

Executive Summary for FY 2002-2003

<Processes>

Domain Co-Leaders

- Dr. Beverley Hale, Land Resource Science, University of Guelph
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Projects included in <Processes> Domain in FY 2002-2003

Project Title	Principal/Co Investigators	Affiliation
B1 Post-depositional mobility of trace metals in boreal forest ecosystems: root-soil interactions.	Hale, BA Hendershot, W	Land Resource Science, U of Guelph Natural Resources, McGill University
B2 Development of rational models for relating metal accumulation by aquatic animals to metal concentrations in their environment: relative importance of ambient metal sources.	Hare, L Tessier, A Yan, N	INRS-ETE, INRS, U du Québec INRS-ETE, INRS, U du Québec Ontario Ministry of the Environment, York University
B4 Metal speciation in freshwaters, soil pore waters, through-fall precipitation, atmospheric precipitation and in aqueous solutions resulting from wetting of atmospheric particulates.	Chakrabarti, C Grégoire, DC	Dept. Chemistry, Carleton University GSC, Natural Resources Canada
B5 The availability of trace metals in the rhizosphere of contaminated soils from the Sudbury area.	Courchesne, F	Dept. of Geography, U de Montréal
B6 Metal budgets of lakes and catchments on the Precambrian Shield: compartment sizes and fluxes between compartments.	Dillon, P Watmough, S	Environmental and Resource Studies / Chemistry, Trent University
B7 Importance of reduced sulphur species in controlling metal speciation in surface waters on the Canadian Shield.	Wang, F Tessier, A	Dept. of Chemistry, U. of Manitoba INRS-ETE

Progress toward Achievement of the Objectives

The <Processes> domain currently includes six projects that focus on partitioning of metals among terrestrial and aquatic environmental compartments. The studies focus on: cycling of metals between soils and plants; bioaccumulation of metals in the aquatic environment related to differences in organism exposure routes; validation of methods for speciating metals in dilute aqueous solution; speciation of non-essential metals in the rhizosphere; speciation of metals relative to the oxic state of sulphur in water; and, watershed mobility of microelements. The broad questions addressed in the <Processes> Domain are:

- *What are the relationships among total metal, bioavailable metal and bioaccumulation in environmental compartments?*
- *What is the role of organic and mineral surfaces in metal binding in abiotic compartments of the environment and how does this metal binding affect metal availability?*

Project B1 Post-depositional mobility of trace metals in boreal forest ecosystems: root-soil interactions (B.A. Hale, University of Guelph):

This research project has two main objectives. The first is to develop and test a comprehensive soil – soil solution – root model to predict metal bound to root surface as a function of soil chemistry and environmental conditions. Work on this objective is advancing well. To date a number of modeling approaches have been tested to describe the adsorption of trace metals on both mineral and organic soil materials. The NICA-Donnan model describes the behaviour of the system very well and this model has been calibrated using surface adsorption data. It has also been determined that the adsorption of trace metals on roots can be described using binding constants for the acetate ligand (with some minor adjustments). The second objective is to determine the metal binding capacity of decomposing fine roots and foliage in order to predict when they might act as metal sources or sinks to soils. Progress on this objective is tangential, as the graduate student who was to start in Fall 2002, declined in the first week of September. There was no immediately available student to take her place, so D. Johnson was hired as a post-doctoral fellow until December 2002, for the purpose of writing manuscripts. Three have been submitted, including a summary paper to appear in the June 2003 issue of *Human and Ecological Risk Assessment*, and two more are being written. Since January, Paula Cypas (PhD student) has been supported by MITE-RN; her project has been to develop conditional stability constants for Cu binding to roots, using wheat and hydroponic solutions.

Project B2 Development of rational models for relating metal accumulation by aquatic animals to metal concentrations in their environment: relative importance of ambient metal sources (L. Hare, INRS, Université du Québec):

This project involves three main research objectives. The first is to understand the exposure of burrowing animals to sedimentary metals. Significant progress was made by developing a means of measuring the velocity of the currents that invertebrates produce in their burrows. By measuring the diffusive loss of a tracer gas through a membrane-tipped micro-sensor the low current velocities (< mm per second) produced by the burrowing mayfly *Hexagenia limbata* (Ephemeroptera) can be measured. This data is currently being analysed for publication. Measurements have also been made on the impact of sedimentary metals on invertebrate behaviour. Behavioural endpoints included burrow length, form and depth measured on radiographs, as well as the duration of irrigation, walking and feeding movements recorded by infrared camera. A second objective was to determine the relative importance of food and water for insect larvae in nature. Progress was made on this objective by comparing Pb uptake by the alderfly *Sialis velata* from food and water in a field setting and by measuring Pb losses by *Sialis* from a contaminated lake (Dufault, Rouyn-Noranda). A further field experiment to compare the relative importance of food and water as sources of several metals was conducted. Preliminary results indicate that *Sialis* larvae take up nearly all of their Cd, Cu and Pb from their food. Because food is the major metal source for *Sialis*, its trophic position in various lakes could influence its metal concentrations. Therefore N isotope ratios were (and are) being measured as a means of comparing trophic positions. A third objective to determine the site(s) of Cd²⁺-H⁺ competition in the food chain leading to *Chaoborus* has also been pursued. Laboratory experiments have been completed and

further data analyses and a complementary field experiment will be conducted in 2003.

Project B4 Metal speciation in fresh waters, soil pore waters, through-fall precipitation, atmospheric precipitation and in aqueous solutions resulting from wetting of atmospheric particulates (C.L. Chakrabarti, Carleton University):

Two interrelated objectives of this research project are: i) to determine the environmental factors that control free metal ion availability in freshwaters, soil pore waters and atmospheric precipitation, and ii) to develop new techniques for determination of metal speciation parameters including the dissociation rate coefficient (which is a measure of the chemical reactivity), the diffusion coefficient (which is a measure of the mobility), and the stability constant (which is a measure of the equilibrium availability of free metal ions). Substantial progress has been made in developing and applying metal speciation techniques and methods for determining metal speciation in soil pore water samples and rain throughfall samples from Sudbury and Rouyn-Noranda provided by Project B1 and in lake water samples from Rouyn-Noranda provided by Project C3. Metal speciation techniques that have been developed and applied to the MITE samples include: Competing Ligand Exchange and Adsorptive Cathodic Stripping Voltammetry, Anodic Stripping Voltammetry using a Rotating Disk Electrode, Classical Anodic Stripping Voltammetry at a Hanging Mercury Drop Electrode, and Competing Ligand Exchange and Graphite Furnace Atomic Absorption Spectrometry for the kinetic speciation of metals. Important progress has also been made in applying the new equilibrium speciation model, WHAM/VI, to the MITE samples of Projects B1 and C3.

Project B5 The availability of trace metals in the rhizosphere of contaminated soils from the Sudbury area (F. Courchesne, Université de Montréal):

Significant progress has been made on both the field and laboratory portions of this project. Soils were collected at three locations in the Sudbury area and these sampling sites were chosen among a series of sites already studied by researchers in Project B1 and are the same as those used in the fall of 2001 to sample the rhizosphere of white birch (*Betula papyrifera*). The separation of soil samples into bulk and rhizosphere components (both inner and outer rhizosphere) was completed in the laboratory. The textural and mineralogical analyses of 2001 samples were conducted in April-May 2002 together with pH (H₂O) and organic C determinations. Synchrotron – XRF and XANES analyses were also conducted on selected rhizosphere aggregates from the Rouyn site. The fractionation of trace metals in the rhizosphere and the bulk soils and the subsequent analyses by ICP-AES or ICP-MS started last March. The H₂O, BaCl₂ and pyrophosphate extractions for Al, Cd, Cr, Co, Cu, Fe, Mn, Ni, Pb, and Zn on the 9 sites from Rouyn under *Populus tremuloïdes* was completed in December 2002. All analyses should be completed in June 2003. Method development (ion selective electrode) for measuring the free Cu²⁺ ion activity in water extracts from the rhizosphere under *Betula papyrifera* was initiated early December 2002 and method development for the oxalate extraction will be done next spring.

Project B6 Metal budgets of lakes and catchments on the Precambrian Shield: compartment sizes and fluxes between compartments (P. Dillon, Trent University):

This project was initiated in mid-2001, and data collection has been underway for seventeen months. The purpose of the project is to establish the size of the compartments of metals (including but not limited to the five key metals, Cu, Ni, Zn, Pb, Cd) and the fluxes between compartments in a catchment (Plastic Lake, Haliburton County, Ontario) that is not impacted by local point sources of metals. This is an integrated study of the terrestrial and aquatic portions of the catchment, and includes analysis of the transport of metals between the land and water, the role of both acid deposition and dissolved organic carbon (DOC) in this transport, and the evaluation of the major sinks and sources of metals within the lake and its catchment. Almost all of the stated objectives in the 2002-2003 proposal have been met with only a few slightly behind schedule. The pool or compartment sizes have all been estimated with the exception of the wetland (plant material and sediment) and the lake sediments. These will be completed before the summer of 2003. Measurement of the fluxes between compartments is ongoing, with all instrumentation in place and data collection underway. Work has recently begun to separate the particulate ($>0.45 \mu\text{m}$) and dissolved fractions of the metals as the first step in speciation. This has included extensive QA/QC studies of various filters. As well new studies focussing on the use of stable isotope ratios for source identification using the new high resolution MS instrumentation at the Trent Water Quality Centre have now begun (funded independently of MITE at this point), with a focus on Pb.

Project B7 Importance of reduced sulphur species in controlling metal speciation in surface waters on the Canadian Shield (F. Wang, University of Manitoba):

The objectives of this project are: i) to investigate the presence of metal complexes with reduced sulphur species (RSS) in oxygenated surface waters on the Canadian Shield, and ii) to determine the relative importance of metal-RSS complexes in controlling metal speciation in these surface waters, as well as in sediment interstitial waters. The year 2002 marked the second year of this project and was characterized by intensive studies on the stability of metal-sulphide species in oxic waters and the structural identification of these species. Significant progress was made on the development of analytical techniques for the measurement of total sulphide. The Cr(II)-reducible-sulphide (CRS) method was found to effectively recover the sulphide in the Cd-S and Cu-S species. As a result, two different analytical methods were used for all the subsequent studies: the AVS method for the study of sulphide species of Fe, Mn, Zn and Pb, and the CRS method for sulphide species of Cd and Cu. In order to identify metal-sulphide species by mass spectrometry (MS) two direct structural analytical methods have been tested: electrospray ionization – mass spectroscopy (ESI-MS) and high performance liquid chromatography – high resolution mass spectroscopy (HPLC-HRMS). The electrochemical determination of RSS and metal-RSS complexes was started in January 2002 to develop methods for determining metal-sulphide and metal-polysulphide species by voltammetry. Methods were developed to make the solid-state Au-Hg microelectrodes. Unfortunately, this investigation was subsequently stopped in May 2002 when the graduate student relocated to another university to pursue other interests. As a result, the electroanalytical determination of metal-RSS species has been delayed until a suitable graduate student is available. The determination of formation constants for Hg-RSS complexes was initiated in November of 2002 with the arrival of a new postdoctoral research fellow and will be continued for most of Year 3. A new ultra-trace analytical technique for the analysis of

mercury is being developed with a state-of-the-art DRC II ICP-MS (Perkin Elmer) in the metal-free Ultra-Clean Trace Element Laboratory. Progress was made on field sampling and analysis of metal speciation. In addition to the four lakes studied in Year 1, two more lakes in western Ontario, Lakes 658 and Wabigoon, were added in the Year 2's field study. Each lake was visited once in the summer and overlying water peepers were used to collect dissolved water samples from the surface epilimnion layer. In addition to the AVS and CRS, samples were also collected for analysis of the 8 metals of interest (Fe, Mn, Cd, Cu, Hg, Ni, Pb and Zn), as well as pH, major cations (e.g., Ca^{2+} , Mg^{2+} , Na^+ , K^+), anions (DIC , SO_4^{2-} , Cl^-) and DOC. Once all the analyses are completed, calculations will be made to estimate the relative importance of metal-sulphide species in determining metal speciation in these surface waters. Investigation of biogenic thiols in surface and sediment pore waters was initiated in the summer of 2002 and will be carried on by a PDF for most of Year 3.

Partnerships and Collaboration

In the <Processes> domain, Projects B1 and B5 work on the same forest sites, and, as rhizospheric processes are widely assumed to modify metal bioavailability, the rhizosphere soil project (B5) will help bridge the work on trace metal activity and speciation in the bulk soil solution to that on metal accumulation in the vegetation, being carried out in Project B1. The laboratory-derived methods of measuring metal speciation in solution (B4) are being applied to field-collected samples of surface water, precipitation and soil solution, collected in Projects B1 and C3. This benefits both projects, as it allows validation of the techniques for B4 investigators, and provides speciation information that B1 and C3 investigators can incorporate into their biological investigations. The flux model for a catchment not influenced by local sources of metals (B6) is in notable contrast with the box model being developed in B1, a catchment that is influenced by local sources; the outputs from these two models form the basis for a very powerful comparison.