

## ECOLOGICAL RISK ASSESSMENT SUMMARY OF MITE-RN STUDIES

October 28, 2003 VERSION

PROJECT/TITLE	WHY WAS THIS STUDY DONE?	WHAT WERE THE KEY FINDINGS?	WHY SHOULD REGULATORS AND NON-SCIENTISTS CARE ABOUT THESE FINDINGS?
<p><b>A1:</b> Differentiation of metals on aeolian dust (particulates) from natural sources <u>{Grant Edwards and Goretty Dias}</u></p>	<p>Metals can originate from natural or anthropogenic sources, and although metal releases to the atmosphere have been quantified with some reliability for major anthropogenic sources, natural source estimates of metals have high uncertainties, and representative values for Canada are needed. Mercury de-gassing from bedrock and windblown dust contributes to natural sources of metals. Mercury background levels vary according to the underlying rocks and the soils overlying them. Windblown dust from natural sources can contribute significantly to the atmospheric loading of particulates, the impact of which will depend on the metal chemistry and size distribution of the particulates. This study was conducted to provide better estimates of the magnitude and variability of natural metal releases to the environment in gaseous (mercury) and particulate form, and to determine the chemical make-up and size distribution of particulates at background sites. Additionally, reliable methods to distinguish natural and anthropogenic sources at receptor sites are needed. Therefore, experimental methods to distinguish the source(s) of metals were developed and incorporated in order to enhance existing techniques for distinguishing sources (receptor models).</p>	<p>Four sites, 3 remote or background, and one downwind of a smelter, were monitored. Gaseous mercury emissions were proportional to mercury concentrations in bedrock or soil, and were also affected by temperature, net radiation and precipitation. These relationships are currently being investigated further. Metal concentrations (Cd, Cu, Hg, Ni, Pb, Zn) on particulates at the four sites were within values reported for other background and remote sites. Using experimental and receptor model methods, Cu, Zn and Ni were largely found to originate from local and soil factors at two of the sites, while Cu and Zn largely originated from long-range transport at the third site. Source fingerprinting was not possible at the fourth site. Experimental methods developed included: 1) geological surveys of the study sites to determine natural variation of metals in the soils; 2) development of methods to measure the total gaseous mercury flux based on chamber and micrometeorological techniques; 3) collection of particulates by wind direction and atmospheric conditions to distinguish sources of metals by air masses and atmospheric factors; and 3) collection of particulates by height to aid in determining which metals originated from the surface at the study site, and which were deposited from other sources. These experimental methods have been coupled to receptor models to aid in distinguishing sources.</p>	<p>The overall issue is whether observed metal loadings to various ecosystems are due to atmospheric deposition from anthropogenic activities or from natural sources. To conduct a proper ERA, the link between metal sources and metals present in the affected environment must be established. In Canada, there is concern that unnecessarily stringent environmental regulation of the industrial sector, based on incomplete knowledge of natural sources, may result in severe economic consequences with no measurable benefit to Canadians or the environment. Better estimates of natural contributions to metals in the environment and the ability to conduct experiments which will aid in distinguishing the sources are important for both regulators and industries who are asked to meet regulatory guidelines, and will lessen the uncertainty associated with knowledge of the origin of metals.</p>

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<p><b>A2:</b> Chemical speciation of air particulates related to particle size</p> <p>{Marc Lamoureux}</p>	<p>The emergence of X-ray Absorption Fine Structure (XAFS) spectroscopy has allowed determination of the chemical nature (i.e., chemical speciation) of airborne metal species. XAFS and other methods were used to speciate and differentiate airborne metal species due to natural sources from those due exclusively to industrial or man-made activities. The relationship between particle size and chemical speciation of airborne metal species is important (i.e., is the chemical speciation of an airborne metal species different at different particle sizes?) because small particles that may pose a health hazard to living organisms may some distance under high wind conditions and thus affect area that may not have surrounding industrial activities. The current practice for determining the impact of metal loading in the environment from aerosol deposition is based on total concentration of metals and not on concentration of metal species. Furthermore, analysis of collected airborne particulates is done using analytical techniques that lack sensitivity and are prone to sample contamination problems. The development of alternative techniques for the direct analysis of airborne particulate matter that require minimal sample preparation would increase the level of accuracy of the results. Therefore, knowledge about the actual concentration of each airborne metal species, as measured directly from the sample with minimal sample preparation, will allow appropriate actions to be taken only when the concentration of a metal species that poses a serious health hazard exceeds the regulated limit.</p>	<p>Speciation of copper changes with particle size, and speciation of copper from a sample collected about 9 km upwind from a smelter stack is different, regardless of the particle size, from a sample collected about 24 km downwind (nearly diametrically opposite to the upwind sampler). At least two chemical forms of copper co-exist in airborne particulate matter, a water-soluble species (copper sulfate) and a water-insoluble species (copper oxyde). Cu, Ni, Cd, and Pb particle size-dependent concentration profiles are significantly different between upwind and downwind samples taken relatively close to the stack. The lead isotope ratio (<math>^{206}\text{Pb}/^{207}\text{Pb}</math>) from downwind samples is significantly different from that obtained from upwind samples. The above-mentioned last two pieces of evidence can be used jointly to assess metal loading exclusively due to an anthropogenic source such as a metal smelter.</p>	<p>Our findings provide regulators and industries the ability to differentiate between natural and anthropogenic sources of airborne metal copper. Similar findings are expected for other metals. As well, source apportionments can be done more accurately based on airborne metal species (e.g., Pb, Cd, Cu, and Ni) instead of total airborne metals. This will allow regulatory limits to be set based on a more meaningful concept, i.e., based on metal species distribution as a function of particulate size, as opposed to simply total metal concentration on a given particle size cut-off.</p>

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<p><b>A3:</b> Chemical speciation in atmospheric wet deposition; metal content of wet/dry particulates</p> <p>{A. Chatt}</p> <p>[COMPLETED 2001]</p>			
<p><b>A4:</b> Geochemical mobility / diagenesis of metals in surface sediments</p> <p>{Richard Carignan}</p>	<p>Lake sediments are often used to reconstruct the history of metal deposition and to determine the relative importance of anthropogenic versus natural sources of metal contamination without due consideration to chemical, physical and biological processes in the sediments that could obscure this historical record.</p>	<p>We determined under what circumstances lake sediments can provide true historical records of trace metal loadings from the atmosphere. We discovered that Hg supply to aquatic environments is influenced in a major way by wildfires in their watersheds.</p>	<p>Incorrect conclusions drawn from the interpretation of sediment trace metal profiles could have serious ecological and economic implications.</p>

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<p><b>A5:</b> Analytical speciation of metals on atmospheric particulates / aerosols</p> <p>{<a href="#">Julia Lu</a>}</p>	<p>Identification and quantification of individual forms of mercury is important in understanding not only the mechanisms of reactions/interactions involving mercury in industrial processes and in the natural environment, but also reactivity, bioavailability, and toxicity of this element. The atmosphere receives most of the mercury emissions (more than 90%) from industrial activities (e.g., coal-burning) and it is, in return, the primary source of mercury input to water bodies and land. Particulate phase mercury plays an important role in the atmospheric depositional process. However, there are no analytical methodologies for identifying and quantifying mercury species associated with atmospheric particulate matter/aerosols.</p>	<p>We have developed a novel method to analyze mercury species associated with atmospheric particulate matter/aerosols. This method uses an all-quartz-mini-sampler for collecting airborne particulate matter/aerosols, thermal desorption for separating mercury species, and ICP-MS for mercury identification and quantification. The method has been evaluated using samples of coal fly-ash spiked with different mercury compounds (e.g., HgO, HgCl<sub>2</sub>, Hg<sub>2</sub>O, and HgS) and with a standard, certified reference material. Applications of the method to the analysis of samples of airborne particulate matter and of suspended particulate matter in rainwater reveal distinct mercury species in the samples and evidence of chemical transformation of mercury in the natural environment.</p>	<p>Information on mercury speciation is important to regulators because it can be used to identify the forms of mercury that are released from point sources, to predict the movement of mercury after release, and to assess the influence of mercury movements on ecosystem and human health.</p>

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<p><b>A6:</b> Chemical analysis of aerosolic particulates</p> <p>{Graeme Spiers}</p>	<p>Initially this project focused on the development of a new version of the energy dispersive miniprobe using monochromatic radiation suitable for the analysis of a variety of environmental sample types, including single grains collected from soils, sediments or aerosols (EMMA). With the successful construction of the instrument, the focus moved to analytical applications in support of a variety of projects examining the effects of smelter emissions in the Sudbury smelter footprint, with continuous sensitivity improvement being gained with more difficult or smaller sample types (e.g., window wipes).</p>	<p>Key findings revolve around the utility of the EMMA instrument to effectively and efficiently provide excellent low-level quantitative data of potentially hazardous trace metals in diverse environmental samples with minimal sample preparation. A key benefit is the non-destructive nature of the analytical approach, with the sample being available for subsequent examination by alternative non-destructive techniques such as scanning electron microscopy or following successful EMMA analysis. The development of the EMMA instrument has enabled analysis of a range of samples including vegetation powders, soils and sediments, aerosols on filter media and single particles of historic and modern aerosols of diameters greater than approximately 20 micro-m. For example, analysis of aerosolic materials filtered from winter snow pack has provided firm information enabling the distinction between long-range transport and local materials from the Sudbury industrial complex. This information has, for example, indicated that current emissions may possibly be detected some 175 or more kilometers to the north east of the smelter region, even with the confounding influence of industrial effects in the region. Further analysis using isotopic techniques may be necessary to provide a final answer to this tentative conclusion.</p>	<p>This information is providing information not currently available, information that may be of great significance in unravelling sources of risk to human and ecological health with the Sudbury smelter footprint. The information will be very useful in the community risk assessment process, and will allow information transfer to the public to allay fears of potential health risk. The research program has provided an opportunity to collect information invaluable in addressing potential questions that must inevitably arise during the public review process of both Ecological and Human Health Risk currently ongoing in the Sudbury Region. The information from this analytical approach has the great advantage of being accurate, rapid and non-destructive, making the approach a powerful screening tool for obtaining data to drive more detailed investigations.</p>

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<p><b>A7/AF10:</b> Examination of mineral weathering and release of trace elements in selected soil profiles</p> <p>{Jeanne Percival / William Hendershot}</p>	<p>The study was done to find out whether there was a natural source of trace metal entering the ecosystem in the vicinity of the smelters at Sudbury and Rouyn. If metals are being released from the soil particles and entering the biological cycles of the forests, then the impact of metals added by atmospheric deposition need to be viewed as a partial contribution and not "the" source of contaminants.</p>	<p>Preliminary findings indicate that the additions by mineral weathering are on the same order of magnitude as the amounts being added from the atmosphere.</p>	<p>Other scientists and regulators need to be aware that the amount of metal in soils is a function of contributions from both natural and human sources and so control of natural sources will not result in zero additions to the environment. Part of the message is also that areas around smelters are likely to be naturally rich in trace metals due to the properties of the parent materials, and human activities have only modified the amounts by a degree yet to be determined.</p>

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<p><b>AF7:</b> Physical and chemical evolution of aerosols in smelter and power plant plumes.</p> <p>{Cathy Banic}</p>	<p>National and international concern about the health effects and continued use of Pb, Cd, As, and Hg as well as other metals has defined a need for improved estimates of the long term risks to ecosystems and human health from metals released from mining, metallurgical, and energy production activities. A research aircraft was used to determine the microphysical and chemical properties of airborne particulate metal emissions from the Nanticoke coal-fired power generating station located on the north shore of Lake Erie, Ont., the Horne copper smelter at Rouyn, Que. and from a natural wildfire. These properties are critical to the determination of the deposition rates of metals emitted, and hence their potential to have impacts on local or distant ecosystems. The measured properties are being used in existing atmospheric models to predict the concentrations and deposition patterns of current emissions of metals in particulates from both individual point sources and to estimate the proportion subject to long range transport.</p>	<p>The size distribution of particles emitted from the sources, the metal content of the particles (with emphasis on Ni, Cu, Pb, Zn, Cd, As, Se and Hg), and the distribution of metals by particle size were determined. The plumes were observed to contribute to the particle volume at particle diameters from 0.03 to 30 micrometers, with metals emitted in varying, but sizeable, proportion in the small size fraction (i.e., less than 2.5 micrometers in diameter). A 3-dimensional modelling study is underway with realistic emission rates to estimate the concentration of metals in air and their deposition to the surface on both local and regional scales. Mercury was predominantly emitted as gaseous elemental mercury from all three sources. Gaseous elemental mercury has a long lifetime in the atmosphere and will be transported on global scales. The modelling studies to date have shown that most of the particles observed in the plumes will not be subject to processes which will lead to dry deposition, that dry deposition is smaller than wet deposition in both winter and summer for both industrial sites, that dry deposition is smaller at Nanticoke compared with Horne because of the higher level of the plume central core, and that large particles have greater deposition than medium and small particles.</p>	<p>The data collected in this study are needed for policy decisions regarding emissions of metals from different sources.</p>

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<p><b>AF8:</b> Redistribution of metals in lake sediments by bacterially mediated oxidation-reduction reactions</p> <p>{W. D. Gould}</p>	<p>Our overall project objective is to infer the role of microbial activity on the distribution (or redistribution) of metals in lake sediments through simulation experiments. The implications of this work are significant for the degree to which metal profiles in fresh water sediments can be interpreted as historical records of anthropogenic metal loading. The intent of this project is to directly address the goal of the Sources Domain to estimate “release of trace metals from the solid phase receiving anthropogenic deposits, and from natural sources”.</p>	<p>A series of microcosm experiments were set up to study the key hypotheses in the lake sediment study based on fresh sediment samples. The experiments consisted of 10-cm diameter core tubes containing a 1-cm layer of amended sediment, which was then covered with 6 cm of unamended sediment and 4 cm of overlying lake water. The cores were incubated at 6°C and were sampled over a time series, once in January 2002 and also in October 2002. Preliminary results indicated that elevated concentrations of soluble iron in the porewater fraction were observed throughout most of the sediment column when ferrihydrite was added. Increased concentrations of solid phase iron were observed in the 2 cm of sediments above the ferrihydrite-amended layer. Additional experiments will be done in order to determine if the effect is due to mobilization and redeposition of iron or to an artifact of the sampling procedure.</p>	<p>Elevated metal concentrations in surface lake sediments are typically attributed to increased industrial activity, however there are a number of mechanisms that could potentially redistribute metals in sediments, including bacterially mediated redox reactions (e.g., iron and manganese reducing bacteria can use metals as alternate terminal electron acceptors under anaerobic conditions). The activities of these reducing bacteria can solubilize metals that have been incorporated with oxyhydroxides. Solubilized metals can migrate by diffusion and potentially re-precipitate at other locations within the sediment profile. This project will provide a greater understanding of metal transformations in lake sediments. Knowledge gained on the kinetics of geochemical processes and the relationship between anthropogenic and naturally occurring loadings of sediments will be useful in assessing the impact of mining and smelting activities on receiving waters and lakes. An understanding of the relative ability of remobilized metals to produce toxicity will reduce ERA uncertainties.</p>

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<p><b>AF9:</b> Role of bacteria in mobilisation of arsenic from mine impacted tailings</p> <p>{<u>Vince Palace and Frank Rosenzweig</u>}</p>	<p>Gold and uranium mining activities are often associated with elevated concentrations of several metals in biotic and abiotic compartments. Arsenic is one of the major elements of concern for many of these operations. Whereas environmental managers may be aware of the primary factors governing arsenic release from contaminated sediments, recent evidence suggests that other less understood factors, including bacterial activity, can affect the rates of release of arsenic from contaminated sediments to the overlying water column. These studies were undertaken to examine the contribution of bacterial activity to arsenic release from sediments contaminated by mining activity.</p>	<p>This study has identified specific bacteria species that are capable of respiring using arsenic. The respiration of arsenic by these bacteria as part of their energy metabolism, transforms arsenic from the oxidized state, arsenate, to the reduced state, arsenite. This transformation results in greater solubility and, hence, greater mobility of arsenic, which allows it to move into surface waters and subsequently into biota.</p>	<p>The key issue identified by this project is that the mobility of arsenic can change with changing conditions at a contaminated site. Specifically, we have seen that, as bacterial communities colonize areas of high arsenic (e.g., mine impacted sediments), the rates of release of arsenic from those sediments can also change. Predictions regarding how much arsenic will move from the deposited sediments and into potential human exposure pathways (i.e., drinking water and fisheries resources) will be strengthened by including the data generated from this project.</p>
<p><b>B1:</b> Trace metal dynamics in contaminated northern forest ecosystems</p> <p>{<u>Beverley Hale, William Hendershot</u>}</p>	<p>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 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. 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.</p>	<p>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.</p>	<p>The database developed and the development and calibration of predictive models provide regulators with a tool to evaluate the effects of smelter emissions on the boreal terrestrial ecosystem. Non scientists should be reassured that the metals in these ecosystems are mainly in highly stable forms with little chance of causing ecological harm.</p>

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<p><b>B2:</b> Models relating metals in animals to metals in the environment</p> <p>{<u>Landis Hare,</u> <u>André Tessier</u>}</p>	<p>Human activities have increased the movement of metals such as cadmium and copper to lakes where they can enter living organisms and have toxic effects. Our goal is to understand from where and by what means aquatic animals take up these metals. Using this information, we can develop models that will allow us to relate metal concentrations in animals to those in their surroundings and thereby use animals as metal biomonitors.</p>	<p>We cannot assume that metal concentrations in sediment or in water will represent those to which animals are exposed. Animals determine in part from where their metals come, and how much they accumulate, through their burrowing and feeding behaviours. For example, animals living in sediments do not necessarily take up their metals from sediments because they pump water through U-shaped burrows, which minimizes their exposure to sedimentary metals. Metal exposure is also influenced by an animal's feeding behaviour because some animals take up most of their metals from food rather than from water. Thus metals are transferred along food chains. We used models based on this type of information to relate metal concentrations in animals to those in their surroundings.</p>	<p>Information on metal uptake by organisms is useful to determine in what medium we should measure metal concentrations to assess metal exposure to the biota in lakes and streams. Alternatively, organisms themselves can be used as biomonitors to assess metal exposure in nature. Lastly, information on metal uptake can improve laboratory tests designed to measure the effects of metals on animals by making them more ecologically sound and thus environmentally relevant.</p>

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<p><b>B3:</b> Quantification and modelling of metal mobility</p> <p>{<a href="#">Les Evans and Miriam Diamond</a>}</p> <p>[COMPLETED 2001]</p>	<p>A question that is often asked is, "if we release an amount of metal into a lake, what will the concentration be in the system and how might this affect the fish in the lake?". We have developed a mathematical model that relates the amount of metal released into a lake with the resultant concentrations. We have taken the model to a more sophisticated level by accounting for the complex chemistry that the metal will undergo upon its release. Accounting for this complexity increases the accuracy of our model estimates. The results can be used by experts in ecotoxicology to determine if the resultant concentrations, and more specifically, the concentrations of particular metal species predicted by the model, will cause potential harm to the biota in the lake.</p>	<p>The model provides reasonable estimates that connect metal releases with lake concentrations. To arrive at this conclusion we applied the model to a lake that has high concentrations of zinc in its sediments and for which the chemistry is relatively complicated. Our model was able to simulate the concentrations in the lake (note that the model is based on scientific principles and is not used to "fit" the data). We also used the model to estimate future concentrations in the lake given different amounts of zinc released and changes in lake chemistry.</p>	<p>The model provides regulators with a tool to help them regulate. Specifically, the model will assist regulators with setting reasonable limits for the release of metals into lakes where that limit is set to protect the health of the lake's ecosystem. The model provides industry, such as mining companies, with a tool that will help them meet regulatory guidelines</p>
<p><b>B4:</b> Metal speciation in freshwaters from lakes, soil pore waters, and through-fall precipitation samples</p> <p>{<a href="#">Chuni Chakrabarti</a>}</p>	<p>Environmental regulators and water resources managers need to know the maximum permissible loading of toxic metal species in effluents to freshwaters, and they depend on the scientific community to provide science-based answers to these questions that can eventually form the basis of environmental regulations to protect aquatic ecosystems. The problem is that it is not the total concentration of a metal - it is the metal speciation that determines ecotoxicity. We have sought to answer this challenge by developing metal speciation models that are applicable to the freshwater environment. We have sought to establish experimentally the following linkage: Metal Speciation ↔ Bioavailability ↔ Ecotoxicity.</p>	<p>Freshwaters are dynamic systems, often far removed from equilibrium, mainly because coordination equilibrium involving transition metals is typically slow. The result is that the equilibrium assumption (on which the principal, environmental regulatory models, FIAM and BLM, are based) may not be valid. Three factors were found to influence the dissociation kinetics of trace metal complexation: 1) metal-to-ligand ratio; 2) charge-to-radius ratio; 3) ligand field stabilization energy. Incorporation of kinetic speciation is essential for slow rates characteristic of double exchange reactions involving transition metals, Ni(II), Cu(II), Cd(II), or Zn(II). For Ni(II), Cu(II), Cd(II), or Zn(II) complexes in freshwaters.</p>	<p>Our results provide science-based tools that can enhance the usefulness of currently-used bioavailability models (FIAM and BLM) by incorporating kinetic speciation, which will result in better protection of the freshwater environment. Because freshwaters are non-equilibrium systems, ERA based only on equilibrium-availability of free metal ion concentrations may underestimate the real risk. ERA should take into consideration both equilibrium and the kinetic speciation.</p>

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<p><b>B5:</b> Availability of trace metals in the rhizosphere of contaminated soils from the Sudbury area</p> <p>{<u>François Courchesne</u>}</p>	<p>The main purpose of this study was to generate new knowledge to help increase our capacity to relate the uptake and storage of nutrients and trace metals by plants to the elemental content of the soil materials. Most, if not all, of the scientific approaches available to estimate plant uptake are based on the chemical composition of the solid and/or of the liquid phases of the bulk soil. Although we recognize that bulk soil content is involved in the process of elemental uptake by plants, we also believe that our ability to understand the transfers of matter between the pedosphere and the biosphere will be drastically improved by taking a closer look at the soil: root interface. In short, the rhizosphere is a soil environment that we need to explore thoroughly in order to better understand, manage and protect the soil-plant systems of the Earth's surface.</p>	<p>The data gathered during the project clearly indicate that the rhizospheric environment systematically acts as a sink for trace metals such as Cd, Cu, Ni, Pb and Zn when compared to the associated bulk soil materials. This observation is termed the rhizosphere effect. Moreover, this effect is proportionally more pronounced for the bioavailable forms than for the less soluble metals. We have studied the environmental factors that are susceptible to control the increased metal levels in the rhizosphere, and we found that the impact of tree species is of a rather limited extent for most metals and that it is generally lower than a factor of two. The impact of soil contamination by metal compounds on the rhizosphere effect can reach up to a factor of five and varies substantially with metal type. The role of organic matter and of soil microorganisms is also under investigation.</p>	<p>The advances in the area of rhizosphere research resulting from this project will: 1) have a profound impact on our understanding of the role of roots, microorganisms and organic matter on the uptake of trace metals by plants; 2) challenge our current concept of the strategies that the plants implement when exposed to contaminants of anthropogenic origin; 3) allow identification of key indicators of the response of soils to environmental stresses; and, 4) generate knowledge on the chemistry of the rhizosphere that will prove very useful for the development of new bioremediation technologies for the cleanup of metal-contaminated soils</p>

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<p><b>B6:</b> Metal budgets of Canadian Shield lakes and catchments</p> <p>{<u>Peter Dillon and Shaun Watmough</u>}</p>	<p>Most research on trace metals in the Canadian environment has been conducted on severely affected sites. Much less is known about the levels and cycling of trace metals under either natural or background conditions, or in systems where long-range transport is the most significant source of metals rather than local point sources. In both of these cases, metal levels are typically much lower than in those systems affected by point sources. The role of acid deposition in mobilizing metals from catchments to lakes is well known for some of the non-trace metals such as Al, Fe and Mn, but much less understood for the metals found in trace amounts. This study was intended to provide a baseline against which more heavily impacted sites can be gauged, providing targets for remediation, and to assist in developing a better understanding of how ecosystems function naturally.</p>	<p>The information that has been collected is still being synthesized and summarized into key findings, so it is premature to address this question at this time. The data collected at our principal study site will be useful for comparison with other MITE-RN sites that focus on more heavily impacted areas near smelters. Ongoing MITE-RN projects can use our site, although not a true reference or background site, to provide comparable data at low metal levels. These data will also be used for development and testing of fate and transport models. We will also partition the sources of some of the metals between anthropogenic and natural components.</p>	<p>The results will provide regulators with some of the tools needed to help them set acceptable metal levels in the environment. Specifically, the information will assist regulators with setting reasonable limits for levels of metals in lakes by establishing natural or background levels.</p>

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<p><b>B7:</b> Role of reduced sulphur species in controlling metal speciation in surface waters on the Canadian Shield</p> <p>{Feiyue Wang}</p>	<p>One of the key questions in the exposure assessment phase of a metals ERA is how to take into account metal speciation and to distinguish bioavailable from non-bioavailable metal species. Metal speciation studies in surface waters have long centered on the role of organic matter in determining metal speciation and bioavailability. At the beginning of this project, new studies were published suggesting that metal-sulfide species might also be present in surface waters, but little was known about their identities and relative importance. We started this project specifically to answer the following three questions: (i) can metal-sulfide species be stable in oxic waters? (ii) if they can, what are their chemical identities (i.e., complexes, clusters, or colloids)? and (iii) how important are they in determining metal speciation in surface waters on the Canadian Shield?</p>	<p>After 3 years of investigation, we are able to draw the following conclusions to the three questions: (i) Whereas some metal-sulfide species (e.g., Fe-S, Mn-S, Ni-S) are not stable in oxic waters, other metal-sulfide species (e.g., Pb-S, Zn-S, Cd-S, Cu-S) can be stable in oxic waters for prolonged periods of time (weeks to months). (ii) Multiple lines of evidence suggest that those oxidation-resistant metal-sulfide species in laboratory solutions are indeed a mixture of truly dissolved metal-sulfide complexes and dynamic colloids; they are not soluble metal-sulfide nanoclusters as previously reported in the literature. (iii) Field studies and thermodynamic modeling indicate that truly dissolved metal-sulfide complexes play a negligible role in determining metal speciation in surface waters on the Canadian Shield. New analytical techniques are needed to determine the relative importance of dynamic metal-sulfide colloids in those waters. Although metal-sulfide nanoclusters are not found in synthesized oxic waters, they may be present in natural surface waters if appropriate stabilizing agents are available. This possibility warrants further investigation.</p>	<p>First, our results have removed one uncertainty associated with exposure assessment of metals, that is, regulators can neglect metal-sulfide complexes when assessing metal speciation and bioavailability in most natural surface waters on the Canadian Shield. Second, regulators should be aware that some metal-sulfide colloids and/or clusters may be present in surface waters, the importance of which needs to be further studied. Finally, we have provided revised metal speciation models (WHAM and HYDRAQL), which can help regulators to assess metal speciation in waters where sulfide concentration is relatively high (e.g., hypolimnetic waters and sediment interstitial waters).</p>

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<p><b>BF1:</b> Biochemical cycling in the boreal forest – Metal concentrations in woody tissues</p> <p>{<u>Christian Bégin</u>, <u>Martine Savard</u>}</p>	<p>Previous dendrogeochemical investigations of a series of six forest sites in the Rouyn-Noranda region have shown that some of the metals emitted from the Horne smelter accumulate in woody tissues. The significance of this and how these anthropogenic metals would be incorporated and cycled in the forest system were uncertain. This study was intended to provide a quantitative assessment of the total metal pool in boreal forest vegetation. This is the first step to calculate the long-term return of these metals to forest soils. Such investigations will directly contribute to global understanding of metal biogeochemical cycles in the boreal ecosystem.</p>	<p>A method was developed for evaluating metals concentrations in standing wood and used to develop new data on metals loadings from the Horne smelter into boreal forest areas – metals contamination was at least 13 times higher than in areas of the forest unaffected by the smelter. Broad leaf species are particularly efficient at absorbing and accumulating metals in their woody tissues. The additional contamination by anthropogenic metals impairs the assimilation of some metals (e.g. Cu) naturally involved in physiological processes. Accumulation of metals follows a lag phase (uptake is not foliar, but via the roots)</p>	<p>Canada is among northern countries identified as important sources of airborne metal concentrations. Some of those metals are absorbed by forest vegetation. Knowledge of the extent and significance of this metals “sink” in boreal forests is required as this is an increasingly important issue for managers and the public. This study provides previously unknown information.</p>

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<p><b>C1:</b> Metals effects in aquatic biota <u>{George Dixon, Uwe Borgmann}</u></p>	<p>Risk assessments and management decisions regarding metals in the aquatic environment rely heavily on water (WQG) and sediment (SQG) quality guidelines. However, these guidelines are often unreliable for predicting toxic effects for several reasons. First, WQGs are either single numbers, or contain only a correction for water hardness. However, hardness is often not the main or only factor actually controlling metal toxicity in water. Second, WQGs are based on single contaminants and do not take the reality of metal mixture effects into account. Third, SQGs are also single numbers and do not take overlying water chemistry into account. However, water chemistry strongly affects both the partitioning of metals between water and sediment, and the uptake of metals from water. Fourth, neither WQGs nor SQGs take metal uptake from food into account. However, some organisms obtain most of their metals from food, and present guidelines might not be sufficient to protect against dietary exposure to metals. We have, therefore, conducted studies to determine: (1) The relationship between Ni and Cd bioaccumulation and chronic toxicity in freshwater to <i>Hyalella azteca</i> with all major water chemistry components (calcium, magnesium, sodium, potassium, pH, alkalinity, dissolved organic matter) to develop a “biotic ligand model” (BLM) to accurately describe toxicity in a wide variety of water chemistry types. (2) Bioaccumulation and chronic toxicity of As, Co, Cr and Mn to <i>Hyalella</i> (data previously not available), and then determine the toxicity of mixtures of 10 metals (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Tl, Zn) when present simultaneously. (3) The effect of different natural lake waters, with widely differing chemistry, on metal accumulation and chronic toxicity to <i>Hyalella</i> for sediments collected from different lakes near smelters. (4) Accumulation and chronic toxicity to <i>Hyalella</i> of Cd in food-only exposures using food grown in the presence of Cd (i.e., not artificially spiked).</p>	<p>In all of these studies metal bioaccumulation has been measured and compared directly to toxicity because toxicity is a function of metal accumulated and not total metal in the environment. Observations to date indicate that: (1) Ni toxicity is predictable from Ni accumulation and is a function of calcium and pH, but not magnesium, sodium, or potassium. The BLM accurately predicts toxicity. Studies with Cd and the effects of organic matter on Ni and Cd are underway. (2) Toxicity of 10 metal mixtures is less than predicted (i.e., less than strictly additive) with the commonly used “toxic unit model”, which assumes that effects can be predicted by adding together the concentrations of all metals, after applying a weighting factor which accounts for the different potencies of the different metals. However, toxicity is slightly greater than predicted using an “effects-addition” model, which sums predicted effects for all single metals in the mixture. (3) Accumulation and toxicity of Ni in sediments is not affected strongly by water chemistry, but accumulation and toxicity of Cd in sediments is much higher when the overlying water is softer and of lower pH. Use of the BLM accurately predicted Ni bioaccumulation and use of the effects-addition model closely predicted observed toxicity in <i>Hyalella</i> exposed to field-collected sediments. (4) We have succeeded in growing algae in the presence of Cd and creating a “naturally” contaminated (i.e., environmentally relevant) food source which retains most of the Cd when fed to <i>Hyalella</i>. This food was toxic to <i>Hyalella</i> in initial tests. Further experiments to determine dose-response relationships are in progress.</p>	<p>This research will provide managers and regulators with more reliable predictions of impacts from metals in the environment. For example, toxic impacts for single metals can be predicted, even under widely varying water chemistry conditions, using BLM type models. In fact, the USEPA is currently developing a BLM-based criterion for copper. In addition, our research will allow better prediction of the impacts of multiple metals present simultaneously, and will help adjust guidelines to take dietary exposure into account, if necessary. Our results also demonstrate how water chemistry effects can be incorporated into cause-effect based SQGs to more accurately predict effects of metals in sediments.</p>

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<p><b>C2:</b> Biological effects of chronic metal exposures in fish</p> <p>{<a href="#">Chris Wood</a>, <a href="#">Gordon McDonald</a>}</p>	<p>The primary objectives of our research are to use laboratory-based studies to understand and model the chronic impacts of metals (Cu, Cd and Zn) on the health of fish in the natural environment. In this context, we are particularly focusing on the Biotic Ligand Model (BLM) approach, which is becoming well accepted globally as a new cost-effective strategy for performing ecological risk assessment for metals in the aquatic environment. The BLM is a mechanistic model that relates the binding of free ionic species of a metal in the biotic ligand (e.g., fish gill) to toxicity in reference species, and is currently used only for assessing acute toxicity in freshwater organisms (fish and daphnids). Our ultimate goal is to develop BLMs for assessing chronic toxicity of metals in freshwater fish that will take into account both waterborne and dietary exposure routes of metals.</p>	<p>The present versions of the BLMs consider that only water chemistry variables can influence the bioavailability of a metal and thereby its toxicity in fish. However, we have demonstrated mechanistically how different environmental conditions, especially during chronic exposures (e.g., metal levels in water and diet, and dietary quantity and quality), and acclimation can produce dramatic alterations in the metal-binding properties of the biotic ligand, and subsequently in the toxicological sensitivity of freshwater fish to metals. We have also delineated several chronic endpoints that are indicative of chronic toxicity of different metals, both via water and diet. Overall, our findings strongly indicate that the chronic history of the fish needs to be integrated into the present version of BLMs in order to use them for assessing chronic impacts of metals.</p>	<p>All of our findings are significant steps towards the development of chronic BLMs for Cu, Cd and Zn. The intended chronic BLMs, once developed, will be of great significance, particularly in Canada and Europe where the regulatory emphasis in ERA is on chronic impacts. Application of the cost-effective, site-specific BLM approach for addressing ERA issues of chronic toxicity will provide better environmental protection, will ease the regulatory burden for industry, and will help protect the export market of Canadian metal producers.</p>

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<p><b>C3:</b> Relationships between metal body burdens and effects</p> <p>{<a href="#">Peter Campbell</a>, <a href="#">Alice Hontela</a>, <a href="#">Joe Rasmussen</a>}</p>	<p>This study was done to help define the impacts of metals on aquatic ecosystems and help develop credible water quality guidelines for metals. Government regulators working in this area have traditionally relied on laboratory experiments carried out under defined conditions (toxicity tests) and, to a lesser extent, on field observations on impacted indigenous populations. To link these two approaches, one needs a common measure of metal exposure in laboratory and field settings. The determination of metal concentrations or burdens in tissues (or whole organisms) has been suggested as a means of achieving this linkage. More specifically, this field-based project was designed to determine (i) whether relationships exist between metal body burdens in indigenous fish and metal-induced effects at the organism and population levels, and (ii) whether these relationships improve when the metal body burdens are expressed not as total metal, but rather in terms of the metal's partitioning within particular target tissues. Different life stages of yellow perch (YP: <i>Perca flavescens</i>) were chosen as trial biosentinel organisms.</p>	<ul style="list-style-type: none"> <li>• Essential and non-essential metals are handled differently by YP.</li> <li>• Food may be an important source of Cd (and other metals?) to yellow perch. If this observation is confirmed for other fish species, it should trigger consideration of the question whether PNECs expressed in terms of dissolved metal will be under- or over-protective.</li> <li>• Metal “spillover theory” does not seem to apply in the case of chronic / life-long metal exposures (evidence for incomplete metal detoxification even in moderately contaminated lakes, and the apparent absence of a threshold exposure concentration below which the incoming metals are completely detoxified).</li> <li>• Competition by ambient Ca<sup>2+</sup> or H<sup>+</sup> ions at metal uptake sites did not have a major influence on bioaccumulated Cd, Cu, Zn or Ni in feral yellow perch, in contrast to (short-term) results obtained from laboratory exposures of fish to waterborne metals (limited usefulness of BLM to predict metal bioaccumulation in indigenous yellow perch).</li> <li>• Indirect, food-web mediated effects of metals on YP in the most contaminated lakes. The most common indication of such indirect effects on YP is severely stunted growth coupled with a high degree of zooplankton dependence throughout their life.</li> </ul>	<p>The absence of a clear threshold metal concentration, above which YP cannot detoxify incoming metals (i.e., the apparent failure of metal “spillover theory” to apply under chronic exposure conditions) runs counter to prevailing thinking about metal toxicity.</p> <p>The demonstration of food-web mediated effects of metals on consumers serves as a reminder of the importance of the “less-noble” or forage aquatic species, i.e. those that serve as the prey base for the top consumers.</p>

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<p><b>C4:</b> Accumulation and effects of metals on wildlife</p> <p>{<u>Laurie Chan</u>}</p>	<p>The objectives of this study were to investigate: Hg accumulation in target wildlife species and their prey in ecosystems near mining/smelting activities, and near areas having naturally high geological sources of Hg in Canada; the interaction between Hg and Se in biological tissues; and potential biomarkers of Hg exposure and damage in fish-eating wildlife.</p>	<p>Our most important finding was that, in all 3 of our study sites (lakes in the Noranda, QC area; lakes near Clyde Forks, ON; and lakes in the Pinchi, BC region), having a wide range of soil- and sediment-Hg concentrations, Hg accumulation in small fish was generally not sufficiently high to be of toxicological concern for most fish-eating wildlife. Sediment/soil Hg concentrations in these areas are not good predictors of corresponding fish-Hg concentrations. Large increases (&gt;20 fold) in sediment-Hg do not necessarily translate into comparable increases in Hg in fish, or in fish-eating wildlife (2-3 fold). Hg accumulation in fish is strongly influenced by water chemistry (e.g. - lake pH), and the dominant chemical form of Hg in sediments, as well as by the amount of Hg present. Environmental Hg present predominantly as HgS (cinnabar) probably has low bioavailability for methylation, compared with other inorganic Hg complexes; availability to bacteria for methylation is a key requirement for Hg biomagnification. Hg also forms complex with Se in common loon tissues. This may provide a protective mechanism for Hg toxicity.</p>	<p>Our findings are relevant to helping government and industry develop sound, science-based policies regarding Hg in the Canadian environment.</p>

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<p><b>C5:</b> Population and physiological effects of industrial metal contamination on wild fish</p> <p><u>{Patrice Couture and Greg Pyle}</u></p>	<p>Given recent Canadian regulations requiring metal mining and smelting companies to monitor the effects of their activities on fish populations and to assess the ecological risk of new projects in the receiving environment, there is an urgency to validate laboratory models and to critically examine commonly used indicators of condition in wild fish. Although metal effects on fish have been extensively studied in the laboratory, the effects on wild fish, which are the primary concern of regulators, remain underrepresented in the literature. Our research examined a large number of yellow perch from the widest size range available in five lakes from each of two of the most metal-contaminated aquatic systems in Eastern Canada, Sudbury ON and Rouyn-Noranda QC. Yellow perch are ubiquitous in Eastern Canada and can be found in lakes ranging from pristine to highly metal contaminated. The objectives of this research were to characterize the extent and variability of metal effects on fish condition and physiology and to identify sensitive end-points in wild fish inhabiting metal-contaminated systems.</p>	<p>Condition factor of wild yellow perch was significantly impaired in metal contaminated lakes relative to uncontaminated sites. However, condition factor was strongly influenced by age, gender, location (Sudbury vs. Rouyn-Noranda), and season. Moreover, fish living in metal contaminated sites were generally smaller than those from clean sites at a young age, but grew more rapidly than those from reference sites, indicating that varying ecological conditions along the metal gradient (for example competition and predation) likely interfere with metal effects on fish growth and condition. Although growth was more rapid in contaminated lakes, fish did not live as long as those from clean lakes. Tissue metal accumulation patterns suggested that essential metals, like copper and nickel, are under tight homeostatic control. However, when these essential metals accumulate beyond some critical threshold that our large database will allow us to define, homeostatic control is lost and metal accumulation is rapid and significant. Non-essential metals, like cadmium, are not under homeostatic control and metal accumulation typically reflects metals in the environment. Our data also indicate that diet is a significant source of metals in wild fish, and may actually be more important for explaining some of these effects than dissolved metals. Finally, our results confirmed earlier studies in our laboratory that metal-contaminated fish are aerobically impaired. However, our results suggest that aerobic impairment varies with fish age, being measurable in small fish and disappearing in larger fish.</p>	<p>Our research should receive careful attention by regulators, because it indicates that metal contamination of receiving environments likely causes effects through dietary more than aqueous uptake (such are not presently adequately considered by predictive models such as the BLM), that younger fish are aerobically impaired, which may be an effect of dietary preferences, and that growth and morphometric condition may in some situations be very high in metal-contaminated yellow perch.</p>

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<p><b>CF1:</b> Assessment of profundal benthic invertebrate communities in metal-contaminated lakes and meta data analyses</p> <p>{<u>Lee Grapentine</u>}</p>	<p>Regulators and the concerned public want to know whether or not discharges from metal mining activities damage ecosystems. Lakes in the Rouyn-Noranda metal mining and smelting area exhibit a distinct gradient in concentrations of metals in water and sediment, ranging from uncontaminated to substantially contaminated. This study was conducted to examine how natural communities of sediment-dwelling (benthic) organisms change across a series of increasingly metal-contaminated lakes.</p>	<p>Deep-water benthic invertebrate communities in the lakes with the highest concentrations of metals in water and sediment were impoverished compared to communities in the less contaminated lakes. The results suggest that lakes far from or upwind of the smelter are mainly influenced by natural conditions such as water hardness, sediment grain size and organic content. However, in lakes near to and downwind of the smelter, concentrations of several metals (including Cd, Cu, Pb and Zn) appear as more important in controlling benthic community composition.</p>	<p>When evaluating potential environmental impacts of mining activities such as those in the Rouyn-Noranda area, regulators and other non-scientists will be able to see how much metal contamination lakes can handle before the insects, crustaceans and other organisms living in sediments are adversely affected.</p>
<p><b>CF2:</b> Quantitative synthesis of aquatic environmental effects studies for metal mines of the Precambrian Shield</p> <p>{<u>Lee Grapentine</u>}</p>	<p>Adverse effects of industrial activities are of most concern when they are seen to impact natural communities (i.e., groups of organisms that are resident in the environment). This study was done to pull together all available information on assessments of metal-mining activities on communities of aquatic organisms of the Canadian Shield, and to determine if, "on the balance", effects of mining activities are negative, positive or not large enough to be noticeable.</p>	<p>Suitable information was available only to assess effects on benthic invertebrate communities. Overall, benthic invertebrate communities in areas exposed to metal mining activities are depauperate (fewer types of organisms and fewer individuals) compared to those in areas unexposed to metal mining activities.</p>	<p>These findings can be used as evidence of actual effects of mining activities. They indicate impacts to real groups of organism residing in their natural environment. The information can be viewed as "ground truthing" for results obtained from laboratory or theoretical (modeling) studies.</p>

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<p><b>CF3:</b> Impacts of metal-contaminated forest soils from the Canadian Shield on terrestrial organisms</p> <p>{Richard Scroggins}</p> <p>[COMPLETED 2002]</p>	<p>This study was mutually beneficial to MITE-RN and Environment Canada's Method Development and Application Section. MITE-RN got some soil effects data for terrestrial plants, earthworms and soil arthropods (Collembola) and Environment Canada completed further soil toxicity method validation using a boreal forest soil.</p>	<p>The three test methods worked well with the forest soil. The soil sample collected closest to the Sudbury smelter site (one of three sample locations along the Hale/Hendershot gradient) was toxic to plants and soil biota at sublethal concentrations.</p>	<p>These findings extend the applicability of soil toxicity tests for determining whether contamination of forest soils is causing toxicity to representative biota.</p>

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<p><i>Industrial Intern</i> {Collins Kamunde}</p>	<p>The presence of two potential pathways of metals exposure in fish presents unique problems in determining the source of the metal exposure for risk assessment in aquatic environments. To date the relative importance of food and water as vectors of metals in fish remains largely undetermined. Possibly as a result of this paucity of information, current ERA methodologies for metals in fish do not predict the true ecological risk because the two pathways of exposure are not considered. Moreover, without accurate characterization of exposure, the value and relevance of any ERA of metals in fish would be significantly diminished. Accurate prediction of exposure (e.g., accumulation of a metal of interest) is important because a link between a contaminant of concern and effects in receptors (organisms) of concern has to be demonstrated in ERA. The present study was therefore carried out to address the gap in information on pathways of metals exposure in fish by developing kinetic bioaccumulation models for delineating and quantifying metals accumulation from both water and food. The models were tested site-specifically in yellow perch (<i>Perca flavescens</i>) in metals contaminated lakes of Southeastern Canada.</p>	<p>The models demonstrated that metal accumulation from food is, under most circumstances, greater than that from water. Laboratory-derived kinetic bioaccumulation model values predicted site-specific metal accumulation in the field with an acceptable degree of accuracy. Moreover, model values were applicable across species, although predictions using a larger number of fish species are necessary to derive a persuasive conclusion. In uncontaminated environments the models predicted that food was the main pathway of exposure and accumulation of copper, zinc, and cadmium. In contaminated environments, diet remained the main pathway for accumulation of copper and cadmium while both water and diet were important for zinc accumulation. Bioaccumulation of all three metals from water was best predicted using the free metal ion concentration (i.e., <math>\text{Cu}^{2+}</math>, <math>\text{Zn}^{2+}</math>, or <math>\text{Cd}^{2+}</math>) rather than dissolved or total metals concentrations.</p>	<p>First, the findings underline the importance of dietary metals exposure in metal accumulation in fish. Regulators can therefore not continue to ignore potential effects of dietary metals exposure. Second, by predicting metals accumulation via the two principal pathways of uptake the kinetic models developed here provide more accurate estimates of exposure and potential for effects than models that rely on one pathway of exposure. Metals regulation and ERA would therefore be more precise and realistic if these models were used. Third, while equilibrium models like the Biotic Ligand Model (BLM) are more useful for predicting acute effects, kinetic models are likely better at predicting chronic effects. Regulations based on protection against adverse chronic effects are more realistic because they offer protection over the entire lifespan of the organism. Fourth, there is potential for utilizing these models in conjunction with other predictive models such as the BLM. It is probably pointless to carry out BLM predictions when the main pathway of exposure is food.</p>

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<p><b>Government Intern</b> {Richard Goulet}</p>	<p>Species sensitivity diagrams (SSDs) often show that aquatic invertebrates are among the most sensitive to metal exposure. Their early disappearance from an ecosystem can lead, for example, to stunted growth in fish. It is important to develop bioaccumulation models and determine at which internal concentration acute and chronic effects are occurring. Presently, the biotic ligand model (BLM) is the only model available that relates exposure to acute effects. The BLM was validated by short exposures of animals to metals in water only. Thus, the BLM should be used mainly for acute exposure scenarios such as chemical spills. Under chronic exposure scenarios, aquatic organisms will continue feeding and metal uptake through this activity may be significant. What is the importance of dietary metal uptake on metal bioaccumulation and what will be the associated effects? This study was done to get an early answer to these important questions.</p>	<p>Research focused on predicting metal accumulation in sensitive aquatic invertebrates. More precisely, a bioaccumulation model was used, which integrates dietary and water uptake pathways, to predict Cd accumulation in <i>Daphnia magna</i>. Modeled internal Cd concentrations in <i>D. magna</i> agreed well with laboratory measurements, suggesting that the model can accurately predict Cd accumulation under laboratory conditions. In a risk assessment example, the model was used to estimate a range of <math>[Cd^{2+}]</math> over which no chronic effects are expected (<math>[Cd^{2+}] &lt; 0.1 \mu g L^{-1}</math>).</p>	<p>Regulators must consider metal uptake from food during chronic exposure scenarios. Presently, most toxicity data (LC50 or EC50) are from toxicity tests where animals are exposed to metals in water only. Similarly, during chronic toxicity tests, animals are exposed to contaminated water and fed with uncontaminated food. Scientists in Belgium observed that when daphnids were fed with increasingly contaminated algae, their biomass increased accordingly. This result suggests that in chronic exposure scenarios, metal accumulated by algae are less toxic to the daphnids, or that grazing activity supplies energy to the daphnids, which transfers into increased resistance to stress caused by metal exposure. This surprising result suggests that LC50 values presently used by regulators are overprotective.</p>