
# ESS- MITE Program Final Report
June 2006

**Program Manager: Dr. Andrew Rencz**

**To provide the geoscience knowledge necessary to assess and support the management of risk posed by metals in the environment to ecosystem and human health.**

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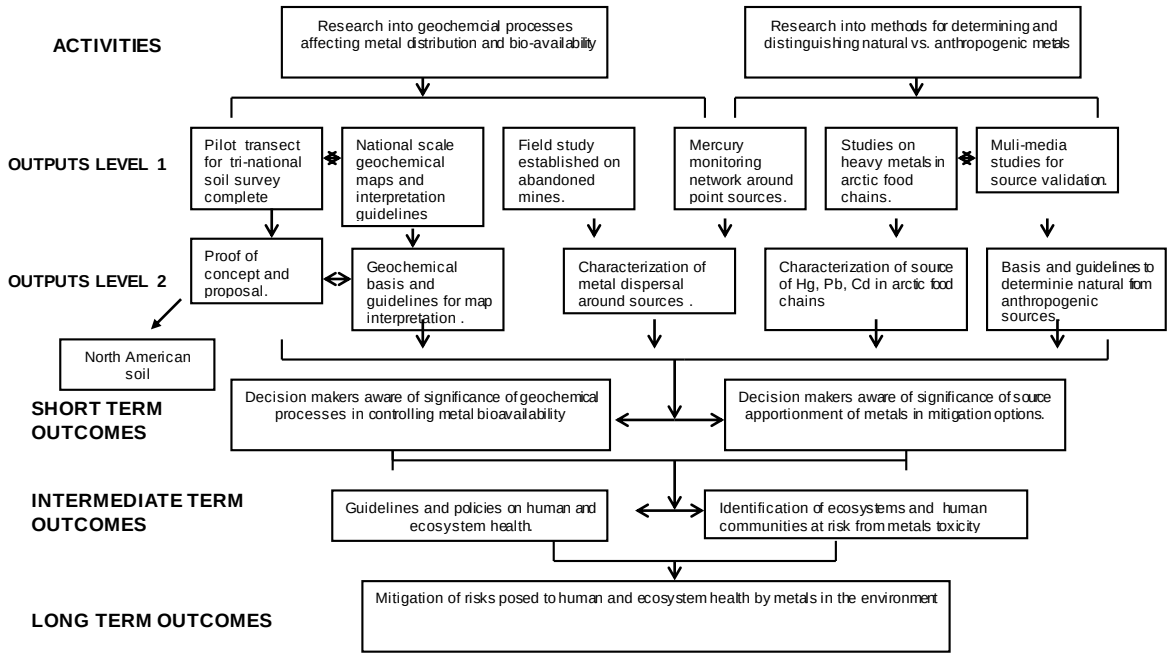
## Program Overview

The Earth Science Sector established the original MITE (Metals in the Environment) Initiative in 1997 to provide an environmental focus for activities within the department. Following the successful completion of the program in 2002 a second MITE program was initiated. The objective of the program was similar to the original program, seeking to assure that regulatory decisions to ensure a clean environment were, when appropriate, based on sound geoscience. Whereas the first program focussed on issues surrounding point sources the second initiative addressed a new set of issues, typically dealing with identifying environments of concern and providing geosceitnific knowledge to reduce the risk in these environments.

The second MITE initiative started in 2003 with a three year annual funding level of $260 K (O&M) and a salary component of approximately $ 1.1 million. Each year additional funds were derived through outside partnerships. The objective of the program was to

**Table 1: Logic model for the MITE program.**




provide the geoscience knowledge necessary to assess and support the management of risk posed by metals in the environment to ecosystem and human health. The logic model for the program is presented in Figure 1.

To address these issues the program was conducted as three projects, each with a number of activities:

**Project 1**: Metals in the Environment: Sources, Fate, and Risks

Activity 1: Multi-disciplinary investigations of risks associated with abandoned metal mines
Activity 2: Geochemical baseline protocols for soil monitoring
Activity 3: Geochemical modeling of soil mineralogy
Activity 4: Risk-assessment mapping, background estimation, and metadata development

**Project 2:** Natural vs. Anthropogenic Metals

Activity 1: Multi-media validation studies
Activity 2: Hg and Cd source apportionment in traditional northern foods
Activity 3: Improving analytical methodologies and process understanding

**Project 3:** Emission and deposition of elements and particles as related to geogenic and anthropogenic sources

Activity 1: Canada Wide Standard of Mercury emissions from coal-fired utilities, speciation of As, Cr and Ni and characterization of particles emitted from coal-fired power plants
Activity 2: Delineation of the environment that may cause health risk in the vicinity of large stationary sources
Activity 3: Inter-disciplinary techniques to identify the processes that distribute and redistribute metals in lake sediments
Activity 4: Integration and interpretation of the potential redistribution of metals in lake sediments

**Figure 1: Location of study si**


Each project defined a set of scientific needs that targeted a specific government priority. The resolution of these issues were beyond the mandate of NRCan; typically residing within mandates of Environment Canada, Health Canada, Indian and Northern Affairs or within the realm of provincial jurisdiction. Consequently the success of the program was based on developing sound partnerships with stakeholders who required the information for fulfilling their mandate.

In order to provide environmental solutions a multi-disciplinary scientific approach was required. This was done through partnerships with a variety of academic and other government institutions. These partnerships were crucial to the multi-disciplinary approach that provided an overview of the issue.

The program touched on a wide variety of issues that affect Canadians and several projects have international connections. As shown in Figure 2, field work was conducted across Canada and one project was undertaken in India. The projects included regional geochemical surveys which provided information for the estimation of background concentrations of metals across Canada. From this knowledge risk assessments were better informed as they were able to put site specific information into a broader perspective. Several targeted projects investigated environments of concern where disturbances were recognized as posing a risk to the health of Canadians. This included environments around abandoned gold mines, areas affected by mercury deposition from a variety of sources with a focus on coal fired power plants. A fundamental point in these studies is recognizing the source of the pollutant, specifically if the contaminant arises from a natural or anthropogenic source. This knowledge is fundamental to developing remediation policies which most directly target the cause of the problem while not imposing undue hardship on the industrial sector.

Details of the projects and sub-activities within each of the projects are provided in this report. The report provides an overview of the findings by activity within each project. Further details of the activities can be found in the attached CD-see APPENDIX A for a list of activities and the associated powerpoint PowerPoint presentation. At the end of each of the project descriptions is a list of the publications and presentations as of March 31, 2006. The total number of publications is presented in Table 1. Further details are available by contacting the researchers as there will be as significant number of papers being published following the publication of this report.

**Table 1: Presentations from the MITE program**

| **Presentation** | **Num.** |
|---|---|
| Peer reviewed papers | 36 |
| Conference proceeding papers | 13 |
| Reports | 17 |
| Theses supervised | 6 |
| Conference presentations | 19 |
| Manuals | 3 |
| Assessment reports | 1 |

It should be noted that the MITE program formally ended in April of 2006, however significant elements of the program are being continued under a new program: Environment and Health.

Thank you,

Dr. Andrew Rencz
Program Manager, MITE

# Project Descriptions

## *Project 1: Metals in the Canadian Surface Environment: Sources, Fate, and Risks - Michael B. Parsons, Project Leader*

### Introduction

The objectives of this multi-disciplinary project were to:

1. Provide decision-makers and stakeholders with geoscience knowledge essential to assess and manage risks posed by metals in the environment;
2. Identify areas, through appropriately designed activities, where Canadians may be exposed to chemical species of ecosystem and human health concern, and to characterize critical processes involved in metal release, transport, and fate to assist in developing risk-management strategies;
3. Provide the appropriate geoscience knowledge to manage risk—specific examples are provided in the activity reports below; and
4. Contribute, through each project activity directly to achieving the overall MITE program goal of providing sound scientific information to help mitigate risks associated with metals in the environment.

This three-year (2003–2006) project has characterized the distribution, chemical form, and potential risks associated with metals released into the Canadian surface environment from natural sources and activities related to their exploitation. Multi-disciplinary studies have defined areas that pose risks to both ecosystem and human health, and have led to a better understanding of processes that affect the distribution and fate of metals. This knowledge has contributed to the assessment and mitigation of risks, and is being used directly by various stakeholders to help develop environmental quality guidelines and risk-management strategies.

The project consisted of four main activities: (1) multi-disciplinary investigations of metal(loid) release, transport, and fate near abandoned gold mines; (2) development of models and protocols to support the implementation of a North American soil-monitoring program; (3) development of geochemical models to improve understanding of soil mineralogy and facilitate the use of mineralogical data in risk assessments; and (4) risk-assessment mapping, metadata development, and geochemical background estimation based on legacy datasets and newly acquired National Geochemical Reconnaissance (NGR) data. Collaborative studies and effective communication of the results to clients responsible for policy development (e.g. Environment Canada (EC), Health Canada (HC), Fisheries and Oceans Canada (DFO), Nova Scotia Department of Health) have ensured that ongoing risk-management decisions are informed by ESS data.

## Summary of Outputs

In the past three years, supported by project funding, ESS staff, partner scientists, and students have authored or co-authored 5 peer-reviewed journal papers, 10 internal reports, 6 student theses, and 22 conference presentations. Project participants also contributed several chapters to a 320-page Mineralogical Association of Canada Short Course Volume entitled *Mercury: Sources, Measurements, Cycles, and Effects* (edited by Michael Parsons and Jeanne Percival). This short course took place at the Annual GAC/MAC meeting in Halifax in May 2005, and was accompanied by a one-day Special Session on "Mercury in the Environment" (organized by Percival and Parsons). A list of completed publications from this MITE project is included in Appendix A. At least 14 more journal papers are in preparation as part of a special issue of *Geochemistry: Exploration, Environment, Analyses* devoted to recent MITE investigations at abandoned gold mine sites in Nova Scotia. In addition to traditional scientific outputs, metadata and map products have been prepared for internet distribution, and a coloured brochure has been created to advertise the new Geochemical Metadata Catalogue (available through the Geoscience Data Repository at http://gdr.nrcan.gc.ca/geochem/index_e.php). Results from recent MITE investigations of gold mine sites in Nova Scotia led to the formation of a Federal-Provincial Historic Gold Mines Advisory Committee in May 2005, which is assessing human and ecosystem health risks associated with these sites, and actively managing acute health risks at some mines. This committee has a website (http://www.gov.ns.ca/enla/goldmines), and has issued two press releases (June 2005: http://www.gov.ns.ca/news/details.asp?id=20050623004, December 2005: http://www.gov.ns.ca/news/details.asp?id=20051216001) that have been featured on local and national television, radio, and in various newspapers. Finally, over the last three years, ESS staff (particularly Bob Garrett) have responded to many direct requests from other government departments, the private sector, academics, and private citizens for ESS geochemical data and interpretations (Appendix B). Most of these requests were for natural background levels of metals in various earth materials in support of risk assessments or guideline development. These non-traditional scientific outputs are often time-consuming, make direct use of legacy ESS data and recent MITE results, and represent an important means by which ESS data are communicated to various clients in direct support of risk-mitigation activities.

## Summary of Project Findings

### Activity 1: Multi-disciplinary investigations of risks associated with abandoned metal mines

*(ESS Project Staff: Michael Parsons, Gwendy Hall, Jeanne Percival, Al Sangster (retired))*

This study is a multi-disciplinary, multi-partner investigation of the dispersion, transformation, and fate of metals and metalloids in freshwater and marine environments surrounding abandoned gold mines in Nova Scotia. The main goal of this work is to provide data that can be used to assess environmental and human health risks and support

better informed land-management decisions. Project partners include ESS, the Nova Scotia Department of Natural Resources, Environment Canada, Fisheries and Oceans Canada, and four universities (Queen's University, University of Ottawa, Dalhousie University, and the Royal Military College). Characterization of the marine environmental impacts associated with these gold mines has been carried out concurrently through the Geoscience for Oceans Management (GOM) program (http://gom.nrcan.gc.ca/), and two abandoned mine sites have also been mapped using remote sensing methods as part of a project in the Sustainable Development Through Knowledge Integration (SDKI) program. (http://sdki.nrcan.gc.ca/mine/impacts_e.php). Detailed studies of metal(loid) speciation in dusts and near-surface particulates from selected mine sites have been funded in part by the Metals in the Human Environment – Research Network (MITHE–RN), Project I2 (http://www.mithe-rn.org/research/project_details.cfm?resProjectID=12).

From 2003 to 2005, samples of tailings, soil, till, rock, sediment, water, and/or vegetation were collected at 15 past-producing gold mines. Field studies reveal that most mines contain large volumes of unconfined tailings, which have historically been deposited down-gradient of mill sites in surrounding rivers, swamps, lakes, and the ocean. In some districts the tailings have been transported significant distances (>2 km) offsite by local streams and rivers. At most mines, the tailings are overgrown and often difficult to recognize; however, some tailings deposits have recently been disturbed by human activities (e.g. gold panning, fill excavation, off-road vehicle usage). Chemical analyses of more than 500 tailings and downstream sediment samples show high concentrations of mercury (Hg) (<5 ppb to 350 ppm; mean 7 ppm) and arsenic (As) (9 ppm to 31 wt.%; mean 1 wt.%). The highest Hg levels are found near mill structures, reflecting Hg loss during amalgamation and retorting. Arsenic concentrations are highest in areas containing arsenopyrite concentrates, or where weathering of the tailings has concentrated As in secondary phases (e.g. scorodite [$Fe^{III}AsO_4 \cdot 2H_2O$], Ca-Fe arsenates, As-bearing ferric oxyhydroxides). Water chemistry data indicate that dissolved As concentrations are very high at some locations, as compared to background values of generally <25 ppb. Most dissolved As is present as arsenate ($As^{5+}$); however, high concentrations of the more toxic arsenite ($As^{3+}$) are present near groundwater discharge areas, and in low-oxygen settings (e.g. swamps, tailings pore waters). Dissolved Hg concentrations in surface waters are relatively low even in close proximity to tailings with high levels of Hg, suggesting that most Hg is present in relatively insoluble forms. Detailed multi-disciplinary studies with project partners have characterized the background levels, speciation (e.g. mineralogy, oxidation states), mobility, and bioaccumulation of metal(loid)s in both freshwater and marine systems. A wide variety of methods have been employed, including sequential extractions, synchrotron-based X-ray absorption spectroscopy (XAFS), measurements of microbial activity and methylmercury generation, biological sampling (plants, fish, frogs, clams, invertebrates, mice, hares), and sediment/water toxicity testing.

Several of the gold mine sites are located in close proximity to residential developments, and are frequently used for recreational purposes. Very high concentrations of As in the windblown and vehicle-raised dust from these tailings sites may pose a potential acute health risk to recreational users of these areas, and a chronic risk to nearby residents who

are exposed to tailings-derived dust. Furthermore, studies by project partners (EC, DFO, RMC) demonstrate that both As and Hg are entering the food chain in some areas, which may pose a risk to human health. Results from this study have recently led to the formation of a Federal-Provincial Historic Gold Mines Advisory Committee (http://www.gov.ns.ca/enla/goldmines). This committee is continuing to evaluate the potential ecological and human health risks associated with gold mines throughout Nova Scotia, and is developing recommendations for management of these tailings sites.

## Activity 2: Geochemical baseline protocols for soil monitoring

*(ESS Project Staff: Robert Garrett (Emeritus), Gwendy Hall, Rod Klassen, Fari Goodarzi)*

This activity has developed sampling, field, and analytical protocols in collaboration with partners in Canada, the U.S.A., and Mexico in support of a proposed North American soil-monitoring program. Key project partners include the U.S. Geological Survey (USGS), Agriculture and Agri-Food Canada (AAFC), and the Servicio Geologico Mexicano. The database resulting from this long-term, continent-wide survey would enhance our ability to recognize and quantify changes in soil composition caused by urbanization, industrialization, agriculture, waste disposal, and other human activities. The proposed survey addresses a well-established need for high quality soil data, including geochemistry and mineralogy, to support risk assessment and management decisions by various agencies. The main objectives of this MITE activity are to test and refine sampling and analytical protocols for the proposed soil geochemical survey of North America, and to develop a report for ESS Management on the relevance, benefits, costs and resource/logistical requirements for implementing a Canadian national soil ambient level monitoring program as an interdepartmental collaborative effort.

Following a series of meetings in 2003 and 2004, the Canadian component of a 4000-km-long N-S soil sampling transect (from northern Manitoba to the US/Mexican border) was planned for Summer 2004 in partnership with staff from AAFC. In August 2004, Garrett and Klassen collected soil samples from 36 sites along the North Dakota - northern Manitoba segment of the N-S continental transect. The samples represent geologically diverse soil parent materials, including glacial lake sediment and till derived from the Canadian Shield and Phanerozoic sedimentary bedrock. Samples from each site include: (1) soils collected by horizon (O-, A-, C-horizons, where present) for multi-element four-acid and weak soluble extraction analyses and determination of soil texture; (2) A-horizon samples collected for soil moisture and microbiological characterization; and (3) topsoils collected from 0-5 cm for multi-element chemistry and determination of selected pesticides and other organic compounds. Most of these samples were sent to the USGS for analysis. Additional chemical / gamma-ray measurements were conducted by the GSC, including the development of a suitable analytical protocol (Gwendy Hall) for use in the water extractions of all transect samples (essential for characterizing the labile metal concentrations in soils). Garrett presented an overview of the study results at the MITE Final Workshop in February 2006, including a proposal for continued activity under the new ESS Environment and Health Program. Papers describing the transects will be published in a special issue of *GEEA* in 2007. Key results from the study will

also be summarized in a report to ESS Management that can be used to help decide if Canada should participate in a full North American soils-monitoring program.

## Activity 3: Geochemical modeling of soil mineralogy

*(ESS Project Staff: Rod Klassen, Robert Garrett (Emeritus), Ross Knight, Peter Davenport)*

This activity has employed geochemical modeling to improve understanding of soil mineralogy and metal bioavailability, and to facilitate the use of mineralogical data in risk assessments. These models help to explain the sources of elements in soils, how quickly metals become available through weathering and soil formation, and what phases host metals in soils. In 2003, Klassen developed a website (http://gsc.nrcan.gc.ca/geochem/model/index_e.php) describing the importance of geochemical modeling for understanding mineralogical controls on geochemical background variation, and the apportionment of trace elements among minerals and sample media. The techniques described in this website have been applied to legacy soil data collected from across Canada (Labrador, Nunavut, South Ontario), and the results are summarized in a series of publications prepared during the current MITE program. At the request of the MITE Program Manager, a report on the geoscience factors affecting geochemical background variation was also prepared for Health Canada in support of their risk-assessment programs.

As a contribution to the pilot study for the proposed soil geochemical survey of North America, C-horizon soil samples were collected from all 36 sampling sites along the North Dakota - northern Manitoba transect to investigate the potential for geochemical modeling of soil mineralogy. The chemical composition of silt and clay-sized fractions from the transect soils were determined, and used as input for geochemical modeling of soil mineralogy based on approaches developed by the Geological Survey of Finland. The purpose of this ongoing study is to indicate geochemical differences among grain size fractions, including the <2 mm fraction analyzed for the pilot study, that may be due to mineral partitioning resulting from geological processes. The modeling will provide a basis to interpret soil geochemistry in terms of its mineralogy and potential environmental reactivity.

## Activity 4: Risk-assessment mapping, background estimation, and metadata development

*(ESS Project Staff: Peter Friske, Stephen Day, Robert Garrett (Emeritus), Rick McNeil, Martin McCurdy, Graeme Bonham-Carter (Emeritus), Wendy Spirito, Stephen Adcock, Eric Grunsky)*

This MITE activity has provided geoscience knowledge on the geochemistry of soils and tills in Canada, and developed procedures for geochemical background estimation in support of risk-management activities. The main objective of this activity was to facilitate and encourage the use of ESS geochemical data by risk assessors in the

federal, provincial, and public arenas, and to communicate to the public the reality that Canada's surface environment is geochemically variable and that the prime control on that variability is the geology of the underlying materials.

***National Atlas compilation of NGR data for Cu, Ni, Hg & Zn:*** This sub-activity has prepared a series of national-scale maps (1:7.5 million and 1:1 million scale), tables, and descriptive texts based on legacy (1974-present) and recent NGR surveys to show background levels of Cu, Ni, Hg and Zn in lake and stream sediments, and to identify regions of elevated levels of these metals where risks to human and ecosystem health may occur. Contour maps for all four elements have been prepared, together with maps based on drainage basin and ecoclassification frameworks. ESS staff have worked closely with National Atlas staff to develop explanatory web text for use in "Learn More" windows concerning applied geochemistry and MITE issues. Draft maps have been posted on a National Atlas internal test website, and final maps (including explanatory text) are expected to be uploaded to the public National Atlas website later in 2006. A draft of the Hg map is shown on the ESS MITE program website (http://mite.nrcan.gc.ca/index_e.php).

***NGR Surveys in the Northwest Territories and Yukon:*** NGR data have been, and continue to be, used by Environment Canada and other clients for developing environmental quality guidelines (e.g. CEPA Risk Assessments, Canada-Wide Standards, and Sediment Quality Guidelines through the CCME). Within the ESS MITE program, roughly 40,000 $km^2$ of Canada's landmass have been covered by eight new stream sediment and water surveys totalling over 2,768 sites, including 459 bulk sediment samples from the Northwest Territories and Yukon. Surveys have been conducted in the Macmillan Pass / Sekwi Mountain area (NWT), the Travaillant Lake area (NWT), and the Old Crow region (YK). Data from these surveys have been / will be published as GSC Open Files, incorporated into the NGR database, and used to augment National Atlas geochemical compilation maps. Survey data from the Macmillan Pass / Sekwi Mountain area, containing stream sediment and water data for 916 sites, illustrate the sharp geochemical contrast between the geochemically unique Selwyn Basin, the mid-Cretaceous Selwyn Plutonic Suite, and the predominately carbonate sedimentary rocks. Data from the Edéhzhíe stream sediment, bulk sediment, and water survey will form the basis of a non-renewable resource assessment under NWT's Protected Areas Strategy. Stream sediment and water data obtained through the Old Crow surveys will also form the basis of a non-renewable resource assessment. These assessments are critical in the selection of protected areas (parks and others), aboriginal land claim negotiations, as well as general land-use planning and are based on the best geoscience available. Data from these NGR surveys will support better-informed land-use decision-making by Deh Cho, Tetlit Gwich'in, Gwichyah Gwich'in and Vuntut Gwich'in aboriginal groups, and the Northwest Territories and Yukon Governments.

***Determination of background levels of metals:*** Through the MITE Program, ESS has been working with other government agencies to determine background levels of metals in the environment across Canada. In 2004, Bonham-Carter and Garrett wrote a guidance document on statistical methods of defining geochemical background. This document was prepared in response to a specific request from Environment Canada for assistance in

developing new water quality guidelines for the protection of aquatic life, but will also be of use to other agencies tasked with environmental protection. The document text has been incorporated into EC's new "Protocol on Deriving Water Quality Guidelines for the Protection of Aquatic Life". ESS has also been providing Health Canada with knowledge on the geochemistry of soils and tills, including background values to support risk-management decisions as part of the Federal Contaminated Sites Program. A background study of metals in Canada (Adcock, Garrett, Bonham-Carter, Rencz) was started in 2004 using data from 20 GSC till surveys, and a summary report on this work will soon be published as GSC Open File 5084. Finally, in collaboration with the New Brunswick Dept. of Natural Resources, ESS (Adcock, Grunsky, Rencz, Spirito) has compiled till data for approximately 9400 sites and conducted statistical analyses to determine the natural variability in trace metal concentrations. Approximately 400 samples (20 samples from each of 20 original surveys) have been re-analyzed by a consistent method to check the reproducibility of the geochemical data, and to assess the need for leveling in this large dataset. The compilation will soon be made available as a joint GSC/NBDNR digital publication.

***Metadata development for Health Canada**:* This subactivity provides Health Canada with a direct means to determine what soil and till geochemical data are available for their areas of interest across Canada. ESS staff (Spirito, Rencz, Adcock) have developed metadata for both GSC and Provincial geochemistry data, which are now available (in English and French) through a map-based interface on the GDR website (http://gdr.nrcan.gc.ca/geochem/index_e.php). The catalogue currently contains 524 entries, including data for 304 soil/till/peat samples, and 220 records consisting of data for NGR lake and stream sediments, biogeochemistry surveys, and several miscellaneous geochemical surveys. This represents an estimated 70% of the GSC's data holdings, and something less than 50% of the Provincial data holdings. For many surveys, the raw geochemical data are available for download. A GSC Open File (5085, supercedes OF 4703) has been produced summarizing these metadata, and a coloured brochure has also been developed to advertise the ESS Geochemical Metadata Catalogue. These outputs support risk-management decisions as part of the Federal Contaminated Sites Program, and were highlighted at the Federal Contaminated Sites workshop in March 2006.

## Appendix: Contributions to Outcomes

## Appendix 1A: List of Reports, Publications, and Conference Presentations

***Theses***

**2006**

Corriveau, M.C. (2006) Characterization of Arsenic-Bearing Near-Surface and Airborne Particulates From Gold Mine Tailings in Nova Scotia, Canada. M.Sc. thesis, Queen's Univ., Kingston, ON, 124 p.

**2005**

Murimboh, C.A. (2005) New Insights on the Chemical Speciation of Nickel and Copper in a Naturally Metal-Rich Soil from the Thetford Mines Area, Quebec. Unpublished M.Sc. Thesis, Department of Graduate Studies (Chemistry), Carleton University, Ottawa, ON. (supervised by R. Klassen).

Stanley, N. (2005) Effect of Various Biogeochemical Processes on Mercury Methylation in Cu-Zn and Au Mine Tailings. M.Sc. thesis, University of Ottawa, Ottawa, ON, 158 p.

**2004**

Mosher, A.L. (2004) Environmental Impacts of Historical Mine Tailings Disposal at Cochrane Hill Gold District, Nova Scotia. B.Sc. Honours thesis, Dalhousie University, Halifax, NS, 60 p. (+ 4 app.).

***Reports***

**2005**

Corriveau, M.C., Jamieson, H.E., Parsons, M.B., and Campbell, J.L. (2005) Characterization of metal(loid)s in mineral dusts from gold mine tailings. GAC-MAC-CSPG-CSSS Joint Meeting, Halifax, Nova Scotia, Abstracts Volume 30, p. 36.

Garrett, R.G. (2005) Natural distribution and abundance of elements. Chapter 2 of *The Essentials of Medical Geology* (Ed. in Chief O. Selinus). Elsevier Academic Press, Amsterdam, the Netherlands, pp. 17-41.

Garrett, R.G., Drew, L.J. and Sutphin, D.M. (2005) Estimating soil geochemistry from stream sediment geochemistry. *In*: Proceedings of IAMG 2005, GIS and Spatial Analysis. Qiuming Cheng and G. Bonham-Carter (eds) Toronto, Ontario, August 21-24, 2005, vol. 1, pp. 452-457.

Parsons, M.B., Smith, P.K., Goodwin, T.A., Hall, G.E.M, and Percival, J.B. (2005) Arsenic and mercury contamination from historical gold mine tailings in Nova Scotia. *In:* Mining Matters for Nova Scotia 2005, NS Dept. of Natural Resources, Report ME 2005-2, (ed.) D.R. MacDonald, p. 19 (abstract).

Winch, S., Fortin, D., Lean, D.R.S., Praharaj, T., and Parsons, M.B. (2005) Controls on MeHg in tailings from Nova Scotia Au mines and Timmins, Ontario base-metal mines. Program and Abstracts of the Joint International Symposia for Subsurface Microbiology (ISSM 2005) and Environmental Biogeochemistry (ISEB XVII), p. 65.

**2004**

Goodwin, T.A., Smith, P.K., and Parsons, M.B. (2004) Multi-element distribution in humus, soil, till, rock and tailings associated with historic gold districts of the Meguma Terrane, Nova Scotia, Canada. *In:* Mineral Resources Branch, Report of Activities 2003; Nova Scotia Department of Natural Resources, Report 2004-1, pp. 7–14.

**2003**

Parsons, M.B., Smith, P.K., Goodwin, T.A., Hall, G.E.M, Sangster, A.L., and Percival, J.B. (2003) Distribution and speciation of elements associated with historical mine tailings at selected lode gold deposits of the Meguma Terrane, southern Nova Scotia. *In:* Mining Matters for Nova Scotia 2003, NS Dept. of Natural Resources, Report ME 2003-2, (ed.) D.R. MacDonald, p. 11 (abstract).

***Conferences***

**2006**

Garrett, R.G., Chorlton, L.B., Friske, P.W.B., Rencz, A.N. and Klassen, R.A. (2006) The use of the next geological Map of Canada for the National Geochemical Reconnaissance Program and the National Atlas of Canada, GAC/MAC Joint Annual Meeting, 2006. Special Session 10: The Next Geology Map of Canada, Montreal (abstract).

**2005**

Corriveau, M.C., Jamieson, H.E., Parsons, M.B., and Campbell, J.L. (2005) Potentially hazardous mineral dusts from abandoned gold mine tailings. Gananoque Environmental Science and Engineering Student Conference, Gananoque, ON, February 5, 2005.

Daniels, C.M., Parsons, M.B., Jamieson, H.E., Hall, G.E.M. and Vaive, J.E. (2005) Arsenic in gold mine tailings and co-existing porewaters in freshwater and marine settings. Gananoque Environmental Science and Engineering Student Conference, Gananoque, ON, February 5, 2005.

Garrett, R.G., Friske, P.W.B., McNeil, R.J., Day, S.J. and McCurdy, M.J. (2005) Regional geochemical maps for risk assessors. *In*: 8th International Conference on the Biogeochemistry of Trace Elements, Adelaide, Australia, April 3-7, 2005, Book of Abstracts, pp. 412-413.

Smith, P.K., Parsons, M.B., and Goodwin, T.K. (2005) Geology and Environmental Geochemistry of Lode Gold Deposits in Nova Scotia. Guidebook for Field Trip FT-B5, Joint Annual Meeting of the Geological Association of Canada and the Mineralogical Association of Canada, 105 p.

Klassen, R. and Garrett, R. (2005) Geochemical modeling of soil parent material mineralogy. Soils, Sediments, and Water. Soil Geochemical Background on a Continental Scale, Amherst, MA, p. 176. (abstract and oral presentation).

**2004**

Jamieson, H.E., Walker, S.R., Andrade, C.F., Parsons, M.B., and Lanzirotti, A. (2004) Using synchrotron-based microanalysis to predict environmental risk associated with mine waste. 87th Canadian Chemistry Conference and Exhibition, London, ON

Mosher, A.L., Parsons, M.B., and Zentilli, M. (2004) Geochemistry and mineralogy of tailings at the Cochrane Hill Gold District, Nova Scotia. *In:* Proceedings of the Annual General Meeting of the Atlantic Geoscience Society, Moncton, NB, *Atlantic Geology* 40 (1): 151.

Parsons, M.B., Smith, P.K., Goodwin, T.A., Hall, G.E.M, Sangster, A.L., and Percival, J.B. (2004) Distribution, cycling, and fate of mercury and associated elements at historical lode gold mines in Nova Scotia Canada. *RMZ – Materials and the Geoenvironment* 51 (1): 185–189 (extended abstract for a presentation at the 7th International Conference on Mercury as a Global Pollutant, Ljubljana, Slovenia, June 27-July 2, 2004).

Stanley, N. and Fortin, D. (2004) Effect of Various Biogeochemical Factors on Hg Methylation in Sulfidic Mine Tailings. *RMZ – Materials and the Geoenvironment* 51 (1): 267–271 (extended abstract for a presentation at the 7th International Conference on Mercury as a Global Pollutant, Ljubljana, Slovenia, June 27-July 2, 2004).

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**2005**

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**2005**

Parsons, M.B. and Percival, J.B. (eds.) (2005) Mercury: Sources, Measurements, Cycles, and Effects. Mineralogical Association of Canada Short Course volume no. 34, 320 p.

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***Open File***

**2006**

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Day, S.J.A., Lariviere, J.M., Friske, P.W.B., Gochnauer, K.M., MacFarlane, K.E., McCurdy, M.W., and McNeil, R.J. (2005) National Geochemical Reconnaissance (NGR): Regional stream sediment and water geochemical data, Macmillan Pass - Sekwi Mountain, Northwest Territories. Geological Survey of Canada, Open File 4949.

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Bonham-Carter, G.F. and Garrett, R.G. (2004) Establishing natural background in geochemical surveys. Report submitted to Environment Canada (soon to be released a GSC Open File), 42 p.

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Spirito, W.A., Rencz, A.N., Kettles, I.M., Adcock, S.W., Stacey, A.P. (2004) Compilation of soil and till geochemical metadata for Canada. Geological Survey of Canada, Open File 4703 (will be superceded by OF 5085 "Compilation of Soil and Till Geochemical Metadata for Canada").

***Website***

**2003**

Klassen, R. (2003) Geochemical Modeling. Contribution to the ESS Metals in the Environment (MITE) Program Website. http://gsc.nrcan.gc.ca/geochem/model/index_e.php

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**2005**

Reimann, C., Filsmozer, P. and Garrett, R.G. (2005) Background and threshold: critical comparison of methods of determination. *Science of the Total Environment*, 346 (1/3): 1-16.

Reimann, C. and Garrett, R.G. (2005) Geochemical background - Concept and reality. *Science of the Total Environment*, 350 (1/3): 12-27.

**2004**

Grosz, A.E., Grossman, J.N., Garrett, R.G., Friske, P., Smith, D.B., Darnley, A.G. and Vowinkel, E. (2004) A preliminary geochemical map for arsenic in surficial materials in Canada and the United States. *Applied Geochemistry*, 19(2): 257-260.

**2003**

Richardson, G.M., Mitchell, I.A., Mah-Paulson, M., Hackbarth, T. and Garrett, R.G. (2003) Natural emissions of mercury to the atmosphere in Canada. *Environmental Reviews* 11(1): 17-36.

# Appendix 1B: Requests for ESS Background Geochemistry Data (compiled by R.G. Garrett)

| Requestee | Organization | Location | Date | Media | Elements | Notes |
|---|---|---|---|---|---|---|
| Guy, Martha | National Water Resources Inst., EC | Burlington, ONT | Nov 03 | Soils | P, Na, K, Al, Fe & Mn | Support for Athabasca River basin, Alberta, agricultural nutrient study |
| Ralston, Nick | Energy & Environmental Res. Centre | Grand Forks, ND | Dec 03 | Soils | Se | Prairie soils |
| Schierow, Linda | Library of Congress | Washington, DC | Feb 04 | General | Hg | Natural sources of Hg to the environment |
| Smart, Meg | Vet. Sci., Univ. of Saskatchewan | Saskatoon, SAS | Feb 04 | Soils | Al | To support her work as an expert witness, re Penner, ALT. Supplied copy of report written to support PSL-2 Risk Assessment in 1998 |
| Schuehammer, Tony | Canadian Wildlife Service, EC | Hull, PQ | Jun 04 | Till | Hg | To provide information on geogenic sources for a study of Hg in loons in eastern Ontario |
| David, Jacinthe | HC, Contaminated Sites Program | Toronto, ONT (?) | Nov 04 | Soils | Zn | Request to support human health soil quality guidelines (Mark Richardson project @ HC) |
| Moore, Christine | Cantox Environmental Inc. | Halifax, NS | Dec 04 | Soils | | Request re Avalon Peninsula, Argentia clean-up. No GSC data, pointed her to NFLD provincial agencies |
| Code, Sylvie | HC, Contaminated Sites Program | Ottawa, ONT | Jan 05 | Soils | Cu & Se | Request to support human health soil quality guidelines (Mark Richardson project @ HC) |
| Dodge, Jeff | HC, Contaminated Sites Program | Ottawa, ONT | Jan 05 | Soils | Cd | Request to support human health soil quality guidelines (Mark Richardson project @ HC) |
| Grenier, Mike | Canadian Wheat Board | Winnipeg, MAN | Feb 05 | Soils | As, Cd, Cr, Cu, Hg & Pb | To support wheat export program re quality of Sakatchewan soils |
| Dowbenk, Ray | Agrium | Calgary, ALT | Feb 05 | Soils | As, Cd, Cr, Cu, Hg & Pb | Supplied copy of material sent to Mike Grenier, CWB |
| Bruulsema, Tom | Potash & Phosphate Inst. of Canada | Guelph, ONT | Mar 05 | Soils | As, Cd, Cr, Cu, Hg & Pb | Supplied copy of material sent to Mike Grenier, CWB |
| Alexander, Paul | HC, Contaminated Sites Program | Toronto, ONT (?) | Mar 05 | Soils | Sb | Request to support human health soil quality guidelines (Mark Richardson project @ HC) |
| Goldacker, Suzanne | Cantox Environmental Inc. | Toronto, ONT | Mar 05 | Soils & Lake Seds | As, Co, Cu, Ni, Pb & Se | Ontario data only. To support Sudbury Area Risk Assessment |
| Amid, Amir | Concordia Univeristy, Civil Eng. | Montreal, PQ | Mar 05 | Soils | | Request for soil data for Montreal via Mike Parsons. Could not assist, provided pointers to Will Hendershot and Sebastien Sauve |
| Goulet, Richard | EC, Existing Substances Branch | Hull, PQ | Apr 05 | General | | Supplied commentary on regional geochemical backgrounds and the metalloregion concept |
| Dwyer, Bob | International Copper Association | New York, NY | Apr 05 | Soils & Stream Waters | | Reviewed confidential report to European Metals Industry by IC Group (JAP et al.) on FOREGS data and related bioavailability issues |
| Mroz, Rita | EC, EPB, Waste Management & Remediation | Dartmouth, NS | Apr 05 | Soils | | Request to review JWEL report on and proposal for a spatial framework for soil ecotox studies. Report supplied and completed in |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | | | | May |
| Thorleifsson, Harvey | Minnesota Geological Survey | St. Paul, MN | May 05 | Soils & Tills | Se & Te | Request for information on background levels and possible sources of high Se & Te Tills in up-ice Manitoba |
| Grenier, Mike | Canadian Wheat Board | Winnipeg, MAN | Jun 05 | Soils | Hg, Cd, Pb, As, Cr & Cu | Follow on to February request, preparation of a report to support the CWB's application for Green Food certification with China |
| Brown, David | Private Citizen | St. Lazarre, PQ | Jun 05 | Soils | Mn | Same Mn in soils issue re school site at Pierrefonds, April-May, 2001 (see lzh file in E_MITE) |
| Macfarlane, Ronald | City of Toronto, Public Health | Toronto, ONT | Jul 05 | Not specified | | How to estimate background, supplied copy of STE_346(1-3)1-16.pdf |
| Miller, Corey | MacDonald Env. Sci. Ltd. (MESL) | Nanaimo, BC | Jul 05 | Natural Waters | As, Cd, Co, Cu, Pb, Hg .. | Extensive list of 19 elements (some listed). Supplied information on ESS data sources and current NGR/National Atlas compilation |
| Kettles, Ines | Stephen MacDonald & Associates | Almonte, ONT | Aug 05 | Soils | Ba | Background levels in the Almonte area, supplied summarty stats and graphics on the basis of the Sharpe data |
| Goulet, Richard | EC, Existing Substances Branch | Hull, PQ | Aug 05 | General | | Review ESB Guidance Document #4, Geochemical background and naturally occurring substances, for Sept 14th EC-GSC meeting |
| Grenier, Mike | Canadian Wheat Board | Winnipeg, MAN | Sep 05 | Soils & Grains | Cd | Provide information to support Canada-Japan grain sales negotiations |
| Jardine, Bryce | DINA, Environmental Protectiont | Regina, SAS | Oct 05 | Soils | As | Information on natural background levels of As in Saskatchewan soils to support a site specific RA on an Indian reservation |
| Hopkins, Debra | Golder Associates, Ltd. | Calgary, ALT | Nov 05 | Soils | Al, Mn, Co, Mo & B | Natural background levels in Alberta soils. Prepared a min1-report. No B data, and only C-horizon Al data |
| Kapaj, Simon | Univeristy of Saskatchewan | Saskatoon, SAS | Feb 06 | Soils & Tills | As | Natural background levels in Saskatchewan for a groundwater project. Provided background information, already had maps |
| Salminen, Reijo | Geological Survey of Finland | Espoo, Finland | Feb 06 | Stream sediments | Wide range | Summary stats for NGR SS data for a table of international background levels in the FOREGS survey data interpretation volume |
| Hsia, Sophie | Blake, Cassels & Graydon LLP | Calgary, AB | Feb 06 | Soils | Cr | Range of background levels for Cr in Alberta to support land sale near Fort Saskatchewan |

## Project 2: Source Apportionment and Natural Archives of Metals in Northern Canada - P.M. Outridge, Project Leader

### Introduction

The objectives of this multi-disciplinary project were to:

1. Evaluate the validity of the protocols and natural archives (lake sediments, peat bogs, trees, glacial snow and ice) that environmental scientists use for source apportionment studies of metals in atmospheric deposition in remote regions;
2. Investigate the archives' chemical and physical characteristics that influence archive reliability;
3. Conduct apportionment calculations of priority metals (Hg, Cd, Pb) in deposition and traditional country foods in the Arctic to aid clients' on-going science assessments; and
4. Develop better conceptual understanding and analytical procedures that will improve the accuracy and reliability of source apportionment of metals.

The project outputs are aimed to influence: the national and international organizations conducting environmental science assessments in the Arctic (Northern Contaminants Program (DIAND), and the Arctic Monitoring and Assessment Programme), which rely extensively on these natural archives; northern communities and NGOs which have expressed concern about long-range metal pollution in their environment and traditional foods; and the awareness of the public and policy-makers about the sources of environmental metals (natural vs. anthropogenic; local vs. distant).

### Summary of Outputs

In the past 3 years, supported by project funding, ESS and partner scientists authored or co-authored 10 peer-reviewed journal papers, 8 conference presentations and 1 scientific assessment report .At least 8 more papers are planned or in preparation. In addition, the Devon Island ice core research of Zheng, Shotyk, Fisher and Zdanowicz attracted considerable media attention in Canada and Europe, resulting in (among other coverage) a half-page article in the *Ottawa Citizen*, and in *The Regina Leader-Post*, Feb. 6 2006, which mentioned the GSC several times, an CBC North interview with James Zheng, and a four-page article in a German universities science magazine

## Summary of Findings

## Activity 1: Archive validation

**(summarized by C. Zdanowicz)**

While reanalysis of some parameters from the peat core component is still awaited, the overall conclusion is that ice cores, tree rings and peat appear to accurately reflect atmospheric deposition histories of priority metals (Hg, Pb and Cd). Lake sediments suffer from having a relatively high natural metal background (compared to ice and peat), and from biological turnover of upper sediment layers (in the sub-Arctic and boreal lakes studied). Diagenetic movement of Hg is also possibly a problem in some lakes. These processes act to mask or smear any anthropogenic input histories in sediments. The Hg profile in our High Arctic lake (Amituk Lake) was significantly associated with greatly increased phytoplankton productivity (seen in sediment diatom abundances) in the latter half of the 20$^{th}$ century. This association suggest that Hg profiles in some Arctic sediments may be influenced by climate warming, through greater biological scavenging of Hg from the water column.

**High Arctic region (Cornwallis and Devon Islands) –** J. Zheng, C. Zdanowicz, D. Fisher, J. Percival, P. Outridge (GSC), G. Stern and P. Wilkinson (DFO).

***Glacial ice:*** The reconstructed Pb and Cd deposition histories from Devon ice cap show large increases in atmospheric metal pollution starting in the late 19th century, with maximum levels in the latter half of the 20th century, and a return towards pre-industrial levels in the early 2000s. However, the most recent Pb-isotope data (2004) show that human-derived Pb still accounts for over 95% of total Pb in the Devon ice cap glacier. The Pb history agrees well with ice cores from central Greenland but also shows noticeable differences, suggesting the influence of different atmospheric Pb contamination source(s) on Devon than on Greenland. Devon Island seems to receive more wintertime airborne transport from Eurasia.

***Lake sediments:*** In contrast to the Devon Island ice core, profiles of [Pb] and [Cd] in Amituk Lake sediment cores show no evidence of major anthropogenic inputs. The profiles show wide concentration variations associated with variable sedimentation rates. Lead isotope ratios measured in a previous (1989) core were remarkably uniform throughout the record, and essentially identical to the pre-anthropogenic period. The Hg profile displays a large increase after the 1960s peaking in the early 1980s, which is highly correlated with sediment diatom abundance increases over the same period.

***Comparison with historical or instrumental records:*** The 1989 Hg and Pb profiles for Amituk Lake compare well with the 2003 cores taken from this lake, suggesting that there has been little diagenetic movement of these sedimentary metals over that 15 year interval. Airborne aerosol data from the Environment Canada station near sea-level at Alert (Ellesmere Island) for 1980-1995 show that atmospheric [Pb] declined by a factor of ~3-4 during this period, which compares reasonably well with the [Pb] record in the high-altitude Devon Island ice core. Airborne [Cd] measured in Resolute and Coral Harbour over the period 1973-2000 also declined similarly to the ice core. The

atmospheric [Cd] record, however, is too noisy and coarsely resolved to be compared with the ice core and lake records.

**Subarctic region (Belcher Islands and SE Hudson Bay) –** M. Hermanson (U. of Pennslyvania), J. Percival, P. Outridge (GSC), N. Givelet and W. Shotyk (U. of Heildelberg)

***Lake sediments:*** Results from Imitavik Lake (Belcher Islands) cores show that fluxes of Pb and Hg in the lake sediments were relatively constant prior to 1800, and began to increase markedly after ~1850 (for Hg) to 1900 (for Pb), with the steepest increases occurring after ~1940. Results for Cd, albeit "noisier", show a trend comparable to that of Pb in the post-1900 period, but Cd data are lacking prior to this date. In general, the observed trends are consistent with those found in cores extracted from Imitavik Lake in 1983, 1990 and 1993. However the metal fluxes calculated from the 2003 cores were lower than for older cores, owing to a greater 210Pb burden in the sediment.

***Peat:*** *A comparison is unavailable at the time of writing owing to a need to reanalyse the* $^{210}$Pb *profiles in the cores.*

***Comparison with historical or instrumental records***: The 2003 sediment Hg profile from Imitavik Lake did not resemble the 1993 cores taken from this lake, although the Pb profiles in 1983, 1993 and 2003 were all similar. This suggests significant diagenetic movement of dissolved Hg over time. Atmospheric Hg data are available from the air monitoring station in Kuujuarapik, Québec, but the period of record, which began in 1999, is too short for significant trends to be identified, let alone compared with the much longer record developed from peat and lake sediments.

**Boreal region (Flin Flon, Manitoba) –** C. Begin, P. Outridge, J. Percival, R. McNeely (GSC), J. Frank, N. Givelet and W. Shotyk (U. of Heidelberg)

***Lake sediments:*** In cores from Kotyk Lake and Sask Lake 4, [Pb], [Cd], [Cu], [Zn] and [Cd] begin to rise in the late 1890s to early 1900s, >30 years before the Flin Flon smelter opened (1931). This may indicate that lakes in the area were already receiving atmospheric metal inputs from distant anthropogenic sources, or that post-depositional diffusion or mixing processes "smoothed" the metal profiles in the sediments. This latter explanation is supported by $^{210}$Pb and $^{137}$Cs evidence of mixing in the upper layers of sediments in both study lakes. Most metal profiles also show decreasing levels after the mid-1980s, presumably due to implementation of emission control measures at the Flin Flon smelter at that time.

***Peat:*** At the time of writing, $^{14}$C and $^{210}$Pb dating of the peat cores is still underway. Interpretation of the deposition histories for Pb, Cd and Hg are therefore preliminary.

The rise in [Pb], [Cu] and [Zn] in peat cores from "background" levels is sharp and presumably corresponds with the start of smelter activity in Flin Flon. Metal concentrations in peat are generally higher near Kotyk Lake, 30 km from the smelter, than near Sask Lake 4, ~55 km further away. Profiles of [Pb], [Cu] and [Zn] show several maxima at different depths and vary from site to site. It is unclear if these differences are related to changes in the nature of smelter emissions over time, as there is no correspondence with the smelter metal emission profiles. Compared with these other metals, the [Hg] profile in the Kotyk Lake peat bog shows a smoother, more gradual upward trend with a broad maximum between 15-25 cm depth, and a decreasing trend above. This suggests either that smelter-emitted Hg is being remobilized at depth in the

peat profile (relative to other metals), or that part of the Hg increase is related to other, distant sources, natural or anthropogenic.

***Tree-rings:*** Tree-ring dendrochemistry from the catchments of Meridian and Kotyk Lakes indicate that contamination from the Flin Flon smelter began to impact forest stands immediately after its startup in 1931, but this impact became most pronounced after the early-1940s. At that time, the rate of increase for [Pb], [Cd] and [Zn] in tree-rings rose steeply, while tree growth curves declined sharply from those of normal, healthy trees. An abrupt change in the $^{206}Pb/^{207}Pb$ ratios in tree-rings at Kotyk Lake ca. 1930 shows that smelter-emitted Pb deposited in forest soils was almost immediately assimilated by the trees. As seen in the lake sediments, [Pb] and [Cd] in tree rings began to decline after the mid-1980s and , $^{206}Pb/^{207}Pb$ ratios began to shift back towards pre-smelter values, presumably due to emission control measures at the smelter.

***Comparison with historical or instrumental records:*** Data from a 1985 sampling of Kotyk Lake was similar in Hg content and profile to the 2004 sampling, suggesting little movement of Hg up core. However, reanalysis of remaining 1985 sediments in 2004 showed that Hg contamination during storage was a significant problem. The official metal emission data for Flin Flon smelter, provided by Hudson Bay Mining and Smelting (HBM&S), suffers from discrepancies which make its reliability questionable. The Hg emission data, in particular, are unreliable prior to 1976. This makes any comparison with reconstructed deposition histories from natural archives difficult. For example, maximum metal [Pb] and [Cd] in tree-rings occur between the late 1950s and the mid-1970s, a period for which the HBM&S record actually shows unusually low particulate emissions for all metals. In general, there is better agreement between the various proxy time series of metal accumulation and the cumulative emission data, rather than with the annual emission data.

## Activity 2: Hg and Cd source apportionment in traditional northern foods

**Long-term changes of Hg in Western Arctic ringed seals** – P. Outridge

Archeological field work, supported by the project, near Holman, N.W.T. in 2003 returned several dozen samples of ringed seal jaws with teeth from the 14th century, and 6 from the late 19$^{th}$ Century. To these were added several dozen Holman seals (2001-03) supplied by DFO. Mercury concentrations in seal canine teeth in recent years were at least 7 times higher, on average, than historical and pre-industrial samples, which exhibited consistently low values - below detection in most cases. Stable C and N isotope ratios, which can be interpreted as markers of feeding behaviour, did not change during this time; thus, the Hg increase was not due to altered feeding patterns of the seals. The results suggest that human-derived Hg constituted at least 85% of total Hg on average in modern seals. These results support earlier published work on an adjacent population of Beaufort Sea beluga, which displayed an average 10-fold Hg increase in teeth over the last 500 years. The results have been reported to the Fisheries Joint Management Committee (N.W.T.), which financially supported this work.

Cadmium in caribou meat is a public concern in the Yukon. Holocene caribou teeth, retrieved from receding glaciers in theYukon, and modern caribou teeth from the same area, were analysed for Cd, Pb, Pb-isotopes and other elements. This work showed that

current Cd levels are no higher than they have been during the Holocene, and are in fact lower than a maximum of 3,000 years ago; thus, modern Cd is likely entirely natural in origin. Normalizing Cd against geogenic elements (Al, La) lead to the same conclusion. Anthropogenic Pb is present is modern teeth, according to isotopic analyses, but Pb concentrations in meat are extremely low, and thus are not a human health concern.

**Micro-analysis of teeth for stable carbon and oxygen isotopes** – B. Taylor and H. Mirnejad

Source apportionment of Hg in animals, using their teeth as proxy archives of body burden, could be severely compromised if diets or feeding location change over time and cause Hg intake to change, and this change is not recognized. For example, increases in tooth Hg due to dietary change could be mistaken for anthropogenic pollution if trends in stable carbon and nitrogen isotope ratios were not concurrently measured. Oxygen isotope records from teeth could provide a temporal record of temperature change. This research aims to develop the capacity for laser-based, *in situ* fine-scale (high spatial resolution) isotopic analysis of animal teeth, to aid the reconstruction of animal feeding and of possible climate proxy records.

Preliminary results show that consistent C and O isotope values can be retrieved from within annual growth layers of a test tooth of a beluga, using laser sampling at 100 μm spot sizes. In situ isotopic variability needs to be further investigated, as does inter-calibration between powdered and laser-assisted samples. Future work will focus on developing a continuous-flow sample introduction system.

## Activity 3: Improving analytical methodologies and process understanding

**Metal transport experiments in lake sediments** – S. Alpay

The objective of this work was to examine the role of microbial activity on the distribution of metals in simulated lake sediments through column experiments. The experiments test the hypothesis that bacterially mediated redox reactions redistribute metals within the sediment column under natural conditions. Metal redistribution could seriously compromise deposition histories in sediment archives.

Isotopically labeled ($^{57}$Fe isotope) experiments verify that the migration of Fe in sediment columns is due to mobilization and redeposition. Further evidence of Fe mobility is the elevated concentrations of $^{57}$Fe in the pore water fraction and in the overlying water of the columns. However, Fe mobility is not apparent in the abiotic control experiments, which confirms that the reactions controlling its transport are, indeed, microbially mediated within the time frame of the experiments.

**Multicollector ICP-MS Methods for metal isotope determination** – C. Gregoire / W. Doherty

Isotope ratios offer a potentially powerful source apportionment and tracer technique, however, with the exception of Pb, none of the isotope systematics have been developed for trace metals of environmental significance. The first step in this field is analytical method development.

Although there are over a hundred MC-ICP-MSs in service around the world, little systematic research has been completed on the sources and control of mass discrimination and isotope ratio imprecision arising from sample introduction, the plasma, interface and extraction and focusing lenses. Part of the program for integrating the MC facility into the laboratory system at the GSC is developing generalized rapid procedures for the preparation of samples and the measurement of isotope ratios of many elements. This R&D is divided into three phases: 1) hardware; 2) instrument calibration; 3) analyte separation.

***Hardware:*** Modifications to the MC-ICP-MS sample introduction system resulted in much improved short term precision (expressed as %RSD) of an isotope ratio measurement, of between 0.0005% and 0.0008%, independent of the analyte of interest. The short term stability (expressed as %RSD) ranged from 0.05% to 0.3%.

***Instrument Calibration:*** Failure to account for all potentially major measurement errors will result in methods which are unreliable. A unique internal standardization technique has been developed for the following standardization schemes: 1) Self internal (SI) standardization; 2) the analyte and internal standard (IS) are different elements but the required signals can be measured simultaneously (e.g. Pb-Tl); 3) the analyte and IS are different elements but their signals cannot be measured simultaneously.

Using our new calibration approaches, for analytes where the mass separation is 1 amu (for mass ranges from ca. Ba to U), the following long term reproducibilites can be expected: SI: 3-6 ppm; simultaneous analyte-IS pairs: 5 to 8 ppm; non-simultaneous analyte-IS pairs: 6 to 11 ppm. These errors are superior to those reported in the literature for other MC-ICPMS instruments. Using NBS 982 Pb Isotopic Standard as an "unknown sample", the MC-ICP-MS was accurate to within 0.007% to 0.02% of certified values, and well within the reference error statistics. There was a 0% rejection rate on over 300 determinations and no results which were 'outliers'.

***Analyte Separation:*** The goal of this phase is to select and develop a simultaneous analyte separation scheme that is fast, reliable, and applicable to a generalized sample dissolution procedure, and which produces matrix-free solutions containing Pb, Hg, Ni, Co, Pt, Cd and Zn, as well other transition metals. Multi-collector ICP mass spectrometers work best if solutions to be analyzed are virtually free of matrix components.

Long-established solvent extraction techniques using diphenylthiocarbazone provide a fast and effective means of separating analyte metals from matrix components. Extractions are completed in less than a minute. This is many times faster than current column separation methods. To date, experiments have demonstrated that the approach works well, albeit some further work is required to optimize separation and recoveries. ICP-OES is being used to evaluate the quality of separated solutions prior to their measurement on the multi collector ICP-MS.

## Appendix: Contributions to Outcomes

## Appendix 1A: Peer-reviewed journal articles, conferences, scientific assessment and reports

***Peer-reviewed journal articles***

**2006**

Zheng, J., Fisher, D., Blake, E., Hall, G., Vaive, J., Krachler, M., Zdanowicz, C., Lam, J., Lawson, G. and Shotyk, W. An ultra-clean firn core from Devon Ice Cap, Nunavut, Canada, retrieved using a specially-designed titanium drill for trace element studies. *Journal of Environmental Monitoring.* (in press)

**2005**

Krachler, M., Zheng, J., Koerner, R., Zdanowicz, C., Fisher, D. and Shotyk, W. Increasing atmospheric antimony contamination in the northern hemisphere: snow and ice evidence from Devon Island, Arctic Canada. *Journal of Environmental Monitoring* 7: 1169-1176 (2005).

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Outridge, P.M., Hobson, K.A. and Savelle, J.M. 2005. Changes in the mercury and cadmium concentrations and feeding behaviour of beluga (*Delphinapterus leucas*) near Somerset Island, Canada, during the 20$^{th}$ Century. *Science of the Total Environment* 350: 106-118 (2005).

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***Scientific Assessment and Reports***

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## Project 3: Emission and Deposition of Elements and Particles as Related to Geogenic and Anthropogenic Sources - F. Goodarzi, Project Leader

### Introduction

The objectives of this multi-disciplinary project were to:

1. Provide Canada with essential data concerning the emission and deposition of elements in the vicinity of large stationary sources to provide decision makers (Environment Canada and Health Canada) with knowledge essential for setting guidelines for the health of Canadians (i.e. Canada-wide Standard for Mercury), to inform NRCan senior managers (ESS; ADMs; DM), to identify possible remediation practices for reduction of elements (such as Hg), and provide information on toxicity of As, Cr, Hg and Ni emissions associated with coal-fired power plants;
2. Delineate the environment health risk where health risk may occur in the vicinity of large stationary sources;
3. Combine inter-disciplinary techniques to identify the processes that distribute or redistribute metals in lake sediments in order to characterize the pre-industrial lake sediment record as well as lake response to mining and smelting operations; and
4. Evaluate these effects in two lakes with different geochemical settings, but similar distances and prevailing wind directions from a major anthropogenic point source of metals (the Horne smelter in Abitibi-Timiskaming, Quebec).

The project outputs were aimed to: influence national and international organizations conducting environmental science assessments and the setting of guidelines, particularly Environment Canada; and, to increase the awareness of the public and policy-makers about the nature and toxicity of emitted elements (As, Cr, Hg and Ni) from stationary sources and possible remediation strategies for their reduction.

### Summary of Outputs

In the past 3 years, supported by project, OGD and Industrial funding, ESS and partner scientists authored or co-authored 23 peer-reviewed journal papers and 8 conference proceeding papers, 18 conference presentations and 6 scientific assessment reports. At least 10 more papers are planned or in preparation. Also, four PhD and one MSc studies are/were being conducted in the Universities of British Columbia, Guelph, Victoria and Royal Road College that are/were supervised and supported by this project. Two PhDs are finished.

## Summary of Findings

# Activity 1: Canada Wide Standard of Mercury emissions from coal-fired utilities, speciation of As, Cr and Ni and characterization of particles emitted from coal-fired power plants

**(summarized by F.Goodarzi).**

### Sub-Activity 1. Speciation and mass-balance of mercury from pulverized coal-fired power plants burning western Canadian subbituminous coals; Canada-wide Standard for Mercury Emission

In this activity, the speciation and mass-balance of mercury emitted from coal fired power plants, was examined. This activity was interdisciplinary and involved Environment Canada (AAP Directorate), Canadian coal-fired power plants (Alberta, Saskatchewan, Manitoba, Ontario and Nova Scotia) and CANMET. The data were supplied to Environment Canada by power plants and the Electrical Association of Canada and were also included in the "*Agreement respecting the Canada–wide Standard for Mercury Emissions from Coal-fired Electric Power generation Plants*" (Dion, 2005)

The data indicate that the variation in mass balance of mercury for the six power plants studied is mostly related to the variability of the coal feed rate and is within the acceptable error range. Most of the mercury emitted is in the form of gaseous elemental mercury (GEM, $Hg^0$) and emitted at a rate of 6.6 to 12.6 g/h. The reactive gaseous mercury form (RGM, $Hg^{2+}$) is emitted at a rate of 0.34 to 3.68 g/h. There is very little RGM emitted from power plants equipped with hot side ESP. The rate of emission of particulate mercury ($Hg^p$) is low, with the range of 0.005 to 0.076 g/h, indicating that ESP's capture most of the particulate mercury (Goodarzi, 2004, 2005a). The variability in the rate of capturing mercury is due to petrological differences between coals (Goodarzi and Rose, 2003, Goodarzi and Goodarzi, 2004, Goodarzi and Sanei, 2003).

The data are a further indication of how difficult it is to develop a baseline for the reduction of mercury even if the feed coal is of the same rank (subbituminous). It is shown that even within the same coal rank and within a narrow range of mercury content in feed coals (0.051-0.075 mg/kg) there are parameters that may influence the rate of emission of mercury. The most important finding of this study is that mercury, like any other element, can be captured by particulate control equipment. Furthermore, depending on the configuration of the particulate control and the nature of the feed coal, up to 57.6% of the mercury may be retained (Goodarzi, 2004, 2005a, 2006).

The abundant inertinite (natural char) in feed coal equates to more unburned carbon in ESP fly ash, and to enhanced capture of mercury in cold-side ESP fly ash. This indicates that the inertinite content of a coal seam may be indicative of the percentage of unburned carbon, and the percentage of mercury captured by a cold-side ESP (Goodarzi, 2004, Goodarzi et al., 2005, 2006, Goodarzi et al., 2005b).

### Sub-Activity 2. Speciation of As, Cr and Ni

This activity was carried out jointly with Canadian coal fired power plants and the University of Kentucky (Department of Chemical Engineering). The species of As, Cr and Ni in the feed coals and ash by-products from seven Canadian power plants

(including one with a fluidized-bed combustor) were analyzed. The power plants burned local subbituminous and bituminous coals with sulphur contents ranging from 0.30 to 3.5 wt. % and were examined using XAFS spectroscopy.

***Nickel:*** Nickel present in both subbituminous and bituminous coals is predominantly non-toxic $Ni^{+2}$ in coordination with oxygen in the coals. The presence of metallic nickel ($Ni^0$) in a feed coal is probably due to contamination from stainless steel used for coal preparation and/or transportation equipment (Goodarzi and Huggins, 2003, 2004). The results of these studies were supplied to industry and also Environment Canada for possible use in guidelines.

***Arsenic:*** About 50% of the arsenic in most sub-bituminous feed coals is in the form of $As^{3+}$ and about 50% is in the form of arsenate arsenic (Goodarzi and Huggins, 2003, 2004).

Virtually all (>95 %) of the arsenic in both sub-bituminous and bituminous fly ashes from the ESPs or baghouse and stack fly ash appears to be in the form of the less-toxic arsenate ($As^{5+}$) (Goodarzi and Huggins, 2002, 2005a).

***Chromium:*** The chromium in most Canadian feed coals and bottom ash samples are mostly (>95%), if not entirely, non-toxic $Cr^{3+}$. The fly-ash samples derived from combustion of most subbituminous and bituminous coals contain little or no $Cr^{6+}$ (<5%). Not all of the chromium in the feed coals or ash products is related to minerals in the coal. Convincing evidence for metallic chromium ($Cr^0$) contamination, in the form of stainless steel, was noted for the feed coal at one plant and for the fly ash in a second plant (Goodarzi, 2002,Goodarzi and Huggins, 2003, 2005b).

**Sub-Activity 3. The rates of emissions, morphology and chemistry of fine particles emitted from some Canadian coal-fired power plants.**

The particles emitted from stacks are classified based on their morphologies and chemistries into the following forms: unburnt carbon; feed-coal minerals such as quartz; and by-products of the dissociation, fractionation, and contamination by minerals in coal. (Goodarzi 2005c, 2006a). The rates of emitted particulates from the three power plants are 9.9 to 53.4 $mg/m^3$ (dry), 30 to 90 kg/hr (dry), and 0.039 to 0.118 kg/MWh, respectively. The total emissions of particulates from two power plants are below the Canadian Guideline for emission from a coal-fired power plant (0.095 kg/MWh), while the third power plant is slightly higher than the Guideline (0.118 kg/MWh). The malfunctioning of control technology may result in unrealistic and wide variation in the measured rates of emitted particles (Goodarzi, 2005c, 2006a, b).

The concentrations of elements in coal ashes are related to their volatilization upon combustion. The most refractory elements are concentrated in the combustion ashes as indicated by enrichment indices. Only a small quantity of the hazardous elements present in milled coal was emitted, and that bottom and ESP ashes capture most elements, including some Hg (Goodarzi, 2005, 2006c). The calculated input of elements of environmental concern (As, Cd, Hg, Ni, and Pb) emitted in the air (ng/m3) by the power plant at the zone of maximum impact and at ground level are lower than the Health Guidelines in both Canada and the USA (Goodarzi, 2006c). The concentrations of these elements in air, calculated based on their emissions, are low compared to the ambient concentrations in either rural or urban air (Goodarzi, 2005c, 2006c).

## Activity 2: Delineation of environments that may cause health risk in the vicinity of large stationary sources

**Sub-Activity 1. Moss-monitoring**

The moss-monitoring survey has been a successful research project since the mid 90's. Moss-monitoring is a low cost passive monitoring method to detect the aerial deposition of particulate elements. An extensive study has been carried out at Trail, BC in the area surrounding the Teck-Cominco smelter. The study was extended to up to 30 stations, which were monitored every 3 months. The study continued for 5 years providing long term results on metal deposition to populate a database for this area. The findings on fugitive dust and various hot spots in the region resulted in immediate actions by Teck-Cominco Metals to investigate the issues (Goodarzi etal, 2002a&b, 2003, 2005). *The result of the second phase is still under preparation for release. The results of the moss-monitoring survey in Trailare the key data for ERA around Trail smelter.* Similarly, moss-monitoring studies were carried out in the vicinity four coal-fired power facilities in Alberta: Sheerness (Hanna, Alberta); Battle River (Stettler, Alberta); Wabamun (Stony Plain, Alberta); and Milner (Grand Cache, Alberta). The findings of moss monitoring study around the Wabamun station *were a key document in a EUB hearing for the expansion of TransAlta Keephills power plants.*

**Sub-Activity 2. Variation of metals in stream sediments and peat**

The stream sediments from 12 creeks in vicinity of the Teck-Cominco smelter in Trail, British Columbia were examined. It was found that organic matter in sediments is mostly natural (char from forest fires). There is also anthropogenic organic matter, mostly coke particles associated with small-scale smelters unrelated to the activity of Teck-Cominco (Reyes et al., 2005). In another study, that covered the background site as well as some streams draining in proximity to the Trail smelter, the concentration of heavy metals was determined to delineate the impacted area by the Teck-Cominco smelter, define the geochemical background of metals in the region and the general distribution of metals in the tributary systems in the region (to be used for determining the effects of metals in the sediments on the aquatic organisms, flux of metals to the connected larger water bodies (Columbia river, Lake Roosevelt, etc.) The results of this study have been the *significant base for the Environmental Risk Assessment study of the Trail area for Teck-Cominco. The data collected for stream sediments in Trail area is still one of the main documents in this region*. The results of this study are also used as reference *in the EPA report for Lake Roosevelt, and the Golder Associates Environmental Risk assessment.* A detailed study of peat in the vicinity of Teck-Cominco indicates that peat sampled close to smelters has higher concentrations of Pb and Zn and their concentration remains constant with depth (Hawke, Ph.D. Thesis, 2004)

## Activity 3: Inter-disciplinary techniques to identify the processes that distributes or redistributes metals in lake sediments

The lake sediment study in central Alberta uses geochemical and petrological approaches to reveal more detailed information on the processes involved in the

distribution of trace elements in the sediments of the Wabamun region. A multi-elemental analysis of the recent sediments in conjunction with other inorganic and organic geochemical factors provided valuable information on the sources, quantity, and processes involved in the distribution of trace elements in the study region (Sanei and Goodarzi, 2003, Sanei et al., 2005 a-c). The results of this study provide a new insight into the way that the sediment data can be interpreted. There has been *great interest expressed by the government, local residents, and industry stakeholders (coal-fired power generating companies)* in such studies since they would indicate the possible effects of the industrialization and urbanization in the region.

The achievements of the lake sediment study in Alberta are: (i) determining the age of sediments and sedimentation rate in ten lakes and creating the most comprehensive $^{210}Pb$ flux data base for this study region; (ii) determining the temporal variation and spatial distribution of trace elements in the recent sediments from the wide geographic region in the Wabamun area; (iii) the detail process-oriented studies on mobility of trace elements during the early diagenetic processes and geochemical interactions between sediments and porewater; (iv) studying the affinity of trace elements with organic and inorganic compounds and the geochemical factors influencing metal distribution; (v) characterizing the mineralogy and morphology of sediment particles; and (vi) characterizing the organic compounds in the sediment using organic geochemistry/petrology approaches (Sanei, Ph.D. Thesis, 2005).

## Activity 4: Integration and interpretation of the potential redistribution of metals in lake sediments.

In this activity, interdisciplinary data from diatom studies, solid and aqueous phase geochemistry, isotopic determinations, and bacterial enumerations have been combined to examine the processes that distribute or redistribute metals in lake sediments and characterize the pre-industrial lake sediment record as well as lake response to mining and smelting operations. These effects were evaluated with a focus on two lakes with different geochemical settings, but similar distances and in the prevailing wind directions from the Horne smelter in Abitibi-Timiskaming, Quebec. The Activity is a partnership between CANMET (MMS-NRCan), Environment Canada (NWRI, NGSO), University of Calgary (Geology), Queens University (Biology) and GSC under a research agreement.

Highlights include publication of site selection criteria that were developed for 99 reconnaissance lakes studied by Kliza and Telmer (2001). These were applied to identify two acidic kettle lakes (Alpay et al., 2005) within the zone of influence of the Horne smelter. Alpay et al. (in press) show that the modern spatial distribution of pH in the 99 lakes is affected not only by industrial $SO_2$ emissions, but also by other anthropogenic and natural factors, including buffering capacity from the regionally expansive calcareous glaciolacustrine deposits left by glacial lakes Barlow and Ojibway. Interpreting the modern regional distribution of pH, ranging from 3.7 to 9.3, is comparable to Abitibi-Timiskaming where wind-transported emissions and buffering from calcareous glaciolacustrine deposits can yield similar spatial trends.

At the study site scale, several indicators have recorded the timing of anthropogenic emissions from the Horne smelter. Identification and enumeration of diatoms (single-

celled algae; bio-indicators of pH) from 50 lakes were used as a surface sediment calibration set for northwestern Quebec (Dixit et al., in press). Of the key environmental variables considered, canonical correspondence analysis indicated that diatom species distributions were most strongly correlated to pH. Dixit et al. (in press) developed a weighted averaging calibration model for pH inferences and applied it to $^{210}$Pb-dated sediment cores for a paleolimnological reconstruction of the two study lakes. Although naturally acidic (pH 5.5 in the mid-1800s), the acidification of Lac de la Pépinière has accelerated since 1927, probably as a result of acidic deposition from smelter emissions (pH 4.8 in 1998). Lac Perron has remained acidic through time, but its diatom species have shifted, likely in response to increased metal loading (e.g. Fe, Al) and to a transition from organic to mineral acidity starting in the 1920s as a result of emissions from the Horne smelter. Additionally, increases in Fe, Pb, and In concentrations (emission constituents) and a decrease in the $\delta^{34}$S values of total sulphur in sediment cores from both lakes coincide with the start-up of the smelter in 1927 (Mayer et al., in prep). More active bacterial (dissimilatory) sulphate reduction prevailed in the late 1920s after smelting began and when anthropogenic sulphate loading to the lakes increased; increased bacterial sulphate reduction gave rise to an increase in sulphur isotope fractionation and, hence, more negative $\delta^{34}$S values in the sediments. Although sulphur isotope ratios are useful tracers to record the onset of metal-laden acidic deposition in the two previously sulphate-limited lakes; total sulphur concentrations alone are not. Additional findings show that the nature of pore water chemistry shifts temporally in Lac de la Pépinière, as likely do the mechanisms of aqueous metal transport within the sediment column. Two intended activities within the Activity, combining the lake sediment record with the tree ring record and interpreting pore water dynamics and historical metal loads will be deferred.

## Appendix: Contribution to Outcomes

## Appendix 3A: Publications, Proceeding Conferences, Abstract, Reports and Open Files

The scientists in this project produced two Ph.D. theses, published one GSC Bulletins, 22 papers (published and in review), delivered 28 talk and posters, 11 reports (including those in review), and one open file.

***Ph.D. Thesis***

Hawke, M.I. 2004. Elemental characteristics of organic deposits from an Area surrounding a Lead-Zinc smelter: concentration, distribution, mode of occurrence and mobility.. Department of Earth and Ocean Sciences, University of British Columbia.

Sanei H. 2005: Environmental geochemistry and petrology of the recent sediments from lakes in the vicinity of the coal-fired power plants in central Alberta, Canada, School of Earth and Ocean Sciences, University of Victoria, British Columbia, Canada.

***Bulletin***

Goodarzi F., Sanei H., and Duncan W. F., (2003): Deposition of trace elements in the Trail region, British Columbia; An assessment of the environmental effect of a base metal smelter on land. *Geological Survey of Canada Bulletin # 573*.

***Edited Journal Special Issue:***

Gentzis T. and Sanei H., 2006: New Horizons in Coal Science, Organic Petrology and Geochemistry, *International Journal of Coal Geology*, Volume 65, Issues 1-2, Pages 1-170, Elsevier.

***Papers Published and in Reviews***

**2006**

Goodarzi, F., 2006a. The rates of emissions of fine particles from some Canadian coal fired power plants. Fuel, 85; 425-433.

Goodarzi, F., 2006b. Assessment of elemental content of feed coal, combustion residues and stack emitted materials for a Canadian pulverized coal fired power plant, and their possible environmental effect. International Journal of Coal Geology, 65;17-25.

Goodarzi, F. 2006c. Morphology and chemistry of fine particles emitted from some Canadian coal-fired power plants. Fuel, 85; 273-280.

Goodarzi, F., Reyes, J. Schulz, J. Holman, D. and Rose, D. 2006. Variation in mercury emission over thirty-nine weeks – Parameters influencing the variation. International Journal of Coal Geology, 65; 26-34.

Goodarzi F., Sanei H., Stasiuk L.D., Bagheri-Sadeghi H., and Reyes J., 2006. A preliminary study of mineralogy and geochemistry of four coal samples from northern Iran. International Journal of Coal Geology, 65; 33-50.

Pentari, D., Typou, J., Goodarzi, F. and Foscolos, A.E. 2006: Impact of elements in natural and reclaimed soil from abandoned coalmines on wheat crops, in northern Greece. International Journal of Coal Geology, 65; 51-58.

Reyes J., Goodarzi F., Sanei H., Stasiuk L.D., and Duncan W., (2006): Petrographic and geochemical characteristics of organic matter associated with stream sediments in Trail area British Columbia, Canada, International Journal of Coal Geology, 65; 146-157.

**2005**

Goodarzi, F. 2005, Petrology of Subbituminous feed coal as guide to capture of mercury by ESP-Influence of depositional environment. Inter Journal of Coal Geology, 61;1-12

Goodarzi F. and Huggins F.E. 2005a, Speciation of arsenic in Canadian subbituminous and bituminous feed coals and their ash byproducts. Energy and Fuel, 19; 905-915.

Goodarzi F. and Huggins F.E 2005b. Speciation of chromium in Canadian subbituminous and bituminous feed coals and their ash byproducts. Energy and Fuel, 19; 2500-2508.

Sanei, H., Stasiuk, L.V. and Goodarzi, F. 2005. Petrological changes occurring in organic matter from recent lacustrine sediment during thermal alteration by Rock-Eval pyrolysis. Organic Geochemistry, 36; 1190-1203.

**2004**

Goodarzi, F. and Goodarzi, N.N. 2004, Factor influencing the mercury content of western Canadian subbituminous coal-a weighted average study. International Journal of Coal Geology, 58; 251-259.

Goodarzi F. and Huggins F.E. 2004, Speciation of nickel in Canadian subbituminous and bituminous feed coals and their ash byproducts. Journal of Environmental Monitoring, 6; 787-791.

Papanicolaou, C. Kotis, T., C. Foscolos, A.E. and Goodarzi, F., 2004. Coals of Greece: a review of, uses and future prospectives. International Journal of Coal Geology, v. 58; 147-170.

Goodarzi, F. 2004, Speciation and mass-balance of mercury from coal fired power plants burning western Canadian subbituminous coal, Alberta, Canada. Journal of Environmental Monitoring, 6; 792-798.

***2003***

Goodarzi F., Sanei H., and Duncan W. F., 2003: Deposition of trace elements in the Trail region, British Columbia; An assessment of the environmental effect of a base metal smelter on land. Geological Survey of Canada Bulletin # 573

***Papers in press***

Sanei H., Goodarzi F., and Hilts H., (*submitted*): Assessment of Site-specific background concentrations of elements in soil around a metal smelter in Canada, *Geochemistry: Exploration, Environment, Analysis (GEEA)*.

Goodarzi F., Sanei H., Garrett R. G., Labonté M., and Duncan W. F., (in press): The moss monitoring survey around the Trail smelter, British Columbia-a review. *Geochemistry: Exploration, Environment, Analysis (GEEA).*

Stasiuk, V. Bagheri-Sadeghi, H. and Goodarzi, F. in press. Petrology, rank and liquid petroleum potential of Jurassic coals from the Central Alborz Region, Northern Iran. International Journal of coal Geology.

Alpay, S., J.J. Veillette, F. Rosa and M. Douma. Rationale, research approach, and study sites for investigating vertical metal distributions in lacustrine sediments. *IN:* Geological Survey of Canada Bulletin 584, Metals in the environment around smelters at Rouyn-Noranda, Quebec, and Belledune, New Brunswick: Results and conclusions of the GSC-MITE point sources project, *ED:* G.F. Bonham-Carter, Geological Survey of Canada, Ottawa.

Alpay, S., Veillette, J.J., Dixit, A.S., and Dixit S.S. *in press.* Modern and historical distributions of lake-water pH within a 100-km radius of the Horne smelter in Rouyn-Noranda, Quebec (Canada). Geochemistry: Exploration, Environment, Analysis.

Dixit, A.S., Alpay, S., Dixit, S.S., and Smol, J.P.. Paleolimnological reconstructions of Rouyn-Noranda lakes within the zone of influence of the Horne smelter, Québec (Canada). Journal of Paleolimnology.

**Proceeding of Conferences**

**2005**

Goodarzi, F. 2005a. Mercury emission and passive reduction strategies- A Canadian example. Proceedings of International Conference on Coal Science and Technology. October 9-14, Okinawa, Japan. 3A03, pp.1-13

Goodarzi, F. 2005b. Factor influencing the particulate emission from coal-fired power plants. Canada. International Conference on Coal Science and Technology. October 9-14, Okinawa, Japan. 2P501:1-8.

Goodarzi F., Reyes J., Sanei H., and Huggins, F. 2005. Assessment of elemental contents of the feed coal, combination by-products, and stack emitted materials for a Canadian pulverized coal-fired power plant. Proceeding of the International Conference on Coal Science and Technology (ICCS&T) Okinawa, Japan, October 9-14. 3P503, pp.1-10.

Goodarzi F., Reyes, J., and Rose, D. 2005. Variations of mercury content in feed coal and fly ash from a coal-fired power plant over thirty-eight weeks; Parameters influencing the variation International Conference on Coal Science and Technology (ICCS&T) Okinawa, Japan. October 9-14. 2P107, p.1-12.

Goodarzi, F. and Sanei, H. 2005. Aerial deposition of particle and elements in vicinity of power plants in Alberta, Canada. Proceedings of International Conference on Coal Science and Technology. October 9-14, Okinawa, Japan. 3P504, pp. 1-15.

Sanei, H. and Goodarzi, F. and Telmer, K. 2005. Geochemistry of the recent sediments from lakes in the vicinity of the coal-fired power plants in central Alberta, Canada. Proceedings of International Conference on Coal Science and Technology. October 9-14, Okinawa, Japan. **,** 2A07, pp.1-13.

Sanei, H. and Goodarzi, F and Telmer, K. 2005. Spatial distribution of Hg & other trace elements in the recent lake sediments located in the vicinity of the coal-fired

power plants. Proceedings of International Conference on Coal Science and Technology. October 9-14, Okinawa, Japan.3P509, pp.1-11.

**2004**

Duncan, W.F.A., Mattes, A.G., Gould, W.D. and Goodarzi, F. 2004. Multi-stage biological treatment system for removal of heavy metal contaminants.. *In* Waste Processing and Recycling in Mineral and Metallurgical Industries. Fifth International Symposium. S.R. Rao, F.W. Harrison, J.A. Kozinski, L.M. Amaratunga, T.C. Cheng and G.C. Richards (eds). Hamilton, Canada, Aug. 22-25, 2004. p. 469-483.

**2003**

Sanei, H. and Goodarzi, F. 2003. The influence of coal-fired power plants on lake sediment in Central Alberta, Canada (work in progress). Proceeding of 12th International Conference on Coal Sciences, November 2-6, Cairns, Australia Paper 8P15: 7p.

Goodarzi F. and Sanei H., 2003. Concentration and distribution of elements in milled-coal., power plant ashes and stack emitted materials in a Canadian coal fired power plants. Proceeding of 12th International Conference on Coal Sciences, November 2-6, Cairns, Australia. Paper 12P17, 7p

Goodarzi F. and Huggins F.E. 2003. Chromium and nickel speciation in Canadian feed coals, bottom and fly ashes. Proceeding of 12th International Conference on Coal Sciences, 2nd-6th November Cairns, Australia. Paper 7B3: 16p.

Goodarzi, F. and Rose, D. 2003. Petrology of feed coals and chars in ESP fly ash as related to mercury retained in pulverized coal-fired power plants. Proceeding of 12th International Conference on Coal Sciences, November 2-6, Cairns, Australia. Paper 12P16, 7p.

Stasiuk, V. Bagheri-Sadeghi, H. and Goodarzi, F. 2003. Petrology, Rank and liquid petroleum potential of Jurassic coals from the Central Alborz Region, Northern Iran. Proceeding of 12th International Conference on Coal Sciences, November 2-6, Cairns, Australia. Paper 12P18, 10p.

***Abstract***

**2005**

Goodarzi, F. 2005. Is pre-combustion reduction of mercury emitted from pulverized coal-fired power plants possible? An Alberta experience. In Web site of 2nd international Experts Workshop Mercury Emission from Coal (MEC2) May 24-2, 2005, Ottawa, Canada.

Goodarzi F. and Sanei H. 2005. Spatial distribution of antimony and other trace elements in soil in the vicinity of a coal-fired power plant in Alberta, Canada, 1st International Workshop on Antimony in the Environment, Institute of Environmental Geochemistry University of Heidelberg (Germany), May 16-19, 2005.

Goodarzi F., Sanei H., Reyes J., and Duncan W.F. 2005. Distribution of Antimony in stream sediments in the vicinity of a zinc-lead smelter in Trail, British Columbia, Canada, 1st International Workshop on Antimony in the Environment, Institute of

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***Report***

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## Appendix 3B: Requests for Advice and Data Gathered

| Requester | Organization | Location | Date | Media | Data /Knowledge Required | Discussion and Nature of Inquiry |
|---|---|---|---|---|---|---|
| **F. Goodarzi an example for year 2003 only** | | | | | | |
| J. Bolton | TransAlta, | Edmonton, Alberta | Jan. 16 | Particulate emission | Hg | Speciation of emitted mercury |
| J. Morton | Morton Ltd | Calgary | March 18 | Oil Shale | Trace metal | Trace metal in oil shale |
| A. Hickenbotham | TransAlta Utilities | Edmonton, Alberta | March 29 | Coal | Elemental Content | Washing and cleaning of coal |
| J. Cran | Cran & Stenning Technology Inc. | Calgary, Alberta | May 6 | Coal | Geochemical Properties | Reactivity of coal |
| R. McCanddles, | Environment Canada | Vancouver, BC | May 15 | Coal Seam | Characteristics | Advise on nature of self burning of coal |
| ESS-Assessment group | ESS-NRCAN | BC and Alberta | Mar. 17, 2003 | Coal | Elemental and Geochemistry | Fording Coal Expansion and Brook power plants |
| J. Cran, | Cran & Stenning Technology Inc. | Calgary, Alberta | May 20 | Coal | Geochemical Properties | To discuss the coal type and activity. |
| A. Hickinbotham, | TransAlta Utilities, | Edmonton, Alberta | June 2 | Coal | Mineralogy | Mineralogy of coal |
| W. Kluit | Teck-Cominco Ltd. | Trail, BC | June 17 | Smelter | Emission | Advised on impact of stack emission on land |
| O. Collingham | Collingham Consultants | Calgary, Alberta | June 22 | Coal | Elemental and Mineral | Mineral and elements in Alberta coal |
| R. McCanddles | Environment Canada | Vancouver, BC | June 25 | Fly ash Carbon | Hg | Reactivity of char and Hg |
| J. Cran, J. Shults, J. Eber | | N. Dakota, USA | July 11 | Coal | Geochemical Properties | Underground burning of coal seams |
| H. Cohen | Beer Shiva University, Israeli | Beer-Shiva Israel | July 14 | Coal | Hydrogen | Role of H in self combustion of coal |
| Prof. N. Saghdi, Eean-ul-Shams | University of Cairo | Cairo, Egypt | July 15 | Coal | Geochemical Properties | Nature of Megara coal in Egypt |
| J. Tingly, | ATCO Electric | Hanna, Alberta | Sept to Nov. | Coal | Stack Emission | Deposition of particles on land |
| J. Perry | Northwest Ltd. | Calgary Alberta | Sept 11 | Coal | Geochemical Properties | Advise on coal in China |
| P. Valupadas | Alberta Environment | Edmonton, Alberta | Sept 16 | Coal | Stack Emission | Deposition of elements in Alberta |
| B. Peel | ATCO Electric | Edmonton, Alberta | September 22 | Coal | Emission Monitoring | Moss-trap studies |
| R. McCanddles | Environment Canada | Vancouver, BC | October 15 | Coal | Geochemical Properties | Reactivity of self-burning coal |

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| S. Andurchik | EPCOR | Edmonton, Alberta | Nov 10 | Coal and Ashes | Hg | Speciation of Hg in coal and ashes |
| S. Murphy, B. Mayer, L .Lyons | University Calgary | Calgary, Alberta | | Fossil Fuel | Elemental and Mineral | Environmental aspect of fossil fuel |
| T. Foscolos | University of Crete | Greece | Dec 22 | Coal | Full Elemental | Elemental composition of coal |
| **Julito Reyes** | | | | | | |
| David Espenhain | Teck Cominco Ltd. | Trail, BC | May 27 2003 | Stack emission | Particle size | Data on previous particle size analyses |
| B. Duncan | Teck-Cominco | Trail, BC | Jan. 13, 2004 | Stream Sediments | Full Elemental | Stream sediment and elements |
| D. Hollman and J. Shultz | EPCOR | Edmonton, Alberta | Jan. 13, 2004 | Coal and Ashes | Hg | Canada wide Standard of mercury |
| Zahra Sahebi. | University of Tehran | Tehran, Iran | Oct. 10, 2004 | Coal | Petrology and Geochemistry | Petrology and geochemistry data of Iranian and Canadian coal. |
| J. Tingly | ATCO Electric | Hanna, Alberta | Feb 14, 2006 | Coal | PAH | Emission of PAHS |

**H.Sanei, an example for 2005**

1. **Golder Associates:** Stream Sediment report, Soil report, Soil Background Report, Moss-bag deposition data, Stack-slag and ore concentrate data
   -2005-Participating in the report by the Golder Associates on the Lake Sediments in the Wabamun Lake, determining the input of gravel washing operation on the shore of the Wabamun Lake.

2. **Seacor Environmental Inc.:** Acquiring the moss-bag deposition data and Atmospheric Mercury Flux (AMF) data and our expert opinion.

3. **Cantox Environmental Inc:** Acquiring the stream Sediment report, soil report, soil background report, and moss-bag deposition data.

4. **Larkspur Biological Consultants Ltd.:** Acquiring NRCan soil reports, soil background report, and moss-bag deposition data. Consulting with our experts to design a sequential extraction scheme.

5. **Loda Electronics Co.:** Co-designing the 2005 version of the Mercury Deposition Collector, manufactured by Loda Electornics, IL, USA (Model 2005 Sanei/NRCan/Canadian version).

6. **Morrow Environmental Consulting:** Consulting with our scientists and asking for expert opinions regarding the soil, metal deposition on the Rossland, BC. area

7. **RSLS Environmental Networks Inc.:** Collaboration with NRCan in the Atmospheric Mercury Flux sampling in Carstair, Alberta. Collaboration with

NRCan in designing the suitable modifications of the equipments and collectors for the extreme winter condition (winterizing).

8. **Ministry of Water, Land and Air Protection (British Columbia):** (Mr. Timothy Bennett): Consulting with ESS scientists and asking for expert opinion regarding the soil, metal deposition on the Rossland, BC.
   -(June 2005) The NRCan-ESS soil and Moss-bag deposition data was the key data in the Rossland Golf Course dispute between Teck-Comince Metals, Rossland Property Investments Ltd., and the Ministry of Water, Land and Air Protection, British Columbia.

9. **The Parkland Airshed Management Zone (PAMZ):**
   -Official member of The Parkland Airshed Management Zone (PAMZ), one of the active airshed under the Clean Air Strategic Alliance (CASA) - representing NRCan-ESS in the board meetings. Atmospheric Mercury Flux activity is supported and partially funded by PAMZ. The board consists of the representatives from public (mainly local residents), Government (e.g., Alberta Environment, Environment Canada, NRCan), industry, NGOs, and Municipalities.

10. **The West Central Airshed Society (WCAS):** Training and issuing the training certificates for operation the Atmospheric Mercury Flux (AMF) site by the ESS (Calgary) scientist.

## Acknolwedgements:

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## APPENDIX

## Appendix A: Powerpoint presentations for each activity.

| **Project 1:** Metals in the Environment: Sources, Fate, and Risks | Presentation |
|---|---|
| **Activity 1**: Multi-disciplinary investigations of risks associated with abandoned metal mines | P1.0-Project1.0_Overview_Parsons.ppt<br>P1.1-Source_Fate_Risk_Mineralogy_Percival.ppt<br>P1.1-Source_Fate_Risk_Mines_Parsons.ppt |
| **Activity 2**: Geochemical baseline protocols for soil monitoring | P1.2-Source_Fate_Risk_Triantional_Garrett.ppt |
| **Activity 3**: Geochemical modeling of soil mineralogy | P1.3-Source_Fate_Risk_Models_Klassen.ppt |
| **Activity 4**: Risk-assessment mapping, background estimation, and metadata development | P1.4-Source_Fate_Risk_Background_level_Grunsky.ppt<br>P1.4-Source_Fate_Risk_Background_Spirito.ppt |
| **Project 2:** Natural vs. Anthropogenic Metals | Presentation |
| **Activity 1**: Multi-media validation studies | P2.0-Project2_Overview_Outridge.ppt<br>P2.1-Source_Apport_IceCores_Zheng.ppt<br>P2.1-Source_Apport_InterSiteCompare_Zdanowicz.ppt<br>P2.1-Source_Apport_Peat_Shotyk.ppt<br>P2.1-Source_Apport_Seds_Alpay.ppt<br>P2.1-Source_Apport_Seds_Percival.ppt<br>P2.1-Source_Apport_TreeRings_Begin.ppt |
| **Activity 2:** Hg and Cd source apportionment in traditional northern food | P2.2-Source_Apport_Northern Foods_-Outridge.ppt |
| **Activity 3**: Geochemical modeling of soil mineralogy | P2.3-Source_Apport_Isotopes_Taylor2.ppt |
| **Activity 4:** Improving analytical methodologies and process understandin | |
| **Project 3:** Emission and Deposition of Elements and Particles | Presentation |
| **Activity 1:** Canada Wide Standard of Mercury emissions from coal-fired utilities, speciation of As, Cr and Ni and characterization of particles emitted from coal-fired power plants | P3.0-Project3_overview_Goodarzi.ppt<br>P3.1-Deposition_coal_Goodarzi.ppt<br>P3.1-Deposition_Speciation_Huggins.ppt |
| **Activity 2**: Delineation of the | P3.2-Deposition_monitoring_Sanei.ppt |

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| environment that may cause health risk in the vicinity of large stationary sources | |
| **Activity 3**. Inter-disciplinary techniques to identify the processes that distribute and redistribute metals in lake sediments. | P3.3-Deposition_LakeSeds_Sanei.ppt |
| A**ctivity 4** –Integration and interpretation of the potential redistribution of metals in lake sediments. | P3.4-Depostion_Seds_Alpay.ppt |