Executive Summary for FY 2002 - 2003
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Domain Co-Leaders

- Dr. Marc Lamoureux, St. Mary's University
- Dr. Robert G. Garrett, NRCan, Geological Survey of Canada

Projects included in <Sources> Domain in FY 2002 - 2003

Project Title	Principal/Co-Investigators	Affiliation
A1 Development and application of methods for measurement of metals on aeolian dust from natural settings	Edwards, G.C. Campbell, J.L.	School of Engineering, U. of Guelph Dept. of Physics, Univ. of Guelph
A2 Chemical speciation and quantitative determination of some metal pollutants associated with airborne particulate matter of varying sizes	Lamoureux, M.	Dept. of Chemistry, St. Mary's Univ.
A4 Geochemical mobility of metals in surface sediments: influence of sediment diagenesis	Carignan, R. Tessier, A.	Dépt. Sci. Biologiques, U. de Montréal INRS-ETE, Univ. du Québec
A5 Development, evaluation and applications of analytical methods for chemical speciation of mercury associated with atmospheric particulate matter/aerosols and with suspended matter in wet precipitation	Lu, J.Y.	Dept. of Chemistry, Biology & Chem. Engineering, Ryerson Univ.
A6 Application of sensitive techniques for the chemical analysis of aerosolic particulates	Spiers, G.A.	Centre for Environmental Monitoring, Laurentian Univ.
A7 Rates of trace metal release due to mineral weathering	Hendershot, W.	McGill University
AF8 Redistribution of metals in lake sediments by bacterially mediated oxidation-reduction reactions	Gould, D. Alpay, S.	Mining and Mineral Sciences Laboratory, NRCan Geological Survey of Canada, NRCan
AF9 The role of bacteria in the mobilization of arsenic from mine impacted sediments	Palace, V.	Freshwater Institute, DFO
AF10 Examination of mineral weathering and release of trace elements in selected soil profiles	Percival, J. Hendershot, W.	Geological Survey of Canada, NRCan McGill University

Progress Toward Achievement of Objectives

The research objectives in the <Sources> domain involve: i) estimating site-specific metal loadings in differing ecosystems due to the atmospheric deposition of metals from anthropogenic and natural sources; and ii) determining if diagenetic processes modify chemical records in lake sediments preventing them from being interpreted as records of historical deposition. These studies address the issue of origin in the ecosystem of metals that may pose public health and/or environmental threats, and will help identify appropriate risk management strategies. The objective will be achieved by addressing the following research questions:

- *What is the magnitude of metal emissions from natural sources? What are the metal species present in natural particulate fluxes?*
- *What are the most appropriate criteria and methodologies for source apportionment, natural vs. anthropogenic, of metal releases?*
- *What is the speciation of metals deposited from the atmosphere? Is the speciation determined by source characteristics or by transformations during transport?*

Studies in the <Sources> domain involve both field and laboratory components. Field work is undertaken both up- and down-wind from known metal sources to the atmosphere, and at remote sites. Laboratory studies include experiments under controlled conditions, and the development and use of appropriate analytical chemistry tools. In addition to the seven ongoing projects (A1-A6) from 2001-2002, two new projects were initiated in 2002-2003. These two new projects (A7 and AF10) will fulfill an important knowledge gap, and the main question to be studied is:

- *What is the rate of trace metal release from particulate matter due to mineral weathering?*

Project A1 Development and application of methods for measurement of metals on aeolian dust from natural settings (G. Edwards, University of Guelph): Due to the resignation of Professor Edwards as Associate Professor, mercury lab research and the PM modeling component have been cancelled from the objectives. A field intercomparison of the PIXE cascade impactor technique with other particulate collectors was completed, and sample analysis will begin as soon as the PIXE facility renovations are completed. As part of the evaluation of appropriate lab methods for studying fractionation of soils into aerosols and to understand the effect of friction velocity on aerosol fractionation and composition, an existing wind-tunnel at the School of Engineering was evaluated. The wind-tunnel was found to be inadequate due to problems of providing a clean air source and acquiring the amount of soil needed for such a study. Thus, a resuspension chamber has been built which houses PIXE cascade impactors and stacked filter units to collect particles by size. Its characteristics will be evaluated shortly, followed by the study of aerosol-soil fractionation in the chamber. This part of the study is still in progress. Preliminary relationships between field and lab data, and soil and aerosol data, will be finished by end of winter 2003 (March). Although not in the original proposal, a field study to collect aerosols from a bare soil has been completed and soil collected will be analyzed and tested in the chamber.

Project A2 Chemical speciation and quantitative determination of some metal pollutants associated with airborne particulate matter of varying sizes: Samples collected in the Rouyn-Noranda vicinity have been analysed by ICP-MS. The quantitative determination of Pb, Ni, Cu, Cd, and Zn was completed for the July/August 2000 and the October 2001 collection. Results

showed that Zn is not a good indicator of the impact of the Horne smelter stack on the environment, but Pb and Cu are definitely more abundant in particulates that are downwind from the Horne smelter compared to particulates collected upwind from the stack. The Pb isotope ratio was determined for the July/August 2000 collection and showed that the Pb isotopic signature for airborne particulate matter collected downwind from the Horne smelter stack is different from that collected upwind. The Pb isotope ratio determination for the October 2001 collection is in progress. The determination of Cu, Ni, Pb, Cd and Zn using laser ablation ICP-MS on the October 2001 and future sample collection from the Sudbury region began at the end of the Fall 2002. Chemical speciation, using x-ray absorption fine structure (XAFS), of Cu, Ni and Pb for the July/October 2000 is completed and Cu was completed for the October 2001 collection. Results show that the chemical nature of Cu and Pb from particulate matter collected downwind is different from the upwind samples. Furthermore, the speciation is particle size dependent. Collections of airborne particulate matter from the Sudbury area are scheduled to begin at the end of Fall 2002 (collaboration with Project A6). Samples from wet events from the Rouyn-Noranda and Sudbury areas (under W. Hendershot's supervision - Project A7) are being collected and will be investigated during Fall 2002/Winter 2003 for chemical characterization (quantitative and speciation).

Project A4 Geochemical mobility of metals in surface sediments: influence of sediment diagenesis (R. Carignan, Université de Montréal): **Main project**. Duplicate sediment cores were collected in July 2002 in three lakes at a low metal loading site (Île René-Levasseur on Manicouagan Reservoir). Total Hg, total carbon and nitrogen, ^{137}Cs, ^{210}Pb, ^{214}Pb, ^{226}Ra and ^{241}Am measurements are underway and will be completed in February 2003. Chemical digestion of the sediment samples are underway and should be completed by the end of December 2002, and measurements of Al, As, Cd, Cu, Fe, Mn, Ni, Pb, Ti and Zn will be completed in March 2003. Similar analyses for the samples collected in 2001(Rouyn-Noranda) are complete and ready for archiving. Measurements of Al, As, Cd, Cu, Fe, Hg, Mg, Mn, Na, K, Ni, Pb and Zn in the porewater samples from L. Despériers (Rouyn-Noranda) are complete. The WHAM 6 speciation computer code was modified to include metal complexation by polysulfides and metal speciation calculations were completed for porewaters from the three regions. Diagenetic modelling is well underway and results to date indicate that post-depositional remobilization appears to be negligible for Pb and Hg, intermediate for Cu, and important for As, Cd and Zn. Results shows a potentially important effect of wildfires on Hg cycling at the watershed scale and on Hg deposition chronologies in lakes. To confirm this phenomenon, other boreal lakes were cored (August 2002) in the Haute-Mauricie region, where the fire history is well documented. Total Hg combined with geochronological analyses confirm the importance of wildfires on Hg cycling. Charcoal measurements on these samples will be completed early in 2003. **High-resolution porewater sampling.** The Diffusive Gradient in Thin-films (DGT) approach was abandoned because extensive measurements of metal species diffusion within the types of hydrogels currently used in DGT samplers indicated that sampling with this technique is prone to artifacts. **Stable Pb isotopes**. Sediment cores (August-September 2002) were obtained from the vicinity and extended region of Rouyn-Noranda for Pb and ^{206}Pb/^{207}Pb, ^{206}Pb/^{208}Pb and ^{206}Pb/^{204}Pb measurements. Pore waters using peepers were also collected in that region to determine Pb mobility. Fish and *Hexagenia limbata* (Ephemeroptera) were collected for measurement of Pb

isotopic ratios. Measurements of Pb ratios are complete for L. Vose sediments while the other measurements are underway. The large differences in isotopic signature between L. Vose and L. Tantaré indicate that the geographical influence of smelter emissions can be traced using lake sediments. **Ag and platinoids**. Two projects on Ag and platinoid metals geochemistry were initiated. Cores and porewater samples from L. Tantaré and L. Vose are currently being analyzed.

Project A5 Development, evaluation and applications of analytical methods for chemical speciation of mercury associated with atmospheric particulate matter/aerosols and with suspended matter in wet precipitation (J.Y. Lu, Ryerson University): Temperature programs that combine step-wise and linear ramping have been developed and tested, and have been compared with the linear ramping program for separating mercury species associated with airborne particulate matter. Samples of airborne particulate matter have been collected in an industrial area in the Nanticoke region (with support from Mr. Robert Kozopas, OPG) and in the Arctic (in collaboration with Dr. W.H. Schroeder, Environment Canada). Samples of suspended particulate matter in rainwater have also been collected (in collaboration with Dr. W. Hendershot) from Sudbury, Ontario, and Rouyn-Noranda, Québec. The methodology for mercury speciation using Electrothermal Vaporization-Inductively Coupled Plasmas-Mass Spectroscopy (ETV-ICP-MS) developed in the lab has been tested using the samples collected from the industrial area and the Arctic. The samples of suspended particulate matter in rainwater are to be analyzed. Since the homogeneity of the coal-fly ash samples spiked with solid mercury compounds is poor, a new methodology using vapors of mercury compounds has been developed for preparing standards containing mercury compounds.

Project A6 Application of sensitive techniques for the chemical analysis of aerosolic particulates (G.A. Spiers, Laurentian University): In May 2002, a new generation Energy-dispersive Miniprobe Multi-element Analyzer (EMMA) incorporating a specially designed high resolution Ge detector for small samples was installed. This EMMA system is designed to allow analyses of soil and sediment powders, finely ground organic samples, materials on filters, and small individual grains. Students and staff have been trained in operation and quality control techniques on the new EMMA, with analyses currently proceeding on the filters collected from snowpack during the previous winter. Collections from a smaller number of sites (~25) at varying distances from the smelter heartland through to the Quebec border are planned for the upcoming winter. Another project utilizing the MITE-RN support includes a detailed examination of road dusts within the Ramsey Lake watershed, the major drinking water source for the Greater City of Sudbury. The road dusts will be analysed for chemical, mineralogical and morphological properties. At selected sampling sites adjacent to both high and low density use roads, as well as car parks, modern anthropogenic aerosols will be collected and characterized. Preliminary data from this undergraduate thesis project should be available for presentation at the MITE-RN workshop in 2003. The recent arrival of the Cascade Air Samplers from Dr. Lamoureux will enable a collaborative research program to be initiated, with Stage I being with research projects examining the nature of aerosol and road dust input to Ramsey Lake, the Sudbury drinking water supply. Then the samplers will be installed at selected sites from the snow aerosol-sampling program completed over the past two winters. Selected samples will be

shipped to Dr. Lamoureux (Project A2) for detailed speciation analyses. Samples of colloidal material from the soil lysimetry project established by Dr. Hendershot (Project B1) will also be analysed by EMMA on arrival at the CEM laboratories in Sudbury. Examination of the morphological, chemical and mineralogical nature of the mobile colloidal phase of these soil solutions from soils in industrially contaminated sites will be compared with those collected previously from soils under mixed aspen-spruce from pristine sites. Columns from the "Rates of trace metal release due to mineral weathering" (Hendershot, Project A7) will be impregnated at the end of the leaching experiments. The columns will then be sectioned and analyzed by electron beam techniques at CEM to quantify the removal of selected metals from mineral grain surface layers.

Project A7 Rates of trace metal release due to mineral weathering (W. Hendershot, McGill University) Two series of whole soil weathering experiments have been conducted to test and perfect the methodology to determine the rate of input of trace metals into the soil environment by weathering of trace metal rich minerals or polymineralic fragments. The column leaching protocol appears to be working very well with stable and repeatable results. In the proposal, the importance of being able to measure the amounts of trace metal released from the mineral phase and then re-adsorbed was stressed since it was thought that the metals released by weathering would not remain in solution. The experimental results confirm that this is the case. However, the EDTA solution used to displace the re-adsorbed metals seems to be working and it is expected release rates will be measured. The chemical analysis from the second experiment is underway and a final decision on the details of the methodology will be taken in January 2003. At that time, soil fractions from collaborator Jeanne Percival (NRCan, GSC) will be the focus of further weathering experiments. Another objective is to use the data obtained to calibrate a mineral weathering model that will predict the release rate of trace metals as a function of mineralogy and environmental conditions. A working model that will simulate the behaviour of the leaching columns is being developed and combines solution speciation, surface adsorption and mineral weathering.

Project AF8 Redistribution of metals in lake sediments by bacterially mediated oxidation-reduction reactions (D. Gould, Natural Resources Canada): A series of microcosm experiments were set up in November 2001 to study key hypotheses in the lake sediment study based on fresh sediment samples taken by divers in September 2001. The cores incubated at 6^{o}C were sampled over a time series, in January 2002 and in October 2002. The room temperature samples without organic matter addition were sampled in January 2002 and in August 2002. Chemical analyses of the sediments from the last sampling of the microcosm experiment are currently being completed and the microbial data and the available chemical data from the microcosm study are presently being interpreted. Preliminary results indicate that elevated concentrations of soluble iron in the porewater fraction are observed throughout most of the sediment column when ferrihydrite was added. Also increased concentrations of solid phase iron were observed in the two cm of sediments above the ferrihydrite-amended layer. Additional experiments will be undertaken in order to determine if the effect is due to mobilization and redeposition of iron, or to an artifact of the sampling procedure. The addition of organic matter had no effect on either the microbiology or the chemistry of the microcosms, an observation that supports the view that

electron acceptors rather than electron donors are limiting in these particular sediments. Future plans involve a series of triplicate microcosm studies at 6°C with and without ferrihydrite and an abiotic control (gamma radiation sterilized). Labelled iron (^{57}Fe) and nickel (^{61}Ni) will be used.

Project AF9 The role of bacteria in the mobilization of arsenic from mine impacted sediments (V. Palace, Dept. of Fisheries and Oceans): This project aims at studying the community structures of iron, arsenic and sulphate reducing bacteria in Balmer Lake sediments. Results will be used to focus further studies on the most relevant organisms for As release from sediments. As well, physiological and genetic characterization of arsenic, iron and sulphate reducers has been continued. To this date, studies to determine total diversity of microbial colonies with sediment depth have been completed. The microbial numbers have also been correlated with arsenic and iron concentrations at each depth. Phylogenetic characterization of the iron, arsenic and sulfate reducing microbes present at each depth are continuing. Total diversity studies are also ongoing using primer specific analysis by PCR. An arsenic respiring bacteria from Balmer Lake sediments has been isolated and phylogenetic characterization has been completed. An analysis of arsenic flux in lab microcosms under varying redox regimes has been initiated at the University of Montana laboratories. These experiments are comparing the biotic driven release of arsenic from sediments relative to sterilized cores. This work will continue through the 2003-04 study year.

Project AF10 Examination of mineral weathering and release of trace elements in selected soil profiles (J. Percival, Geological Survey of Canada): This project aims at providing a detailed mineralogical characterization of six soil profiles located in Sudbury and Rouyn-Noranda. Specifically, the determination of trace minerals that can be a source of trace metals in the weathering environment was undertaken. Detailed mineralogical analyses by X-ray diffraction and scanning electron microscopy determined that some minerals may be potential substrates for metal retention, including biotite, chlorite and Fe-oxides. SEM analyses to X-ray map specific metals have not yet started, but polished thin sections of grain mounts are in hand. The identification and preparation of appropriate grain size fraction or discrete minerals for weathering experiments is another objective to be achieved. Sample fractionation was completed on 6 B/C soil samples from the Rouyn-Noranda and Sudbury soil stations that are instrumented with bulk precipitation collectors, through-fall collectors and lysimeters. Samples were also separated into magnetic and non-magnetic heavy mineral fractions. Discussion with W. Hendershot (Project A7) to select appropriate fraction(s) for weathering experiments are in progress. The sequential extraction of trace metals from selected samples to determine mobility potential is earmarked for 2003-2004.

Partnerships and Collaboration

Participants in the <Sources> domain include: Iain Campbell and Zdenek Nejedly (A1, Department of Physics, University of Guelph); Pat Rasmussen (A1, Health Canada); Bill Schroeder, Cathy Banic and Sunling Gong (A1 & A5 [except S. Gong], Meteorological Service of Canada); Dr. T. Sholtz (A1, Ortech International Inc.); Conrad Grégoire (A2 & A5, Natural Resources Canada); Grant Edwards (A5, University of Guelph); Andriy Cheburkin, (A6, Laurentian University); F. Rosenzweig (AF9, University of Montana); J. McGeer, C.W. Smith,

and J. Dutrizac (AF8, Natural Resources Canada); W. Hendershot (A6 & AF10, McGill University), R.G. Garrett and G.E.M. Hall (AF10, GSC); J. Percival (A7, GSC); D. Pearson (A6, Laurentian University); M. Lamoureux (A6, Saint Mary's University). In summary, 26 scientists from 15 institutions (universities, Federal departments and industry) are collaborating in 9 funded projects. Networking is strengthened by participation of some scientists in more than one project. In addition, the 9 projects are supporting 7 students working towards graduate degrees and 8 undergraduates; and are supported by 9 PDFs and research assistants, and 5 technicians.