

Physical and Chemical Evolution of Aerosols in Smelter and Power Plant Plumes

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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 located on the north shore of Lake Erie, Ont. and the Horne copper smelter at Rouyn-Noranda, Que. 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 measurements made by the aircraft were complemented by remote sensing of the plume by a scanning lidar and by ground-based sampling of regional-scale aerosol. In addition, the emissions from a natural wildfire were studied. The presentation will focus primarily on particles emitted from the Horne smelter.

Industry performed in-stack sampling for metals during seven flights into the plume of the Horne copper smelter. In-situ chemical and microphysical properties of the particles emitted were measured in the plume as it evolved over distances of 2 to 27 km during winter and summer of 2000. The estimated dilution factors of the plume for the samples collected by the aircraft ranged from 2,000 to 70,000. The relative emissions of As, Cu, Pb and Zn into the size fractions $<2 \mu\text{m}$, $2-8 \mu\text{m}$ and $>8 \mu\text{m}$ aerodynamic diameter were established based on cascade impactor measurements of the particulate in the plume. The combination of the emission data from the industry and the aircraft sizing provide input needed to initialize models to predict the deposition and dispersion of the emissions.

A three-dimensional numerical modeling study of the characterization of particles emitted from the smelter at Rouyn (Quebec) was conducted using the BLFMAPS-a Mesoscale Boundary Layer forecast and Air pollution prediction system. The modeling system simulated meteorology and the air concentration, dry deposition and wet deposition of particulate matter emitted during February and July 2000. Particle concentration and deposition were simulated as a function of three aerodynamic mean mass particle diameters of 0.25, 4 and $20 \mu\text{m}$ (fine, medium and large, respectively). Coarser particles have a stronger deposition rate than the finer particles. Finer particles have a longer lifetime in the atmosphere and transport over long distances.

Comparison of scanning electron microscope analysis of particles collected in the plume and deposited to snow shows that metal-containing particles in the snow are compositionally more variable and complex than those found in the plume or ambient air.

The Pb isotope results obtained in this study suggest that aerosols emitted from the Horne smelter are transported into northeastern North America. However, point source apportionment in future will be difficult due to the fairly recent practice of processing recycled material containing industrial Pb from various sources at the Horne smelter.

Studies of mercury species in the atmosphere

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A methodology is developed and evaluated for the analysis of inorganic mercury species associated with atmospheric particulate matter. This methodology combines thermal desorption for separating mercury species with ICPMS for mercury detection and quantification. The applications of this methodology to the studies of mercury speciation in the atmosphere reveal (1) atmospheric gaseous elemental mercury (GEM) is oxidized to mainly water soluble mercury species each spring in the Arctic; (2) mercury species associated with airborne particulate matter appear to be a mixture of elemental and soluble mercury species and the distribution of these species in the particulate phase varies with location. (3) mercury species associated with suspended particles in rain water are mainly non-soluble forms; (4) transformation of mercury from more soluble forms to less soluble forms in the atmosphere.

Chemical speciation and quantitative determination of some airborne metal contaminants of varying particle sizes: General trends and limitations.

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This project has been ongoing for four years, with the fifth year being a phasing out year. Results reported here are for the Rouyn-Noranda region, in the vicinity of the Horne smelter. Sampling and analysis of samples from the Sudbury area is in progress. Samples were collected using a pair of high volume samplers each equipped with a 5-stage cascade impactors (cutoffs at 7.2, 3.0, 1.5, 0.95, 0.49, <0.49 μm). Samplers were positioned generally up (South West) and down wind (North East) from the smelter stack at distances that varies from 2 to 25 km. Some method development were performed initially to improve our ability to measure small concentration of metals in airborne particulate matter. Even though the analysis of Cu, Pb, and Ni using ultrasonic sampling GFAAS technique worked well, the availability of ICP-MS at the end of year 2 prompted us to restrict the analyses to only ICP-MS because it provided greater sample throughput with the additional ability of doing isotope ratio determination. The effectiveness of laser ablation coupled to inductively coupled plasma mass spectrometry (LA-ICP-MS) to determine quantitatively Cu, Ni, Pb, Cd, and Zn has been demonstrated and has been used for the analysis of samples from the October 2001. The analysis of particulate matter using LA-ICP-MS was also carried out at the Analytical Services Lab of the Geological Survey of Canada (Ottawa) to ensure quality of results. The quantitative determination of Pb, Ni, Cu, Cd, and Zn using ICP-MS showed that airborne 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. $^{206}\text{Pb}/^{207}\text{Pb}$) determined from the July/August 2000 collection showed that the lead isotopic signature for airborne particulate matter collected downwind from the Horne smelter stack is different from that collected upwind. However, when increasing the distance (October 2001 collection) that separates the smelter stack from the samplers, the ability to distinguish background level lead from suspected smelter lead (via lead's isotopic signature) was significantly compromised. This may indicate that the lead isotope ratio signature is either highly dependent on the smelting process, which can be quite variable at the Horne Smelter, or that the dilution effect plays a significant role in damping the lead isotopic signature as sampling is done further away from the stack. Chemical speciation of Cu, Ni, and Pb airborne species using synchrotron x-ray absorption fine structure (synchrotron XAFS) was and is still currently being investigated (it will require one more year of XAFS analysis in order to be completed). The chemical speciation of Cu, Ni, and Pb for the July/October 2000 indicates 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. Comparison between samples collected from Rouyn-Noranda and Sudbury in terms of their respective chemical speciation is not available.

The investigators wish to acknowledge and thank MITE-RN, Environment Canada (Youth Internship) and NSERC (Discovery Grant) for their financial support.

Rate of potentially toxic metal release by soil mineral weathering.

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Mineral weathering is one of the natural sources of trace metals found in terrestrial ecosystems and understanding the relative contribution from this source is essential to evaluating the impacts of human activity on ecosystem metal loading. In the case of trace metals, measurement of the release rate from soil minerals is confounded by the presence of trace metals in the coatings found around soil minerals and by the likelihood that metals released by the weathering of the crystal lattice will re-precipitate as part of the amorphous material common in podzolic soils. To avoid these obstacles, we developed a method that takes into account the amounts of trace metals in the coatings at the beginning and end of an 8-week weathering period. Weathering was carried out in miniature leaching columns using an artificial soil solution consisting of 1 mM CaCl₂ at pH 3 or 4. EDTA (ethylene-diamine-tetraacetic acid) was used to extract the trace metals from sub-samples of the soils either prior to or following the weathering experiments. Trace metals in the CaCl₂ leachates were also measured so that the total metal release could be calculated; metals were analysed by ICP-MS.

Difficulties were encountered in conducting the weathering experiments because of the inherent variability of the soil samples and hence the amounts of metals released from different sub samples of the same soil. To a certain extent these errors could be decreased by combining the leaching solutions from all 8-weeks of the experiment into a single sample.

The results show that the rates of release of trace metals varied between the two principle transects at Rouyn and Sudbury, as well as at different sites along the transects. Rates were also compared to those of soils sampled in a non-mining area, i.e., Plastic Lake. Rouyn had the highest release rate of metals, followed by Plastic Lake and then Sudbury. Mean Ni release rate in Sudbury ($6.6 \times 10^{-8} \mu\text{g g}^{-1} \text{s}^{-1}$) were three-fold those in Rouyn and more than 10-fold those in Plastic Lake. Nickel released in Sudbury increased with closer proximity to the smelters. Release rates of Zn were slightly above $2.1 \times 10^{-7} \mu\text{g g}^{-1} \text{s}^{-1}$ in both Rouyn and Plastic Lake, but mean rates were $8.3 \times 10^{-8} \mu\text{g g}^{-1} \text{s}^{-1}$ in Sudbury. The intermediate sites in Rouyn and Sudbury showed the highest and lowest release rates of Zn, respectively. Mean release rates of Cu were highest in Rouyn ($6.0 \times 10^{-8} \mu\text{g g}^{-1} \text{s}^{-1}$), followed by Sudbury ($3.3 \times 10^{-8} \mu\text{g g}^{-1} \text{s}^{-1}$) and then Plastic Lake ($0.41 \times 10^{-8} \mu\text{g g}^{-1} \text{s}^{-1}$). For both Cd and Pb, rates across the sites did not exceed $2.1 \times 10^{-8} \mu\text{g g}^{-1} \text{s}^{-1}$, with the exception of Pb in Plastic Lake that had a mean of $3.7 \times 10^{-8} \mu\text{g g}^{-1} \text{s}^{-1}$.

Despite the large relative errors in some cases, the data on weathering rates is on the same order of magnitude as what was measured in studies on the dissolution of primary minerals using continuous flow-through fluidized bed reactors: H⁺ consumption rates at pH 3 varied between 8.3 and $10 \times 10^{-6} \mu\text{mol m}^{-2} \text{s}^{-1}$ of soil.

A summary of method development and measurement of particulate concentrations and gaseous emissions of metals at remote sites.

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The research objectives for A1 were to assess the relative contributions of natural and anthropogenic sources of metals to the environment by determining the magnitude of metal emissions from natural sources and determining the metal species (chemical and physical characteristics) present on particulates from natural sources. The quantification of natural inputs of metals to the environment through biogeochemical cycling is important for providing risk assessments and determining the potential benefits of anthropogenic emission control. The project was designed to quantify contributions of metals on particulates arising from windblown dust and from air-surface exchange of gaseous mercury from natural sources.

Overall we have met and exceeded the objectives as outlined in the original proposal. While the focus of the research was monitoring and method development extensive data sets were obtained especially for gaseous mercury. The mercury data set has been useful in understanding some of the processes affecting mercury emissions. We were also successful at characterizing particulate metal concentrations at remote and rural sites and in the development of field methods to aid source apportionment. Preliminary methods were developed to differentiate natural from anthropogenic sources through experimental field design (size-fractionated concentrations, profiles, wind direction analysis), and these should help identify with greater certainty sources of metals at receptor sites.

In summary the research accomplished within Sources Project A.1 has provided experimental methods for and measurement of gaseous mercury and metal on particulates in Canada. These results are important to regulators and non-scientists for several reasons. The overall issue for these interest groups is whether observed metal loadings to various ecosystems are due to atmospheric deposition from anthropogenic activities or from natural sources. To conduct a proper environmental risk assessment (ERA), the link between the metal sources and the metals present in the affected environment must be established. In Canada, there is concern that unnecessarily stringent environmental regulation of the industrial sector, based on incomplete knowledge of natural sources may result in severe economic consequences with no measurable benefit to Canadians or the environment. Better estimates of natural contributions to metals in the environment and the ability to conduct experiments, which will aid in distinguishing the sources, are important for both regulators and industries who are asked to meet regulatory guidelines, and will lessen the uncertainty associated with knowledge of the origin of metals.

Historical records of metal loadings from the atmosphere in Canadian Shield lakes

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This study examined the chemical behavior and determined the post-depositional mobility of trace elements (As, Cd, Cu, Hg, Ni, Pb and Zn) in recent lake sediments of unperturbed boreal Shield lakes located in the Province of Quebec (Canada) and exposed to high, medium and low levels of atmospheric pollution. Sediments cores, obtained at the deepest sites of each lake, were dated (²¹⁰Pb, ¹³⁷Cs, ²⁴¹Am) and analysed for trace elements, stable Pb isotopes and other geochemical variables. Porewaters, obtained at the same sites by *in situ* dialysis, were analysed for trace elements, major cations and anions, sulfide, elemental sulfur, organic and inorganic carbon. To estimate the importance of post-depositional redistribution of metals in lake sediments we used two approaches: i) concentration gradients in porewaters coupled to diagenetic modeling and ii) comparison of sediment metal profiles from lakes exposed to high and low metal loads from the atmosphere. Our results indicate that dated sediment metal profiles obtained at sites near important emission sources faithfully reflect chronological deposition trends. However, for remote lakes, the profiles of some metals can be influenced by diagenetic processes. They show also that there has been a progressive and substantial decrease in metal deposition over the last 20-30 years, indicating the success of recent measures to control atmospheric emissions. Lastly, stable Pb isotopes are used successfully to identify sources (e.g., coal, leaded gasoline, smelting activities) of lead to lake sediments and to evaluate their relative historical importance.

Acknowledgment. Funding from the MITE Research Network (Mining Association of Canada, Ontario Power Generating Company and Natural Sciences and Engineering Research Council of Canada) is gratefully acknowledged.

Indium and thallium in two Canadian Shield lakes: Sources, geochemistry, and implications for contaminant monitoring

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Dated sediment cores (²¹⁰Pb) from the deepest sites in Lake Tantaré, near Quebec City, QC, and Lake Vose, near Rouyn-Noranda, QC were analysed for In and Tl, as well as for several other geochemical variables. Samples of interstitial and overlying water were also collected at the same sites by *in situ* dialysis and analysed for In, Tl, major ions, sulfide, organic and inorganic carbon and pH. Atmospheric deposition is the main source of anthropogenic contaminants in those two uninhabited Canadian Shield headwater lakes, but because of their location, L. Tantaré and Vose are exposed to different emission sources of trace metal pollution. The porewater data are used, together with information on infaunal benthos, in the diagenetic reaction-transport equation for solutes which is solved numerically with the code PROFILE. Information generated by PROFILE includes rates of In and Tl production or consumption as a function of sediment depth; this result is used to calculate the diagenetic contribution to the In and Tl solid profiles and then, to estimate the deposition chronology of these metals. This information is useful for *a posteriori* monitoring of the contaminant fluxes. Our results indicate a significant decrease in Tl and In deposition over the last 20 - 30 years, indicating the success of atmospheric emissions control measures. Thermodynamic calculations such as saturation indices are used to identify the diagenetic reactions responsible for In and Tl consumption from the porewaters. Comparison of In and Tl profiles with those of other contaminants (e.g., PAHs, Pb stable isotopes) measured at the same site allows identification of the main atmospheric sources of these two trace metals. Our results suggest that Tl and In are useful tracers for atmospheric emissions from coal combustion and metal smelters, respectively.

Acknowledgements. Funding from the MITE Research Network (Mining Association of Canada, Ontario Power Generating Company and Natural Sciences and Engineering Research Council of Canada) is gratefully acknowledged.

A century of atmospheric lead deposition around Rouyn-Noranda: What can lake sediments tell us?

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Total Pb concentration and its stable isotopic composition were measured in dated (²¹⁰Pb, ¹³⁷Cs and ²⁴¹Am) sediment cores from four headwater lakes of the Canadian Shield with uninhabited and undisturbed watersheds, and situated along a West-East transect comprising Rouyn-Noranda : L. Despériers, L. Vose, L. Carpe and L. N56 (10 km SO, 25 km E., 150 km E and 300 km E of Rouyn-Noranda, respectively). Porewaters were collected at the same sites by *in situ* dialysis and analyzed for Pb.

Diagenetic modeling indicates that post-depositional redistribution of Pb is negligible in all cases and that Pb profiles in the solid phase represent the historical variations of Pb deposition. The isotopic ratios ²⁰⁶Pb/²⁰⁷Pb and ²⁰⁶Pb/²⁰⁸Pb reveal the occurrence of two isotopically-distinct types of anthropogenic Pb in each of the four lakes. Lakes Despériers, Vose, and Carpe have been contaminated by the same two types of Pb. One of these (²⁰⁶Pb/²⁰⁷Pb ~ 1.00) has a Pb isotopic signature similar to that of the ore processed at the smelter, most likely the main source of contaminant Pb in L. Despériers and Vose, 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 results on polycyclic aromatic hydrocarbons (PAHs) in the same cores. The influence of Pb from the smelter is not observed in Lake N56. Our isotopic data for this lake suggest a dominant type of Pb 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.

Our results 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.

Acknowledgments. This study was supported by grants from the Natural Sciences and Engineering Research of Canada, the Ontario Power Generating Company and the Mining Association of Canada. (MITE-Research Network)

Chronology of platinum and palladium deposition in two Canadian Shield lakes: Evidence of regional contamination by aerial transport

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The use of automobile catalytic converters since 1975 in Canada and the United States has greatly reduced urban air pollution by NO_x, CO and hydrocarbons. Recently however, the results of several studies have shown that the operation of car catalytic converters containing Platinum Group Elements (PGEs) can lead to platinum (Pt), palladium (Pd) and rhodium (Rh) contamination of the environment with the potential for biological effects. Moreover, analyses of recent snow in Greenland have revealed a global scale of atmospheric contamination by PGEs that is apparently linked to automobile emissions. We report on the results of a study designed to measure the deposition fluxes of Pd and Pt in two Canadian Shield lakes over the last century. Sediment cores were collected in pristine Lake Tantaré, located in an Ecological Reserve near Québec City, and in Lake Vose, located downwind from a metal smelter. Atmospheric deposition is the main source of anthropogenic metals to the uninhabited drainage basins of these two lakes. The sediment cores were dated by several methods (²¹⁰Pb, ¹³⁷Cs, ²⁴¹Am) and analysed for Pt and Pd by isotope dilution ICP-MS. Spectral interferences were resolved by both mathematical correction and matrix separation on an ion exchange resin. The sedimentary Pt profiles indicate that the Pt deposition flux was 10 times higher in 2001 than at the beginning of the 20th century. However, because Pt fluxes started to increase before the introduction of car catalytic converters, other anthropogenic sources must have contributed to atmospheric Pt contamination. The Pd atmospheric deposition flux has also significantly increased over the last century.

Acknowledgements. Funding from the MITE Research Network (Mining Association of Canada, Ontario Power Generating Company and Natural Sciences and Engineering Research Council of Canada) is gratefully acknowledged.

Zinc and PAHs in the sediment of a Canadian Shield lake

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This study took place in the westernmost basin of the pristine lake Tantaré, located in an ecological reserve about 40 km Northwest of Québec City. L. Tantaré watershed has not been affected by forest fires or wood harvesting, and it remains uninhabited. Concentrations of zinc, thirteen parent PAHs and other geochemical variables were measured in a dated (^{210}Pb) sediment core obtained at the deepest site. Porewaters sampled by *in situ* dialysis on seven occasions at the coring site were analysed for pH, Zn, major ions, sulfide and organic and inorganic carbon. Dissolved Zn concentrations were consistently higher in the overlying water than in the porewaters; the dissolved Zn profiles indicated a diffusion of zinc from the overlying water to the sediments. The porewater data and population densities of benthic animal were used in a one-dimensional transport-reaction diagenetic model for solutes which was solved for the reaction rate of zinc consumption from the porewaters. With this latter information, we estimated that the contribution of diagenesis to the total Zn profile is about 30-40%. Calculation of saturation indexes suggests that Zn consumed from the porewaters is fixed to the sediments by precipitation as sulfide or by coprecipitation. Total Zn concentrations increased sharply from a background value of $0.7 \pm 0.1 \mu\text{mol g}^{-1}$ below 13 cm ($<1851 \pm 21$) to a maximum value of $5.3 \pm 0.1 \mu\text{mol g}^{-1}$ at 5.25 cm (1944 ± 3) and then decreased progressively to a value of $1.1 \pm 0.1 \mu\text{mol g}^{-1}$ at the sediment surface. Comparison of the total Zn profile with another profile obtained 13 years earlier at the same site shows a downward shift of the peak by 1.75 cm due to burial, but no noticeable change in neither Zn peak height nor width, suggesting that bioturbation is small at this site. The ΣPAH profile peaks between 4.75 and 5.75 cm (between 1949 ± 2 and 1938 ± 3) is highly correlated with that of Zn. The specific composition of PAHs and their chronology of deposition point out to coal combustion as their main source. All this information concurs to suggest that coal combustion was the main source of zinc in L. Tantaré.

Acknowledgments. This study was supported by grants from the Natural Sciences and Engineering Research of Canada, the Ontario Power Generating Company and the Mining Association of Canada. (MITE-Research Network)