

# Regional source discrimination of atmospheric aerosols in Europe using the isotopic composition of lead

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## ABSTRACT

$Pb^{206}/Pb^{207}$  and  $Pb^{208}/Pb^{207}$  isotope ratios were measured in a series of daily atmospheric aerosol samples collected in southern Sweden between 9 February and 30 May 1988. The ratios were observed to vary considerably, depending on the origin of air. 5-day back-trajectories were used to classify the samples according to source region: Northwest, Western Europe, East, Eastern Europe, or a combination of two regions. Significant differences in the isotope ratios were found. Unique signatures based on the  $Pb^{206}/Pb^{207}$  and  $Pb^{208}/Pb^{207}$  ratios could be assigned for each region. The signatures were generally consistent with isotope ratios of Swedish and other European gasolines, and with literature values of the isotope ratios of economically significant lead ores used in Europe. A comparison was made between the regional signatures and the  $Pb^{206}/Pb^{207}$  ratios observed in Arctic aerosol samples. Excellent agreement was observed between the Arctic  $Pb^{206}/Pb^{207}$  ratios (1.160) and an average source signature (1.156) calculated from observations in this study using equal contributions from Western Europe, Eastern Europe, and the East as predicted by a chemical transport model.

## 1. Introduction

Atmospheric lead (Pb) is of interest in environmental studies because of its potential toxicity and its characteristic association with specific sources of atmospheric pollutants, such as automobile exhaust and smelter emissions (Nriagu and Pacyna, 1988). Because it is concentrated mostly in sub-micrometer particles when it is released to the atmosphere, it can be transported long distances and deposited over large areas of the Earth. For instance, anthropogenic lead well in excess of natural lead has been detected in Antarctic glaciers (Boutron and Patterson, 1987) and in the Arctic atmosphere (Sturges and Barrie, 1989b).

Reliable identification of sources of lead in the environment is normally difficult to achieve because of the difficulty in discriminating between sources of lead solely by the lead concentration. Two approaches have been devised to overcome this problem. One involves identifying differences in the multielemental composition of atmospheric aerosols. Swietlicki (1989) has utilized this approach to investigate sources of many elements, including lead, observed in atmospheric aerosols in southern Sweden. The other approach, used in this paper, exploits differences in the lead isotopic composition. The isotopic composition can vary significantly in different ore bodies, reflecting differences in geological age and geochemical cycling processes. The four stable isotopes of lead are  $Pb^{204}$ ,  $Pb^{206}$ ,  $Pb^{207}$ , and  $Pb^{208}$ . They are present in nature in average proportions of 1:17:15:37. If major sources of lead in the environment utilize lead from different ore bodies, then an isotope signature can be used to assess the relative impacts

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of various sources. This has obvious application to control strategies and emission reduction policies.

The lead isotope signature technique has been used many times in the past (e.g., Rabinowitz and Wetherill, 1972; Stukas and Wong, 1981), but it has most often been limited to local studies or specific site problems. More recently, it was applied on a large scale (Flegal et al., 1989) following the discovery that in North America in the mid-1980's there were significant differences in the  $Pb^{206}/Pb^{207}$  ratio in atmospheric aerosols originating from American automobiles, Canadian automobiles, and Canadian non-ferrous smelters (Sturges and Barrie, 1987). The major differences were attributed to the widespread use of organo-lead anti-knock additives in gasoline, and to national economic influences in the selection of sources of lead for these additives. The observed variations in  $Pb^{206}/Pb^{207}$  ratios were used to carry out a source apportionment for atmospheric lead at monitoring sites far removed from some of these sources (Sturges and Barrie, 1989a; Hopper and Barrie, 1988).

Studies of isotopic differences of atmospheric lead on a similar large scale have not previously been carried out in northern Europe. A study of the historical record of lead concentrations and lead isotope ratios in Belgian pond sediments (Petit, 1983) indicated that anthropogenic emissions of lead have dominated "natural" levels in the past century, and that the  $Pb^{206}/Pb^{207}$  ratio in the sediments has changed significantly with time. Both of these are necessary conditions for the application of the isotope signature technique. However, these data represent integrated measurements and have neither the accompanying source signatures nor the time resolution required to perform a source apportionment. An exploratory study by Maring et al. (1987) using atmospheric aerosol samples suggested that the technique might be successfully applied in southern Europe, but the limited number of samples analyzed in that study prevented source identification on a broad scale.

The present study was undertaken to measure atmospheric lead concentrations and isotopic composition at a site in northern Europe in order to assess the potential for regional source identification. If such an application proved feasible, then it would give valuable insights into the predominant sources of lead-containing atmo-

spheric aerosols in the European community, and into the long-range transport of these pollutants. Moreover, the monitoring site was located along one of the principal pathways by which atmospheric pollutants are introduced into the Arctic. Much of the air pollution in the Arctic atmosphere is believed to originate from Eurasian sources (Barrie, 1986; Akeredolu et al., 1990). Better knowledge of the isotopic composition of lead in northern Europe combined with observations of lead isotopic composition in the Arctic (Sturges and Barrie, 1989b) could assist in determining the possible contributions of European source regions to lead in remote northern regions.

## 2. Experimental

### 2.1. Sample collection

The sampling site was located at Aspvreten, Swedish Environmental Protection Board, Air Chemistry Laboratory, on the eastern coast of central Sweden (Fig. 1). Stockholm (1986 population 1,450,000), 100 km north of the site, is the largest anthropogenic source of atmospheric aerosols in the area. Two smaller cities, Nyköping (population 64,000) and Nörrköping (population 84,000), may have influenced samples collected during periods of westerly or southwesterly flow, but their contributions are believed to be small. In addition, a steel mill at Oxelösund, 25 km southwest of Aspvreten, releases about 15 tonnes  $a^{-1}$  of Pb. Despite these local sources, the sampling site was well placed to observe uninterrupted transport from the Soviet Union and Eastern Europe. Air trajectories from the United Kingdom and Western Europe crossed Danish and southern Swedish sources before reaching Aspvreten, but Scandinavian sources are not expected to have dominated the observed lead at Aspvreten during strong transport situations. This has been well documented for aerosol sulphate (Rodhe et al., 1972), which can be used as a reasonable surrogate for aerosol lead (Ross, 1986; Ross, 1987). Thus, samples collected during strong transport situations should be representative of the regional plumes from Europe.

Daily aerosol samples were collected between 9 February and 30 May 1988, on 20 cm  $\times$  25 cm Whatman 41 filters using a Sierra high-volume sampler with 15  $\mu$ m size-selective inlet operating at

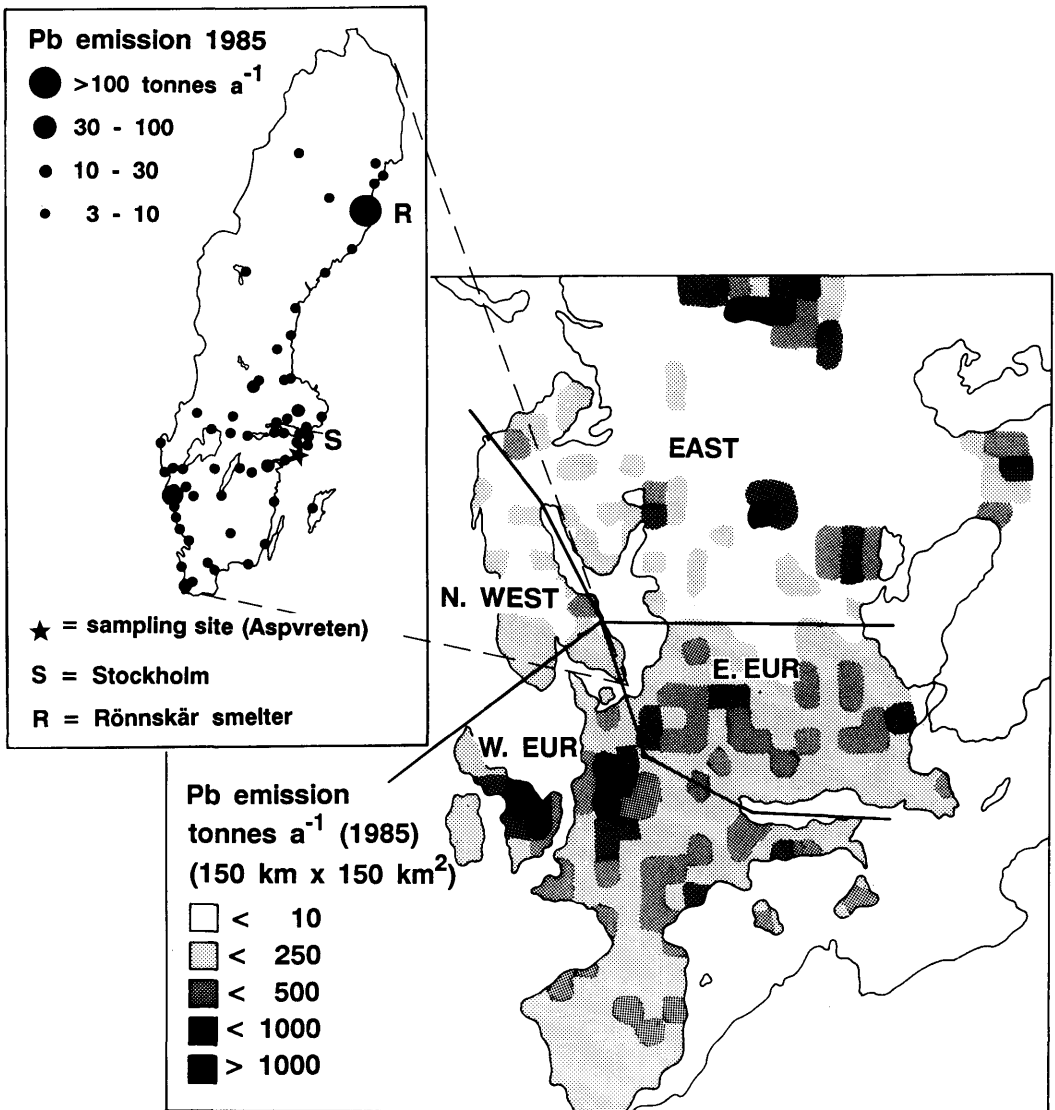


Fig. 1. The distribution of annual Pb emissions in Europe in 1982 and in Sweden in 1985 (Semb and Pacyna, 1988; Monitor, 1987). Boundaries of the regional sectors used for trajectory classification have been superimposed.

18.9 liters s<sup>-1</sup>. Samples were changed each day at 15.00 hours local time. The collector was located on the roof of a small building in a forest clearing. During the first week of the sampling period, two filters were loaded back to back in the sampler to check the collection efficiency. A field blank was taken each week by loading a blank filter into the collector but not sampling through it. Field blanks were subsequently handled identically to the

sample filters. Additional samples were collected in Stockholm at the end of the sampling period to provide an indication of the isotopic composition of Swedish automobile lead.

Field blanks and exposed filters were placed in sealed plastic bags for transport to the University of Stockholm. There, under Class 100 clean room conditions, the filters were cut into four equal portions. A portion of each filter was analyzed for lead

concentrations and lead isotope ratios by ICP-MS (inductively coupled plasma, mass spectrometry) at the central laboratory of the Ontario Ministry of the Environment, Toronto, Canada. Samples and field blanks were treated identically, and were always handled in a protected environment using clean plastic gloves.

### 2.2. Sample preparation

Filter portions were placed in 100 ml Pyrex beakers, covered with a watch glass, and ashed in a muffle furnace (1 h with a linearly increasing temperature from 20°C to 475°C, then a constant 475°C for 2 h). The ash was digested with high-purity (Aristar, BDH Limited) hydrochloric and nitric acids, and a thermal treatment. The final extracts were prepared as 1 ml concentrated HNO<sub>3</sub> and 30 ml DDW (distilled de-ionized water).

All glassware and sample tubes were cleaned before use by soaking in 20% HNO<sub>3</sub> for at least 24 h, followed by soaking in DDW for another 24 h, then a rinse with fresh DDW and low-temperature (60°C) drying in a sealed oven. Glassware and tubes were sealed in polyethylene bags until use.

Sample and field blank filter portions were processed in batches. Each batch was nominally comprised of 14 sample filters, at least 1 field blank filter, and several quality control (QC) samples. The latter consisted of one or more of each of the following: method blank (empty beaker, carried through ashing, digestion, and analysis); reagent blank (1 ml concentrated HNO<sub>3</sub> and 30 ml DDW, prepared at end of a batch digestion, for analysis only); composite QC (1 to 5 ml of an aqueous composite solution containing 14 metals at a concentration of 5 µg ml<sup>-1</sup> each, added to a clean beaker and carried through ashing, digestion, and analysis); SRM QC (weighed amounts of powdered Standard Reference Materials such as NBS1648 Urban Particulate Matter, NBS1633a Trace Elements in Coal Fly Ash, and NRCC MESS-1 Marine Sediment Reference Material, weighed into an empty beaker and carried through ashing, digestion, and analysis).

### 2.3. Sample analysis

ICP-MS was used to determine lead isotope ratios and lead concentrations simultaneously. The instrument has a typical precision of

0.2%–3% RSD (Relative Standard Deviation) for 5 replicate measurements of an isotope ratio. This can be compared to thermal ionization mass spectrometers which have a precision of 0.01%–0.1% RSD. However, the advantage of ICP-MS is a much higher sample throughput.

ICP-MS instrument settings were optimized for Pb<sup>208</sup> before analyzing each batch of samples. The Pb<sup>206</sup>/Pb<sup>207</sup> and Pb<sup>208</sup>/Pb<sup>207</sup> ratios were measured in each sample and the raw isotope intensities were also recorded. The lead concentration and lead isotope data reported here are averages of 5 replicate measurements of ion intensities for each lead isotope. Two quality assurance solutions were prepared from standard reference materials (NBS981, NBS982) with a certified lead isotopic composition. A 100 ng ml<sup>-1</sup> solution of NBS981 was analyzed every 5 samples, and a normalization factor calculated from the measured and certified isotope ratios. Linearly interpolated normalization factors were then used to correct sample isotope ratios for slight offsets due to mass calibration or instrument drift. Such correction factors were normally very small; ratio corrections caused by instrument drift were usually less than 0.4% h<sup>-1</sup>, and never exceeded 0.7% h<sup>-1</sup>. Dilute solutions of NBS982 were analyzed occasionally to verify that this mass normalization procedure was working satisfactorily and to assess the accuracy of the method. At lead concentrations of 10 times the instrument detection limits or higher, the differences between the measured and “true” NBS982 isotope ratios (calculated from the certified isotope abundances) were always less than the precision of the measurements.

A “total” lead concentration was calculated from the sum of the ICP-MS ion intensities of the stable lead isotopes in each sample. This was referenced to a similar “total” lead concentration in the 100 ng ml<sup>-1</sup> NBS981 standard. The concentration of this standard was verified by ICP-OES (ICP optical emission spectroscopy) and atomic absorption spectroscopy. By calculating lead concentrations in this manner, determinate errors in the total lead concentration caused by variability in the isotopic composition of the sample were minimized. A regression of ICP-MS “total” lead against ICP-OES concentrations for 77 samples showed no significant difference between the two measurements ( $r^2 = 0.95$ , slope =  $0.96 \pm 0.03$ , intercept =  $8.53 \pm 29.1$ ).

The ICP-MS instrument detection limit for lead concentration was less than  $0.1 \text{ ng ml}^{-1}$ . Method detection limits were actually limited not by the instrument sensitivity, but by trace amounts of lead in the filters, acid reagents, and contamination during handling of the filters. The mean lead concentration in the field blank filter portions was  $3.24 \pm 0.72 \text{ ng ml}^{-1}$  (approximately equivalent to  $0.25 \text{ ng m}^{-3}$  of aerosol lead) which, based on results from the different types of quality control blanks, was divided roughly 40:60 between sample handling, and reagents/filter media.

Results from seven breakthrough test samples indicated an average retention efficiency on the first filter of 93%–98%. Percent recoveries of lead for the digestion method averaged 98% for the composite QC (an aqueous spike), and 84% for the powdered SRM QC materials. Corrections for less than 100% recoveries have not been applied to the lead concentrations reported here. While the recoveries from the powdered SRMs were lower than the essentially complete recoveries obtained with the aqueous spikes, the powdered SRMs were used only as approximate surrogates for Swedish atmospheric aerosols in order to verify a reasonably high recovery with solid materials.

The measured concentrations and isotope ratios were screened for detectability (i.e., significantly above blank levels) by two criteria:

- I reject if total lead concentration  $< 5.4 \text{ ng ml}^{-1}$
- II reject if  $\delta$  ratio  $> 1\%$   
or if  $\delta$  ratio  $> \% \text{RSD}$  of sample measurement

where  $\delta$  ratio is the normalized concentration-weighted bias added to the observed sample ratio from the filter media.

Criterion I compared the sample lead concentration to the mean plus three times the standard deviation of the lead concentration in the field blanks ( $5.4 \text{ ng ml}^{-1}$ ). There were no samples that failed this criteria. Criterion II assessed the effect of trace lead from the blank filters and sample preparation on the isotope ratios at low sample lead concentrations. An estimate of the perturbation in each sample ratio caused by the finite amount of lead in the blanks was calculated from the measured sample concentration and isotope

ratios (assumed to be the sum of lead from aerosols, and lead from the filters and reagents), and the mean concentration and ratios in the field blanks. Because the lead concentrations in the field blanks were so low, several portions of different field blank filters were pooled to provide reliable ratio measurements. The average  $\text{Pb}^{206}/\text{Pb}^{207}$  and  $\text{Pb}^{208}/\text{Pb}^{207}$  ratios in the field blank filters were 1.18 and 2.45, respectively. The calculated perturbations in the ratios were then compared to the measurement precision of the ratios, and would have been rejected if the calculated error exceeded the measurement error. Again, there were no samples that failed this criteria.

The validity of these criteria was substantiated during early attempts to include sample ratios based on  $\text{Pb}^{204}$  abundances; a significant fraction of samples were rejected after failing to pass these criteria, and  $\text{Pb}^{204}$  was subsequently dropped from the analysis program. Either higher lead concentrations in extracts, on the order of  $100 \text{ ng ml}^{-1}$  or more, or longer integration times are required for reliable ICP-MS  $\text{Pb}^{204}$  ratios because of the relatively low abundance of this isotope.

### 3. Observations

#### 3.1. Lead concentrations and isotope ratios

The observed total lead concentrations,  $\text{Pb}^{206}/\text{Pb}^{207}$  ratio, and  $\text{Pb}^{208}/\text{Pb}^{207}$  ratio in daily samples from Aspveten from 9 February to 30 May 1988 and from Stockholm on 4 days in June 1988 are listed in Table 1 and Table 2. Time series of the Aspveten data are also plotted in Fig. 2 and Fig. 3. Aerosol lead concentrations are similar to those reported in other studies for this area. Of note are the occasional episodes of elevated lead concentrations. Values of the isotope ratios for these groups of samples are fairly homogeneous within an episode, indicating consistency in sample collection and analysis. The mean precision of the ratios is indicated by the average 1-sigma error bars in Fig. 3. The range of variations in the  $\text{Pb}^{206}/\text{Pb}^{207}$  ratio significantly exceed the precision of individual sample measurements, suggesting at least two sources with distinct lead isotope signatures. The same inference can also be drawn from the  $\text{Pb}^{208}/\text{Pb}^{207}$  ratios (Fig. 3b), although there is considerably more noise caused by less precise measurements of this isotope ratio.

Table 1. *Aerosol Pb concentrations, Pb isotope ratios, and back-trajectory classifications at Aspveten, Sweden, from 9 February 1988 to 8 April 1988*

| Sample Date | Total Pb [ng m <sup>-3</sup> ] | Pb <sup>206</sup> /Pb <sup>207</sup> | Pb <sup>208</sup> /Pb <sup>207</sup> | Trajectory Sector | Sample Date | Total Pb [ng m <sup>-3</sup> ] | Pb <sup>206</sup> /Pb <sup>207</sup> | Pb <sup>208</sup> /Pb <sup>207</sup> | Trajectory Sector |
|-------------|--------------------------------|--------------------------------------|--------------------------------------|-------------------|-------------|--------------------------------|--------------------------------------|--------------------------------------|-------------------|
| 09-Feb      | 23.1                           | 1.146 ± 0.019                        | 2.411 ± 0.037                        | 0                 | 10-Mar      | 8.6                            | 1.116 ± 0.014                        | 2.399 ± 0.032                        | 0                 |
| 10-Feb      | 19.0                           | 1.142 0.017                          | 2.410 0.041                          | 1                 | 11-Mar      | 2.7                            | 1.124 0.012                          | 2.405 0.025                          | 2                 |
| 11-Feb      | 22.4                           | 1.148 0.009                          | 2.402 0.020                          | 1                 | 12-Mar      | 4.0                            | 1.127 0.009                          | 2.408 0.026                          | 2                 |
| 12-Feb      | 24.6                           | 1.110 0.010                          | 2.343 0.026                          | 0                 | 13-Mar      | 6.9                            | 1.126 0.016                          | 2.391 0.027                          | 2                 |
| 13-Feb      | 18.8                           | 1.130 0.011                          | 2.396 0.026                          | 0                 | 14-Mar      | 7.9                            | 1.150 0.017                          | 2.411 0.050                          | 2                 |
| 14-Feb      | 47.3                           | 1.128 0.011                          | 2.380 0.018                          | 1                 | 15-Mar      | 10.1                           | 1.149 0.011                          | 2.428 0.021                          | 2                 |
| 15-Feb      | 50.1                           | 1.166 0.015                          | 2.421 0.037                          | 6                 | 16-Mar      | 13.2                           | 1.142 0.010                          | 2.405 0.017                          | 0                 |
| 16-Feb      | 47.8                           | 1.177 0.014                          | 2.449 0.036                          | 6                 | 17-Mar      | 12.5                           | 1.155 0.007                          | 2.430 0.014                          | 4                 |
| 17-Feb      | 7.2                            | 1.161 0.009                          | 2.442 0.023                          | 5                 | 18-Mar      | 20.1                           | 1.137 0.006                          | 2.410 0.017                          | 2                 |
| 18-Feb      | 3.1                            | 1.162 0.017                          | 2.425 0.028                          | 4                 | 19-Mar      | 8.5                            | 1.114 0.011                          | 2.379 0.028                          | 2                 |
| 19-Feb      | 9.0                            | 1.133 0.014                          | 2.401 0.028                          | 4                 | 20-Mar      | 13.2                           | 1.151 0.010                          | 2.426 0.024                          | 3                 |
| 20-Feb      | 11.3                           | 1.105 0.016                          | 2.364 0.037                          | 2                 | 21-Mar      | 16.7                           | 1.141 0.010                          | 2.410 0.018                          | 5                 |
| 21-Feb      | 4.7                            | 1.156 0.021                          | 2.421 0.037                          | 0                 | 22-Mar      | 13.3                           | 1.144 0.007                          | 2.425 0.019                          | 4                 |
| 22-Feb      | 4.7                            | 1.154 0.015                          | 2.426 0.034                          | 5                 | 23-Mar      | 11.3                           | 1.141 0.015                          | 2.417 0.027                          | 4                 |
| 23-Feb      | 25.4                           | 1.164 0.012                          | 2.444 0.029                          | 4                 | 24-Mar      | 11.4                           | 1.150 0.018                          | 2.422 0.031                          | 5                 |
| 24-Feb      | 29.1                           | 1.166 0.016                          | 2.445 0.035                          | 4                 | 25-Mar      | 10.6                           | 1.148 0.015                          | 2.414 0.034                          | -9                |
| 25-Feb      | 25.6                           | 1.157 0.009                          | 2.437 0.023                          | 4                 | 26-Mar      | 12.9                           | 1.130 0.005                          | 2.404 0.014                          | -9                |
| 26-Feb      | 23.4                           | 1.159 0.021                          | 2.432 0.047                          | 4                 | 27-Mar      | 25.5                           | 1.143 0.012                          | 2.397 0.033                          | -9                |
| 27-Feb      | 11.5                           | 1.140 0.018                          | 2.412 0.024                          | 3                 | 28-Mar      | 15.2                           | 1.148 0.014                          | 2.412 0.032                          | -9                |
| 28-Feb      | 14.8                           | 1.168 0.010                          | 2.439 0.016                          | 4                 | 29-Mar      | 10.5                           | 1.153 0.020                          | 2.423 0.056                          | -9                |
| 29-Feb      | 22.6                           | 1.156 0.016                          | 2.433 0.035                          | 4                 | 30-Mar      | 23.1                           | 1.157 0.015                          | 2.417 0.035                          | 0                 |
| 01-Mar      | 17.9                           | 1.158 0.013                          | 2.426 0.031                          | 3                 | 31-Mar      | 23.8                           | 1.153 0.014                          | 2.415 0.026                          | 5                 |
| 02-Mar      | 14.2                           | 1.138 0.016                          | 2.417 0.039                          | 3                 | 01-Apr      | 20.8                           | 1.156 0.014                          | 2.432 0.034                          | 5                 |
| 03-Mar      | 25.8                           | 1.159 0.014                          | 2.436 0.038                          | 0                 | 02-Apr      | 17.6                           | 1.144 0.010                          | 2.420 0.018                          | 4                 |
| 04-Mar      | 36.9                           | 1.155 0.007                          | 2.423 0.022                          | 0                 | 03-Apr      | 19.6                           | 1.134 0.009                          | 2.397 0.019                          | 3                 |
| 05-Mar      | 8.2                            | 1.113 0.011                          | 2.350 0.027                          | 0                 | 04-Apr      | 33.3                           | 1.104 0.011                          | 2.335 0.033                          | 0                 |
| 06-Mar      | 9.4                            | 1.117 0.008                          | 2.379 0.020                          | 0                 | 05-Apr      | 7.6                            | 1.115 0.012                          | 2.391 0.027                          | 2                 |
| 07-Mar      | 14.1                           | 1.150 0.014                          | 2.430 0.034                          | 4                 | 06-Apr      | 16.3                           | 1.104 0.007                          | 2.375 0.025                          | 2                 |
| 08-Mar      | 16.4                           | 1.154 0.011                          | 2.435 0.026                          | 3                 | 07-Apr      | 9.8                            | 1.103 0.010                          | 2.385 0.026                          | 2                 |
| 09-Mar      | 19.4                           | 1.154 0.014                          | 2.440 0.033                          | 0                 | 08-Apr      | 1.8                            | 1.135 0.016                          | 2.428 0.039                          | 2                 |

na = data not available.

Trajectory Classification Codes:

|   |          |                                |    |        |  |
|---|----------|--------------------------------|----|--------|--|
| 1 | W. Eur.  | Western Europe.                | 5  |        | western USSR + Finland + eastern Europe. |
| 2 | N. West. | Sweden + northwest background. | 6  | E Eur. | eastern Europe.                          |
| 3 |          | Local (Sweden) + western USSR. | 0  |        | unclassified (ambiguous).                |
| 4 | East.    | western USSR + Finland.        | -9 |        | missing trajectory data.                 |

### 3.2. Trajectory analysis

In order to assist identification of source regions, 5-day back-trajectories of air parcels reaching Aspveten during the sampling program were calculated. The three-dimensional Lagrangian computer model used has been described previously (Olson et al., 1983). The back-trajectories of air parcels terminating at the 925 hPa level (i.e., approximately 750 m above sea level) every six

hours (12, 18, 00, 06, and 12 GMT) were plotted and grouped to correspond to the 24-h period of each sample. Trajectories associated with each sample filter were then reviewed and classified according to the sector outlines shown in Fig. 1. The sectors were chosen to correspond to major socio-economic blocks in Europe.

The accuracy of the classifications from this procedure depends not only on the accuracy of the computer model and calculations, but also on the



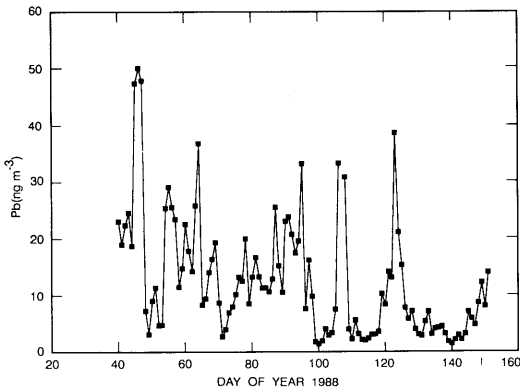


Fig. 2. Time series of daily average total aerosol Pb at Aspveten Sweden during spring 1988.

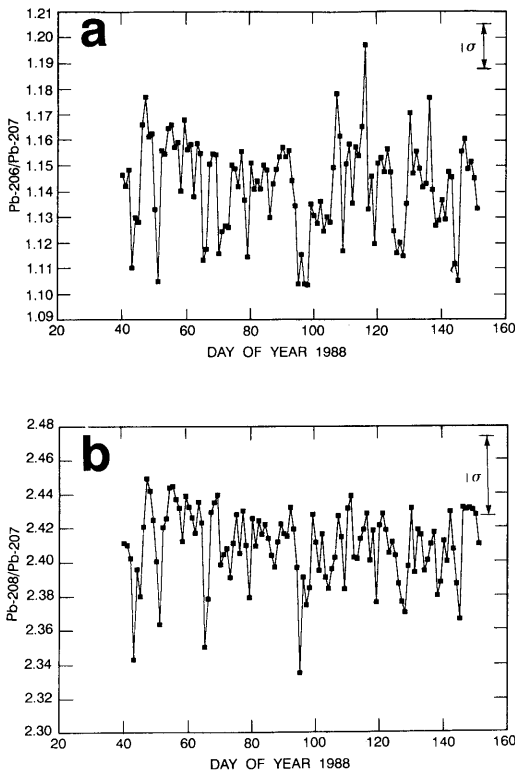


Fig. 3. Time series of the observed isotope ratios (a)  $Pb^{206}/Pb^{207}$  and (b)  $Pb^{208}/Pb^{207}$ . The 1-sigma bar indicates a typical precision for the isotope ratio measurements.

was reached between the trajectory analysts. The coded trajectory classification results are included in Table 1 and Table 2. Twenty-three percent of the trajectories meandered so much that they were not classified by the current scheme. This subset was not included in any of the calculations of regionally representative isotope ratios.

The dependence of  $Pb^{206}/Pb^{207}$ ,  $Pb^{208}/Pb^{207}$  and total lead concentration on trajectory sector is shown in Fig. 4 and Fig. 5. Only samples with classified trajectories were used to prepare these plots. In Table 3 characteristic ratios for the four source regions Eastern Europe, East (i.e., mainly Soviet Union), Northwest (i.e., Sweden, Norway and northern background) and Western Europe are listed. A consistent pattern for the isotope ratios is apparent. Of the six possible different pairs in the four source region set, three are significantly different at the 95% confidence level in both isotope ratios: Eastern Europe/Western Europe, Eastern Europe/Northwest and Northwest/East. One additional pair are different in  $Pb^{208}/Pb^{207}$  ratio only, namely Western Europe/East. The only source pairs that cannot be distinguished are those for the Eastern Europe/East and Western Europe/Northwest groups. The class of samples having trajectories from two sectors (Fig. 4) have isotope ratios that fall between those having trajectories solely from one or the other sector. This is consistent with a mixture of aerosols from the two regions.

The dependence of total lead concentration on trajectory sector (Fig. 5) shows that for the spring of 1988 the highest concentrations were from Eastern Europe (median  $48 \text{ ng m}^{-3}$ ) and then in order of decreasing lead came Western Europe, the East and the Northwest at 21, 13 and  $4 \text{ ng m}^{-3}$ , respectively.

These sector median concentrations agree reasonably well with the results of Swietlicki (1989). That study collected continuous 12-h samples from 3 island monitoring stations off the southeast coast of Sweden for more than a year, ending in December 1986. Samples were grouped into nine sectors according to air mass back-trajectories, but only  $\frac{1}{3}$  of the samples could be classified. When the 1986 sector geometric mean Pb concentrations are averaged to correspond to the sectors used in the current study (after weighting by the number of classified samples in each sector), the results are 19, 20, 3.4, and  $4.5 \text{ ng m}^{-3}$  for the East-



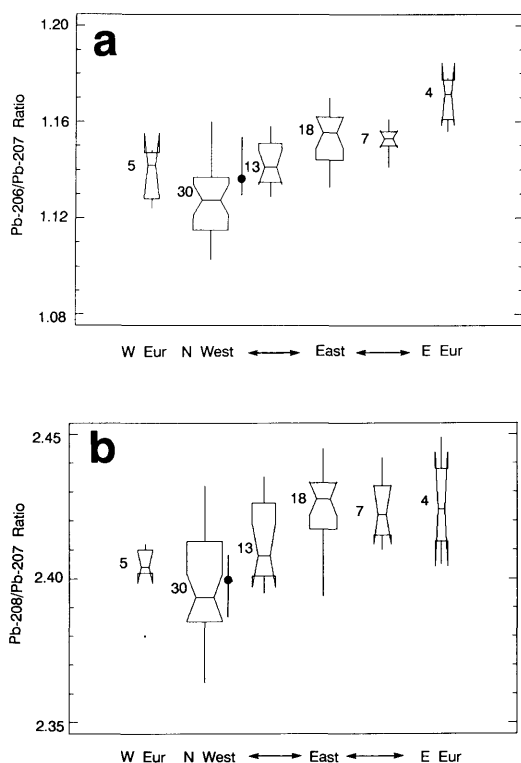


Fig. 4. The dependence of (a)  $Pb^{206}/Pb^{207}$  and (b)  $Pb^{208}/Pb^{207}$  ratios on the trajectory sectors defined in Fig. 1. The distribution of observations in each sector is represented by a notched box and whisker plot. The average and range of four Stockholm samples is included beside the Northwest box.

ern Europe, Western Europe, East, and Northwest sectors. The most significant difference is between the results for the Eastern Europe sector. It is unlikely that Pb emissions have doubled in Eastern Europe between 1986 and 1988. The high concentrations observed in spring 1988 are based

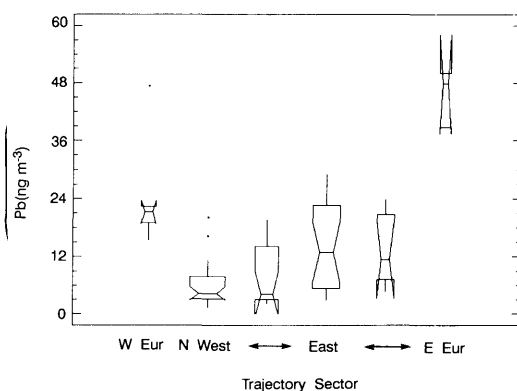


Fig. 5. As in Fig. 4, but for total Pb concentration.

on only a few samples, which may represent anomalously strong direct transport episodes from this sector. While these samples over-emphasize contributions from the sector, and would be inappropriate for apportionment calculations on an annual basis, this set does seem to represent an emission profile unobscured by emissions from other sectors so that the derived isotope signatures are clear and unambiguous.

Additional confidence in the current trajectory classification scheme can be gained from an examination of the relationship between  $Pb^{206}/Pb^{207}$  and  $Pb^{208}/Pb^{207}$  in daily samples for those days when the origin of air was clearly defined by trajectories (Fig. 6a) and when it was not well-defined (Fig. 6b). In Fig. 6a, symbols are used to differentiate samples from different sectors, and the median isotopic composition of each major source region from Table 3 is also plotted. On the days when the origin of air was clearly defined there is an approximately linear relationship between the two ratios. This picture would not change significantly if the data were added from those

Table 3. Characteristic lead isotopic composition for each of the regional sources (Fig. 1); the median and the 95% confidence limits (in brackets) on the median for pairwise comparison are given

| Source region              | $Pb^{206}/Pb^{207}$  | $Pb^{208}/Pb^{207}$  |
|----------------------------|----------------------|----------------------|
| Eastern Europe             | 1.172 (1.160, 1.185) | 2.424 (2.407, 2.443) |
| East (USSR, Finland)       | 1.153 (1.148, 1.162) | 2.428 (2.421, 2.433) |
| Northwest (Sweden, Norway) | 1.128 (1.222, 1.135) | 2.394 (2.385, 2.410) |
| Western Europe             | 1.142 (1.130, 1.155) | 2.405 (2.400, 2.410) |

samples when mixed air came from two sectors (Northwest-East, East-Eastern Europe).

The line calculated from the least squares regression of  $Pb^{206}/Pb^{207}$  on  $Pb^{208}/Pb^{207}$  is plotted in Fig. 6b. The samples used for this calculation included all samples with classified trajectories

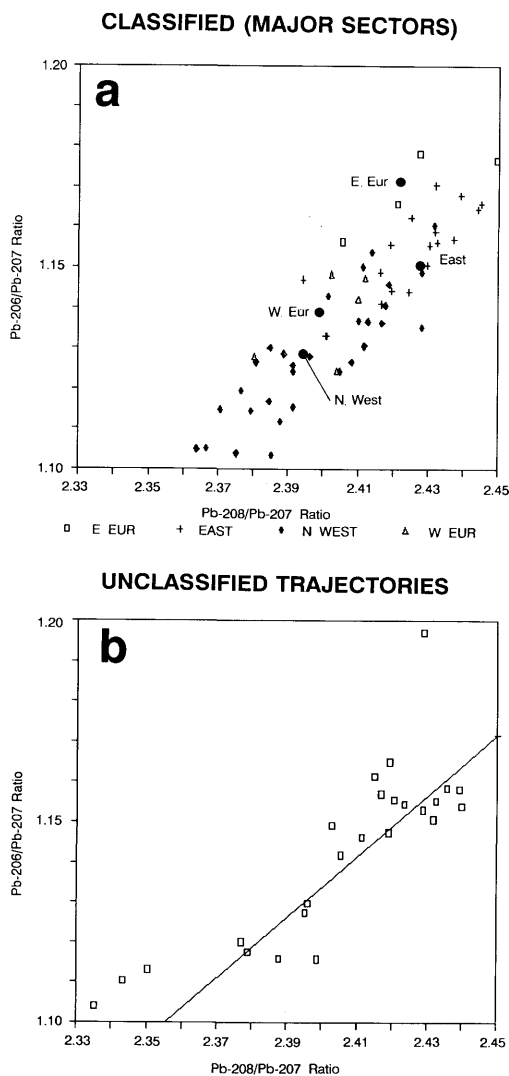


Fig. 6. (a)  $Pb^{206}/Pb^{207}$  versus  $Pb^{208}/Pb^{207}$  ratios for samples with well-defined trajectories originating in one of the four sectors. Median ratios for the four sectors are also indicated; (b)  $Pb^{206}/Pb^{207}$  versus  $Pb^{208}/Pb^{207}$  ratios for samples with ill-defined origin of air. The line is the least squares regression of  $Pb^{206}/Pb^{207}$  on  $Pb^{208}/Pb^{207}$  for all samples with classified trajectories.

(i.e., samples in Fig. 6a plus those samples with well-defined classified trajectories that crossed two sectors). To Fig. 6b have been added individual points for those days when the origin of air was ill-defined (Fig. 6b). Most of these points are scattered about the regression line calculated for those data of well-defined origin. This suggests that little or no systematic error was introduced into the characteristic regional ratios by the trajectory classification scheme. However, there are three outliers with low values of both isotope ratios. They are associated with somewhat high lead concentrations ( $24.6$ ,  $8.2$  and  $33.3 \text{ ng m}^{-3}$ ), and may have been influenced by a local industrial source.

There is an additional outlier in Fig. 6b with a very high  $Pb^{206}/Pb^{207}$  ratio which occurred on a day with a lead concentration of  $3 \text{ ng m}^{-3}$ . A number of other samples had very similar trajectories which passed over Finland and the Kola peninsula and, while the isotope ratios in those samples were very similar to one another, they were significantly different from the ratios observed in this sample. We have no explanation for this singular observation at this time, except to postulate a random analytical error in the measurement of the  $Pb^{207}$  isotope abundance, or a point source with a unique lead isotope signature.

## 4. Discussion

### 4.1. Relationship between sources of anthropogenic lead and regional lead isotope ratio signatures

Fig. 1 summarizes atmospheric emissions of Pb in Sweden and Europe for 1985 (Monitor, 1987; Semb and Pacyna, 1988). While total emissions of Pb to the atmosphere have decreased since these inventories were compiled, the qualitative picture of Pb emissions in Europe remains similar (J. M. Pacyna, personal communication). The largest changes have occurred in Western Europe, with the introduction of unleaded gasoline and with decreasing Pb content of other vehicle fuels. It is estimated that in 1988 the relative fraction of Pb originating from auto exhaust had decreased to 50% or less (J. M. Pacyna, personal communication). Nevertheless, automobile exhaust remains a major source of Pb in atmospheric aerosols in Europe, and will still be the predominant source of emissions from regions where lead-free fuels are

not yet widely available. Any discussion of lead isotope ratios in atmospheric aerosols must recognize the still significant influence of gasoline additives.

Table 4 is a compilation of lead isotope composition for major ore bodies that are sources of lead used in Europe. However, a direct comparison between the isotopic composition of ores and aerosols is difficult. There is little information in the open literature regarding the geological origins of lead used in fuel additives, and information on sources and suppliers is often considered confidential by commercial consumers. Some inferences can be drawn from sources within the industry and by making reasonable deductions.

Western European gasoline lead additive manufacture is dominated by the British company Associated Octel (AOC) and its European subsidiaries. Additives for gasoline in the United Kingdom are manufactured from a mixture of Australian and British Columbian ores, giving a probable average  $Pb^{206}/Pb^{207}$  ratio of around 1.09. Some tetra-alkyllead is imported from the United States which, assuming 25% imports with a  $Pb^{206}/Pb^{207}$  ratio of 1.20, will increase the probable average ratio to 1.12. The French, German and Italian subsidiaries of AOC are believed to use a

mixture of Australian and Moroccan ores which have  $Pb^{206}/Pb^{207}$  isotope ratios of around 1.04 and 1.16-1.17 respectively (Brown, 1962).

Previous measurements of lead isotope ratios in European atmospheric aerosol samples are summarized in Table 5. The  $Pb^{206}/Pb^{207}$  ratios measured in Western Europe are roughly consistent with the current estimate for United Kingdom gasoline, and the range of observed values confirms that significant differences do indeed exist between different regions. However, these literature values cannot be used as representative regional isotope signatures in the present study because the ratios can also vary with time. The choice of ore sources by industrial consumers is heavily influenced by changing economic, technological, and political circumstances. Hence reliable comparisons can only be made with isotope ratios measured during the same period.

The  $Pb^{206}/Pb^{207}$  and  $Pb^{208}/Pb^{207}$  ratios in the four Stockholm air samples average  $1.140 \pm 0.010$  and  $2.402 \pm 0.011$ , respectively (Table 2; Table 6). These samples were collected near a large highway in order to provide a current estimate of the average ratios in Swedish automotive fuels. These mean values are similar to the Western Europe signature of Table 3. Contact with the Swedish

Table 4. Lead isotope ratios in some major European, North African, and Soviet ore deposits (from Brown (1962) and Doe (1970) except as noted); if data for more than one ore body are available, an average and standard deviation for the region are listed

| Region   | No. ores | $Pb^{206}/Pb^{207}$ | $Pb^{208}/Pb^{207}$ |
|--|----------|---------------------|---------------------|
| Germany/Austria                                | 4        | $1.171 \pm 0.005$   | $2.457 \pm 0.003$   |
| Italy  | 2        | $1.161 \pm 0.017$   | $2.448 \pm 0.021$   |
| Greece   | 1        | 1.193               | 2.474               |
| Spain  | 1        | 1.167               | 2.469               |
| Sweden/Finland                                 | 4        | $1.010 \pm 0.025$   | $2.300 \pm 0.028$   |
| Eastern Europe <sup>1</sup>                    | 3        | $1.193 \pm 0.013$   | $2.486 \pm 0.015$   |
| Poland <sup>2</sup>                            | 1        | 1.179               | 2.469               |
| North Africa <sup>3</sup>                      | 5        | $1.173 \pm 0.012$   | $2.468 \pm 0.007$   |
| USSR (central/south)                           | 8        | $1.152 \pm 0.016$   | $2.437 \pm 0.017$   |
| USSR (Kola peninsula)                          | 2        | $1.065 \pm 0.054$   | $2.345 \pm 0.028$   |
| USSR (Siberia)                                 | 3        | $1.170 \pm 0.005$   | $2.459 \pm 0.007$   |
| USSR (small deposits) <sup>4</sup>             | 18       | $1.156 \pm 0.012$   | $2.439 \pm 0.024$   |
| USSR (average of above, except Kola peninsula) | 29       | $1.156 \pm 0.014$   | $2.441 \pm 0.022$   |

<sup>1</sup> Poland, Hungary, Yugoslavia.

<sup>2</sup> From Russell and Farquhar (1960).

<sup>3</sup> Morocco, Algiers.

<sup>4</sup> Mostly central/southern USSR.

Table 5. Literature values of lead isotope ratios in European atmospheric aerosol samples

| Reference                     | Location                    | Pb <sup>206</sup> /Pb <sup>207</sup> | Pb <sup>208</sup> /Pb <sup>207</sup> |
|-------------------------------|-----------------------------|--------------------------------------|--------------------------------------|
| Maring et al. (1987)          | Mediterranean:              |                                      |                                      |
|                               | NW Africa (1981)            | 1.156                                | 2.430                                |
|                               | E. Europe, Italy (1983)     | 1.149                                | 2.422                                |
|                               | Marseilles (1983)           | 1.118                                | 2.389                                |
| Petit et al. (1984)           | Belgium (1983)              | 1.125–1.145                          |                                      |
|                               | Belgium (1983) <sup>1</sup> | 1.12 –1.14                           |                                      |
| Elbaz-Poulichet et al. (1984) | Paris (1981)                | 1.101                                | 2.409                                |
| Facchetti et al. (1984)       | Turin (1981)                | 1.185                                |                                      |

<sup>1</sup> car exhaust.

Petroleum Institute confirmed that additives are purchased mainly from AOC in the UK, and our results are consistent with this. The available data and information suggest that the Stockholm data are reasonable values for Swedish vehicle emissions. That the mean ratios in the Stockholm samples are closer to the Western Europe signature ratios than those for the Northwest sector suggests that vehicle emissions are less significant sources of atmospheric Pb in non-urban areas of Sweden and Norway.

Additional information was gained from direct ICP-MS analysis of gasoline samples from several European locations, following extraction with bromine and nitric acid. The samples were collected from retail or other outlets at the endpoints of the normal industrial and consumer distribution systems in each country. A comprehensive sampling and analysis program for European vehicle fuels was beyond the scope of the current study,

Table 6. Lead isotope ratios measured in samples of European gasolines; the year of sample collection, and the experimental precision (1 standard deviation) of each ratio measurement, are also shown

| Origin                            | Year | Pb <sup>206</sup> /Pb <sup>207</sup> | Pb <sup>208</sup> /Pb <sup>207</sup> |
|-----------------------------------|------|--------------------------------------|--------------------------------------|
| Sweden<br>(inferred, see Table 2) | 1988 | 1.140 ± 0.010                        | 2.402 ± 0.011                        |
| Poland                            | 1988 | 1.174 ± 0.005                        | 2.418 ± 0.002                        |
| Vienna                            | 1990 | 1.111 ± 0.006                        | 2.371 ± 0.003                        |
| Hungary                           | 1990 | 1.072 ± 0.008                        | 2.339 ± 0.004                        |
| Holland                           | 1990 | 1.062 ± 0.019                        | 2.320 ± 0.006                        |

and the results of these individual samples should not be construed as representative regional averages.

Despite this, it is evident that the general pattern in Table 6 is consistent with the pattern that emerged from the aerosol samples and the sector averaging scheme (Table 3). Pb<sup>206</sup>/Pb<sup>207</sup> and Pb<sup>208</sup>/Pb<sup>207</sup> ratios are generally lower in Western Europe samples (aerosols or gasolines) than in Eastern Europe samples. Of particular note is the good agreement between the ratios measured in the sample of Polish gasoline (Table 6), the ratios for the Eastern Europe sector (Table 3), and the ratios for Polish and East European ore bodies (Table 4). It is likely that such good agreement among disparate data sources is fortuitous. Thus these results should not be interpreted as evidence that Polish ores are the only source of atmospheric Pb in Eastern Europe. Gasoline samples, for instance, may be a blend of several fuels containing Pb from several sources. The available information on ore distribution and consumption does not exclude other Eastern Europe or Soviet sources of ores.

Fig. 7 shows that the isotope signature for samples associated with air trajectories from the East (essentially from the USSR), agrees well with the ratios in Central and Southern Soviet lead bearing ores. This Eastern signature also agrees very well with samples from the islands of Hopen and Ny-Alesund in Svalbard, collected during episodes of atmospheric transport out of the USSR (Sturges and Barrie, 1989b). Those samples had a mean Pb<sup>206</sup>/Pb<sup>207</sup> ratio of 1.154 ± 0.006, compared with the mean Eastern signature in this work of 1.153 (Table 3), and gives us considerable confidence in

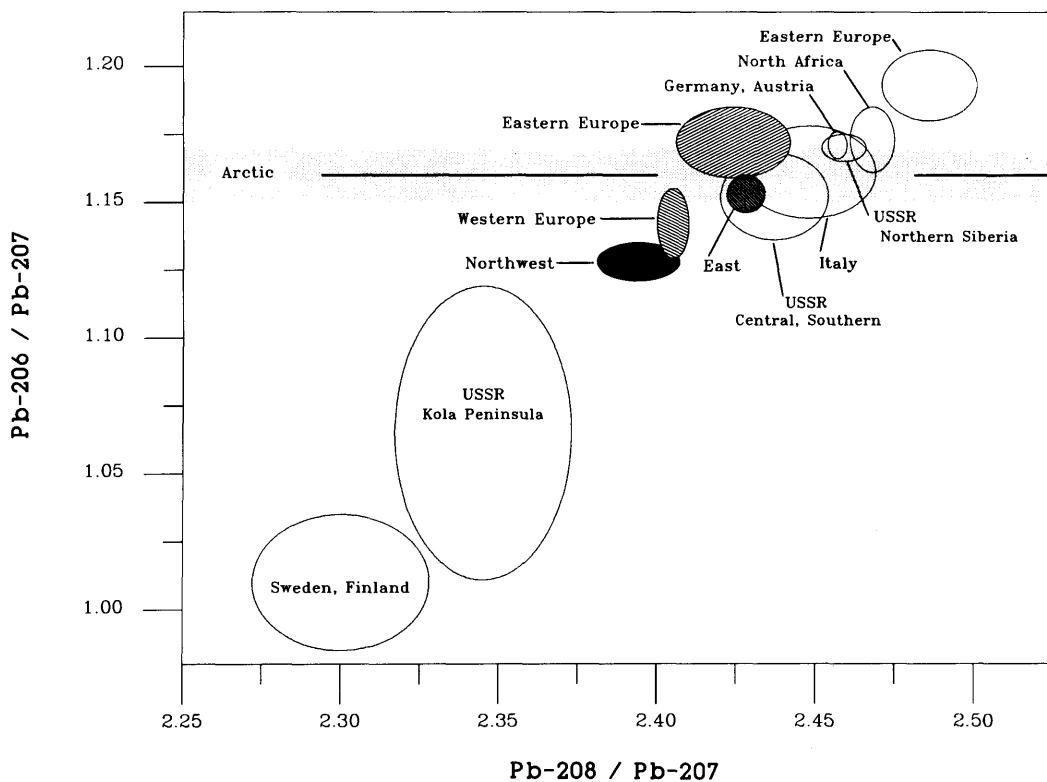


Fig. 7. Characteristic  $Pb^{206}/Pb^{207}$  and  $Pb^{208}/Pb^{207}$  ratios for sectors and regional ore bodies. Areas are centered on the appropriate mean ratios, with widths equal to the standard deviations for the group. Shaded areas are sector data (Table 3); open areas are literature data (Table 4). The  $Pb^{206}/Pb^{207}$  ratio observed in Alert samples is also shown (heavy line = mean; shaded bar = standard deviation).

our assessment of the lead isotope signature for the Soviet Union.

There are significant limitations to the conclusions that can be drawn from analysis of isotopic composition alone. A case study of these limitations follows, using the current data set. Commercial ore bodies in the north of Sweden and Finland contain exceptionally non-radiogenic lead (that is, the relative abundance of  $Pb^{207}$  is high). As Fig. 7 illustrates, the ratios in these ores are very different to those in atmospheric lead in the Northwest sector. It may be concluded that the atmospheric lead associated with this sector is predominantly derived from Swedish automotive emissions, with a smaller contribution from northern industrial activity, or even from Soviet smelting activity on the Kola Peninsula, across the border from

Finland (Fig. 1). Atmospheric sampling on the USSR border in Finland (Sturges and Barrie, 1989b) has confirmed that Soviet industrial activity in that area does indeed release atmospheric aerosols with a low  $Pb^{206}/Pb^{207}$  ratio (1.08 to 1.11). Averaging by sector may in fact hide the presence of some samples with very low lead isotope ratios. Close inspection of Table 1 and Table 2 will show that there were five samples in the Northwest sector with  $Pb^{206}/Pb^{207}$  ratios between 1.103 and 1.105, and  $Pb^{208}/Pb^{207}$  ratios between 2.34 and 2.39. These are very close to the isotopic composition of Swedish/Finnish ores, as well as those of the Kola peninsula. From the isotope data alone, one might reasonably infer an industrial point source origin of the lead in these samples but it would be incorrect to assume a

Soviet source. A detailed inspection of the associated back-trajectories revealed a consistent pattern for four of these samples (one trajectory was ambiguous and unclassified), with straight westerly or west-northwesterly flow originating over the North Atlantic and crossing southern Sweden.

#### 4.2. Relevance to Arctic Pb isotope ratios

In an attempt to discern the origin of lead pollution in the Arctic, Sturges and Barrie (1989b) examined the  $Pb^{206}/Pb^{207}$  isotope ratios in atmospheric particulate matter collected at Canadian High Arctic stations. The average ratios were similar at Alert ( $1.160 \pm 0.010$ ) and Mould Bay ( $1.161 \pm 0.006$ ). From a comparison with lead isotope ratios of likely Soviet and other ores (refer to Sturges and Barrie, 1989b, for literature sources), the Arctic ratios were deduced to be in good agreement with the ratios in certain Soviet lead ores. This is illustrated most clearly in Fig. 7, where the expected ranges of the  $Pb^{206}/Pb^{207}$  ratio in several ore bodies, including ores from Siberia and Central/Southern USSR, overlap the mean value observed in the Arctic.

However, the similarity of the Arctic ratios to isotope ratios in these ores does not necessarily mean that these are the sole or even dominant sources of lead in Arctic aerosols. Additional information is required to assess their validity. For example, Fig. 7 also shows that Italian ores have the closest agreement with the observed Arctic  $Pb^{206}/Pb^{207}$  ratio but, given the known source distributions and strengths (Fig. 1), it is improbable that Italy is a dominant contributor to Arctic aerosol lead.

Because of the long residence times of aerosols in the Arctic atmosphere (Barrie, 1986), the Arctic data represent relatively long-term averages that likely include significant contributions from multiple regions. Contributions from regions with low characteristic lead isotope ratios may well be offset by contributions from one or more regions with high values of the ratios.

This can be illustrated by a calculation incorporating results from a recent Arctic aerosol transport modelling study (Akeredolu et al., 1990), which showed roughly equal contributions on an annual basis to Arctic aerosol lead from three regional sources: Eastern Europe, USSR, Western Europe. Because most of the annual inputs to the

Arctic have been found to occur between October and May (Barrie, 1986), which includes the period for which lead isotope data are available, the results of Akeredolu et al. (1990) can be used to estimate the relative contribution to the Arctic from the different European source regions. If the regional atmospheric  $Pb^{206}/Pb^{207}$  ratios from Table 3 are given equal weight and averaged (excluding the Northwest signature, which is more indicative of a local or background signal), then a mean  $Pb^{206}/Pb^{207}$  ratio of 1.156 is obtained. This is not significantly different from the mean  $Pb^{206}/Pb^{207}$  ratio of 1.160 observed in the Canadian Arctic.

By themselves, the current lead isotope data do not allow greater discrimination between the possible contributing regions for lead in the Arctic atmosphere. The current study reduced the number of major source regions to four, but there are only two unique parameters ( $Pb^{206}/Pb^{207}$ ,  $Pb^{208}/Pb^{207}$ ) available for balancing the unknown contributions from these regions. Additional measurements, such as the  $Pb^{208}/Pb^{207}$  ratio in Arctic aerosols or covariate regional trace element signatures, would help to clarify the situation.

Fig. 7 and Table 3 show that the  $Pb^{208}/Pb^{207}$  ratio for the Western Europe sector is significantly different from the ratios in the East and Eastern Europe sectors. If a  $Pb^{208}/Pb^{207}$  ratio of approximately 2.43 is observed in Arctic aerosols, then there would be firm evidence that Western European sources were negligible because a simple mass balance shows that such a high  $Pb^{208}/Pb^{207}$  ratio could not be obtained if there were sizeable contributions from the Western Europe and Northwest sectors.

## 5. Conclusions

Differences in the isotopic composition of European atmospheric lead observed at a location in Sweden in spring 1988 have been characterized on a regional scale. The combination of the  $Pb^{206}/Pb^{207}$  and  $Pb^{208}/Pb^{207}$  ratios could be used to clearly differentiate between four regions: Northwest (Norway, Sweden), East (Soviet Union, Finland), Eastern Europe and Western Europe. The use of a single isotope ratio permits some regional discrimination but the signatures

are not always unique. Both isotope ratios are necessary for the confident resolution of regional-scale sources.

The observed differences in the lead isotope ratios arise from the use of lead from different ore bodies for gasoline additives and industrial operations. The observations are consistent with the isotopic composition of lead in Stockholm and European gasolines, literature values for various ore bodies, and with estimated ore usage.

The observed lead isotopic composition in the Arctic is consistent with the estimated regional European lead isotopic signatures from this study, and with chemical transport model estimates of equal contributions of lead to the Arctic from Western Europe, Eastern Europe and the Soviet Union. Contributions to the Arctic from the Northwest (Norway, Sweden) appear to be minor.

$Pb^{206}/Pb^{207}$  and  $Pb^{208}/Pb^{207}$  ratios in typical Swedish ores are very low. From mass balance considerations, they cannot form a sizeable fraction of the observed Arctic aerosol without an unduly large contribution from source regions with very high isotope ratios.

## 6. Acknowledgements

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