

# Soil: source of trace elements to the atmosphere, and sink for trace elements from the hydrosphere

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Polar snow and ice as well as peat cores from ombrotrophic bogs provide records of atmospheric lead (Pb) deposition extending back 15,000 years. Natural fluxes of Pb to the atmosphere were dominated by mineral particles derived from soils, illustrating the importance of soils for the chemistry of the atmosphere. Both archives show that human activities have dominated atmospheric Pb emissions for more than 3,000 years. Although Pb emissions to the atmosphere have been declining for several decades, the legacy of industrial Pb in the soils of Europe and northeastern North America probably amounts to 1-10 g/m<sup>2</sup>. The fate of this potentially toxic trace metal in soils, subsequent to deposition from the atmosphere, is a matter of great interest, and not without some controversy.

Using the clean lab methods and ICP SMS which have been used successfully to study Pb in polar snow and ice, we have followed the Pb flows from the atmosphere to soils, and from there into some streams and lakes of the Great Lakes-St. Lawrence forest region. Lead isotopes (<sup>206</sup>Pb, <sup>207</sup>Pb, and <sup>208</sup>Pb) clearly show that the lakes are dominated by Pb from anthropogenic sources, but the concentrations in the aqueous phase may be extremely low (comparable to ancient arctic ice) because of various processes in soils, as well as the removal of soil-derived particles and colloids from the water column.

To further illustrate the efficient removal of Pb and other metals by soils, we have compared a range of trace metals in recent groundwater (less than 30 years old) from artesian flows (Simcoe County, Ontario) with contemporary snow in the recharge area. Potentially toxic, chalcophile elements are highly enriched in snow today, relative to their natural abundance in soils, with enrichment factors (calculated using Sc) ranging from ca. 100 to 1000x for Ag, Bi, Cd, Cu, Mo, Pb, Sb, Te, Tl and Zn. Relative to M/Sc ratios in snow, however, groundwater samples significantly **depleted** in these elements, as well as Cr and V. The removal from the waters of these elements is presumably due to such processes as physical entrapment of metal-bearing atmospheric aerosols by organic and mineral soil components as well as adsorption and surface complexation of ionic species onto organic, metal oxyhydroxide and clay mineral surfaces. In addition, soils are home to a diverse array of natural biofilters, namely living organisms. In the case of Pb, the removal processes are so effective that apparently “natural” ratios of Pb to Sc are found in the groundwaters. Remarkably, some of the groundwater samples contain less Pb than the cleanest layers of ancient arctic ice (ie < 1 ng/L). To put these findings in perspective, these Pb concentrations are at the lowest levels ever measured anywhere on earth, and are testimony to elaborate and efficient removal processes in soils.

Soils are much more than simply rooting media: they represent important reservoirs of water and plant nutrients, sinks for atmospheric carbon and nitrogen, and form the basis of agriculture, forestry, and many ferrous metal mines. In addition, they play a vital role in regulating the chemical composition of the atmosphere, including its variation with global climate change, and are unsurpassed water filters.

## **Biographical Sketch, William Shotyk**

**William Shotyk** was born in the Village of Swansea, now part of the City of Toronto, in Ontario, Canada. He received his B.Sc. (Agr.) in Soil Science and Chemistry from the University of Guelph in 1981 and a Ph.D. in Geology from the University of Western Ontario in 1987. Following postdoctoral research at the University of California, Riverside and UWO, he worked at the University of Berne in Switzerland where he completed a Habilitation in Geochemistry, in 1995. After 12 years at the University of Berne, he became Professor at the University of Heidelberg and Director of the Institute of Environmental Geochemistry, in October of 2000. His research group is responsible for Inorganic Environmental Geochemistry, with state-of-the-art metal-free clean lab facilities and sector-field ICP-MS for measuring trace elements and Pb isotope ratios at extremely low concentrations. The main research areas are human impacts on the geochemical cycles of potentially toxic trace elements such as Pb, Sb, As, Cd and Hg, including archives of atmospheric change (ombrotrophic peat bogs and polar ice cores), fate in soils and sediments, and impacts on natural freshwaters. A member of the American Chemical Society, American Geophysical Union, and the Geochemical Society, he has published more than 170 articles, including 130 in refereed journals, as well as in conference proceedings, books, and newspapers.