

TRACING THE SOURCES OF ATMOSPHERIC POLLUTION ON A GLOBAL SCALE VIA LEAD ISOTOPES IN AEROSOLS

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Abstract

Colleagues and associates operating easy to use sampling kits have collected more than 400 aerosol samples from ~170 sampling sites distributed worldwide. Sampling occurred over two periods: 1994-96 and 1997-99. Spot sampling was carried out in the early period, whereas selected sites were sampled continuously in the latter period. A global map of $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ isotopic signatures in aerosols has been established. At the sampling sites where leaded petrol is still in use, the isotopic composition of airborne Pb was mainly determined by the alkyllead used in petrol as an antiknock agent. Changes in comparison with isotopic ratios reported earlier were detected in the U.S. and Europe and are due to both, an increase in the relative contribution of industrial Pb to the atmospheric Pb levels and long- and mesoscale transport of Pb.

1. Introduction

Organic Pb-compounds introduced in the 1920s as antiknock agents in leaded petrol significantly polluted the environment with Pb. Due to health risks the average Pb content of leaded petrol was reduced in 1982 and finally it was phased out in 1989 in the U.S. (Nriagu, 1990). Today, the largest sources of Pb in the U.S. are metal processing plants. In Canada the phasing out of leaded petrol began in 1987 and was complete in 1992. In Europe, Austria was the first country to ban leaded petrol, Sweden and Germany followed in the 1990s and were joined by the U.K. and France in 2000. However, as leaded petrol is still available in many countries and emission regulations are poor, imbalances in global Pb emission fluxes lead to an effective dilution of Pb in some countries and contamination of others via long and meso-scale transport. Differences in source isotopic signatures provide an effective mean of monitoring this transport of pollution. Also, due to the introduction of unleaded petrol, the relative contribution of industrial emissions to the atmospheric Pb increases. Provided the petrol and industrial Pb have different isotopic compositions this will be reflected in a shift in the isotopic composition of aerosols.

Large variations in lead isotope abundance exist in nature and provide the basis for following the path of lead through the environment. The lead isotopes ^{206}Pb , ^{207}Pb and ^{208}Pb are formed by the radioactive decay of ^{238}U , ^{235}U and ^{232}Th , respectively, ^{204}Pb is primordial only. Variations in isotopic composition arise from differences in the age of ore bodies and the initial chemical composition of their source rock. Mixing of lead from different primary ores during industrial processing and recycling reduces the variations, but they are still large compared with the available precision of thermal ionization mass spectrometry.

Most investigations using Pb isotopes to study the pollution of the atmosphere have been regional. Few data are available for the southern hemisphere and many of the Pb isotopic signatures available originate from times when leaded petrol was a major source of atmospheric Pb. U.S. aerosols have been characterized by $^{206}\text{Pb}/^{207}\text{Pb}$ ($^{208}\text{Pb}/^{207}\text{Pb}$) isotopic ratios of 1.18 - 1.22 (2.42 - 2.47); Canada 1.15 - 1.19 (2.42 - 2.44), Eastern Europe 1.15 - 1.18 (2.41 - 2.43), Western

Europe 1.10 - 1.16 (2.38 - 2.41), or Asia 1.07-1.21 (2.34-2.46) (Flegal et al., 1993; Mukai et al. 1993; Rosman et al., 1994; Carignan and Gariépy, 1995; Monna et al., 1997). Our study significantly expands the available Pb isotope data.

2. Sampling and Methods

Sampling kits consisted of a small diaphragm type aquarium-pump modified to invert the airflow, 2-3 m of PVC tubing and a polystyrene housing fitted with a Teflon backing filter (pore size 30-60 μm) and a Teflon front filter (pore size 0.45 μm). The filters collected air for periods of 1-60 days. A sector of the filter was leached in 0.4M HBr for one hour under HEPA-filtered air flow and Pb was separated from the leach solution using HBr/HCl column chemistry and Biorad AG 1x8 ion exchange resin. The blank for sample processing was always less than 4% of the total Pb measured.

Isotopic and concentration measurements were carried out with a VG354 isotope ratio mass spectrometer using the multi-collector configuration for high precision. The samples were thermally ionised from a zone-refined rhenium filament and ionisation was enhanced with a silica gel/phosphoric acid mixture. Repeated measurements of NIST SRM981 were used to correct for instrumental fractionation which indicated a bias of (0.12 ± 0.05) % per mass unit for measurements on the Faraday collectors, and (0.24 ± 0.06) % per mass unit for measurements on the Daly collector.

3. Results

3.1. Eastern United States

The most radiogenic $^{206}\text{Pb}/^{207}\text{Pb}$ ($^{208}\text{Pb}/^{207}\text{Pb}$; $^{206}\text{Pb}/^{204}\text{Pb}$) ratios measured in 1994-99 were 1.197-1.231 (2.459-2.470; 18.89-19.39) in Tampa, FL, and Manhattan, NY. The highest Pb level of atmospheric Pb (107 ng per m^3) was detected in Manhattan. Aerosols collected in Woods Hole, MA, in the northeast of the U.S. exhibited comparatively low radiogenic airborne Pb with values of 1.173 - 1.196 (2.437 - 2.451; 18.33-18.69). The range of the isotopic ratios is larger than ranges previously reported for the U.S. (fig. 1) (Rosman et al., 1994).

3.2. Western United States

Isotopic $^{206}\text{Pb}/^{207}\text{Pb}$ ($^{208}\text{Pb}/^{207}\text{Pb}$; $^{206}\text{Pb}/^{204}\text{Pb}$) ratios in the American West as low as 1.159 (2.426; 18.10) have been measured in Berkeley, CA. The most radiogenic ratios of 1.188 (2.446; 18.57) were detected in Pasadena, CA. These ratios are in general lower than ratios previously reported for the Pb isotopic composition of airborne Pb in the Western U.S. Pb concentration was low and ranged from 3-16 ng per m^3 .

3.3. Canada

The most radiogenic ratios in Canada were measured in Toronto, with a maximum of 1.171 (2.433; 18.30). The isotopic ratios of aerosols of that region agree well with ratios previously published by Carignan and Gariépy (1995). Ratios as low as 1.094 (2.365; 16.98) have been measured at a sampling site in Winnipeg and this is possibly caused by local sources. The Pb concentrations amounted to 1-16 ng per m^3 .

3.4. Europe

Whereas the isotopic composition of the aerosols in the UK did not change significantly in the past ~20 years, a change in isotopic composition compared with earlier measurements (Monna

et al., 1997) was detected in other parts of Europe. The $^{206}\text{Pb}/^{207}\text{Pb}$ ($^{208}\text{Pb}/^{207}\text{Pb}$; $^{206}\text{Pb}/^{204}\text{Pb}$) ratios measured in aerosols in the UK were 1.097 - 1.136 (2.372 - 2.412; 17.08-17.69) and are similar to $^{206}\text{Pb}/^{207}\text{Pb}$ ($^{208}\text{Pb}/^{207}\text{Pb}$) ratios of 1.096 - 1.129 (2.373 - 2.407) measured in earlier studies. The ratios measured in France in 1995-99 were 1.105 - 1.142 (2.381 - 2.410; 17.25-17.94) and more radiogenic than ratios reported earlier. This was also the case for German aerosols and a shift from 1.114 - 1.145 (2.377 - 2.420) in earlier data to ratios between 1.133 - 1.165 (2.405 - 2.440; 17.63-18.20) in our study occurred. In Eastern Europe and Russia the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of 1.148 - 1.164 are correlated with previous ratios but the $^{208}\text{Pb}/^{207}\text{Pb}$ ratios of 2.396 - 2.446 tend to be higher (fig. 2). $^{206}\text{Pb}/^{204}\text{Pb}$ ratios are 17.49-18.20.

3.5. Asia

All samples collected in China during our study showed an enrichment in ^{208}Pb . The ratios did not change significantly as compared with earlier studies (Mukai et al., 1993) and are 1.141 - 1.177 (2.435 - 2.467; 17.78 - 18.45). Japanese emissions were characterized by a comparatively small range of isotopic ratios between 1.153 (2.442; 17.94) in Kumamoto to 1.162 (2.443; 18.17) in Hiroshima. This range is in good agreement with values published by Mukai et al. (1993) of 1.159 ± 0.005 (2.433 ± 0.020) for the late 1980s and indicates a very stable isotopic signature of airborne Pb.

4. Discussion and Conclusion

4.1. United States

In 1997-99 there was a significant difference between isotopic ratios measured in aerosols from the East and the West coast of the United States. West coast aerosols were less radiogenic than those from the East coast but slightly higher than ratios measured in Canada (fig. 1). As total Pb emissions of the United States decreased by 98% between 1970 and 1995 industrial emissions and long range transport of pollution are getting relatively more significant in American air. Total Pb emission of Asia for example exceeded those of the U.S. by 3-4 fold in 1989 (Pacyna et al., 1995) and assuming that emissions from Asia did not decrease, a factor of > 10 seems more likely in 1999. A recent study by Jaffe et al. (1999) has shown that Asian emissions reach the West Coast of the U.S. 13% of the back-trajectories reaching the American West Coast crossed over Asia and reached the U.S. within ~10 days. These air-masses carry Asian anthropogenic emissions and might account for the ^{208}Pb enrichment in West Coast aerosols since Chinese aerosol Pb is relatively enriched in ^{208}Pb . However, we can not exclude the possibility that the isotopic composition changed due to a relative increase in industrial emissions of airborne Pb. An enhanced use of Mexican, Peruvian and Canadian Pb ores in primary Pb industries on the West coast could also account for the shift in isotopic ratios. ~30% of refined Pb imports to the U.S. originate from Peru or Mexico, the remaining 70% are imported from Canada (Roskill, 1996). Mixing of domestic Mississippi valley type Pb ores with these imported ores can also explain the shift observed (see fig. 1).

4.2. Europe

In Europe the $^{206}\text{Pb}/^{207}\text{Pb}$ ($^{208}\text{Pb}/^{207}\text{Pb}$) ratios are < 1.135 (< 2.405) at the southwestern sites and increase in a north-easterly direction. Maximum values measured in north-eastern Germany were 1.165 (2.440) similar to Eastern European and Russian emissions. The highest ratios measured in Constance and Plön (Germ.), and Venice (It.) occurred in winter. As the

ambient Pb concentrations do not change significantly between summer and winter samples at these sites a local inversion is unlikely to be responsible for the shift of the isotopic composition of the aerosols. Also, there is no leaded petrol available in Germany so that a change in alkyllead isotopic composition can be excluded. The variation in isotopic composition can best be explained by a seasonal changing influence of emissions from Eastern Europe: relatively more influence in winter than summer. As Constance and Plön are located closer to Eastern Europe and Russia and the concentrations of Pb in ambient air are 2-10 fold less than at the other sites, the influence of Eastern European and Russian emissions is expected to be more pronounced. In addition, the seasonal variations found are consistent with local annual wind patterns at Constance (Wessels, pers. comm.).

We cannot exclude the influence of local sources, e.g. domestic and industrial heating from coal, which usually exhibit relatively radiogenic ratios. This influence is expected to be greater during winter and similar effects might be expected at other sampling sites in Europe. However, this was not evident in the data and we conclude that the variations observed in north-eastern Europe were primarily caused by a relative increase from Eastern European emissions. Because of the similarity between industrial and Eastern European or Russian Pb isotopic signatures the later are more difficult to identify. Isotope data combined with meteorological data could be effectively used to identify the origin of pollutants even when the differences in source signatures are small.

4.3. Asia

Most of the domestic ores from China are enriched in ^{208}Pb relative to other common ores (Quisheng, 1986). The use of these ores for industrial purposes and in the production of alkyllead may be responsible for the relative enrichment of ^{208}Pb in Chinese aerosols. Also, as shown in figure 2, the isotopic ratios of airborne Pb in China are possibly influenced by Pb emissions from coal burning as indicated earlier by Mukai et al. (1993). The reason for the narrow range of the isotopic ratios in Japanese aerosols is not known but may be due to mixing of many different industrial sources. It seems unlikely, however, that the different sources (industries, coal burning, incinerators) mix at the different places to the same extent as discussed by Mukai et al. (1993). The main energy source in Japan is oil and the main automotive fuel is LPG. If one or both of these contain a significant amount of Pb and isotopic compositions were similar (in the refinery process they are manufactured from the same crude oil) this might explain the source and narrow range of the Pb isotopic composition in Japan.

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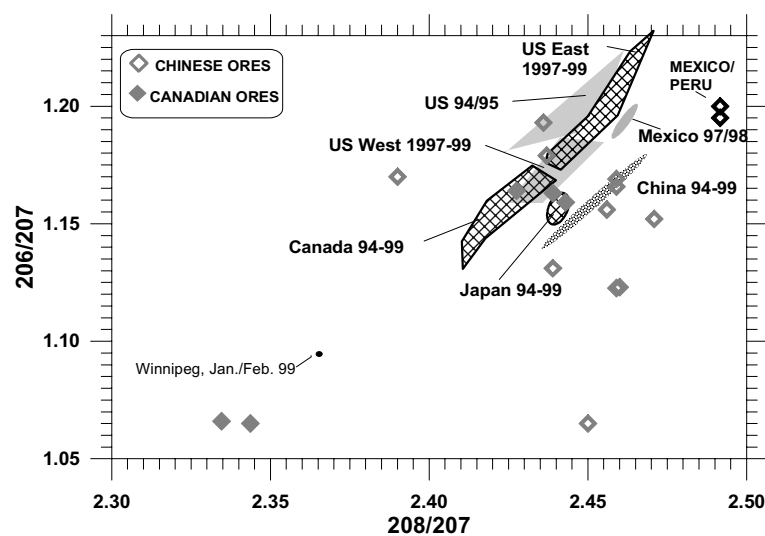


Fig. 1: $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$ of aerosols collected in the U.S., Canada, Mexico, China, and Japan. Diamonds indicate the isotopic compositions of ores (Doe, 1970; Chow et al., 1975; Qiusheng, 1986).

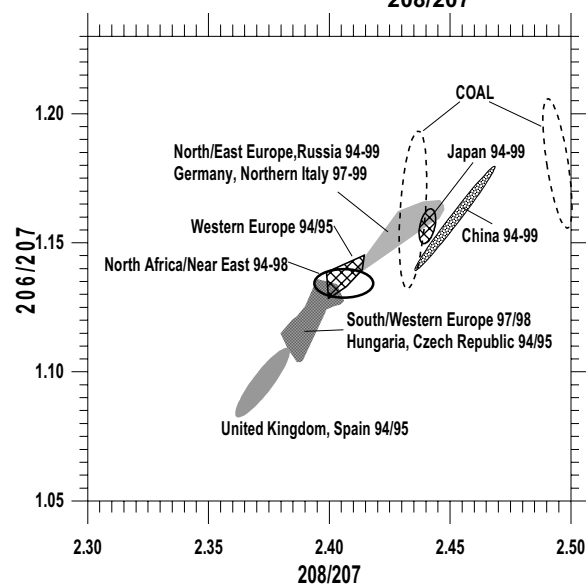


Fig. 2: $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$ of aerosols collected in Europe, North Africa and the Near East. In addition the range for the isotopic composition of Chinese coals is indicated (Mukai et al., 1993).