Tracing sources of atmospheric aerosols using Pb and Sr isotopic composition and elemental concentrations of precipitation from northeastern North America

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A Pb isotope investigation of epiphytic lichens from Québec has previously shown to be an effective tool in tracing the origin and pathways of atmospheric pollution (Carignan and Gariépy, 1995). Results show that lichens record a significant input of anthropogenic Pb emitted to the atmosphere from smelting activities and point to a significant input from US sources. Carignan and Gariépy (1995) suggest that ~60% of the anthropogenic Pb present within the St. Lawrence River valley originates from industrial activities concentrated in the Great Lakes-American Midwest Regions of North America.

An alternative approach to tracing sources of aerosols consists of the isotopic analysis of precipitations (snow, rain) which would aid in quantifying Pb atmospheric pollution at shorter timescales since it is difficult to precisely determine the age of lichens. In this endeavour, we report Pb and Sr isotope ratios and elemental concentrations of snow samples cored during the 1993, and '97 winters along two main transects - the St. Lawrence River Valley and between 47° and 55°N. In 1998, we extended the geographic coverage of our sampling to include the neighbouring areas of SE Ontario, NE United States and the Maritime provinces. The samples of snow profiles provide, therefore, an integrated signal (naturally weighted average), over a period of 3 to 5 months, of the atmospheric pollution affecting NE North America. The aim is to determine the existence of any temporal variation in the sources, and quantify fluxes of atmospheric pollution in Québec.

Pb isotope ratios for ~30 snow cores obtained during the 1993 and 1997 winters show a strong correlation with geographic location, with those from within the St. Lawrence River Valley having the highest $^{206}Pb/^{207}Pb$ ratios (between 1.180 - 1.190). In addition, $^{206}Pb/^{207}Pb$ values decrease from Montréal (~1.190) to the Gaspé-North Shore region (~1.160). Compared to the Pb isotope ratios for snow samples within the St. Lawrence River Valley, those for lichens from proximal areas give similar values; however, marked differences are noted outside the Montréal - Québec City corridor. Along the northern transect (from Noranda to James Bay), $^{206}Pb/^{207}Pb$ ratios for most snow samples decrease systematically (from 1.179 to 1.148). Pb concentrations for most snow samples range from 0.1 to 1.0 ppb, with the highest concentrations found in samples proximal to major urban centres and smelting operations at Noranda (~2.5 ppb). Moreover, Pb concentrations are negatively correlated with pH values (range from 4.1 to 5.1). $^{87}Sr/^{86}Sr$ values for the snow samples are negatively correlated with their Pb isotope ratios, and define a bimodal distribution (<0.708 or >0.709), with those from the northern transect containing the most radiogenic values (~0.710 to >0.720).

Trace element concentrations (obtained by ICP-MS) for various heavy metals (Pb, Cu, Zn, Cd) indicate that they are positively correlated. Pb/Al enrichment factors (*vis.* continental crust) for the snow samples analysed range from 200 to 1500 and are negatively correlated with $^{206}Pb/^{207}Pb$ ratios. Of interest, Zn abundances for snow samples within the Gaspé Peninsula (range from 44 to 165 ppb) are 2 to 5 times higher compared to the remaining samples, and may reflect atmospheric emissions from 'local' smelting activities at Murdochville. In addition, correlations between $^{87}Sr/^{86}Sr$ values and Sr/Al enrichment factors (>50) indicate that atmospheric sea-salts are an important component in snow samples located proximal to Hudson Bay.

One major drawback in using snow profiles is the lack of 'resolution' that is conveyed within a bulk snow profile. It does not permit to distinguish between 'wet' and 'dry' deposition events, which may correspond to radically different climatic conditions, nor delineate between air masses in provenance from different geographic areas.

Consequently, during the past four months we have been using wet-only precipitation samplers from two meteorological stations located within the St. Lawrence Valley, proximal to Montréal. In addition, during the spring and summer of 1998 we will also sample individual precipitation events from a meteorological station located ~900 km northeast of Montréal at the mouth of the St. Lawrence River. The advantages in using this approach are that Pb and Sr isotopic compositions will be obtained for individual, major precipitation events and these results will be combined to simultaneously collected meteorological data used to perform air-mass back trajectory analyses. To-date, Pb isotope compositions were measured for 5 individual precipitation events for each station and $^{206}Pb/^{207}Pb$ ratios are variable (from 1.160 to 1.177). Pb concentrations and pH values are also negatively correlated and vary from 0.2 to 1.0 ppb and 4.2 to 4.7, respectively. Compared to snow profiles retrieved in 1997 from proximal sites within the St. Lawrence Valley, Pb concentrations and pH values measured for the individual precipitation events are similar but the $^{206}Pb/^{207}Pb$ ratios are slightly lower. In addition, $^{206}Pb/^{207}Pb$ ratios for 1998 snow cores retrieved for 6 sites from Vermont and New York states range from 1.170 to 1.197; those sampled north of latitude 44°N (n = 4) give Pb isotope compositions similar to those recorded at the two meteorological stations within the St. Lawrence Valley, whereas the two southernmost samples record more radiogenic values (1.184 and 1.197). Compared to proximal sites sampled in 1997, the less radiogenic Pb isotope compositions measured for 1998 samples and NE United States suggest a smaller contribution of anthropogenic Pb from US sources. A feature which may be attributable to the extremely different climatic conditions prevailing this year as the result of El Niño.

In summary, the Pb isotope data for the snow samples form linear arrays in Pb-Pb isotope diagrams indicative of mixing between at least three distinct end-members. Snow samples within the St. Lawrence River Valley suggest a mixture of anthropogenic Pb from USA ($^{206}Pb/^{207}Pb$ ~1.22) and Canadian ($^{206}Pb/^{207}Pb$ ~1.15) sources, consistent with the interpretation based on the Pb isotope data for lichens from the same region. The third end-member may consist of atmospheric pollution from Eurasia transported over the high Arctic during the winter season. Moreover, the distinct Pb isotope domains based on results for snow samples from Québec may be attributable to seasonal changes in atmospheric circulation pathways, namely southward migration of the polar front from 60–70°N to below latitude 50°N during the winter. During the spring and summer of 1998, we will continue sampling individual precipitation events in order to address the seasonal variability in the transport of atmospheric pollutants over northeastern North America.

References

Carignan, J. and Gariépy, C. (1995) *Geochimica Cosmochim. Acta*, **59**, 4427–33.