

This article was downloaded by:

On: 18 January 2011

Access details: Access Details: Free Access

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

Isotopic Composition as an Indicator of Origin of Lead Accumulations in Surface Soils

J. R. Bacon^a; M. L. Berrow^a; C. A. Shand^a

^a Macaulay Land Use Research Institute, Craigiebuckler, Aberdeen, Scotland

To cite this Article Bacon, J. R. , Berrow, M. L. and Shand, C. A.(1992) 'Isotopic Composition as an Indicator of Origin of Lead Accumulations in Surface Soils', International Journal of Environmental Analytical Chemistry, 46: 1, 71 – 76

To link to this Article: DOI: 10.1080/03067319208026998

URL: <http://dx.doi.org/10.1080/03067319208026998>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

ISOTOPIC COMPOSITION AS AN INDICATOR OF ORIGIN OF LEAD ACCUMULATIONS IN SURFACE SOILS

J. R. BACON, M. L. BERROW and C. A. SHAND

Macaulay Land Use Research Institute, Craigiebuckler, Aberdeen, AB9 2QJ, Scotland.

(Received, 13 March 1991)

Surface accumulation of lead in urban soils is a well-known phenomenon but its marked accumulation in remote, upland areas is less well documented. Such enrichments (up to 500 mg/kg) could be a potential hazard to grazing sheep.

Lead isotope ratios determined by thermal ionization mass spectrometry are reported for three soil profiles from remote, upland areas with highly enriched surface concentrations of lead. Isotope ratios in recent rainwater samples from six widely dispersed sites in Scotland are also discussed.

Lead in current rainwater samples has very low isotope ratios indicating its likely origin from petrol-derived sources. The ratios in soil surface horizons are not as low as those in current rainwater samples which suggests that lead accumulated over many decades is derived from both petrol-derived sources and also from other industrial emissions such as smelting and steel production.

KEY WORDS: Lead isotopes, soil profiles, atmospheric deposition, surface accumulation, rainwater.

INTRODUCTION

Some 47% of the annual production of lead ($> 10^6$ tonnes) is lost to the environment, mainly by combustion of leaded petrol¹. There is considerable evidence that petrol sources are the main contributor to airborne lead in urban areas but less information is available on the long-distance atmospheric transport of lead originating from industrial processes or petrol combustion. Lead isotopic composition has previously been used to trace atmospheric transport of lead originating from industrial processes or petrol combustion; for example Maring *et al.*², showed that the movement of air masses in the Mediterranean region could be followed using this method.

A Norwegian study³ has shown that long-distance atmospheric transport is a major contributor to the higher concentrations (100 to 120 mg kg⁻¹) of lead in topsoils in Southern Norway compared with those in Northern Norway (10 to 20 mg kg⁻¹) and this lead could be entering the food chain via grazing lambs⁴. Some uncultivated, upland topsoils in Scotland contain more than 200 mg kg⁻¹ total lead⁵ and the objective of this study is to characterise and identify the source of these accumulations using lead isotopic composition.

MATERIALS AND METHODS

The isotopic composition of lead varies in nature due to the radiogenic decay of thorium and uranium to lead. Lead from ore deposits can often be the least radiogenic in nature and that used in leaded petrol in the UK from Australian sources has low $^{206}\text{Pb}/^{207}\text{Pb}$ ratios. Trace lead in most rocks has a ratio within the range 1.15 to 1.23. A major Italian environmental study⁶ showed that the use of alkyl-lead in petrol having a ratio of 1.040 was reflected in environmental samples such as rainwater (1.088) but more especially airborne particles (1.064) which both had ratios of 1.16 before the use of lead with a low 206/207 ratio. A source of lead can, therefore, be characterized by its isotopic composition.

Three soil profiles from remote upland areas but with highly enriched surface concentrations of lead were selected for lead isotope analysis in order to establish (1) the variation of isotope ratios through the profiles and (2) the variation of surface lead isotope ratios from site to site.

Rainwater samples collected from a number of monitoring stations across Scotland were also analysed to characterize recent atmospheric inputs into soils.

Soil samples (250 mg) were dissolved in HF (10 ml) and heated to dryness on a steam bath, and the residues redissolved in 2M HCl (10 ml) and dried. Rainwater samples (1 l) were filtered, evaporated to dryness and digested with HCl. The lead was separated in a pure form by anion-exchange procedures and the isotopic composition determined on a VG354 thermal ionization mass spectrometer (TIMS) using the standard silica-gel loading technique. For an accurate isotope analysis a filament loading of 200 ng lead is sufficient. Most soil samples provide more than adequate amounts and for waters 1 litre samples are normally required.

RESULTS AND DISCUSSION

Soil profiles

For studies on the age and formation of rocks, isotope geologists have used the ratios 206/204, 207/204, 208/204, the ^{204}Pb being the single non-radiogenic isotope, and these ratios for the soil profiles examined are reported in Table 1. The lead 206/207 ratio used by Fachetti and Geiss⁶ has generally been accepted as an accurate measure of the origin of lead and is used in this presentation to discuss the results reported.

In profiles 1 and 2 the lead in the surface horizons has significantly lower 206/207 ratios than the underlying horizons consistent with a surface input of lead derived from ores, i.e. of anthropogenic origin. The results for profile No 3 are more difficult to interpret. The upper horizon has the lowest 206/207 ratio of the five upper horizons but there is then a fall in the ratio in the underlying mineral horizons B₁, B₂ and B₃ to values less than the surface horizon. The ratio then rises again in the lowest B₃ and C horizons. This suggests that this profile may be a truncated profile developed on two layers of mineral matter of differing geological origin or the differences may be due to lateral movement of material with a low 206/207 ratio

Table 1 lead isotope ratios in selected soil profiles.

Profile cm	Horizon	L-o-Ign %	Total Pb mg kg ⁻¹	EDTA-Pb mg kg ⁻¹	$\frac{206}{204}$	$\frac{207}{204}$	$\frac{208}{204}$	$\frac{206}{207}$
No 1								
0-5	L&F	87	520	396	17.78	15.50	37.57	1.147
5-25	Oh	84	230	196	18.05	15.52	37.88	1.164
25-35	A	2.1	3.3	0.82	—	—	—	—
35-36	B _{1h}	6.8	10	0.35	—	—	—	1.174
36	B _{Fe}	13	20	1.56	18.13	15.45	37.76	1.174
36-55	B ₃	2.4	6.7	0.34	—	—	—	—
55-95	C _x	1.0	6.0	0.35	18.17	15.46	37.80	1.175
No 2								
0-3	H	56	380	380	18.03	15.54	38.04	1.160
3-8	A ₂	21	155	118	18.06	15.54	38.14	1.1625
13-18	B	13	26	12.8	18.73	15.59	38.44	1.202
No 3								
0-3	L&F	92	440	420	17.92	15.53	37.92	1.154
3-8	H	92	460	420	18.05	15.54	38.00	1.162
8-15	H	91	200	86	18.09	15.56	38.09	1.163
15-25	H	88	40	20	18.00	15.54	38.03	1.158
25-30	A	36	20	6.6	18.14	15.49	37.91	1.171
30-31	B ₁	22	25	5.7	17.63	15.47	37.84	1.139
35-46	B ₂	12	30	0.5	17.69	15.46	37.39	1.145
58-68	B ₃	3.3	30	0.5	17.54	15.45	37.22	1.135
76-86	B ₃	1.7	30	1.3	18.10	15.48	37.86	1.170
96-107	C	1.4	30	0.5	18.05	15.48	37.81	1.166

below the iron pan. If one considers the upper five horizons or 30 cm of the profile the values are comparable with those in profiles 1 and 2. A very high proportion of the total lead in each profile surface horizon is extractable by 0.05M EDTA (Table 1).

Top-soils

The upper-most horizons of all three profiles in Table 1 have 206/207 ratios close to 1.15. Closer examination of all four ratios for these three topsoils and for topsoils from sites 4 and 5 (Table 2), suggests the existence of two distinct groups. The

Table 2 Lead isotope ratios in surface soils.

Site	$\frac{206}{204}$	$\frac{207}{204}$	$\frac{208}{204}$	$\frac{206}{207}$
1	17.78	15.50	37.57	1.147
4	17.84	15.54	37.71	1.147
	17.78	15.53	37.63	1.145
2	18.03	15.54	38.04	1.160
3	17.92	15.53	37.92	1.154
5	18.06	15.57	38.06	1.157
	17.96	15.56	37.87	1.154

locations of the sampling sites are indicated on Figure 1. Sites 1 and 4 have 206/207 ratios 1.145 to 1.147 whereas sites 2, 3 and 5 have ratios in the range 1.154 to 1.160. The other ratios fit a similar pattern. If two soils have all four measured ratios closely matching then this is much stronger evidence for the common origin of the lead than relying on a single ratio. Although the ratios in individual topsoils will depend on a number of factors there does appear to be common patterns for all four ratios in the seven samples from remote areas reported in Table 2. The data set is currently too limited to draw firm conclusions and further data are being accumulated.

Rainwater

To determine the relative proportion of anthropogenic lead in surface soils it is necessary to measure the isotopic composition of lead being deposited from the atmosphere. The 206/207 ratios in some rainwater samples from the remote Cairngorm mountain site at Allt à Mharcaidh (Table 3) are markedly lower than in the soil samples and are very close both to the minimum level reached in the Italian study of 1.088 and to that in the National Bureau of Standards (NBS) common lead of 1.093. This strongly suggests that lead in these rainwater samples is derived from lead ores with a low 206/207 isotope ratio and is of anthropogenic origin. The rainwater samples from all six sites which are in remote upland areas have low 206/207 ratios consistent with the origin of the lead being in petrol additives. Those at the three sites (Chon, Kelty and Hartwood) closer to the industrial belt across the central valley of Scotland tend to have slightly higher values indicating some input from sources other than petrol additives, probably industrial emissions.

CONCLUSIONS

Three soil profiles, from remote upland areas but with highly enriched surface concentrations of lead, have been analysed for lead isotope ratios. Recent rainwater samples from six widely dispersed sites in Scotland have also been analysed.

The lead in current rainwater samples has very low lead isotope ratios which strongly suggests that it is derived from lead ores with low ratios and is of anthropogenic origin.

Table 3 Isotopic composition of rainwater samples taken at various locations.

<i>Sampling site</i>	<i>206/207 ratio in different collections between 7/88 and 2/90</i>
Mharcaidh, NE Scotland	1.082; 1.109; 1.103; 1.106
Glensaugh, NE Scotland	1.112; 1.110; 1.114
Sourhope, SE Scotland	1.106; 1.081; 1.094
Chon, Central Scotland	1.111; 1.098; 1.087; 1.110; 1.118
Kelty, Central Scotland	1.121; 1.141
Hartwood, Central Scotland	1.126; 1.115

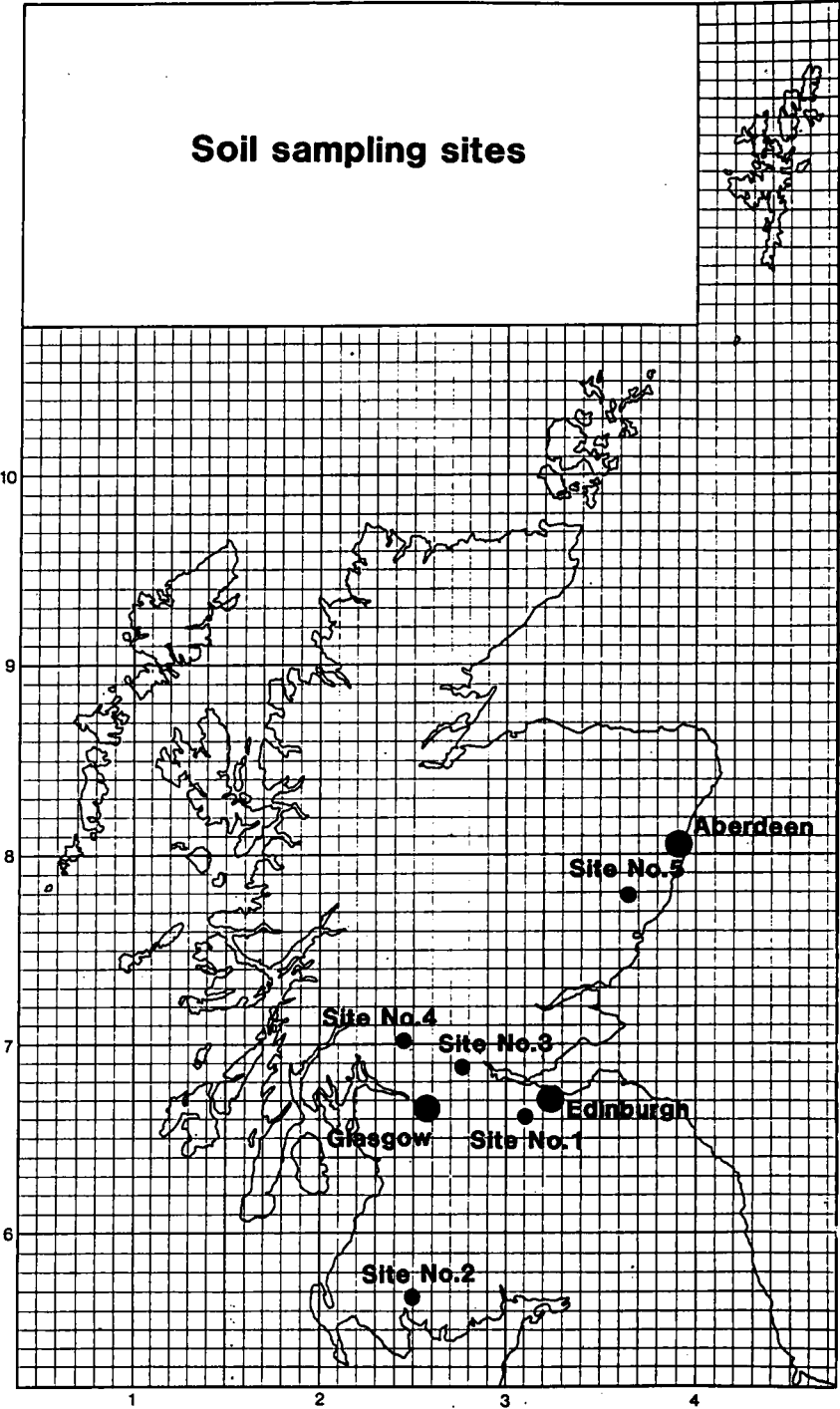


Figure 1

Lead in the surface horizons of all three profiles has isotope ratios of 1.147, 1.160 and 1.154, lower than in underlying horizons in two of the three profiles, indicating anthropogenic inputs of lead. Topsoil samples from two other upland sites have similar ratios.

The ratios in soil surface horizons are not as low as those found in current rainwater samples which suggests differences between lead being currently deposited and lead accumulated over many decades by aerial deposition. The accumulated lead is therefore probably derived from both petrol-derived sources and also other industrial emissions.

References

1. R. L. Boeckx, *Anal. Chem.*, **58**, 275A–288A (1986).
2. H. Maring, D. M. Settle, P. Buat-Menard, F. Dulac and C. C. Patterson. *Nature* (London), **330**, 154–156 (1987).
3. E. Steinnes, in: *Pollutants in Porous Media* (Eds. B. Yaron, G. Dagan and J. Goldshmid, Springer-Verlag, Berlin, 1984) pp. 115–122.
4. A. Froslic, G. Norheim, J. P. Rambaek and E. Steinnes. *Bull. Environ. Contam. Toxicol.*, **34**, 175–182 (1985).
5. M. L. Berrow, W. M. Stein and A. M. Ure. in: *Lead in the Home Environment* (Eds. I. Thornton and E. Culbard, Science Reviews Limited, Northwood, 1987.) pp. 37–45.
6. S. Fachetti and F. Geiss. *Commission of the European Communities*, Report No. EUR 8352 EN (1984).