

ECOLOGICAL RISK ASSESSMENT CONTEXT OF MITE-RN STUDIES

March 1, 2004 VERSION

(Note: no update since November 28, 2002 to Projects A6 and AF8)

PROJECT/TITLE	METALS / ELEMENTS RELEVANT FOR ERA + OTHER METALS/ ELEMENTS	ORGANISMS	ENVIRONMENT COMPARTMENT [AND ERA PHASE]	PREVIOUS ERA STATUS (PRE-MITE-RN) AND EXPECTED (POST-MITE-RN) ERA STATUS		KEY ERA FINDINGS/SUBSEQUENT YEAR PROJECTIONS
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<p>A1: Differentiation of metals on aeolian dust (particulates) from natural sources <u>{Grant Edwards and Goretty Dias}</u></p>	<p>Cu, Pb, Ni, Zn, Cd, Hg, As + Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ga, Ge, Se, Br, Rb, Sr, Y, Zr, Mo, Ag, Sn</p>	N/A	<p>Air-surface exchange including re-emission [HAZARD IDENTIFICATION AND EXPOSURE ASSESSMENT]</p>	Data unavailable / default assumptions	<p>(1) More complete quantification + tools re anthropogenic versus natural sources; (2) modelling of metals transport, emission and deposition rates for ERA; (3) background metal levels in natural dust determined; (4) gaseous Hg fluxes quantified and geochemical and environmental factors analyzed</p>	<ul style="list-style-type: none"> • Both local and regional sources • Methods standardised (tools being developed to assess metal loadings from background dust) • Experimental methods development to aid in source apportionment • Regressions of Hg emissions vs. substrate Hg concentrations • Scaling up approach: modelling

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<p>A2: Chemical speciation of air particulates related to particle size</p> <p>{<u>Marc Lamoureux</u>}</p>	<p>Pb, Cu, Ni (concentration and speciation vs. particle size)</p> <p>Cd, Zn (concentration vs. particle size)</p> <p>²⁰⁶Pb/²⁰⁷Pb (isotope ratio vs particle size)</p>	N/A	<p>Air</p> <p>[HAZARD IDENTIFICATION AND EXPOSURE ASSESSMENT]</p>	<p>Limited chemical speciation possible</p> <p>Limited studies on the relationship between isotope ratio and particle size</p>	<p>(1) Pb isotope ratio vs. particle size for fingerprinting sources; (2) speciation of Cu, Ni, Pb in particulate matter of various sizes from Rouyn-Noranda areas; (3) tools developed for solid-state chemical speciation and particulate size fractionation in dust samples from stack/air/ground.</p> <p>Note chemical speciation of Zn, Cd, Hg possible but will not be done due to time limitations at the synchrotron beam</p>	<ul style="list-style-type: none"> Laboratory study indicates chemical speciation possible for complex mixtures with minimal physical or chemical manipulation which means: (1) aerosols can be fingerprinted; (2) bioavailability can be assessed with aerial exposure; (3) determinations of particle persistence can be made Lower detection limits are being obtained relative to soils metals speciation (but labour intensive and expensive) Airborne particulate matter chemically different downwind vs. upwind of Sudbury smelters as are coarse vs fine particles Pb isotope ratio is sensitive to presence of metal smelters (up to 10 km away from emission source)

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A3: Chemical speciation in atmospheric wet deposition; metal content of wet/dry particulates { <u>A. Chatt</u> }	As, Cd, Cu, Hg, Ni, Zn + Sb, Co, Se, U, Th	N/A	Air-surface exchange [HAZARD IDENTIFICATION AND EXPOSURE ASSESSMENT]	No chemical speciation possible	More complete chemical speciation possible	<ul style="list-style-type: none"> ▪ New methodologies developed [PROJECT COMPLETED 2001]
A4: Geochemical mobility / diagenesis of metals in surface sediments { <u>Richard Carignan / Andre Tessier</u> }	Pb, Hg, As, Cd, Cu, Ni + Cs	N/A	Freshwater lake sediments [HAZARD IDENTIFICATION AND EXPOSURE ASSESSMENT]	(1) Historic deposition / metals mobility uncertain; (2) pore water profiles have low resolution; (3) long-range atmospheric trace metal transport debated; (4) source of atmospheric Pb uncertain	(1) Historic deposition / metals mobility determinable (e.g., via sediment metal profiles); (2) pore water profiles have high resolution; (3) good estimates of metal exposures via pore water and solid phase sediment at short, medium and long range from smelter; (4) sources of atmospheric Pb identified	<ul style="list-style-type: none"> • Hg mobile in pore waters in lake sediments (upper 2-3 cm), thus previous interpretations of deposition rates based on profiles need to be revisited. Hg profiles and surficial concentrations in remote lakes due to both diagenesis and recent deposition. Hg deposition histories strongly influenced by local watershed processes (wildfires, beaver activity) • Zn also mobile in pore waters • Cu, Cd and Ni show no or very little evidence of recent (industrial) enrichment at remote site 700 km NE of Montreal • Order of geographic mobility (long-range atmospheric transport) is: Hg>Pb>Zn=Cd>Cu=Ni

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<p>A5: Analytical speciation of metals on atmospheric particulates / aerosols</p> <p>{Julia Lu}</p>	<p>Hg (primary)</p> <p>As, Se, Cr, Ni, Cd, Zn, Pb</p>	N/A	<p>Air</p> <p>[HAZARD IDENTIFICATION AND EXPOSURE ASSESSMENT]</p>	<p>Reliable methodologies of speciating mercury and other metals or metalloids in airborne particulates were lacking</p>	<p>Development of methodologies for identification and quantification of mercury species associated with airborne particulate matter in wet precipitation</p>	<ul style="list-style-type: none"> • The methodologies developed in previous years is being further validated for analysing Hg speciation in airborne particulate matter and is being modified for mercury speciation in suspended matter in wet precipitation • Samples of airborne particulate matter and suspended matter in wet precipitation are being collected from industrial areas and will be analysed for mercury species • Applications of the method to the analysis of samples of airborne particulate matter and suspended particulate matter in rainwaters reveal distinct Hg species in the samples and evidence of chemical transformation of Hg in the natural environment.

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<p>A6: Chemical analysis of aerosolic particulates</p> <p>{Graeme Spiers}</p>	As, Ca, Cd, Cl, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Se, Tl, Ti, Zn, Zr	N/A	<p>Air, Soils, Sediments, Peatlands</p> <p>[HAZARD IDENTIFICATION AND EXPOSURE ASSESSMENT]</p>	<p>The precursor of this instrument was developed for whole sample analysis, with detection limits in the low ppm levels for all analytes of interest with minimal sample preparation. The technology is conservative of sample, with the sample being subsequently available for analysis by other techniques.</p>	<p>Accurate, quantitative, non-destructive analysis of individual particles and of material captured on filters to provide a realistic understanding of the nature of fugitive site releases from varying industrial processes. Analysis of particles 'filtered' by soils or retained in sediments will enable detailed understanding of historical industrial process releases to environmental media.</p>	<ul style="list-style-type: none"> · New generation instrument constructed. Latest modification on the instrument allows examination of both powders and grains because of installation of a slit type collimator instead of a pinhole. Methods have been developed and validated for material on filters (both aerosols and colloids from waters). Preparation of reference systems ongoing. System used to examine smelter fallout materials from surface soils and snow. Variety of compositions. · Fresh aerosolic particle fallout in smelter footprint contains K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Pb, Se, Sr and Zr. Variety of compositions in single particles, e.g., Fe, Cu, S in one grain; Fe, Cu, Ni, As, Se, Pb in another.

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<p>A7/AF10: Examination of mineral weathering and release of trace elements in selected soil profiles</p> <p>{Jeanne Percival / William Hendershot}</p>	<p>Cd, Cu, Ni, Pb, Zn, Fe, Mn and others as appropriate for mineralogical characterisation</p>	<p>N/A</p>	<p>Soils and parent materials</p> <p>[HAZARD IDENTIFICATION AND EXPOSURE ASSESSMENT]</p>	<p>Knowledge gap concerning the rates of metal liberation from soil parent materials - required for source apportionment studies</p>	<p>Characterise soil materials mineralogically and geochemically; estimate amount of metal present in soils due to natural processes; knowledge will improve ERAs by assisting in placing anthropogenic effects into an appropriate natural process context</p>	<ul style="list-style-type: none"> Analyses in progress on 6 soil samples from two sites associated with project B1.
<p>AF7: Physical and chemical evolution of aerosols in smelter and power plant plumes.</p> <p>{Cathy Banic}</p>	<p>Cu, Pb, Ni, Zn, Cd, Hg, As + Na, Mg, Al, Si, P, S, Cl, K, I, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ga, Ge, Se, Br, Rb, Sr, Y, Zr, Mo, Ag, Sn</p>	<p>N/A</p>	<p>Measured properties and concentrations in air; calculated wet and dry deposition of metals from the plume to ground (soil, vegetation, surface waters)</p> <p>[HAZARD IDENTIFICATION AND EXPOSURE ASSESSMENT]</p>	<p>Data unavailable for evolution of particles and gases in the plume/ default assumptions necessary (e.g. SOP for Cu/Zn smelters)</p>	<p>(1) Calculated patterns of mid-range wet and dry deposition to soil, vegetation and surface waters; (2) concentrations in air/dust on local and regional scales for emissions – data collected 30km from sources; (3) reconciliation of measurements with estimated stack emissions; (4) methods for trace metals speciation/ particle size fractionation in plumes</p>	<ul style="list-style-type: none"> Hg speciation in plumes (fraction emitted as elemental or reactive gaseous, particulate) For metals with high source strength, distribution of metal by particle size, also limited speciation Size distribution of particles in the plume

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<p>AF8: Redistribution of metals in lake sediments by bacterially mediated oxidation-reduction reactions</p> <p>{<u>W. D. Gould</u>}</p>	<p>Fe, Cu, Zn, Ni + Mg, Ca, Sr, Cs, Cr, Mn, Co, K, Zn, Cd, Al, P, S, C, As, Si, Na</p>	<p><i>Daphnia magna</i> in the water column; iron reducing, sulphate reducing, and acid producing bacteria in the sediment column</p>	<p>Samples of the overlying water from control and spiked column experiments will be analysed for metal concentrations and tested for toxicity. These monitors are being used to test potential upward metal mobility from the sediments to the water column.</p> <p>[HAZARD IDENTIFICATION AND EXPOSURE ASSESSMENT]</p>	<p>There is uncertainty with respect to whether the observed vertical distribution of metals in lake sediments is a true chronological record of the actual deposition sequence. Potentially, the observed deposition record is altered by microbially mediated redox reactions during early diagenesis.</p>	<p>1) Determine whether microbial redox reactions (dissimilatory iron reduction) can solubilise and redistribute iron in the sediment column by vertical transport.</p> <p>2) Evaluate the potential for other metals (Cu, Zn, Ni) that are associated with iron oxyhydroxides to also be remobilised by microbial activity.</p>	<p>2001-Year 1: Evidence from field studies indicates that bacterial sulphate reduction may be significant in the upper 10 cm of the lake sediments – sulphate reduction may be a sink for metals near the sediment-water interface</p> <p>2002-Year 2: The role of iron reducing bacteria in redistributing metals vertically within the sediment column and potential release to the overlying water will be investigated. Microcosm studies are in progress.</p>

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<p>AF9: Role of bacteria in mobilisation of arsenic from mine impacted tailings</p> <p><u>{Vince Palace and Frank Rosenzweig}</u></p>	As, Cu, Zn, Ni, Hg + Fe, Mn	<p>Bacteria (strain isolated designated VC-1)</p> <p>Other work: fish (Pearl dace, White sucker) – As, Cu, Cd, Ni, Hg in tissues</p>	<p>Freshwater lake and sediments</p> <p>[HAZARD IDENTIFICATION AND EXPOSURE ASSESSMENT]</p>	<p>Uncertainty regarding contribution of the biotic component of sediments to reduction of As, Fe, Mn and subsequent mobilisation of As from sediments to the water column</p>	<p>Development of sediment and community based model to describe biotic and abiotic mechanisms for As efflux from historically mine impacted sediments</p> <p>Arsenate reducing activity quantification and potential for water column enrichments underway based on laboratory sediment testing.</p>	<p>Confirmation of the presence of arsenic and iron respiring bacteria in historically loaded sediments.</p> <p>Putative sulphate reducing communities also being characterised.</p> <p>Characterisations of activity and specificity are ongoing.</p> <p>Specific strains of both arsenate reducing bacteria and putative sulphate reducer from the test freshwater system have been accomplished.</p> <p>Additional cores from within treated limnocorrals retrieved and primary isolations of bacterial communities underway in Dr. Rosenzweig's laboratory.</p> <p>Results expected to determine bacterial contribution to water column enrichment of arsenic and dissolved iron.</p>

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<p>B1: Trace metal dynamics in contaminated northern forest ecosystems</p> <p>{<u>Bev Hale, William Hendershot</u>}</p>	Cu, Zn, Pb, Ni, Cd	<p>Red pine (<i>Pinus resinosa</i>); Black spruce (<i>Picea mariana</i>); white birch (<i>Betula papyrifera</i>); white spruce (<i>Picea glauca</i>)</p>	<p>Northern forest ecosystems (soil, vegetation, ground waters)</p> <p>[EXPOSURE ASSESSMENT]</p>	<p>Uncertainty re: (1) magnitude of plant-cycling of metals; (2) contribution of groundwater to aquatic metals; (3) current metal burdens in forest ecosystems relative to inputs; (4) cumulative impacts related to metals additions; (5) magnitude of metal cycling between plants and soils, and its relationship to atmospheric inputs; (6) contribution of vadose zone water to downward movement of metals; (7) speciation of metals in vadose zone waters (including binding to soil particles) and its relationship to plant bioaccumulation</p>	<p>Good information on: (1) size of terrestrial inputs to aquatic ecosystems (is terrestrial a closed cycle?); (2) releases due to fires, clear cutting, other alterations; (3) extent and magnitude of metals mobility in forest soil around a smelter; (4) projected metal assimilative capacity of forest ecosystems; (5) determination whether woody tissue accumulation poses a threat to the trees or an exposure route to other organisms; (6) quantity and locations of metals sequestered in forests; (7) decomposition rates of leaves and roots, and the size of this input relative to atmospheric inputs; (8) metal speciation in vadose zone solutions, and relationship to soil characteristics; (9) link between free metal ion in forest soils and bioaccumulation in forest plants</p>	<ul style="list-style-type: none"> ▪ Tree / shrub species dominating plant community biomass control metal dynamics ▪ Plant metal burdens are greater than current atmospheric inputs ▪ Fine roots dominate annual plant metal cycling; play a more substantial role than foliage in cycling of trace metal contaminants • Fine roots dominate both sequestration and cycling of Cu, Ni and Pb, and their effect is disproportionately larger than their proportion of total plant mass • Zn sequestration and cycling are also dominated by fine roots, but in proportion to the size of fine roots relative to total plant mass • Metal binding to soil particles can be predicted using a simplified NICA-Donnan model • Bioaccumulation factors (BAFs) for metals in whole plant, expressed relative to free metal ion concentration, were more similar among sites than BAFs calculated using total metal concentrations

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<p>B2: Models relating metals in animals to metals in the environment</p> <p>{<u>Landis Hare,</u> <u>André Tessier</u>}</p>	Cd, Cu, Ni, Pb, Zn	Phantom midge (<i>Chaoborus</i>); Alderfly (<i>Sialis</i>); mayfly (<i>Hexagenia</i>); aquatic moss (<i>Fontinalis</i>)	Freshwater lakes and streams [EXPOSURE AND EFFECTS ASSESSMENT]	Poor ability to predict bioaccumulation because of uncertainty in: (1) food as a metal source; (2) species differences in accumulation; (3) exposure of burrowers to metals in sediments	Metal bioaccumulation more predictable: (1) estimates for water vs. food as metal sources; (2) differences among related species; (3) metal exposure of burrowers; (4) reliable biomonitors	<ul style="list-style-type: none"> • Food an important Cd exposure route • Temperature changes rate of prey ingestion and thus Cd assimilation (seasonal differences important) • Species of <i>Chaoborus</i> differ in their Cd accumulation (treat individually, don't group) • Exposure of burrowers to metals related to behaviour (living in sediment does not necessarily mean accumulation from sediment) • Moss a promising stream biomonitor; in lakes use <i>Chaoborus</i>

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<p>B3: Quantification and modelling of metal mobility</p> <p>{<u>Les Evans and Miriam Diamond</u>}</p> <p>[PROJECT COMPLETED 2001]</p>	<p>Zn, Cu (modelling at lake scale)</p> <p>Model general to most metals. A version developed outside of MITE-RN is suitable for Hg</p>	N/A	<p>Freshwater lakes</p> <p>[EXPOSURE ASSESSMENT; fate - pathways analysis]</p>	<p>No model of metal speciation/ surface complexation coupled with fate and transport</p>	<p>(1) Aqueous speciation – surface complexation / model coupled with a mass balance model for lakes, and general to most metals; (2) demonstrated model applicability to a range of environmental conditions suitable for retrospective and prospective simulations; (3) applied to Ross Lake, Manitoba, to account for change in lake from sink to source</p>	<ul style="list-style-type: none"> • Aqueous speciation of Zn varies over time and this variation changes Zn fate, specifically changing the lake from a sink to a source • Different Zn species predominate in oxic and anoxic waters, and these species vary in their mobility and presumably their bioavailability • Sediment resuspension and sediment to water diffusion are major modes of Zn transport • Generalised speciation / fate model available for zinc and other metals • Model provides estimates of bioavailable fraction in water column and sediments for exposure studies

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<p>B4: Metal speciation in freshwaters from lakes, soil pore waters, and through-fall precipitation samples</p> <p>{Chuni Chakrabarti}</p>	<p>Freshwater: Ni, Cu, Pb, Cd, Zn</p> <p>+ Ca, Mg</p> <p>Soil solutions: Ni, Cu, Pb</p> <p>[The parameters: pH, conductivity, temperature, DOC, TOC, IC, and the following metals, non-metals, cations and anions are determined in lake waters, soil pore waters, and in through-fall precipitation samples: Cu, Fe, Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, Ag, B, Ba, Be, Bi, NH4+, Cd, Co, Cr, Cs, Ga, In, Li, Mo, Ni, Pb, Rb, Sb, Sc, Se, Sr, Tl, U, V, Zn, Li, Na, K, Mg, Mn, Ca, Sr, Ba, F-, OAc-, Cl-, SO42-, NO3 -, NO2 -, PO43-]</p>	N/A	<p>Freshwater</p> <p>[HAZARD IDENTIFICATION AND EXPOSURE ASSESSMENT]</p>	<p>No certainty: (1) environmental factors that control release of humic-bound metals to lake waters; (2) effects of metal ion/cation competition; (3) metal species in soils and soil solutions</p> <p>Regulators and managers need to know the maximum permissible loading of metal species in effluents to freshwaters, and they depend on the scientific community to provide science-based answers 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.</p>	<p><i>Increased certainty re metals releases and effects of ion/cation competition; (2) better techniques for determination of metal speciation, especially free metal ions in lake waters, soil solutions and soil samples; (3) speciation techniques applied to lake water and soil interstitial water – usable for low total metal concentrations and in presence of natural organic matter. We expect to establish experimentally the following linkage: Metal Speciation ↔ Bioavailability ↔ Ecotoxicity. Our results will provide regulators and managers with science-based tools that can enhance the usefulness of the currently-used models (FIAM and BLM) by incorporating kinetic speciation, which will result in better protection of the freshwater environment.</i></p>	<ul style="list-style-type: none"> Major cations Ca²⁺ and Mg²⁺ crucial for release of humic-bound Ni as Ni²⁺ Voltammetric techniques may provide estimates of free metal ion concentrations in lake waters and soil solutions {From other funding: Natural organic matter (dissolved) influences both metal speciation and toxicity} <p>Freshwaters are dynamic systems, often far removed from equilibrium, mainly because coordination equilibrium involving transition metals is typically slow. Thus 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 the 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, kinetic speciation is a requirement.</p>

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<p>B5: Availability of trace metals in the rhizosphere of contaminated soils from the Sudbury area</p> <p>{<u>François Courchesne</u>}</p>	<p>Soil: Cu, Ni and Cd, Pb, Zn</p> <p>+ Al, Fe, Mn</p>	<p>N/A</p> <p>Rhizosphere collected from white birch (<i>Betula papyrifera</i>), trembling aspen (<i>Populus tremuloides</i>) and red pine (<i>Pinus resinosa</i>) roots</p>	<p>Soil</p> <p>Northern forest ecosystem</p> <p>[EXPOSURE ASSESSMENT]</p>	<p>Poor ability to relate elemental uptake and storage by plants to soil content because of: (1) lack of data on trace metal contents and chemical species in the rhizosphere of forest soils; (2) uncertainty regarding the impact of environmental factors such as tree species and magnitude of soil contamination on the rhizosphere effect; (3) poor understanding of the links between the soil solution, the soil:root interface and plant tissues with respect to bioaccumulation of trace metals</p>	<p>Increased capacity to relate elemental uptake by plants to soil because of: (1) availability of high quality data on the chemistry of trace metals in the rhizosphere and on the impact of tree species and of soil contamination levels; (2) identification of key processes controlling the movement and accumulation of trace metals in terrestrial ecosystems with emphasis on the contribution of the rhizospheric environment (in collaboration with B1); (3) better assessment of the potential of the rhizosphere as a source of indicators of the response of soil-plant systems to environmental stresses.</p>	<p><u>Findings</u> for first two years (02-04): 1) the rhizosphere systematically acts as a sink for bioavailable Cd, Cu, Ni, Pb and Zn (H₂O-soluble and salt-extractable) compared to the bulk soil (i.e., rhizosphere effect); 2) the impact of tree species on the rhizosphere effect is of limited extent (factor of two); and, 3) impact of soil contamination on the rhizosphere effect varies with metal and can reach up to 5x (Zn).</p> <p><u>Plans</u> for on-going year (04-05): 1) include another tree species (<i>Pinus resinosa</i>) in the experimental design; 2) characterize microbial biomass and activity in the rhizosphere and establish links with metal content and species; 3) develop method to measure [Zn²⁺] in water extracts from the rhizosphere and model links between [Zn²⁺], pH, DOC, and dissolved Zn concentration.</p>

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<p>B6: Metal budgets of Canadian Shield lakes and catchments</p> <p>{<u>Peter Dillon</u>, <u>Shaun Watmough</u>}</p>	<p>Cu, Ni, Zn, Pb, Cd; also Al, V, Cr, Mn, Fe, Co, As, Rb, Sr, Tl, Bi, U, Na, Mg, Ca, K, Li, Ba in water</p>	<p>Vegetation (forest trees and wetland plants)</p>	<p>Lakes, streams, sediments, wetlands, soil, forests, aquatic plants</p> <p>[EXPOSURE ASSESSMENT]</p>	<p>Limited information available except for sites near point sources; role of other factors such as climate on metal transport unknown</p>	<p>Development of relationships between metal fluxes and other environmental factors, particularly regional / global stressors including acidification, climate change</p>	<p>Measurement of the pool sizes in the Plastic Lake catchment is complete with the exception of lake sediments; inputs from the atmosphere and fluxes between compartments are being calculated. These data will tell us what metal levels are in a system with no local point sources, and will help elucidate which are of anthropogenic origin. A comparison of total and soluble metals indicated that there is very little metal in particulate form in these systems.</p> <p>Projections: stable isotope studies on Pb are nearing completion; these will assist in determining sources. A mass balance model describing sources and sinks is being used to generate information on removal rates of metals from the water column.</p>

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<p>B7: Role of reduced sulphur species (RSS) in controlling metal speciation in surface waters on the Canadian Shield</p> <p>{Feiyue Wang}</p>	<p>Cd, Cu, Hg, Ni, Pb, Zn</p> <p>+ Fe, Mn</p>	N/A	<p>Freshwater</p> <p>[EXPOSURE ASSESSMENT]</p>	<p>Reduced sulphur species only accounted for in metal speciation in anoxic waters, not surface waters</p> <hr/> <p>KEY FINDINGS (Cont'd)</p> <p>In situ two-dimensional high resolution profiling of sulfide in sediment interstitial waters revealed unprecedented lateral and vertical heterogeneity of sulfide, demonstrating the inappropriateness of using bulk sediment/porewater chemistry/bioassay for ERA of metals in sediments</p> <p>In addition to inorganic sulfide, thiols were also found to be present at considerable concentrations in sediment porewaters, the significance of which is being investigated.</p>	<p>(1) Certainty re the presence and importance of reduced sulphur species in oxic waters; (2) approaches (models) determining metal speciation in oxic and anoxic waters that take into account complexation by reduced sulphur species</p> <hr/> <p>KEY FINDINGS (Cont'd)</p> <p>Computer speciation models such as HYDRAQL and WHAM were revised, and can now readily calculate metal speciation in the presence of RSS. The results suggested that metal-sulfide complexes should play a negligible role in determining metal speciation in oxic waters in the 6 lakes studied. The roles of metal-sulfide colloids and possibly clusters (where stabilizing agents are present), however, cannot be assessed at this time due to the lack of analytical techniques.</p>	<p>In laboratory solutions, some metal-sulfide species (e.g., those with Fe, Mn, Ni) are oxidized rapidly when exposed to air, whereas Cd-, Zn-, Pb-, Cu-sulfide solutions can persist for a prolonged period of time (2 to more than 10 weeks)</p> <p>Nanomolar to sub-micromolar levels of dissolved sulfide (measured as acid volatile sulfide or chromous volatile sulfide) were measured in the oxic epilimnion waters of six lakes on the Shield and in adjacent areas. The sulfide was expected to be in the form of metal-sulfide species.</p> <p>Multiple lines of evidence suggest that the oxidation-resistant metal-sulfide species in oxic waters are a mixture of truly dissolved complexes and dynamic colloids; they are not soluble metal-sulfide clusters as previously reported in the literature.</p>

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<p>BF1: Biochemical cycling in the boreal forest – Metal concentrations in woody tissues</p> <p>{<u>Christian Bégin</u>, <u>Martine Savard</u>}</p> <p>[PROJECT COMPLETED IN 2002]</p>	<p>Cu, Pb, Ni, Zn, Cd, Hg, As</p> <p>+ Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ga, Se, Br, Rb, Sr, Y, Zr, Mo, Pb, Ag, Sn</p>	<p>Black spruce (<i>Picea mariana</i>), balsam fir (<i>Abies balsamea</i>), paper birch (<i>Betula papyrifera</i>), aspen (<i>Populus tremuloides</i>)</p>	<p>Boreal forest ecosystem (Woody vegetation)</p> <p>[EXPOSURE ASSESSMENT]</p>	<p>Poor ability to assess metal biogeochemical cycles in contaminated boreal forest because sparse data on: 1) the total metal content in living standing forest trees; 2) metal content and dynamics in dead and subfossil trees; 3) the return rate of metals from woody tissues to soils.</p>	<p>1) Quantitative assessment of total metal pool in the woody tissues of the four most dominant species (spruce, birch, aspen and balsam fir) in boreal forest. 2) Calculation of metal load at regional scale. 3) Comparison between contaminated and natural sites. 4) Quantification of metal dynamics in dead woody tissues. First steps towards a quantitative assessment of biogeochemical cycling of metals in contaminated and uncontaminated forest sites.</p>	<ul style="list-style-type: none"> • Newly developed method for evaluating inorganics concentrations in standing wood • New data concerning metal load re section of forest near Horne smelter • At the contaminated site, potentially toxic metal load (Pb+Cd) in all investigated species is more than 20 kg / km², which is at least 13 times higher than what it was found under less contaminated conditions Broad leaf species are particularly efficient at absorbing and accumulating metals in their woody tissues. Their metal content at the contaminated site can reach levels ten times higher than for conifers High level of contamination impairs the assimilation of some metals (e.g. Cu) naturally involved in physiological processes • Accumulation of metals follows a lag phase (uptake not foliar, but via roots)

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<p>C1: Metals effects in aquatic biota</p> <p>{George Dixon, Uwe Borgmann}</p>	<p>Cd, Cu, Ni, Pb, Zn, As</p> <p>+ Ti, Co, Cr, Mn</p>	<p>Amphipod, <i>Hyalella azteca</i></p>	<p>Freshwater and freshwater sediments</p> <p>[EFFECTS ASSESSMENT]</p>	<p>(1) Single metal guidelines; (2) no generic relationships between toxicity and body burdens for single metals; (3) minimal data on bioaccumulation routes of uptake (comparison of accumulation via water and food)</p>	<p>(1) Increased certainty re metal interactions for benthic organisms; (2) predictions of toxicity from body burdens for single metals and metal mixtures; (3) BLM for chronic toxicity to <i>Hyalella</i>; (4) better relationship of toxicity and bioavailability to benthic community structure; (5) uptake constants for pharmacokinetic modelling</p>	<ul style="list-style-type: none"> Contaminant critical body residues (CBRs) related to chronic toxicity have been determined for all ten individual metals / elements for <i>H. azteca</i> Predictions of chronic toxicity A biotic ligand model for predicting Ni toxicity to <i>H. azteca</i> under varying water quality conditions is being developed Effects of overlying water (lab waters vs. site water) on metal bioaccumulation and metal-organism BCFs have been determined Effect of uptake route (food or water) on bioaccumulation and toxicity is being determined An effects addition model has been developed to predict chronic toxicity based on bioaccumulated metal concentrations

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<p>C2: Biological effects of chronic metal exposures in fish</p> <p>{<u>Chris Wood</u>, <u>Gordon McDonald</u>}</p>	<p>Cu, Cd, Zn</p> <p>[Ag, Ni, Pb – other funding]</p>	<p>Yellow perch (<i>Perca flavescens</i>) YP;</p> <p>Rainbow trout (<i>Oncorhynchus mykiss</i>) RT</p> <p>[<i>Daphnia</i>, fathead minnow, crayfish – other funding]</p>	<p>Freshwater lakes</p> <p>[EXPOSURE AND EFFECTS ASSESSMENT]</p>	<p>(1) Metals criteria generic, not site-specific; (2) no BLM for chronic toxicity; (3) fish model based on rainbow trout; (4) relationship of diet (quality and quantity) on metal impacts uncertain</p>	<p>(1) Site-specific chronic metals criteria; (2) BLM for chronic toxicity to fish; (3) new fish model (yellow perch); (4) increased certainty in relationship of diet (quality and quantity) on metal impacts both directly (uptake) and indirectly (physiological effects on metal toxicity)</p>	<ul style="list-style-type: none"> • Acute Cd BLM for YP differs from that of RT only in lethal accumulation in gills (LA₅₀), but not in Cd binding affinity (Log K) or total number of binding sites (B_{max}). • Mechanisms for Cd toxicity similar for both YP and RBT; however, Cd produces significantly less inhibitory effect on Ca uptake process in YP compared to that of RT, a probable reason for YP being more resistant to acute Cd challenge than RT. • Acute Cd BLM for YP works reasonably well in clean non-polluted freshwater aquatic environments. However, in fish chronically exposed to metal-polluted aquatic environments, there are substantial changes in the gill Cd binding characteristics, which are not considered in the current version of the BLM. Clear need for further research on chronic changes, especially those occurring under natural exposure conditions. This study was carried out with YP collected from different lakes in Sudbury region and in collaboration with Dr. P Couture's group at Laurentian University.

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<i>C2 (continued)</i>				<p><u>ADDITIONAL FINDINGS:</u></p> <ul style="list-style-type: none"> • Dietary Na reduces the binding affinity for Cu in gills and, therefore, has a protective effect against waterborne Cu. Fresh – water fish prefer Na-enriched food to normal food. However, sublethal waterborne Cu does not produce any further shift towards more Na-enriched food selection. Instead, it severely disrupts their normal preference as well as significantly affects their feeding rate and growth. Na enriched food does reduce waterborne Cu accumulation in target tissues (gill, liver, plasma and kidney) in Cu exposed fish, but only to a limited extent and does not fully protect them against sub lethal water borne Cu stress. These findings indicate the need to better understand the olfactory interactions in fish with waterborne Cu in relation to chronic effects. 	<p><u>ADDITIONAL FINDINGS:</u></p> <ul style="list-style-type: none"> • Elevated Ca content in the diet alters Cd and Zn uptake through the gills, tissue distribution and toxicity; potential implications to BLM and to Cd and/or Zn toxicity in the wild where available food supply and type fluctuate greatly. In Cd- and/or Zn-impacted field situations fish may switch from piscivory to crustacean / mollusk grazing, gaining increased dietary Ca and thus protection from waterborne Cd and / or Zn uptake: indirect effects must be considered in ERA • Both dietary and sub lethal water borne Zn do not cause any significant increase of Zn accumulation in any target tissues. Dietary Zn is the primary source of Zn in juvenile fish and its uptake is not influenced by water borne Zn. Overall, it appears than Zn is very well regulated in fish. 	<ul style="list-style-type: none"> • Gill Cu does not equate well to toxicity and binding characteristics change with acclimation conditions as also observed in the case of Cd. These results signify that a single BLM may not work for ERA. • No clear relationship between tissue Cd or Cu burdens and toxicity; tissue specific bioaccumulation may not be useful in hazard classification or ERA. • Dietary quantity and quality (esp. ion levels) affect uptake of metals from water. Uptake and tissue Cu burdens show different relationships to diet. • Both water borne and dietary Cd reduce water borne Ca uptake, however, only dietary Ca, but not Cd, decreases waterborne Cd uptake. Moreover, increased dietary Ca does not change the effect of dietary Cd on waterborne Ca uptake, important findings for the development of chronic Cd BLM

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<p>C3: Relationships between metal body burdens and effects</p> <p>{<u>Peter Campbell</u>, <u>Alice Hontela</u>, <u>Joe Rasmussen</u>}</p>	Cd, Cu, Zn, Pb, Ni	Yellow perch (<i>Perca flavescens</i>)	Freshwater lakes located along a Cd, Cu, Zn gradient [EXPOSURE AND EFFECTS ASSESSMENTS]	(1) No mechanistic link between intracellular metals speciation and higher-level effects; (2) toxicity not readily predictable from tissue concentrations; (3) no tissue metals criteria	<p>(1) Mechanistic link between tissue metal levels and organism / population-level effects; (2) tissue metals criteria; (3) field testing of FIM- or BLM-type models</p> <hr/> <p>SUBSEQUENT YEAR PROJECTIONS</p> <p><u>Year 5:</u> Comparison of effects levels seen in Rouyn-Noranda and Sudbury Lakes with current CCME water quality criteria for metals (in collaboration with Project C5).</p>	<ul style="list-style-type: none"> • Cd detoxification by MT not complete, even at moderate Cd concentrations; classical MT spillover model does not seem to apply to chronic exposures (metals partitioning data in tissues thus did not improve predictions of toxicity) • Impairment of cortisol stress response offers promise as a biomarker of metals exposure, especially for Cd • Metals appear to be affecting the sentinel species directly (e.g., cortisol response) and, in the most contaminated lakes, indirectly via the food chain by affecting the quantity and quality of forage food resource • Transplantation experiments with 1+ yellow perch show appreciable short-term accumulation of Cd, but not of the essential metals Cu or Zn. <p>Transplantation experiments with 1+ yellow perch suggest that diet / food is an important source of Cd to yellow perch (leading to the question: Are PNECs expressed in terms of dissolved metal going to be under / or over protective?).</p>

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<p>C4: Accumulation and effects of metals on wildlife {Laurie Chan}</p>	Hg + Se	Blood and/or eggs of common loons or other appropriate fish-eating birds (grebes, bald eagles) and their fish prey (perch, sunfish, small trout, etc)	Freshwater lakes; surficial soils and sediments [EXPOSURE AND EFFECTS ASSESSMENT]	(1) Se detoxification of Hg and subcellular binding not fully understood; (2) uncertainty in predictions of adverse Hg effects on fish-eating wildlife; (3) uncertainty of risk of high methylHg exposure in fish-eating wildlife from different sources and chemical forms of environmental Hg; (4) immunologic and genotoxic effects of methyl Hg exposure in wildlife largely unstudied	(1) Understanding of Se detoxification of Hg, and subcellular binding of Hg and Se in tissues; (2) improved predictability of adverse Hg effects on wildlife and mammals, including better understanding of risk of immunotoxic and/or genotoxic impacts from methylHg exposure; (3) improved estimates of Hg toxicity thresholds for avian species; (4) better understanding of links between chemical forms of environmental Hg, water chemistry, and ultimate level of dietary methylHg exposure in fish-eating wildlife	<ul style="list-style-type: none"> • Good correlations between Hg and Se in certain loon and bald eagle tissues (e.g., liver), molar ratio of Se:Hg approaches 1:1 in individuals with highest Hg accumulation; most of this Hg is present as inorganic Hg, not methyl Hg, indicating demethylation in certain tissues • Preliminary evidence of DNA strand breakage in liver cells of birds fed diets with environmentally realistic levels of methyl Hg • White blood cell phagocytosis not adversely affected at realistic blood mercury concentrations; this assay not useful indicator of mercury exposure • Environments with high levels of environmental Hg as Hg sulphide do not necessarily result in fish with toxicologically high methyl Hg concentrations

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<p>C5: Population and physiological effects of industrial metal contamination on wild fish</p> <p><u>{Patrice Couture and Greg Pyle}</u></p>	Cu, Cd, Ni, Zn	Yellow perch Small fish communities	Freshwater lakes (fish, water, sediment) [EXPOSURE AND EFFECTS ASSESSMENT]	Limited data currently available to extend laboratory findings to wild fish regarding metal effects on physiological fitness. Effects of age and season on dietary metal uptake largely unknown.	Data will provide a clear understanding of how laboratory-derived toxicological results extrapolate to real-world conditions. Data will indicate the importance of diet and ontogeny on metal contamination and metabolic inhibition. Collaboration with C2 will provide validation and limitations of BLM.	Will provide full assessment of aerobic and anaerobic capacities, condition indicators, and tissue and dietary metal contamination in yellow perch from a gradient of metal contamination (5 lakes x 2 seasons each), and a full range of body sizes. First collaboration with C2 (2002) completed, manuscript submitted to CJFAS. The latter project will refine our understanding of the potential of BLM for ERA using wild fish. Another collaboration with C2 in 2003 examined the role of dietary Ca and Na on metal uptake. Analyses in progress.

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<p>CF1: Assessment of profundal benthic invertebrate communities in metal-contaminated lakes</p> <p>{<u>Lee Grapentine</u>}</p>	<p>As, Cd, Cu, Hg, Pb, Ni, Zn</p> <p>+ Ag, Al, Ba, Ca, Cr, Co, Fe, K, Mg, Mn, Mo, Na, Sr, V, Y</p>	<p>Benthic invertebrates (63 genera)</p>	<p>Freshwater lakes and sediments</p> <p>[EFFECTS ASSESSMENT]</p>	<p>(1) Single metal guidelines; (2) guidelines generic, not site-specific; (3) relationships between environmental metal concentrations and benthic communities uncertain</p>	<p>(1) Discarding generic metal guidelines to predict effects on benthos; (2) incorporation of effects of site-specific conditions/ confounding factors; (3) prediction of benthic community conditions based on metal concentrations in appropriate environmental compartments</p>	<ul style="list-style-type: none"> • Lakes near the smelter and in the direction of the prevailing winds had elevated water and sediment concentrations of Cd, Cu, Pb and Zn, and impoverished benthos • Natural water and sediment factors correlate with benthic community structure • Effects of smelter-related metals likely limited to the two nearest lakes <p><u>Year 3:</u> Descriptive parameters re benthos, gradient of metal contamination, other variables; examination of correspondence between the benthos compared to predictions (from metal concentrations and guidelines); linked with C1, relations between benthos structure and amphipod toxicity/body burdens</p>

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CF2: Quantitative synthesis of aquatic environmental effects studies for metal mines of the Precambrian Shield { <u>Lee Grapentine</u> }	As, Cd, Cu, Hg, Pb, Ni, Zn	Benthos	Freshwater lakes and streams (water and sediment) [EFFECTS ASSESSMENT]	Degree to which information from individual field observational and experimental studies are representative of overall effects of metals in the environment to natural populations and communities not well known	Meta-analyses should provide unique information on actual, rather than potential effects; generalised responses of aquatic communities relevant to the Canadian Shield	Based on available field studies to date, benthic invertebrate communities in areas exposed to metal mining activity differ from those in reference areas. Exposed communities have fewer taxa and fewer individuals than reference communities.
CF3: Impacts of metal-contaminated forest soils from the Canadian Shield on terrestrial organisms { <u>Richard Scroggins</u> }	Cu, Zn, Pb, Ni, Cd	Plants (Northern wheatgrass, barley), earthworms, spring tails (<i>Collembola</i>), Bait Lamina	Soils [EFFECTS ASSESSMENT]	Lack of understanding of bioavailability and effects of anthropogenic or naturally occurring metals in boreal forest soils	(1) Validation of spiked toxicity testing with well-weathered metals in soils; (2) better understanding of bioavailability	Demonstration that toxicity tests with forest soils are possible Chronic toxic effects are observed in metal contaminated forest soils Effects are not limited to aquatic environments

