SOURCES PLATFORM ABSTRACTS

Metal concentrations and source apportionment of particulates and gaseous elemental mercury at various remote sites in Canada

G.M. Dias, G. C. Edwards
School of Engineering, University of Guelph, Guelph, ON

Metals in the atmosphere, whether anthropogenic or natural in origin, are associated with particulate matter (PM), except for mercury (Hg), which can also be in gaseous form. Both natural and anthropogenic sources can contribute to elevated levels of heavy metals at remote sites, therefore the relationship between various sources and metal particle concentrations at a receptor must be resolved and appropriate tools developed for regulation and mitigation of metals on particulate matter (PM) in the environment. Identifying the source of a metal is an important step in environmental risk assessment (ERA). There are various source apportionment procedures available for identifying metal sources. Project A1, has used novel field experiments to contribute towards source apportionment and quantification of metals at remote sites. A summary of our findings to date is presented. Monitoring and the use of source apportionment procedures are discussed in terms of the state of the science for source apportionment, including limitations which continue to hamper this field. Recommendations are made on appropriate experimental design strategies to maximize source apportionment procedures for ERA at a receptor site.

Chemical speciation and quantitative determination of some metal pollutants associated with airborne particulate matter of varying sizes

[1]Lamoureux, M., [1]J. Samson, [1]N. Warner, [1]J. Enright, [2]C. Grégoire
[1]Saint Mary's University, Halifax, NS; [2]Geological Survey of Canada, Ottawa, ON

This project has been ongoing for four years. During the first three years, sampling was done in the Rouyn Noranda region, in the vicinity of the Horne smelter. In year 4, we began the process of collecting samples from the Sudbury area. This will allow comparison of results from two different industrial sites. Samples are collected using a pair of high volume samplers each equipped with a 5-stage cascade impactors that allows separation of particles in six different size range (7.2, 3.0, 1.5, 0.95, 0.49, <0.49 μm).

Samplers are positioned up and down wind from the smelter stack at distances that varies from 2 to 25 km. Samples collected during year 3 in the Rouyn Noranda vicinity have been analysed by both solution nebulization and laser ablation ICP-MS. The quantitative determination of Pb, Ni, Cu, Cd, and Zn is completed for the July/August 2000 and the October 2001 collection. Results showed that Zn is not a good indicator of the impact of the Horne Smelter stack on the environment, but Pb and Cu is definitely more abundant in particulate that are downwind from the Horne Smelter stacks compare to particulate collected upwind from the stack. The lead isotope ratio (e.g. $^{206}Pb/^{207}Pb$) was determined for the July/August 2000 collection and showed that the lead isotopic signature for airborne particulate matter collected downwind from the Horne smelter stack is different from that collected upwind. This difference in the lead isotope ratio signature was not as prominent in samples from October 2001 collection. This may indicate that the lead isotope ratio signature is dependent on the smelting process that can be quite variable at the Horne Smelter. The ability of using laser ablation coupled to inductively coupled plasma mass spectrometry (ICP-MS) was recently demonstrated and used for the determination of Cu, Ni, Pb, Cd, and Zn in samples from the October 2001. The analysis of particulate matter using LA-ICP-MS is also carried out at the Analytical Services Lab of the Geological Survey of Canada (Ottawa) to ensure quality of results. Chemical speciation of Cu, Ni, and Pb airborne species using synchrotron x-ray absorption fine structure (synchrotron XAFS) will require multiple years of investigation in order to be completed. To this day, chemical speciation of Cu, Ni, and Pb for the July/October 2000 is completed whereas the speciation of Cu, Ni and Pb is nearly completed for the October 2001 collection. Results show that the chemical nature of Cu and Pb from particulate matter collected downwind is different from the upwind samples. Furthermore, the speciation is particle size dependent. For example, copper sulfate is more abundant in the small particulate fraction (0.5 micrometer) of the downwind collection than from the upwind collection. The chemical speciation will resume throughout 2003-2004.

Collections of airborne particulate matter from the Sudbury area are scheduled to begin in the Winter 2003. Samples from wet events from Noranda and Sudbury area have been collected and will be investigated for quantitative metal speciation. This work is currently in progress.

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Speciation of Inorganic Mercury in Airborne Particulate matter/aerosols

James J. Lu, ***Julia Y. Lu,*** Department of Chemistry, Biology and Chemical Engineering, Ryerson University, 360 Victoria Street, Toronto, Ontario M5B 2K3, Canada

D. Conrad Gregoire, Analytical Chemistry Research Laboratories, Geological Survey of Canada, 601 Both St., Ottawa, Ontario K1A 0E8, Canada

Cathy Banic, William H. Schroeder, Meteorological Service of Canada, Environment Canada, Air Quality Processes Research Division, 4905 Dufferin St., Toronto, Ontario M3H 5T4, Canada

A novel method that combines thermal desorption for separation and inductively coupled plasma mass spectrometry (ICPMS) for detection and quantification is used for analysis of inorganic mercury species associated with airborne particulate matter/aerosols. Airborne particulate/aerosol samples were collected using quartz traps and the quartz traps also serve as a pyrolyzer during sample analysis. This approach avoids sources of contamination from the environment and from reagents and solvents. Also, chemical transformation of inorganic mercury species is minimized or eliminated. ICPMS allows simultaneous monitoring of other elements, making possible of detecting anions that may be associated with the mercury species. The method has been applied to analysis of the samples collected from industrial, urban and rural sites.

EMMA at Work: Applications of an Analytical Tool for Chemical Characterization of Aerosols, Sediments, Soils and Vegetation in the Sudbury Smelter Footprint

Spiers, G.A.

Centre for Environmental Monitoring, Laurentian University, Sudbury, ON.

The updated EMMA system is providing data for CEM research projects initiated within the Sudbury Smelter Footprint to provide detailed information describing the Sudbury Fingerprint. The presentation will overview results being obtained for some of the following projects:

- Description of current particle emission profiles within the Sudbury smelter footprint;
- Examination of the emissions history by examination of relict smelter particle distribution in soils, sediments and peatlands of the Sudbury smelter footprint region;
- Analyses of selected ferns and mushrooms from a variety of sites of the Sudbury smelter footprint region to ascertain their abilities to hyperaccumulate potential contaminants of concern such as As, Se, Cd, Sb and Tl;
- Preliminary phases of the quantification of the mobile solid-phase composition, mineralogy and morphology for selected Podzolic pedons within the region.

When results from these applications are coupled with historic data, the current applications for EMMA will definitely enhance our understanding of metal emissions within the region. Data from these studies will be crucial for both human and ecological health risk assessment programs being initiated in the Sudbury region (ERA and HHRA).

The applications of the instrument to a planned collaborative study of aerosol filters in the Sudbury Footprint region to provide new understanding of the variability of metallic loadings to the ecosystems will also be outlined. Data to be obtained using cascade samplers will rapidly provide an understanding of PM_{10}, PM_5, $PM_{2.5}$ composition, mineralogy and morphology, both from regional and within-smelter environments, currently only obtainable with considerable difficulty and cost. This collaborative research initiative will provide hitherto unavailable knowledge of the speciation chemistry of modern aerosols, especially when coupled with more routine observations generated with XRD and SEM-EDS examination.

Physical and chemical evolution of aerosols in smelter and power plant plumes

Banic, C.[1], C. Gariépy[2], A. Simonetti[2], A. Chatt[3], M. Lamoureux[4], J. I. Campbell[5], Z. Nejedly[5], H. Wong[6], J. Skeaff[7], D. Paktunc[7], W. R. Leaitch[1]; K. Strawbridge[1]; S. Daggupaty[1]

[1]Meteorological Service of Canada, Toronto
[2]GEOTOP, University of Quebec at Montreal
[3]Department of Chemistry, Dalhousie University
[4]Saint Mary's University
[5]Department of Physics, University of Guelph
[6]AERB, NWRI, Environment Canada, Burlington
[7]Environmental Laboratory, Mining and Minerals Sciences Laboratories, CANMET, Natural Resources Canada, Ottawa

National and international concern about the health effects and continued use of Pb, Cd, As, and Hg as well as other metals has defined a need for improved estimates of the long term risks to ecosystems and human health from metals released from mining, metallurgical, and energy production activities. A research aircraft was used to determine the microphysical and chemical properties of airborne particulate metal emissions from the Nanticoke coal-fired power generating station and the Horne copper smelter. These properties are critical to the determination of the deposition rates of metals emitted, and hence the potential for these species to have impacts on local or distant ecosystems. The data collected in this study are needed for policy decisions regarding emissions from different sources.

Four intensive field campaigns, each of almost 3 weeks, were conducted in 2000. Plumes were sampled up to 40 km downwind of the source for ageing times of up to 1 hour in a variety of meteorological conditions. Stack sampling for particulates was conducted by the industries for times near the aircraft study. The ambient environment was characterised by measurements made outside the plume and upwind of the sources. The size distribution of particles emitted from the sources, the metal content of the particles (with emphasis on Ni, Cu, Pb, Zn, Cd, As, Se and Hg) and the distribution of metals by particle size were determined. The plumes were observed to contribute to the particle volume at particle diameters from 0.03 to 30 μm. Results of a 3-dimensional modelling study show that the deposition to the surface of metals in the particle size range observed in the plume is insignificant within 100 km of the sources. It was shown that mercury was predominantly emitted as gaseous elemental mercury. Gaseous elemental mercury has a long lifetime in the atmosphere and will be transported on global scales. Hence, long range transport is important for the particles and mercury emitted.

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Trace metal deposition chronologies in boreal shield lakes: distinguishing anthropogenic signals from diagenetic effects.

Carignan, R., A. Tessier, L. Rancourt

Université de Montréal, Montréal, PQ.,., INRS-ETE, Québec, PQ.

Accurate metal deposition records in lake sediments are necessary to assess their present human and ecological risk and to evaluate the effects of current or eventual remediation measures. The interpretation of sedimentary metal profiles as historical records may be complex, however, as these profiles may be influenced by a variety chemical, physical and biological processes occurring naturally near the sediment-water interface. We have used three independent approaches to distinguish the anthropogenic from the natural contributions to the shape of metal profiles. A first approach compares metal profiles obtained in chemically similar lakes exposed to high and low metal loads from the atmosphere. A second approach uses geochemical and diagenetic modelling to evaluate the importance of diffusion as an internal remobilization mechanism. Thirdly, stable isotopes have been used to fingerprint possible sources of Pb to lake sediments and to evaluate their relative importance. Four sites located on the Canadian Shield and presumably subject to high (Rouyn-Noranda), medium (Haute-Mauricie) and low (Manicouagan and Havre St-Pierre) metal loadings from the atmosphere were chosen. In each region, three similar lakes were selected; sediment cores were obtained at the deepest site, extruded, dated (210Pb) and analysed for organic carbon, As, Cd, Cu, Fe, Hg, Mn, Ni, Pb and Zn concentrations. Porewaters samples were obtained with peepers (1-cm vertical resolution) in mid summer in one lake of each region, close to the coring site, for determinations of pH, DOC, major ions, sulfides, polysulfides, As, Cd, Cu, Fe, Hg, Mn, Ni, Pb and Zn concentrations. We have also cored lakes with known fire histories in order to document the effects of wildfires on metal deposition chronologies. Our results show that dated sediment profiles collected near large point sources essentially reflect chronological deposition trends. At remote sites, however, the concentrations profiles of some metals (As, Cd ,Cu and Zn) can be slightly influenced by chemical changes occurring in surficial sediments. Post-depositional metal remobilization appears to be negligible for Pb and Hg. In the case of Hg, however, the boreal fire cycle has an important effect on Hg deposition chronologies, with individual fire events followed by 20-30 years of low Hg deposition in lakes.

Is mineral weathering a significant source of trace metals in soils?

Hendershot, W.H.[1] , J.B. Percival[2] and R.Rowe

[1] Department of Natural Resource Sciences, McGill University, Ste-Anne-de-Bellevue, QC H9X 3V9
[2] Geological Survey of Canada, Natural Resources Canada, Ottawa, ON K1A 0E8

The soils in areas near Cu and Zn mines are often developed on glacial sediments and bedrock that are rich in trace metals. As metals released from this natural source could easily be confused with metals associated with anthropogenic pollution, it is important to quantify the magnitude of this source. Mineralogy is an important aspect of soil studies and provides the analytical and quality control for other studies. Mineralogy is often overlooked with emphasis placed on geochemistry. However, as minerals can be the source of the trace metals of interest, it is imperative that mineralogy and geochemistry be investigated in tandem.

Samples of the BC horizons of six soils from transects near Sudbury and Rouyn-Noranda have been examined in great detail. The samples are composed of common rock-forming minerals such as quartz, feldspar, amphibole and pyroxene. Only minor to trace amounts of illite and chlorite occur. Magnetite is present in the magnetic heavy mineral fraction and ilmenite dominates the non-magnetic fraction with traces of zircon, hematite and titanite. No sulphide minerals were observed in any of the fractions. Some of these minerals can sorb trace or heavy metals, but the concentrations in these soils may be too low to detect using the techniques described in this project.

Two series of whole soil weathering experiments have been conducted to test and perfect the methodology. The column leaching protocol is working well with stable and repeatable results. The key to determining the contribution of weathering is to be able to measure the amounts of trace metal released from the mineral phase and then re-adsorbed, as metals released by weathering will re-precipitate. However, the metal released and re-precipitated is subsequently extracted with EDTA and analysed. Although the rate of trace metal release is low, the technique provides a useful tool for the determination of the contribution of weathering to the amount of metal in more available pools.

The results have direct relevance to the ecological risk assessment as they allow us to distinguish between natural and anthropogenic sources of trace metals in the labile pool of soils.

SOURCES POSTER ABSTRACTS

Stable Pb isotope ratios as indicators of atmospheric Pb sources around Rouyn-Noranda

Gallon, C.1, R. Carignan2, A. Tessier1, C. Gobeil1

1INRS-ETE, Québec, QC.2Université de Montréal, Montréal, QC.

The relative abundance of the four stable Pb isotopes (204Pb, 206Pb, 207Pb, 208Pb) is a characteristic of the ore deposit from which the Pb derives and ratios of these isotopes can therefore be used to identify and quantify the relative contributions of Pb sources in the environment. We measured the total Pb concentration and its stable isotopic composition in dated (210Pb, 137Cs and 241Am) sediment cores from three lakes of the Canadian Shield, located along a West-East transect comprising Rouyn-Noranda : L. Despériers, L. Vose and L. N56 (10 km SO, 25 km E and 300 km E of Rouyn-Noranda, respectively). The sediments of these lakes are minimally perturbed by benthos activity (bioturbation and bioirrigation) at the sampling sites, thus simplifying the interpretation of the historical Pb deposition record. In addition, the watersheds are uninhabited, have been little disturbed by woodcutting or forest fires and receive anthropogenic Pb input exclusively through atmospheric deposition. The isotopic ratios 206Pb/207Pb and 206Pb/208Pb reveal the occurrence of two isotopically-distinct types of anthropogenic Pb in each of the three lakes. Lakes Vose and Despériers have been contaminated by Pb from the same sources. One of their Pb types (206Pb/207Pb ~ 1.00) has an isotopic signature similar to that of the ore processed at the smelter, most likely the main source of contaminant Pb in these lakes with maximum fluxes around 1980. The other type of anthropogenic Pb (206Pb/207Pb ~ 1.32) was dominant in the sediments deposited at the beginning of the 20th century; its signature suggests a combination of several Pb sources including mainly the combustion of North American coal, as also indicated by the concentrations of polycyclic aromatic hydrocarbons (PAHs) in the same cores. The influence of Pb from the smelter in not observed in Lake N56. Our isotopic data for this lake suggest a dominant Pb type with a 206Pb/207Pb of ~ 1.18, most likely Pb from the combustion of leaded gasoline with maximum fluxes in 1973, and a less significant one with a 206Pb/207Pb of ~ 1.22, most likely Pb from coal combustion with maximum fluxes in 1940. These results show large differences in Pb isotopic signatures and indicate that it is possible to identify and quantify atmospheric Pb from various anthropogenic sources in lake sediments from the Canadian Shield. They suggest that the geographical influence of smelter emissions can be traced efficiently by measuring stable Pb isotope ratios in lake sediments. Clarifying the relative inputs of trace elements from natural and anthropogenic sources will provide essential information for making rational environmental decisions. These results will contribute information required for ERA on emission pathways and rates of movement of contaminants in the environment.

Mineralogy of Soils in the Vicinity of Smelters in Rouyn-Noranda and Sudbury Areas

Jeanne B. Percival

R.Rowe*, Department of Earth Sciences, University of Ottawa, Ottawa, ON
K1N 6N5 * Current address: Canadian Museum of Nature, Ottawa, ON K1P 6P4
J.B. Percival, Geological Survey of Canada, Natural Resources Canada, Ottawa, ON K1A 0E8
W. Hendershot, Department of Natural Resource Sciences, McGill University, Ste-Anne-de-Bellevue, PQ H9X 3V9

The distribution and fate of the trace metals Cd, Cu, Ni, Pb and Zn is poorly understood in boreal forest ecosystems. This study forms part of a larger project examining processes that control metal movement in soils and to distinguish between anthropogenic and natural sources. This study characterized the mineralogy of soil samples to identify trace minerals that can be a source of trace metals in the weathering environment and to prepare specific fractions or minerals to be used in future weathering experiments.

Six soils rich in trace metals were sampled from the Sudbury and Rouyn-Noranda areas. Samples were fractionated and the silt-size, clay-size and heavy mineral (magnetic and non-magnetic) fractions from the B/C horizons were analyzed by X-ray diffraction and scanning electron microscopy. Both areas had comparable mineralogy. Quartz, plagioclase and K-feldspar dominate the silt-size fraction with minor amounts of chlorite, and amphibole- and pyroxene-group minerals. The clay-size fractions are dominated by quartz, plagioclase, K-feldspar and amphibole-group minerals with minor amounts of chlorite and illite. Epidote and pyroxene-group minerals dominate the non-magnetic heavy mineral fraction with trace and minor amounts of amphibole-group minerals, titanite, zircon, hematite and ilmenite. The magnetic heavy mineral fractions are composed of ilmenite and magnetite. The mobility of trace metals in the soil profile is controlled by many factors including: total concentration of metals; mobility of metals in the organic layer; and composition and texture of the parent material. Trace metal concentrations of Cd, Cu, Ni, Pb and Zn are all below 40 mg/kg in the B/C horizon samples. However, the concentrations are slightly elevated in the Ae-horizon samples probably reflecting smelter additions to the soil column.Iron oxides, phyllosilicates, feldspars and Ti- and Zr-bearing minerals can host trace metals and, therefore, could be a natural source during weathering. As the samples do not contain significant amounts of clay-size material, the heavy mineral fraction is recommended for future weathering experiments. The rates of metal liberation from soil parent materials due to natural processes were identified by the Science Steering Committee as a knowledge gap. The knowledge from this project will improve ERAs by assisting in placing anthropogenic effects into an appropriate natural process content.