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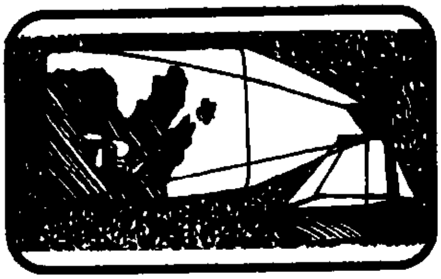

## Trace Metals in the Environment: Mobilization to Remediation

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A one-day symposium entitled "Trace Metals in the Environment: Mobilization to Remediation" was held at the Geological Association of Canada–Mineralogical Association of Canada Joint Annual Meeting in Winnipeg, Manitoba in May, 1996. Past attempts to describe a discipline of "environmental geochemistry" have been criticized for their lack of a central focus and their lack of a common terminology (Fortescue, 1992). It was the goal of this symposium to bring together the diverse fields of research encompassed by "environmental geochemistry," and to focus on the central theme of metal speciation and transport. The symposium was organized by Adrienne Larocque, who chose oral and poster presentations to represent all the components of the comprehensive cycling model shown in Figure 1. The symposium was sponsored by GAC's Environmental Earth Science Division. The proceedings will be published in a special issue of Environmental Geology in 1997.

Adrienne Larocque introduced the symposium by describing different ways of viewing the continuous exchange of matter and energy among the earth's environmental reservoirs (Fig. 1). This conceptual model for metal transport takes into account all reservoirs, whether they represent sources, sinks or agents of transport. Earth is made up of three reservoirs: the solid Earth or geosphere, the liquid layer or hydrosphere, and the gaseous envelope or atmosphere. Living organisms (the biosphere) inhabit the Earth environment, interacting with its component parts. The geosphere is the original source of all terrestrial metals. In addition to being the source, the geosphere may represent a sink for metals. The atmosphere and hydrosphere also may be regarded as sinks for metals; however, from a geological perspective, they are more likely to be considered as agents of transport. Whether we define an environmental reservoir as a sink or as a medium for the movement of metals from one site to another depends on the spatial and temporal scale of observation. For example, the oceans are a vast reservoir for a variety of chemical elements. However, they also are a conduit for elements derived from weathering of rocks to return to the geosphere through sedimentation. Finally, a reservoir may act as a catalyst for changes of state of metals, without actually having incorporated those metals, as in the case of some biologically mediated reactions. Larocque noted that most efforts to remediate metal contamination involve returning metals to their original source: the geosphere.

This overview provided perspective and a unifying framework for the presentations that followed. Some focused on characterization of materials within individual reservoirs, while others documented experiments designed to understand mechanisms of exchange between environmental reservoirs.

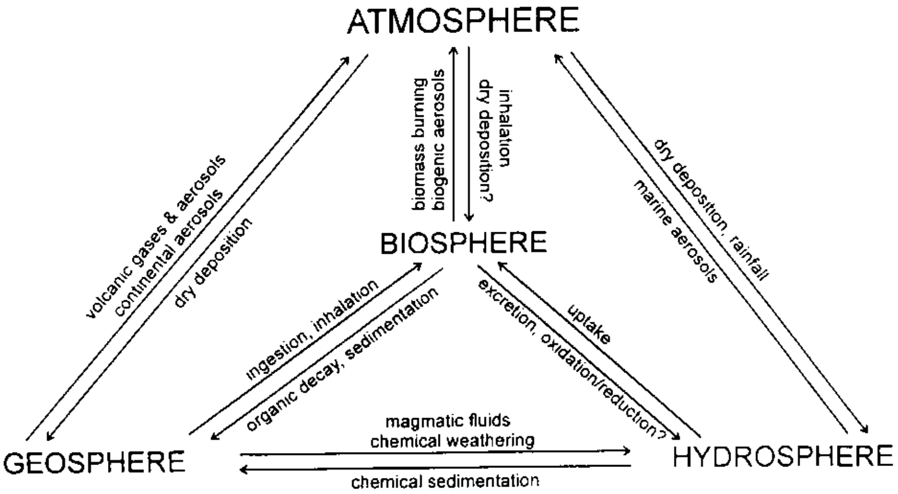

**Figure 1** *Conceptual model which formed the basis for the organization of the symposium (from Larocque and Rasmussen, 1997, Environmental Geology, in press).*

## GEOSPHERE – HYDROSPHERE INTERACTIONS

One of the areas of greatest environmental concern is the weathering of mine tailings and generation of acid mine drainage. The presentations on this topic delivered the clear message that decisions regarding disposal and reclamation require an understanding of metal behaviour specific to the local conditions, including climate, mineralogy, geology and geochemistry, and topography. Shannon Shaw *et al.* described laboratory and field lysimeter experiments to determine optimal dry cover and dam construction materials. Their study of the oxidation behaviour of iron-sulphide minerals intailings showed a positive correlation between the sulphur content of tailings and their acid generating capacity. Richard McGregor *et al.* reported on the mobilization and attenuation of heavy metals in the Copper Cliff nickel mine tailings near Sudbury. Oxidation and dissolution of sulphide minerals release iron, nickel, and cobalt to pore water in the shallow tailings. Subsequently, pH-buffering reactions result in the precipitation of these metals in secondary-phase minerals. The authors reported that goethite, jarosite and vermiculite are sinks for nickel. Chemical extraction experiments demonstrated that significantly higher concentrations of metals are removed in reducing extractions than in acid-leaching extractions. The implication is that some remediation measures may inadvertently destabilize secondary minerals which host heavy metals.

In contrast to temperate regions, areas of low precipitation undergo arid weathering. Bill Chavez *et al.* documented mineral weathering reactions under arid conditions in the southwest United States, where tailings are exposed to alternating periods of oxidation (during spring and fall dry seasons) and leaching (during snow melt and rainy seasons).Their examination of paragenetic relationships of sulphides and oxides in mine tailings indicates that some sites are not actively releasing metals, and thus require different remediation techniques than those that generate acid mine drainage. Careful mineralogical characterization is a necessary step in the evaluation of tailings, as current metal content may have been influenced by grain size variation, lime addition, and variations in residual metal concentration resulting from varying extraction efficiencies. The importance of these factors was documented by Michelle Boulet and Adrienne Larocque in a comparative study of sulphide mine tailings at two sites in New Mexico. The young, relatively unaltered Cyprus–Pinos Altos tailings show variations in metal concentrations that reflect the above factors. In contrast, current metal distributions in the extensively weathered Cleveland mine tailings are a function of the distribution and stability of secondary phases. For example, carbonate-rich hardpan layers immobilize metals released by oxidation of sulphides, through precipitation of metal-rich secondary carbonates. Furthermore, acidic drainage from the Cleveland tailings has much lower concentrations of Pb than other metals because secondary Pb sulphate is highly insoluble.

Jeanne Percival *et al.* reported that total dissolved arsenic concentrations in surface waters draining mine tailings and waste rock near Cobalt, Ontario vary from 11 to 20,000μ g·L$^{-1}$ with strong seasonal variations. Arsenate species (AsV) predominate in strongly oxidizing surface waters, whereas arsenite species (AsIII) are found in ground water. Strong seasonal variations in surface water concentratons are related to the formation of secondary efflorescent arsenate minerals. During dry periods, mineral crusts of gypsum and thenardite form containing secondary arsenates (erythrite, brassite and pharmacolite), and during wet periods these efflorescent minerals are readily dissolved and flushed into surface run-off.

John Kwong documented natural acidification of a lake in Central Yukon. Clear Lake is located adjacent to a buried massive sulphide body, and thus receives subsurface drainage that is acidic and metal-rich. Due to the presence of carbonate rocks flanking the lake, neutralization occurs within one km downstream. Elevated metal concentrations and authigenic sulphides are found in the reducing environment of bog and lake-bottom sediments. Providing contrast to the acidic conditions in the Clear Lake area, Charlie Roots and John Kwong then described the neutral to slightly alkaline surface waters of the Keno Hill Mining District, also in central Yukon. The climate is cold and semi-arid, with no sun in the winter. Here a large volume of unvegetated rock waste has accumulated over 75 years of mining (Ag-bearing galena and sulpho-salts), and has caused elevated metal concentrations in nearby small streams. Metal transport in these streams is limited due to cryogenic precipitation — the surface water is frozen seven months of the year — and co-precipitation and sorption onto suspended particulate matter and the stream substrate. Acid drainage is not widespread in this area, due to the slow rate of sulphide oxidation and continuous neutralization by local carbonate minerals.

## GEOSPHERE – ATMOSPHERE INTERACTIONS

Pat Rasmussen discussed the current debate over the relative significance of natural and industrial emissions of metals to the atmosphere on the global scale. Geoscience perspectives are needed to address the large uncertainties and information gaps associated with attempts to distinguish airborne metal species arising from industrial sources from other species of metals in the atmosphere. These include windblown soil and sediment particles, forest fire debris, biogenic particles (waxes, pollen, spores), seaspray, volcanic particles and gases, low-temperature degassing, and methylation products. Existing estimates of the annual global flux of metals from natural sources vary by orders of magnitude. Thus, conclusions about the relative significance of industrial emissions can depend entirely on which natural flux estimate is chosen. For example, one emissions inventory for lead (Pb) indicated that only 4% of the global Pb flux arises from natural sources (ref 2), while another indicated that at least 90% arises from natural sources (ref 3). This disparity is due entirely to differences in the estimation of the natural Pb flux, as the anthropogenic estimates in the two inventories are virtually identical!

Jim Stimac *et al.* presented evidence of the significance of natural volcanic emissions by documenting the redistribution of Pb and other volatile metals during eruption and devitrification of the Bandelier Tuff, New Mexico. Lead and other incompatible trace metals become strongly enriched in silicic magmas. During eruption, they are partitioned into the vapour phase, and thus may be released directly into the atmosphere in large amounts. During devitrification of matrix glass, vapour is liberated from which metal-rich minerals crystallize. Their fine-grained nature and location in porous tuffs makes these minerals susceptible to mobilization by groundwater. In his poster, Stimac compiled available data on volcanic emissions of metals to the atmosphere. He pointed out the large uncertainties associated with these data, and the necessity of additional research to better constrain volcanic metal fluxes.

Penny Henderson *et al.* studied the distribution of trace metals in humus and till samples in the Flin Flon–Snow Lake area of Manitoba and Saskatchewan, to determine the relative contribution of metals including natural and anthropogenic sources and the fate of metals associated with fall-out from a smelter. Surface humus and underlying till parent material were collected in a regional scale survey and in detailed surveys near the smelter at Flin Flon. Total metal concentrations near the smelter are enriched as much as 250 times above background. Metal concentrations decrease exponentially with distance from the smelter, reaching background levels at distances averaging 40 km from the smelter. Sequential extraction techniques indicate that metal partitioning behaviour varies depending on the element. Smelter-derived particulates were identified using SEM, and consist of distinctive spherical particles, metal particulates, oxides and sulphates. Smelter-derived spherules are present only in humus and not in till, and are rare outside a radius of 100 km from the smelter.

To address the need to characterize natural sources of Pb in the vicinity of the long-range atmospheric monitoring site at Dorset, southern Ontario, Lyn Anglin *et al.* investigated Pb isotopic signatures of natural surface materials from bedrock, till and lake sediments. The study found that Pb isotopic signatures previously attributed to long-range atmospheric transport of metal pollution could arise equally from local natural sources, *e.g.*, windblown dust, pointing to the need for improved methods of distinguishing sources of airborne Pb at rural and remote receptor sites.

## GEOSPHERE – BIOSPHERE INTERACTIONS

In a talk entitled "Trace Metals: the Good, the Bad, and the Ugly," Bill Fyfe provided an overview of the role metals play in health, economics and the environment. Life evolved in the presence of metals in the environment and thus organisms at all levels are adapted to metals. Indeed many metals are essential for health. But at the same time as identifying the usefulness of metals in everyday life, Fyfe emphasized the need to acknowledge mistakes of the past and present, particularly in the face of the increased pressures caused by overpopulation. Geoscientists can make a unique contribution by focussing research efforts on understanding geochemical controls on mobility and bioavailability of metals and improving technologies for the remediation of polluted sites.

A poster by Nikolaos Condoyannis *et al.* documented elevated concentrations of Ag, As, Cd, Cu, Fe, Mn, Pb, Sb and Zn in surface soils and overlying plants on the floodplain of the Coeur D'Alene River in Idaho. The enrichments, which are as much as 186 times higher than in a control area, result from dispersal of mining and milling wastes from a major Ag-Pb-Zn mining district. The authors observed increased mobility and bioavailability, related to increased pH, under wet conditions. Bioavailability also appears to be a function of plant species. Plant-soil metal ratios decrease in the order Potamogeton (spp.) > Equisetum palustre > Phragmites australis > Agrostis stolonifera. The ability of aquatic Potamogeton (spp) to take up metals otherwise considered immobile suggests that it may be a useful accumulator plant for the removal of metals from contaminated soils.

Michael Aide and Gary Cwick examined soil-forming processes that influence nutrient status and metal bioavailability in a boreal forest ecosystem near Thompson, Manitoba, as part of NASA's BOREAS project. Selective, sequential chemical extractions indicate that nutrients and metals in the cation exchange fraction and/or sequestered by the organic matter pool are the bioavailable fractions, while the amorphous and crystalline Mn- and Fe-oxide fractions buffer the more active pools against changing soil conditions. Important soil-forming processes are: decalcification of surface horizon; eluviation-illuviation; pedoturbation; melanization and humification; limited oxide formation, confined to the upper tier of soil; biocycling, *e.g.*, sphagnum decomposition; acidification, in particular leaching of organic acids from Jack Pine; and mobilization of nutrients that support vegetation.

Steve Sheppard and Bill Evenden presented their research on geophagy, a term which refers to the purposeful or inadvertent ingestion of soil. Geophagy may constitute a significant pathway for metal ingestion, but it is a difficult one to quantify, as it is necessary to measure the amount of soil ingested, the total metal concentration of the soil particles ingested, and the bioavailability of the soil-bound metals in the gut. Accidental ingestion by adults is in the order of 60 mg/day. Children, who are more susceptible to the potential toxic effects of metal consumption, also tend to ingest more soil. Geophagous adults may consume as much as 50 g·day$^{-1}$ of soil. Experiments indicate that metals are enriched in the fine soil particles that adhere to human hands (relative to total soil concentrations) because it is the metal-rich clay particles that cling to skin, whereas silicate-rich sand-sized particles do not. Results of experiments on animals indicate that the bioavailability of Cs increases four-fold when Cs-spiked feed is ingested without added soil than when ingested with added soil, as the soil components provide a competitive sink for Cs. In contrast, there is no difference in bioavailability of Pb from feed with or without the addition of soil.

## HYDROSPHERE–BIOSPHERE INTERACTIONS

Rona Donahoe reported that Fe oxyhydroxide adsorption/desorption processes have greater influence than sediment organic matter on the mobility of trace metals in a biologically zoned, riverine freshwater wetland in central Alabama, where the predominant source of trace metals is natural soil weathering reactions. Trace metal cycling involves the adsorption of Pb, As, B, Cd, Sr, and Ba upon surfaces of Fe oxyhydroxide phases, with subsequent release of the metals due to bacterially mediated reductive dissolution of ferrihydrite. Both iron-reducing and sulphate-reducing bacteria are important. In contrast, Al cycling is a function of weathering and clay mineral formation. Released metals may move upward due to diffusion or downward with the hydraulic gradient. Donahoe observed that increased concentrations with depth result in oversaturation and precipitation of Fe and trace metal phases.

Joanne Shwetz *et al.* presented trace element speciation data for bottom sediments from the heavily industrialized St. Clair River, Lake St. Clair and the Detroit River. Total trace metal concentrations indicate diffuse point sources of metal loading in the Lake Huron–Lake Erie corridor. Sequential extractions in-

Erie corridor. Sequential extractions indicate that Cu is associated with the organic fraction, and all other metals are associated with the reducible fraction. In their companion poster, Bryan MacFarlane *et al.* examined trace metal distribution in sediments and zebra mussels from western Lake Erie. Zebra mussels incorporate trace elements into their shells, and thus may be useful biomonitors of metal pollution. The metal concentrations in the shells vary between growth increments, allowing interpretation of changes in trace metal input over time.

## ATMOSPHERE – HYDROSPHERE – BIOSPHERE INTERACTIONS

In their study of boreal forest catchments containing different types of wetlands, Carol Kelly *et al.* reported that all catchments were sinks for total mercury. Upland areas retain methylmercury, whereas wetlands are net sources of methylmercury. Variations in internal hydrology of wetlands result in differences in source strength for methylmercury among wetland types. Yearly differences in water yield also affect methylmercury. Thus, modelling of methylmercury production in any catchment requires a knowledge of percentage and type of wetland area and annual water yield.

Inez Kettles and Keith Bell observed significant vertical variations in Pb isotopic ratios in peat core samples collected from an ombrotophic bog near Detour Lake, northeastern Ontario. The Pb 206/204 ratios are highest in the peat which accumulated during an episode of post-glacial warming, the hypsithermal. The authors concluded that Pb isotopic fingerprinting of peat, in combination with an understanding of the history and context of a bog's development and careful attention to related parameters (bulk density, total Pb abundances, loss-on-ignition), has considerable potential for discriminating among metal sources in the landscape.

## CHARACTERIZATION OF INDIVIDUAL RESERVOIRS: METHODS AND RESULTS

A poster by Jordi Bruno *et al.* reported on research related to the long term oxidative alteration of spent nuclear fuel under natural water conditions. Using SEM, ESEM, XRD, and EMPA, the authors were able to characterize uranophane and its alteration product soddyite. These are secondary phases derived from the alteration of uraninite. Based on their experimental data, the authors also were able to determine a solubility product for soddyite.

Gwendy Hall *et al.* described the application of selective leach procedures to studies of base metal dispersion around several mines in Manitoba, and to the identification of surface geochemical signatures at sites of previous underground nuclear explosions. These authors noted that while phase selective leaches have been around for quite some time, the sensitivity of ICP-MS now allows geochemists to take full advantage of these techniques for environmental research. Some elements remain problematic: mercury, for example, tends to be readsorbed back onto the substrate during leaching. To minimize this effect, the authors recommended changing from a batch to a flow-through mode of operation. Alain Plouffe reported on mercury research in central British Columbia, where cinnabar occurrences in bedrock are responsible for elevated mercury concentrations in surficial sediments. He emphasized that criteria must be established for recognizing mercury derived from natural sources as a prerequisite for effective remedial action. Plouffe used a combination of criteria such as mineral form, regional geochemical patterns, metal associations and depth of sample collection to determine a natural origin for the observed metal distributions.

Rod Klassen discussed the overall significance of regional and vertical variations in metal concentrations in glacial deposits of Canada. He observed that in many places natural concentrations exceed safe-limit criteria established by some jurisdictions! Klassen related the observed compositional variations to variations in provenance, based on determinations of ice flow directions and the history of glacial erosion and transport. In central Newfoundland, for example, As concentrations in till range from 10s ppm to over 1000 ppm at the regional scale, depending on the bedrock source. He emphasized that significant variations of metal concentrations also may occur with depth in a given location. For example, in a sequence of glacial deposits overlying massive sulphide mineralization at Buchans, the lowermost till contains 500 ppb Pb to more than 2000 ppm Pb and 1000 Zn to 2000 ppm Zn. Metal concentrations in overlying sediments at the same site are comparatively decreased (less than 100 ppm Pb and less than 200 ppm Zn). Klassen concluded that a knowledge of natural metal concentrations in soils and soil parent material is a prerequisite for evaluating the impact of human activity, for determining "safe levels" of metals in the environment, and for establishing appropriate clean-up criteria.

## CONCLUDING REMARKS

Large uncertainties in many aspects of trace metal occurrences in the environment, including the contribution and importance of natural processes, make it clear that there is no shortage of challenging research projects for the foreseeable future. Accordingly a second symposium on the theme of trace metals in the environment is being planned for the 1998 GAC–MAC meeting in Quebec City. The symposium will focus on early diagenetic processes in modern sediments, their effect on vertical metal concentration profiles, and their influence on the reconstruction of anthropogenic input histories. If you are interested in participating, or wish to recommend someone else who is doing research in this area, please contact Pat Rasmussen (e-mail rasmussen@gsc.nrcan.gc.ca; phone 613-947-6588) or Jeanne Percival (e-mail percival@gsc.nrcan.gc.ca; phone 613-992-4496).

## REFERENCES

Fortescue, J.A.C, 1992, Landscape geochemistry: retrospect and prospect - 1990: Applied Geochemistry, v. 7, p. 1-53.

Nriagu, J.O. and Pacyna, J.M., 1988, Quantitative assessment of world-wide contamination of air, water and soils by trace metals: Nature, v. 333, p. 134-139.

Kownacka, L., Jaworowski, Z. and Suplinska, M., 1990, Vertical distribution and flows of lead and natural radionuclides in the atmosphere: Science of the Total Environment, v. 91, p. 199-221.