

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TRANSPEC-ERA: An ERA model for metals that is based on metal speciation and fate-transport

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A key objective of the Metals in the Environment Research Network (MITE-RN) is to improve Ecological Risk Assessment (ERA) for metals. With support from MITE-RN, we developed a coupled multi-species metal fate-TRANsport and SPECiation/complexation (TRANSPEC) model (Bhavsar et al. 2004, Bhavsar et al. accepted, Diamond et al. in press). The model links metal loadings (*sources*) to resultant metal species concentrations considering speciation/complexation and fate-transport (*processes*). The next study demonstrated generality of the model by its application to various cationic metals (e.g., Cd, Cu, Ni, Pb and Zn) and to lakes that ranged from eutrophic to oligotrophic and mine-impacted to pristine (Bhavsar et al. in prep). Here we illustrate a possible extension of the model (TRANSPEC-ERA) that connects the estimated metal concentrations to potential ecological risk through exposure and risk assessment.

TRANSPEC loosely couples a speciation/complexation module (e.g., MINEQL+, WHAM) with our fugacity/aquivalence based multi-species fate-transport module. The speciation/complexation module uses site-specific chemistry data and estimates partition coefficients (K_d) and species fraction in truly dissolved, colloidal (bound to DOM) and solid phases. The fate module, using the results from the speciation module, estimates inter-media transport rates and resultant concentrations of metal species in each abiotic media. Next, we have developed ecological exposure and risk assessment modules that use TRANSPEC results to assess the potential risk. The exposure module first estimates metal concentrations in dietary items (e.g, forage fish, aquatic invertebrates and vegetation) using literature derived bioconcentration factors (BCF). The module then calculates daily doses of metals for a variety of juvenile and adult receptors considering various exposure scenarios, exposure factors, body weights, and food and water ingestion rates. The risk assessment module then assesses potential risk in terms of a hazard quotient (HQ) by comparing the daily doses with published toxicity reference values.

A preliminary version of TRANSPEC-ERA has been applied for risk assessment of Zn and Cu in Ross Lake (Manitoba) and Cd in Lake Tantare (Quebec). The results for mine impacted Ross Lake suggest that the potential risk ranges through more than three orders of magnitude depending on the seasonal scenario and receptor considered. The calculated risk may decrease from unacceptable to a tolerable level depending on the use of total (bulk) versus free metal ion concentrations. The results for “pristine” Lake Tantare suggest potential risk for some metals and receptors. Further work will incorporate the biotic ligand model (BLM) instead of BCF for estimating fish concentrations.

Thiols in wetland interstitial waters and their role in mercury and methylmercury speciation

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Organic sulfhydryl compounds, or thiols, are strong complexing ligands with class B metals such as Cu, Hg, and methylmercury (MeHg). Although thiols have been commonly determined in marine waters, little is known about their occurrence in freshwater systems and their role in metal speciation. We determined the concentration profiles of 5 low-molecular-weight thiols (cysteine, thioglycolic acid, glutathione, N-acetyl-L-cysteine, and 3-mercaptopropionic acid) in overlying waters and sediment interstitial waters, at a vertical resolution of 1 cm, in three drastically different wetlands located in the Prairie (Delta Marsh), on the Canadian Shield (Lake 632), and along the St. Lawrence River (Baie St. Francois). All the 5 thiols were detected in the waters, with concentrations ranging from nanomolars to sub-micromolars. In one of the wetlands (Baie St. Francois) where the profiles of Hg and MeHg were also obtained, a co-variation between MeHg and the thiols was observed; both peaked at similar depths below the sediment-water interface. Thermodynamic calculations reveal that at these levels thiols play a negligible role in inorganic Hg speciation in sediment interstitial waters, but they can dominate the speciation of MeHg and Cu. Consistent with recent findings that intracellular MeHg in fish is dominated by MeHg-thiol complexes, this study suggests that thiols also play a significant role in MeHg speciation in the extracellular environment.

Since intracellular thiols are believed to play a dominant role in metal detoxification, the above finding that metal-thiol complexes are also present in the extracellular environment raises immediate questions regarding the bioavailability and toxicity of extracellular metal-thiol complexes, which we believe is one of the critical gaps in conducting ecological risk assessment (ERA) of metals in the aquatic environment.

This work was funded by the Metals in the Environment Research Network (MITE-RN) and the Collaborative Mercury Research Network (COMERN).

Determining the trophic level at which Cd and hydrogen ions compete for biological uptake sites in the food chain leading to the biomonitor *Chaoborus*.

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Protons (H^+) can compete with free metal ions at biological uptake sites on organisms. Because of this competition, it is necessary to take into account ambient pH when predicting metal bioaccumulation and toxicity. This is reported to be the case for *Chaoborus*, whose cadmium (Cd) concentrations in nature depend on those of both H^+ and Cd^{2+} . However, because larvae of this insect take up their Cd entirely from food (zooplankton), this hypothesized competition could take place at several levels in the food chain leading to this predator. We conducted laboratory experiments to determine at what trophic levels this competition takes place. First, we determined whether or not H^+ swallowed by *Chaoborus* could compete with Cd^{2+} at uptake sites on gut wall. To do this, we held *Chaoborus americanus* larvae at a constant Cd^{2+} but at various pH's (4.5, 5.5, 6.5) and fed them cyclopoid copepods that had been raised on green algae rich in Cd. There was no difference in the Cd accumulated by the predator at the various pH's. To explain this lack of competition, we measured the gut pH of *Chaoborus* using pH-sensitive dyes. We found that its gut pH remained circum-neutral, even when ambient pH varied greatly (4.5–9.0). Second, we determined if Cd^{2+} and H^+ compete at biological uptake sites on *Chaoborus*'s prey. To do this, we fed cyclopoid copepods a diet of Cd-rich green algae in the presence of constant $[Cd^{2+}]$ but at various pH's (4.7, 5.5, 6.5). Our data suggest that there is some competition between Cd^{2+} and H^+ at this trophic level, but that it is insufficient to explain the magnitude of the effect at the level of *Chaoborus*. We conclude that H^+ - Cd^{2+} competition on algae best explains the low Cd concentrations in *Chaoborus* from acidic lakes. Funding from the MITE research network supported this research.

Rational development of the biomonitor *Sialis*.

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Measurements of trace metals in aquatic animals allow us to quantify metal exposure and, using an appropriate model, estimate metal concentrations in water or sediment. To be effective, such models should consider the metal's chemistry and the animal's biology. We used a step-by-step approach to develop models relating metal concentrations in larvae of the predatory alderfly *Sialis* to those in its surroundings. Through field and laboratory experiments, we collected key information concerning the behaviour of this insect and the sources of its trace metals. Our findings suggest that this biomonitor accumulates all of its Cd, Cu and Pb from prey. Furthermore, results of measurements of stable sulfur isotopes in *Sialis* and its surroundings suggest that some of the energy (and likely metals) obtained by *Sialis* comes via prey from the compartment comprising anoxic sediment and porewaters. We incorporated this information into a bioaccumulation model describing the relationship between trace metal concentrations in *Sialis* and those in its surroundings. The MITE research network provided funding for our study.

Determination of apoplastic sorption rates and the effect of nickel loading on root copper uptake.

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Biotic ligand modelling involves treating biota as a ligand which competes for free metal with other organic or inorganic ligands in the exposure environment. Developing a biotic ligand model for metals and terrestrial plants will improve the accuracy of accumulation and/or toxicity predictions by considering the ligands and competing cations that are likely to be present in soil solution. Such a model would improve ecological risk assessment of metals by enabling site specific predictions of toxicity and phytoaccumulation.

There are several phases involved in Cu binding to roots: non-specific binding to apoplasm, specific binding to symplasm, and efflux. An attempt was made to separate these components. Fresh whole plants were exposed to a Cu²⁺ solution with an activity of 1.70×10^{-5} M for durations ranging from 5 to 780 seconds; and, plants exposed for 780 seconds to 1.70×10^{-5} M Cu²⁺ were then exposed to a Cu free solution over the same range of times. All exposures were performed at 4 °C to limit respiratory function and therefore limit the specific binding of Cu to symplasm transporters. It is considered that only non-specific apoplastic binding would occur at 4°C. Total root Cu content was measured using AAS. The rate constants for adsorption and desorption were determined to be $8.4 \times 10^{-3} \text{ s}^{-1}$ and $2.3 \times 10^{-1} \text{ s}^{-1}$ respectively. The log value for the equilibrium constant (log K) was -1.44. Comparing this value to a previously determined log K value (4.2) for combined symplastic and apoplastic processes it was concluded that symplastic processes dominate uptake and thus have potentially greater toxicological consequences.

In a separate study, the effect of pre-loading roots with nickel on copper sorption was examined. Mature oat roots grown in soil containing one of two different total Ni concentrations were exposed to buffered Cu solutions for 96 hours. Total root Cu content was again measured with AAS. Soil Ni concentrations were 50 and 2000 ppm and yielded root Ni concentrations of 26 and 527 ppm respectively. Copper exposure solution Cu²⁺ activities were 2.0×10^{-7} , 5.3×10^{-6} , 1.7×10^{-5} , 5.4×10^{-5} and 1.7×10^{-4} M. Binding constants for Cu and roots for both the 50 and 2000 ppm Ni treatments were determined to be 3.3 and 3.7 (log values) respectively. Results showed that increased soil and root Ni concentrations enhanced Cu uptake. This is contrary to expectations when considering Ni as a simple competing cation.

Future research directions include calculation of a log K value for Cu and roots grown and exposed in an artificial soil medium as well as the influence of soil organic matter on the log K value.

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Development of BIOTRANSPEC – Mercury speciation, fate and bioaccumulation model: A mathematical tool for risk assessment

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Fate models are valuable for targeting emission reductions, understanding the connection between emissions and exposure, and drafting reasonable remediation options. Fate models can also be used to assist with human and ecological risk assessments by estimating the concentrations to which receptors are exposed and how this might change under different scenarios. We have developed a mathematical fate and transport model that generates the concentrations, mass and rate of movements of mercury species in environmental media. The steady-state version of “BIOTRANSPEC”, a mathematically linked BIOtic, fugacity/aquivalence multispecies TRANsport model, and aqueous equilibrium SPECiation model, has been developed in order to improve estimates of the fate and biotic uptake of mercury in aquatic systems. BIOTRANSPEC couples the kinetics and aquatic speciation model MINEQL+ with our fugacity/aquivalence model that allows consideration of multiple, interconverting species of mercury. The kinetics module calculates the net production of organic mercury (MeHg) using site-specific rate constants. The speciation model estimates the concentrations and distribution of mercury species that occur as inorganic (Hg^{+2} and Hg^0) and organic mercury (MeHg) species in dissolved, colloidal and particulate phases. In order to accurately estimate the fate of mercury, we have integrated methylation kinetics, speciation and fate models with a simple model of biotic uptake since fish are an important sink for methyl mercury. Model estimated methyl mercury concentrations in various environmental compartments are crucial inputs for the screening-level ecological risk assessment model that evaluates risk posed to most aquatic and terrestrial adult and juvenile receptors through the exposure via air, water, sediment and diet. The risk associated with the estimated exposure is assessed using the literature derived metal species-specific toxicity reference values for the receptors. We illustrate the use of the model through its application to a mercury contaminated aquatic system.