

## PROCESSES PLATFORM ABSTRACTS

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

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In order to assess the fate and mobility of aerially deposited trace metals in forested ecosystems, transects were established along gradients with distance from two point source emitters in Rouyn PQ and Sudbury ON, Canada. In the past, the sites closest to the smelters were exposed to considerable deposition of metals. Now that deposition has been drastically reduced, these sites are returning to a new equilibrium. Using data from samples collected in the field, equations were developed that predict dissolved trace metal concentrations from total trace metal concentrations, soil pH, soil organic matter (SOM) and dissolved organic carbon (DOC) contents. These equations have been integrated into a simple box model that calculates changes in the concentration of trace metals in the organic and upper mineral horizons, and includes a loop for vegetative return of metals to the forest floor, describing changes in the ecosystem compartments over time. Time to reach equilibrium and equilibrium concentrations at different soil pH values, and at different metal loading rates, were calculated. WinHumicV was used to calculate free metal ion concentrations in the soil solutions and then estimates of the biological effects of these concentrations were made. Analysis of plant community metal bioaccumulation factors (BAFs), calculated using total soil metal and free soil metal ion ( $Me^{2+}$ ), found that free soil metal BAFs were more similar among locations than total soil metal BAFs, but that disparity still existed. Mass estimates of phytoaccumulated trace metal contaminants and vegetation transfers to soils demonstrated that accumulation of metals differed significantly among plant vegetation compartments (foliage, fine roots, bark, trunk and branches), and among sampling sites, suggesting an interaction among routes of deposition, as well as plant community structure. Fine roots were found to dominate annual vegetation transfer of Cu, Ni and Pb to soils, relative to foliage; fine root mortality played a smaller role than foliage for Zn plant-soil transfer. Plant-associated metal inputs were found to rival or exceed current estimates of atmospheric metal deposition.

The conclusion of this work is that the receiving environment is profoundly influential of the fate and mobility of metals emitted into forests, and that previously deposited metals cannot be discounted from the ecologically active pool of metals in soils and vegetation.

Development of rational models for relating metal accumulation by aquatic organisms to metal concentrations in their environment: relative importance of ambient metal sources

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Our overall goal is 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 need to better understand the chemical and biological processes involved in metal bioaccumulation. Because metal accumulation precedes toxic effects, such models are an important step towards predicting toxicity. In the case of benthic animals, we recorded their behaviour using an infrared camera and radiographic images to understand their exposure to metals above and below the sediment-water interface. Various types of insects differed in their burrowing and irrigation behaviours (as shown by C. Gallon, A. Gosselin and F. Wang), which almost certainly influences their exposure to metals in anoxic interstitial waters. Thus a 'one size fits all' approach to ERA for sediments would likely exaggerate the exposure of many benthic invertebrates to sedimentary metals. Furthermore, Anne Gosselin showed that the behaviour of a burrowing mayfly (*Hexagenia limbata*) is not altered by Cd added to sediment at concentrations measured in Cd-contaminated lakes near Rouyn-Noranda. Thus the Cd accumulated by mayflies in these lakes is likely to have no effect on their behaviour, which could explain in part their wide distribution in metal-contaminated circum-neutral lakes. We also conducted experiments to determine the relative importance of food and water as metal sources. Louis Croisetière exposed predatory alderfly larvae (*Sialis velata*) to prey (*Chironomus riparius*) that contained either low or high concentrations of metals in combination with either metal-rich or metal-poor lakewater in the field. He contaminated prey by exposing them to metals in situ in a lake near the Rouyn-Noranda smelter (Lake Dufault). He found that water was a negligible source of Cd, Cu and Pb for this predator. We use such information to develop and test mechanistic models that will allow us to use organisms as metal biomonitors in lakes and streams. Work is ongoing on the amphipod *Hyalella azteca*, the phantom midge *Chaoborus*, the alderfly *Sialis* and the moss *Fontinalis*. For example, our previous work showed that for such models to be effective in freshwaters it can be necessary to take into account competition between metal and H ions at biological uptake sites. In this regard, Jord Orvoine conducted experiments to determine the trophic level(s) at which this competitive interaction occurs. He designed a first series of experiments to determine if Cd<sup>2+</sup>-H<sup>+</sup> competition takes place in the gut of *Chaoborus*; that is, between <sup>109</sup>Cd from food (a copepod) and H ions swallowed in lakewater. He found that Cd uptake by the predator was unaffected by changes in ambient pH, suggesting that Cd<sup>2+</sup>-H<sup>+</sup> competition takes place at a lower level in the food chain leading to this predator. Biomonitor models for animals such as *Chaoborus* are useful for estimating metal exposure in the field. 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.

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A new development in defining metal species in aqueous environmental samples

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Smelting operations in Sudbury and Rouyn-Noranda have resulted in metal contamination from atmospheric deposition to surrounding areas. Although the Biotic Ligand Model (BLM) has been successful in predicting metal bioavailability, numerous exceptions have also been reported. The local equilibrium approximation has been an important limitation of current BLM approaches. The objective of this research project was to investigate the impact of metal contamination on chemical speciation (which determines bioavailability) in soil pore waters, throughfall precipitation samples and lake water samples collected near the Sudbury and Rouyn-Noranda smelters. A variety of electrochemical speciation techniques and competing ligand exchange methods were used in this investigation. The key hypothesis in this research project was that the operationally-defined nature of the metal species identified by the current approaches to the study of chemical speciation (e.g. anodic stripping voltammetry) and metal bioavailability result from a failure to account for the analytical timescale of measurement.

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.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ). 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.

The significance of our work is that its findings have shifted the emphasis of environmental research on metals from 'operationally-defined' chemical species to rigorously-defined speciation parameters (i.e. free metal ion concentrations, stability constants, dissociation rate coefficients and diffusion coefficients) that can be used to predict metal bioavailability. Furthermore, we have successfully applied our chemical speciation techniques to small sample volumes (e.g. 10 mL) such as soil pore waters for which our previous chemical speciation techniques requiring larger volumes proved to be inapplicable. The originality of our research lies in the fact that the analytical timescale of measurement was identified as the key parameter for interpreting chemical speciation and predicting metal bioavailability in aqueous samples.

Metal complexes with reduced sulfur species in surface waters

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Reduced sulfur species (RSS) are well known to control the speciation of many metals of environmental concern in sulfidic waters. Less well known is that metal-RSS complexes can also be present in oxic surface waters, despite of the instability of the free RSS in such oxic environments. Here we report our intensive studies on the stabilities and identities of metal-sulfide species in oxic waters and their occurrence in natural surface waters.

The stability testing with synthesized metal-sulfide solutions indicated that, except for Fe, Mn and Ni, the sulfide solutions of all other metals studied (Cd, Zn, Pb, Cu) can be stable in oxic waters for a prolonged period (2 to more than 10 weeks). Electrospray ionization – mass spectrometry (ESI-MS) and liquid chromatography – high resolution mass spectrometry (HPLC-HRMS) suggested that ZnS is the major Zn-sulfide species in the synthetic Zn-S solution. Further transmission electron microscopic (TEM) analysis is undergoing to determine whether the ZnS is a truly dissolved species or a colloid.

Field measurements of dissolved sulfide, along with metals and a variety of other geochemical variables, were conducted in the epilimnetic waters of 6 lakes on the Canadian Shield and nearby areas. The 6 lakes are widespread from northwestern Ontario to Quebec with various degrees of human activities. The dissolved sulfide concentrations ranged from 2.5 nM to 10.4 nM for acid-volatile sulfide (AVS) and from 8.2 nM to 132 nM for chromous-reducible sulfide (CRS).

To further investigate the role of sulfide in controlling metal speciation, an extremely sulfidic prairie wetland (Delta Marsh on the south shore of Lake Manitoba) was studied for the cycling of sulfur. A comparative study on metal speciation in the wetland and in typical Canadian Shield lakes is planned for Year 3 of this project. Analytical techniques for determining thiols in these waters are also on-going.

Our results strongly suggest that ecological risk assessment (ERA) of Class B metals in oxic surface waters needs to take into account the roles of RSS when estimating metal speciation. Equilibrium calculations indicate that Cu, Hg and Ag are most sensitive to sulfide and polysulfide binding, which is coincident with the fact that the dissolved sulfide measured in the surface waters is mainly in the CRS form.

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The availability of trace metals in the rhizosphere of contaminated soils from the Sudbury area

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**Objectives and methods.** The study of the rhizosphere offers an outstanding opportunity to gain knowledge on the interactions between soils, plants and microorganisms, and on the impact these interactions have on the biogeochemical cycling of trace metals. Our long-term objective is to establish the contribution of rhizospheric processes to the cycling of trace metals in terrestrial ecosystems, notably ecosystems that were disturbed by the atmospheric deposition of trace metals. In this context, the specific objective is to contrast the fractionation of trace metals (Cd, Cu, Ni, Pb, Zn) between the rhizosphere and bulk components of forest soils exposed to different levels of contamination by metals and forming under distinct canopies. The study sites are located at three distances along transects of metal deposition in the Sudbury (under *Betula alleghaniensis* and *Pinus resinosa*: 2 species x 3 distances x 5 replicates) and Rouyn (only *Populus tremuloïdes*: 3 distances x 3 replicates) areas. Trace metals were extracted (H<sub>2</sub>O, BaCl<sub>2</sub>, Na-pyrophosphate) 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<sup>++</sup> in H<sub>2</sub>O extracts was also measured using the ISE method.

**Selected results.** The Cd, Cu, Ni and Zn concentrations in the H<sub>2</sub>O, BaCl<sub>2</sub> and, although to a lesser extent, pyrophosphate extractions are systematically higher in the rhizosphere (both the inner and the outer rhizosphere) than in the bulk component of the soils from the Rouyn transect. This concentration difference averages a factor of three; it can reach up to a factor of five for Cd and Ni and sometimes exceeds one order of magnitude for Cu and Zn. In the case of Pb, the contrast between rhizosphere and bulk materials is less pronounced (< four times) and is also less systematic, notably in the pyrophosphate extraction. In the Sudbury soils, the Cu<sup>++</sup> activity is higher in the bulk component and preliminary results suggest that free Cu<sup>++</sup> ions constitute a smaller fraction of total dissolved Cu in the rhizosphere. The gradient in soil contamination as a function of the distance to the city of Rouyn (0.5, 2 and 10 km) is observed only for Zn. For all other metals, higher concentrations were measured at 2 km than at 0,5 km from the facility. Differences among tree species are not systematic and never exceed a factor of three.

**Impact on the ecological risk assessment (ERA) of metals.** Our results could have a critical impact on the way we conduct ERA of metals in terrestrial ecosystems. This is because the data will allow to test the hypothesis that the extent of the functional role of the rhizosphere on the biogeochemical cycle of metals (as revealed here by the magnitude, direction and systematic character of the *rhizosphere effect*) is much larger than the volume fraction it occupies in the field. If this hypothesis is accepted, a scientific approach that specifically integrates the rhizosphere in the study and modelling of the biogeochemistry of metals will need to be developed. Ultimately, this work will help tackle applied questions such as whether the rhizosphere, rather than the bulk soil, should be used for quantifying the exposure to and the uptake of metals by the biota in soils.

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## Trace metal mass balances for Plastic Lake and its catchment

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Plastic Lake is an oligotrophic, dilute lake situated on the Precambrian Shield near its southern boundary in central Ontario. The lake and its catchment, including inflowing stream, wetland and terrestrial ecosystem, have been studied continuously since 1979. The lake and its catchment have been substantially affected by acid deposition, resulting in long-term loss of acid neutralizing capacity, increased sulphate and altered base cation concentrations in the lake, and reduced exchangeable calcium and reduced pH in the soil. Recent decreases in deposition of sulphate have resulted in partial recovery of the aquatic system, but current deposition stills exceeds the critical load for water, and will lead to continued damage to the terrestrial environment. The objective of our project is to measure the size of the pools and the fluxes between the pools of 5 key trace metals (Cu, Ni, Zn, Pb, Cd). In addition, we are measuring pools and fluxes of a number of other elements (Al, V, Cr, Mn, Fe, Co, As, Rb, Sr, Tl, Bi, U, Sc). This is an integrated study of the terrestrial and aquatic portions of the catchment, and includes analysis of the transport of metals between land and water. Measurements include both total and soluble (<0.45  $\mu$ ) metal fractions. Hydrology is measured continuously at a number of points in the catchment, allowing us to partition the whole catchment into sub-components, i.e. upland, wetland, lake. In addition to measuring the pools and fluxes, we are focusing on the roles that deposition of strong acid and that dissolved organic matter (DOM) play in the transport of metals are being studied. To date, the pool sizes of the major compartments of the terrestrial system (soil horizons, forest biomass) and the wetland (plant, peat, water) have been measured. Metal content of the lake water has been measured, and measurement of the sediments is in progress. Fluxes that are measured currently include: input to the system via atmospheric deposition (wet-only and bulk deposition), throughfall (under coniferous and deciduous forest), litterfall, transport through the soil column (using lysimeters), export from the upland portion of the catchment, flux into and out of the wetland, flux into and out of the lake, and sedimentation in the lake. Preliminary results presented will focus on the pool sizes.

## PROCESSES POSTER ABSTRACTS

A method for modeling bioavailability in non-equilibrated systems

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The Biotic Ligand Model (BLM): Can it be applied to higher plants? Time-course experiments for durum wheat (*Triticum turgidum*) were conducted to test the hypothesis that root binding sites equilibrate with copper over time. Live and dead plant roots were exposed to fixed free copper concentrations ( $[Cu^{2+}] = 10^{-7}M, 10^{-6}M$  and  $10^{-5}M$ ) in chemically controlled aqueous media ( $I=0.03M, pe = 15, 20^{\circ}C$ ). After  $HNO_3$  digestion and analysis with F-AAS, multiple regression analyses were performed and tested for best fit. Results demonstrate that copper accumulation by roots continues to increase for both metabolically active ( $r^2=0.979$ ) and inactive ( $r^2>0.960$ ) plants for 384 and 56 hours, respectively. The null-hypothesis was therefore rejected, a conclusion that opposes the equilibrium concept of the classical speciation modeling.

To determine the stability constant and number of root binding sites under non-equilibrium conditions, roots were exposed to nine  $Cu^{2+}$  activities ( $0 - 10^{-3}M, I = 0.03M, pe = 15, 20^{\circ}C$ ) and sampled every four days over a sixteen-day period. Dose-accumulation data were fitted to a separate modified hyperbolic equation ( $\Gamma = \Gamma_{max} (K_{ads} \{Cu\} / 1 + K_{ads} \{Cu\})$ ) for each sampling time within the total exposure length (i.e., 72, 168, 264, 360 hrs). Statistics demonstrated that for all sampling times the maximum variability in the calculated stability constants was 5% of the mean, contrasting the number of root binding sites which varied within 43% of the mean. The changing nature of Cu uptake over time was therefore shown to have stronger implications towards the number of root binding sites ( $15926 + 580 SE \mu g/g.root$ ) than on the conditional stability constant ( $4.26 + 0.07 SE$ ), which proved to be robust across sampling times. Values reported are for 168 exposure hours, chosen because of their high  $r^2$  values and low standard errors.

Understanding the binding capacity of roots for copper takes ecological risk assessment to the next level. By considering plant species-specific metal accumulation, this research recognizes the non-uniformity among plants in assessing the danger for toxicity and accumulation from exposure to contaminated soils. Recognizing that plants exert species-specific control on their environment and translating this knowledge into measures of risk assessment is an important and necessary refinement of existing conceptual models.

Thanks is extended to the Metals in the Environment Research Network and the Canadian Network for Toxicology Centres for providing funding for this project.

## Metal speciation in an extremely sulfidic inland water: (I) Cycling of sulfur species

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A strong metal-complexing ligand, sulfide is known to control the speciation and potentially the bioavailability of many metal ions of environmental concern (e.g., Cd, Cu, Pb, Zn, Hg) in natural waters where sulfide is present. While the sulfide concentrations in most inland waters are usually low (nanomolar to tens of micromolar levels), we have recently reported extremely high sulfide concentrations (up to 1.1 mM) in the sediment porewaters in Delta Marsh, a prairie wetland on the south shore of Lake Manitoba. It is of great interest to study metal speciation in such extremely sulfidic waters to further uncover the role of reduced sulfur species in metal speciation.

Surface waters, sediment interstitial waters and sediment cores from Forster's Bay of Delta Marsh were sampled several times for the period June to August 2002 and analyzed for pH, sulfur species, nutrients, and metals. The sediment-water interface was profiled by dialysis samplers (at a vertical resolution of 1 cm) and by diffusive-gradients-in-thin-films (DGT) probes (at a vertical and lateral resolution of  $\leq 0.4$  cm). The sediment was profiled by cutting the sediment core into 1-cm sections and analyzed for acid-volatile sulfide (AVS), chromous reducible sulfide (CRS), and metals.

The sulfate concentration in the surface water of the marsh was found to be as high as 1.7 mM; tens of micromolar levels of sulfide were present even at 20 cm below the sediment-water interface. Sulfide concentrations in the sediment porewater were extremely high; concentrations of up to 1.1 mM were measured and were highly variable laterally and vertically. The sulfide in the sediments was dominated by CRS, which peaked at 13-14 cm below the interface at a value of 210  $\mu\text{mol/g}$  (dry weight). The sulfur cycling result will be used to design next year's study to compare the metal speciation in Delta Marsh and in typical Canadian Shield lakes.

Our results demonstrate that sulfide can be present at extremely high concentrations in freshwater porewaters, which should be fully understood and incorporated in ecological risk assessment (ERA) of metals in such waters. The two-dimensional heterogeneity of sulfide distribution in the porewaters also questions the current practice of ERA, which is based on the bulk sediment or porewater measurements and ignores and destroys such natural heterogeneities.

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PhyavQL: PhyavQL: A computer model for estimating metal bioavailability and translocation within plants

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ONA chemical aqueous speciation program designed to model metal bioavailability and translocation within plants is currently under development. The Visual Basic application uses MICROQL-based algorithms such as mass-action, mass-balance, Jacobian and Newton-Raphson iterations to calculate metal speciation in aqueous media and on root surfaces. Conditional stability constants for root binding sites (K<sub>root-Cu</sub>) and translocation coefficients (k) developed from hydroponic experiments are incorporated into the database of chemical thermodynamics as competitive ligands. The extent of root-bound metal, or maximum bioavailable fraction, is calculated by sequential comparisons of root-metal binding capacity with that of inorganic nutrients and other compounds in solution. Translocation coefficients relate the maximum bioavailable fraction to predict shoot accumulation. The Visual Basic Windows interface provides a user-friendly template for variable input and graphical illustration of changing speciation respective of pH. The inclusion of higher plants in aqueous speciation modeling has considerable value for the future of ecological risk assessment of metals. PhyavQL has the potential to be a versatile and cost-effective tool for scientists and policy makers in predicting phytoaccumulation of metals for both toxicity and phytoremediation purposes. In its current state this project presents a framework upon which data from collaborative research efforts on plant metal binding can be integrated.

Thanks is extended to the Metals in the Environment Research Network and the Canadian Network of Toxicology Centers for funding this project.

## Metal uptake routes for the biomonitor Sialis

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Measurements of trace metals in biomonitors allow us to quantify metal exposure and, using an appropriate model, estimate metal concentrations in water or sediment. To be effective, such models should be based on chemical and biological knowledge about the organism and the metal. We are currently evaluating the potential of the alderfly *Sialis* as a biomonitor for several trace metals. In our quest to understand how this animal accumulates metals, and thus to put our biomonitor on a solid mechanistic foundation, we are conducting experiments to determine the relative importance of food and water as metal sources for *Sialis*. Understanding how animals accumulate metals will aid in designing effective means to assess ecological risks. In an earlier laboratory study, we showed that Cd is largely accumulated from food. We have now determined that this is also the case in the field for Cd and for several other trace metals. We reached this conclusion by exposing uncontaminated *Sialis velata* larvae to metal-poor or metal-rich prey (*Chironomus riparius* larvae). Metal-rich prey were contaminated for a week in net-covered containers placed at the bottom of Lake Dufault (Rouyn-Noranda). The predator was thus offered metals in either water only, in food only, or in both water and food. However, predators in all treatments were fed; in the water only and control treatments *Sialis* were fed metal-poor laboratory-reared prey. In the water-only exposure treatment, *Sialis* larvae had much lower Cd, Cu and Pb concentrations than did *Sialis* exposed to these metals in prey, suggesting that food is their major source of these trace metals. These new field results are consistent with those of our previous experiments in suggesting that aquatic predators such as *Sialis* obtain much of their trace metal burdens from food. As a consequence, models and laboratory tests designed to estimate metal exposure and explain metal accumulation and effects should consider metal uptake from the diet as well as from water. Funding was provided by MITE-RN, NSERC and the Quebec FRNT.

## Effect of cadmium on the behaviour of a burrowing mayfly (*Hexagenia limbata*)

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Current toxicological paradigms tend to consider extreme biological responses such as lethality, reductions in growth and impaired reproductive success. However, trace metals can have more subtle effects on the behaviour of animals. Given this fact, we conducted experiments to determine the effect of cadmium (Cd) on the behaviour of larvae of the mayfly *Hexagenia limbata* (Ephemeroptera). We chose *H. limbata* for our studies because it is a widely distributed and often abundant insect in lakes and rivers. Furthermore, larvae of this mayfly can be important agents of bioturbation because they resuspend sediment while feeding on it in burrows that they irrigate with oxygenated overlying water. We asked the question: does accumulated Cd modify the behaviour of this ecologically important species? To answer this question, we exposed *H. limbata* to concentrations of sedimentary Cd found in lakes nearby and downwind from metal smelters for several weeks in the laboratory. Larvae exposed to these sediments attained Cd concentrations similar to those measured in *H. limbata* from contaminated lakes near Rouyn-Noranda. We then compared the behaviour of control and Cd-contaminated nymphs by two means: radiographs, by which we measured burrow depth and cumulative burrow length; and infrared video images, by which we measured the time allocated by nymphs to various activities (irrigation, walking, burrowing/feeding, cleaning, turning). Although we observed a wide variation in activity level among individuals, these variations were not explained by Cd, that is, there was no significant difference in the length and depth of burrows constructed by control and Cd-contaminated individuals or in the time spent by these two groups of larvae in various behavioural activities. We conclude that Cd has no measurable effect on the behaviour of *H. limbata* when these larvae contain Cd at concentrations found in impacted lakes near metal smelters. Our results suggest that the *Hexagenia* populations present in lakes near the Rouyn-Noranda smelters are not behaviourally impaired by Cd. We suggest that behavioural endpoints could be a meaningful way of assessing precocious biological effects caused by contaminants.

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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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Larvae of the insect Chaoborus can be an effective biomonitor of Cd concentrations in lakewater, provided that we take into account competition between Cd<sup>2+</sup> and H<sup>+</sup> at Cd uptake sites on organisms. Because the overall goal of our MITE-RN research is to put such models on a better

mechanistic base, we conducted experiments to determine if this hypothesized competition between Cd<sup>2+</sup> and H<sup>+</sup> takes place on Chaoborus itself or at a lower level in the food chain leading to this planktonic predator. In a first series of laboratory experiments, we measured <sup>109</sup>Cd uptake by Chaoborus americanus at various pH's from a copepod (*Diatomus minutus*) that had been previously exposed to Cd in water and its algal food (*Selenastrum capricornutum*). This protocol allowed us to determine if H<sup>+</sup> in lakewater swallowed by Chaoborus could compete with Cd<sup>2+</sup> at Cd-uptake sites in the predator's gut. We held Cd concentrations in prey and Cd<sup>2+</sup> in water constant while varying the pH from 4.7 to 5.7 to 6.7. During the experiment, we measured predation rates to verify that any differences among treatment levels would not be due to changes in ingestion rates with pH (predation rates remained constant). There was no significant difference in larval Cd accumulation at the three pH's, suggesting that Cd<sup>2+</sup>-H<sup>+</sup> competition takes place at biological uptake sites at a lower level in the food chain, that is, on zooplankton prey or on algae at the base of the food chain. To understand why ambient pH does not influence Cd assimilation in the gut of Chaoborus, we used pH sensitive dyes to determine if this predator controls its gut pH and, if so, the pH at which it maintains its gut. Preliminary results suggest that Chaoborus americanus larvae maintain their gut pH at 7.2. If this result is confirmed in subsequent experiments, then this would explain why ambient pH has no influence on Cd uptake in the gut of Chaoborus. Future experiments will be designed to determine if Cd<sup>2+</sup>-H<sup>+</sup> competition takes place at the level of the crustaceans that are the main food for Chaoborus. Through these experiments we hope to put the use of Chaoborus as a Cd biomonitor on a more solid mechanistic base and thereby contribute to the development of biomonitors as an effective tool in ecological risk assessment protocols.

## A kinetic exploration of metal speciation in Sudbury and Rouyn-Noranda areas

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Atmospheric deposition of nickel, copper, zinc and cadmium from nearby smelting operations is a potential ecological and human health hazard. The local equilibrium approximation has been the dominant tool for studying metal speciation. However, natural systems are dynamic and often far removed from equilibrium. Ni(II), Cu(II) and Zn(II) are slow in reaching coordination equilibrium in freshwaters, and stability of their complexes is subject to Ligand Field Stabilization Energy (LFSE), and also Jahn-Teller effect in the case of Cu(II). Because of slow equilibration, kinetic speciation of these metals becomes an unavoidable necessity. The objective of this research was to study the impact of smelting operations on the speciation of these metals in aqueous samples. Competing Ligand Exchange Method/Graphite Furnace Atomic Absorption Spectrometry, Competing Ligand Exchange Method/Adsorptive Cathodic Stripping Voltammetry and Anodic Stripping Voltammetry with a Rotating Disk Electrode were used to investigate the kinetic speciation of these metals in soil solutions (pore waters), and through-fall precipitation samples collected from Rouyn-Noranda (Abitibi, Quebec) and Sudbury (Ontario), respectively. Samples in these regions are affected by acids added for processing of minerals, and metal contamination from current metal mining operations, abandoned mine sites, and atmospheric deposition from nearby smelters.

Total metal concentration and lability were found to be inversely related to the distance from the smelter, suggesting airborne particulate matter as a source of these metals found in these aqueous samples. Exceptions to the observed trend were attributed to the degree of site occupation by the metals (e.g. metal-to-DOC ratio) and competition by major cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . The order of the lability of the metal complexes,  $\text{Ni(II)} > \text{Cu(II)} < \text{Zn(II)}$ , followed the reverse order of the LFSE with the exception of Cu(II); the position of Cu(II) is compounded of LFSE and Jahn-Teller effect.

The significance of this work is that the slow coordination equilibrium of 3d-transition elements, especially of Ni(II) and Cu(II), in freshwaters suggests that the usual equilibrium assumption of BLM and FIAM for freshwaters may not be valid. These kinetic speciation techniques represent an important advance in our experimental ability to investigate lability of the metal complexes in freshwaters, and soil solutions (pore waters) samples, for which the usual equilibrium assumption may not be valid.

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Modeling proton dissociation from organic horizons of podzolic soils.

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Modelling the surface chemistry of soils is complicated by the sheer quantity of information that must be included in the chemical problem. All elements play a role in the surface equilibrium. We have examined the dissociation of  $H^+$  in the organic horizons of podzolic soils using a back-titration technique with a correction for surface dissolution reactions. The dissociation curves were modelled using a simplified version of the NICA (non ideal competitive adsorption)-Donnan model. The differences between model parameters fit to protonated (acid-washed) soil samples and model parameters fit to samples with their exchange complex intact were examined. We observed that the changes in model parameters were predictable and consistent across the soil samples. In an effort to simplify the modelling process we developed a mathematical relationship that related exchangeable cations to a shift in the central pKa of a single site version of the NICA-Donnan model. In these soil samples, the influence of Fe on proton dissociation was found to be important and was integrated into the regression equation. It is demonstrated that if surface complexation models are kept simple, the use of semi-empirical regression equations is an effective means to predict model parameters. These regressions simplify the modelling process and reduce the error in describing the variability in proton dissociation among soil samples of similar origin. The development of simple models to describe the surface charge of forest soils is an essential step in the development of chemical models for use in the assessment of the risk and the fate of emissions of trace metals in terrestrial environments.

## Influence of liming on the fluxes of cadmium in soils observed by DGT (Diffusive Gradient in Thin film)

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The relevant literature concurs that the total quantity of metal in a soil is not a good measurement of its bioavailability and toxicity. The bioavailability of metals can be defined as the proportion of metal that can be taken by biological organisms or that can cause a biological response. This bioavailability depends on the speciation of the metal which is related to several factors like the pH of the soil (1). Moreover, in regard to plants, metals need to be present in the soil solution to be taken by the roots. If the concentration in the soil solution is low, metals can be supplied through desorption from the solid phase (2) or through diffusion. So, the evaluation of the bioavailability of toxic metals in soils needs to consider the chemical speciation in the soil solution, the mobility of the metals and their rates of release from complexed to free metal species as well as release from the solid phase to the solution (3).

The DGT is made up of an exchanging resin which will attract metals and a layer of diffusive gel ( $\Delta g$ ) which makes it possible to analogically limit the speed of ion transport to the resin (4). Thus, the flux ( $F$ ) of ions diffusing through the gel layer can be obtained by these equations:

$$F = D \cdot C_a / \Delta g \quad (1) \quad \text{with } C_a = M \cdot \Delta g / D \cdot A \cdot t \quad (2)$$

The mass  $M$  (extracted from resin) is obtained by ICP-AES. The values of  $D$  (diffusion coefficient in the diffusive layer),  $A$  (exposed area of gel),  $t$  (deployment time),  $\Delta g$  are constant.

The effect of an increase in soil solution pH seems to emphasize desorption of Cd from the solid phase to the solution and has little impact on complexation and the ratio of labile vs. total dissolved concentrations. Therefore, the flux from the solution to the DGT unit were calculated using eq.1 and attributed to net DGT-induced fluxes from soil to solution. Given the logarithmic scale, the flux ( $F$ ) seems to be reduced by over an order of magnitude (10-50 times) following liming from pH 5.4 to 7.0. These results suggest that an increase in pH decreases the rate of metal ion transport from soil to solution. DGT permits the quantitative determination of the potential flux of cadmium from the soil to the solution. The soil used in this study is well buffered by resupply from the solid phase to solution and this both at the natural pH and with carbonate treatment. This confirms the importance of the solid phase labile pool for controlling metal supply to a given sink. A pH increase from 5.4 to 7.0 decreases the concentration of cadmium in the soil solution by about 90 %. These results are in agreement with previous findings that showed that pH is the most important factor controlling heavy metal availability in soils. As DGT can be readily deployed *in situ* in natural soils, it potentially offers the possibility to obtain kinetic information directly in natural systems.

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## Speciation of cadmium in lake waters from Rouyn-Noranda

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The lakes in the Rouyn-Noranda mining area have been affected by cadmium and other metals contamination from current metal mining operations, abandoned mines and atmospheric deposition from a large, nearby smelter that has been in operation since 1927. The objective of this research was to investigate the impact of this metal contamination on metal-impacted lake waters in terms of cadmium speciation which is related to cadmium bioavailability in freshwater. Lake water samples collected in June and July 2001 and in July and August 2002 from Lake Dufault (contaminated) and Lake Opasatica (reference) were investigated using Competing Ligand Exchange Method (CLEM)/Differential Pulse Anodic Stripping Voltammetry (DPASV), with ethylene diamine (EN) as the competing ligand for determination of the cadmium speciation parameters: concentration of free Cd<sup>2+</sup>-ion, concentration of natural organic ligands, and conditional stability constants.

The total dissolved cadmium concentration decreased during the period from June 2001 to August 2002 and the percentage of free Cd<sup>2+</sup>-ion was also found to decrease even more extensively during this period. The conditional stability constants for the Cd(II)-DOC complexes in Lake Dufault increased with decreasing total dissolved cadmium concentrations, whereas the conditional stability constant for Lake Opasatica was nearly constant during this period. Lake Dufault had higher concentrations of Cd<sup>2+</sup> ions compared to Lake Opasatica. The reason for this difference was the higher concentrations of Cu(II), Zn(II) and Pb(II) present in Lake Dufault compared to Lake Opasatica, which compete with Cd(II) for the fewer number of strong binding sites (<10%) of the Dissolved Organic Carbon (DOC), resulting in a greater fraction of Cd(II) binding to the much larger number of weak binding sites (>90%) of the DOC, forming weak Cd(II)-DOC complexes, which were labile. The competition favours complexation by metal such as, Pb<sup>2+</sup> ( $k_{-w} = 7 \times 10^9 \text{ s}^{-1}$ ) and Cu<sup>2+</sup> ( $k_{-w} = 1 \times 10^9 \text{ s}^{-1}$ ) which have higher rate coefficient for water exchange than Cd<sup>2+</sup> ( $k_{-w} = 3 \times 10^8 \text{ s}^{-1}$ ).

The significance of this work is that it has revealed the deleterious effects of discharge of metal-containing effluents to freshwaters, which increases the fraction of weak Cd(II)-DOC complexes which are labile. The originality of this research lies in developing and applying new analytical techniques to determine quantitatively extremely low concentrations of free Cd<sup>2+</sup> ions and other speciation parameters which could not be done before.

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## Stability and characterization of metal-sulfide species in oxic waters

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Most metal ions of environmental concern (e.g., Cd, Cu, Pb, Zn, Hg) tend to form strong complexes with sulfide. Despite the instability of the free sulfide in oxic waters, some metal-sulfide complexes have recently been reported to resist oxidation and can be present in surface waters. However, the stabilities and identities of these complexes in metal speciation remain poorly known. Here we report our results on the stability and characterization of the metal-sulfide species in laboratory solutions.

The stability of metal-sulfide species was studied by exposing the metal-sulfide solution to air over periods of time and measuring the sulfide remaining in the solution. The results indicated that, except for Fe, Mn and Ni, the sulfide solutions of all other metals studied (Cd, Zn, Pb, Cu) can be stable in oxic waters for a prolonged period; considerable amounts of sulfide can be measured even after the solution had been exposed to air for 2 to more than 10 weeks. The sulfide concentration in the Fe-S, Mn-S and Ni-S solutions decreased to below the detection limit within hours. Electrospray ionization – mass spectrometry (ESI-MS) and liquid chromatography – high resolution mass spectrometry (HPLC-HRMS) were then used to study the stoichiometry of the metal-sulfide species. For the Zn-S solution, ZnS appears to be the major species. Transmission electron microscopic (TEM) analysis is undergoing to determine the size and morphology of the ZnS species. The results will determine whether ZnS is a truly dissolved species or a colloid. These techniques will be expanded to other metal-sulfide species.

Once the identities of these metal species are known, they will be included in metal speciation models such as the revised HYDRAQL and WHAM for ecological risk assessment (ERA) of metals in surface waters.

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Effects of acclimation to waterborne copper on copper turnover and gill binding in rainbow trout, *Oncorhynchus mykiss*

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Juvenile rainbow trout (*Oncorhynchus mykiss*) were exposed to an environmentally realistic waterborne Cu level (22 mg/L) in moderately hard water for up to 28 days. Unidirectional copper uptake rates from both the diet and water were assessed weekly using <sup>64</sup>Cu radiolabeled diets and water. Relative to control fish kept at background Cu concentration (2 mg/L), Cu pre-exposed fish displayed decreased uptake of waterborne Cu via the gills but not decreased uptake of dietary Cu via the gut during 48-h exposures to <sup>64</sup>Cu radiolabeled water and diet, respectively. At normal dietary and waterborne Cu levels, the uptake rates of dietary Cu into the whole body (without the gut) were between 0.40 and 0.90 ng/g/h, more than 10-fold higher than those of waterborne Cu into the whole body (without the gills), which were between 0.02 and 0.07 ng/g/h. Waterborne Cu pre-exposed decreased new Cu accumulation in the gills, liver, and carcass during waterborne <sup>64</sup>Cu exposures and in the liver during dietary <sup>64</sup>Cu exposures. A 3-h gill Cu-binding assay showed down-regulation of the putative high affinity-low capacity (HALC) Cu transporters and up-regulation of the low affinity-high capacity (LAHC) Cu transporters at the gills in Cu pre-exposed fish. Exchangeable Cu pools in all the tissues sampled were higher during dietary <sup>64</sup>Cu exposures than waterborne <sup>64</sup>Cu exposures, and previous Cu exposure reduced waterborne exchangeable Cu pools in gill, liver, and carcass. Overall, these results underline a quantitatively greater role for the dietary route of Cu uptake relative to the waterborne route, and important modifications of Cu uptake and transport mechanisms following acclimation to waterborne Cu. Moreover, acclimation-induced changes in gill Cu binding have significant implications in the application of Biotic Ligand Model for ecological risk assessment in natural environments. (Supported by NSERC Strategic, MITE-RN, ICA, ILZRO, NiPERA, Falconbridge, Cominco, and Noranda).

Processes Domain / Poster Abstract