

# Evolving Pb isotope signatures of London airborne particulate matter (PM<sub>10</sub>)—constraints from on-filter and solution-mode MC-ICP-MS

Stephen R. Noble,<sup>\*a</sup> Matthew S. A. Horstwood,<sup>a</sup> Pamela Davy,<sup>b</sup> Vanessa Pashley,<sup>a</sup> Baruch Spiro<sup>c</sup> and Steve Smith<sup>b</sup>

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Pb isotope compositions of biologically significant PM<sub>10</sub> atmospheric particulates from a busy roadside location in London UK were measured using solution- and laser ablation-mode MC-ICP-MS. The solution-mode data for PM<sub>10</sub> sampled between 1998–2001 document a dramatic shift to increasingly radiogenic compositions as leaded petrol was phased out. LA-MC-ICP-MS isotope analysis, piloted on a subset of the available samples, is shown to be a potential reconnaissance analytical technique. PM<sub>10</sub> particles trapped on quartz filters were liberated from the filter surface, without ablating the filter substrate, using a 266 nm UV laser and a dynamic, large diameter, low-fluence ablation protocol. The Pb isotope evolution noted in the London data set obtained by both analytical protocols is similar to that observed elsewhere in Western Europe following leaded petrol elimination. The data therefore provide important baseline isotope composition information useful for continued UK atmospheric monitoring through the early 21<sup>st</sup> century.

## Introduction

This study examines variations in the end-20<sup>th</sup> century London UK aerosol lead (Pb) isotope composition using solution-mode MC-ICP-MS, and reports an initial exploration of laser ablation (LA-) MC-ICP-MS as an alternative analytical technique for atmospheric aerosols typical of an urban environment. Results presented here were obtained from particle deposits on filters, collected during the time when the use of leaded petrol was significantly reduced and then totally phased out (1998–2001).

Pb is a major anthropogenic pollutant originating from mining and smelting, current and historical industrial activities, fossil fuel combustion and incineration. Prior to the turn of the millennium the main source of Pb was the exhaust of vehicles using leaded petrol.<sup>1</sup> Pb emissions from leaded petrol peaked in the 1970s and 1980s at *ca.* 375 000 t a<sup>-1</sup>, with the UK contributing >7000 t a<sup>-1</sup>.<sup>1,2</sup> Atmospheric aerosols are one of the principal media in which this anthropogenic Pb is transported, particularly the inhalable particulate fraction (particles <10 μm in aerodynamic diameter, or PM<sub>10</sub>), and can travel significant distances.<sup>3,4</sup> Facilitated by aerosol transport, Pb contamination of the environment reached global proportions as demonstrated by elevated Pb concentration levels above pre-industrial values as recorded in ice sheets, lake and marine sediments and peat deposits world-wide.<sup>5–13</sup>

TIMS-based studies show that aerosol Pb isotope compositions vary considerably on a global scale.<sup>14</sup> Each major industrial sector's predominant Pb output reflects a few dominant sources

that ultimately derive from a relatively limited number of ore deposits at any one time, or are a relatively constant mix of many Pb sources. There is sufficient regional variation in the Pb isotope signature of aerosols to facilitate apportionment of aerosol Pb sourced from different geographical/industrial domains at a given moment in time. In large complex urban centres and highly industrialised areas the anthropogenic Pb composition is typically a mix of locally-derived, and potentially distally-derived Pb.<sup>15,16</sup> Characterising these isotope compositions at an instant in time and examining the changes over a long time span provides important information concerning the rise and fall of particular anthropogenic inputs.<sup>14,17</sup>

There is strong evidence linking adverse health effects with high overall atmospheric aerosol concentrations in cities.<sup>18–20</sup> Precisely which components of the aerosols are the most damaging remains unknown although PM<sub>10</sub> particles originating from diesel combustion show the strongest association with adverse effects.<sup>21,22</sup> Furthermore, the Pb from the aerosols is known to have an important health impact due to its transfer to the blood stream *via* absorption directly from PM<sub>10</sub> deposited deep in the lungs, which is in addition to the general respiratory and cardiovascular impact of PM<sub>10</sub>.<sup>3</sup> Given these significant health effects it is important to relate the source to the mass contribution of PM<sub>10</sub> deposits, and chemical and isotopic fingerprinting are important in this respect. During the time that tetraethyl Pb was added to petrol, monitoring Pb concentration and isotope composition provided valuable information on traffic-related contributions to PM<sub>10</sub>. Establishing changes in the isotopic signature following withdrawal of leaded petrol is therefore clearly important to source contribution studies in the future.

The UK reduced the Pb content of leaded petrol in 1986 from ~0.34 g l<sup>-1</sup> to 0.143 g l<sup>-1</sup> and after 1987 unleaded petrol sales increased markedly.<sup>2</sup> By 1998 and 1999, emissions had fallen to

<sup>a</sup>NERC Isotope Geosciences Laboratory, British Geological Survey, Nottingham, UK. E-mail: srn@bgs.ac.uk; Fax: +44 936 3302; Tel: +44 936 3555

<sup>b</sup>Department of Biochemistry, King's College, London, UK

<sup>c</sup>Museum of Natural History, London, UK

less than 1000 t a<sup>-1</sup> and yet leaded petrol was still the main contributor to atmospheric Pb emissions. In the period 1970 to the end of 1999, Pb emissions from vehicle exhausts declined by 97% and leaded petrol was finally withdrawn from general sale at the end of 1999. As a consequence, emissions declined even further in 2000 and 2001, resulting in a marked decline in atmospheric concentrations. In central London (Cromwell Road), the annual mean Pb concentration was 1.45 µg m<sup>-3</sup> in 1985, whilst in the years 1990, 1999 and 2002, concentrations were 0.38, 0.068, and 0.027 µg m<sup>-3</sup>, respectively.<sup>2</sup>

## Methodology

### PM<sub>10</sub> characteristics and sample collection

PM<sub>10</sub> are very heterogeneous, comprising inorganic solids, organic substances, elemental carbon and water. This heterogeneity is a function of the diverse sources of this material, which include sea salt, windblown dusts from soils and rocks, forest fires and anthropogenic sources of which fossil fuel combustion is the major source. Additionally, gas to particle reactions in the atmosphere that include fossil fuel combustion gases produce condensed products that make a significant contribution to the mass of PM<sub>10</sub>. In the London UK area specifically, Moreno *et al.*<sup>23</sup> showed that PM<sub>10</sub> are composed of elemental and organic carbon compounds (EOCC), Fe-bearing industrial and traffic-related oxides and alloys, nitrates and silicates, and subordinate sulfates and chlorides. These authors also show that the very fine grained <2.5 µm particles (PM<sub>2.5</sub>) have a higher proportion of EOCC and less Fe-bearing particulates and silicates. EOCC particles are themselves comprised of submicron particles that agglomerate into larger porous composites.<sup>24</sup>

In this study PM<sub>10</sub> were collected on 47 mm Millipore quartz filters at the Marylebone Road air monitoring site using a Rupprecht & Patashnik Partisol model 2000 air sampler. The monitoring site is situated at the kerbside of the busy Marylebone Road which averages 70 000 passing vehicles per day. The air sampler operates at a rate of 16.7 (±7%) litres per minute. The PM<sub>10</sub> samples were collected on a 24 h basis (midnight to midnight GMT) primarily for studies concerned with PM<sub>10</sub> total deposit weights and bulk elemental and organic species characterisation, with this Pb isotope study being an opportunistic addition. Samples were taken from archival material and from new samples collected in September and October 2000 and December 2001. Samples were also collected every 6 days during each sampling period where possible.

It is acknowledged that the stochastic nature of weather is such that the same conditions will not be evident from one year to the next. We have therefore obtained, courtesy of the Met Office and British Atmospheric Data Centre, a summary of the main meteorological parameters and the 5 day wind trajectory for each day on which samples were taken. These are considered in the interpretation of the data.

### Sample preparation and analysis

Pb aerosol isotope studies are typically based on solution-mode analyses employing analytical techniques similar to those used for isotope analysis of geological materials. Generally, chromatographic separation of Pb using ion exchange resins and isotope

ratio determination by TIMS are used,<sup>4,14–16</sup> although some investigators have also used a combination of TIMS and solution-mode quadrupole ICP-MS.<sup>17</sup> TIMS analytical approaches have the advantage of facilitating accurate analysis of very small amounts of Pb with high precision, and the highest possible precision if double or triple spiking methods are used. MC-ICP-MS is also an established method for high precision Pb isotope analysis, particularly if ample sample is available (10's of ng of Pb), and was used here. An important pre-requisite, however, of TIMS or ICP-MS solution-mode analysis is to ensure filters do not contribute sufficient Pb to unduly bias the total Pb isotope composition away from the isotope composition of the filter deposits alone. Rigorously pre-cleaned Teflon filters are therefore typically used to minimize Pb blank, especially for studies in areas where particulate loads are very low.<sup>14</sup>

Unfortunately, the design of many urban sampling programs do not consider isotope measurements and typically employ non-PTFE filters, and it is these types of samples that generally populate filter archives. This was the case with the London filter samples studied here. Nevertheless, although not optimal, it is possible to obtain reliable isotope data from cellulose acetate or glass fibre filters if the total particulate load contains 100's of ng of Pb because filter blank contributions can be sufficiently small compared to the aerosol Pb filter deposits as to not unduly bias the true sample isotope ratios (blank ≤ 5% of total Pb).<sup>16</sup>

The potential reductions in aerosol Pb collected in our 24 h samples as leaded petrol was entirely phased out suggested the possibility that solution-mode filter analyses on relatively Pb-poor deposits might be biased to a greater degree than the older, potentially higher Pb deposits. As a result, a preliminary investigation of laser ablation sampling of filter deposits was pursued as a potentially “cleaner” sampling protocol that could more selectively sample the filter surface deposits, leaving the filter substrate unaffected and relatively unsampled. Only small (<1/4<sup>th</sup>–1/8<sup>th</sup>) slices of the original filters were available for study, but wherever possible these slices were sub-sampled so that LA-MC-ICP-MS analysis could be done in addition to solution-mode MC-ICP-MS.

### Solution mode

MC-ICP-MS solution-mode data obtained in our laboratory on both geological and environmental materials, and also in other MC-ICP-MS laboratories, indicates that organic content and purity of the Pb solution strongly relates to data accuracy and external reproducibility. Every effort, therefore, was made to deliver to the ICP a high purity Pb solution free of high total dissolved solids and separation media.

Sample preparation was done in a class 100 clean laboratory. Reagents were Teflon-distilled twice to minimize Pb contributions during chemistry, and water was prepared to 18.2 MΩ resistivity (Milli-Q). Reagent and water blanks measured by TIMS were on the order of ≤1 pg Pb ml<sup>-1</sup>. Filters were handled with acid-cleaned polypropylene forceps and cut into sections using stainless steel scissors that were pre-cleaned in 2 M HNO<sub>3</sub>, Milli-Q water and distilled acetone. Pb was leached from the filter deposits in 15 ml PFA Teflon vials. The vials were pre-cleaned in 8 M HNO<sub>3</sub> for 24 h, rinsed in Milli-Q water, and refluxed on a hotplate in 6 M HCl for 16 h. Initial filter leaching

was done in 1 M HBr for 2 h at room temperature, in a procedure slightly modified from step 1 in Bollhöfer *et al.*<sup>14</sup> This leaching step was expected to remove Pb from the more highly soluble deposits on the filter. Previous Marylebone Road filter studies indicated a metallic particle contribution from vehicles, including Cu-rich particulates,<sup>25</sup> and so the initial leaching step residues were further treated in sealed PFA vials with 16 M HNO<sub>3</sub> for 16 h at 80 °C. Most of the gray to black carbonaceous material on the filter remained unmoved. The dissolved species from the leach steps were combined, dried down, and taken up in 1 M HBr prior to chemistry.

Pb was separated by anion exchange chromatography using Bio-Rad AG1-X8 resin in polypropylene columns. The chemistry step was repeated to further purify the Pb. Pb separates were dried down and re-dissolved twice in 16 M HNO<sub>3</sub> and the analyte was taken up in 0.45 M HNO<sub>3</sub>. These steps were taken to ensure destruction of residual resin particles to avoid potential organic contamination during mass spectrometry, which has been observed to reduce analytical precision.<sup>26</sup> Pb separates were diluted with ~5 ng g<sup>-1</sup> natural Tl in 2% HNO<sub>3</sub> to a volume of *ca.* 1 ml for introduction into the MC-ICP-MS, with measured <sup>205</sup>Tl/<sup>203</sup>Tl used to correct for instrumental mass fractionation in the plasma.<sup>27</sup> 1998–1999 solutions were analysed on a VG P54 MC-ICP-MS, while 2000–2001 solutions were analysed on an Axiom MC-ICP-MS. The instruments were operated in dry plasma mode with samples introduced into the plasma as a dry aerosol employing an ESI PFA 50 micro-concentric nebuliser (uptake rate of ~50 µl min<sup>-1</sup>) connected to a Cetac Aridus desolvating unit. Running conditions of the P54 and Axiom were virtually the same during the course of this study, and are reported in Table 1 of Horstwood *et al.*<sup>28</sup> Data were collected in the static multicollection mode, in 4 blocks of 25 ratios with inter-block peak-centring and half-mass baseline measurement. Validated washouts better than *ca.* 0.1% of the previous sample were done between runs to avoid cross-contamination. Typical total Pb ion beams were 5–5 × 10<sup>-11</sup> A. Data were normalized to NBS 981 at the time of analysis using the values of Thirlwall.<sup>29</sup> In this way any inaccuracies between analytical sessions were corrected and the sample data were directly comparable (*e.g.* Bouvier *et al.*).<sup>30</sup>

Blank contributions exclusively from the filters, and the total Pb concentrations of some filters, were determined by TIMS on a Finnigan MAT 262. Small segments of the filters (~0.05 g) were leached as above, and the leachate spiked with a high purity <sup>208</sup>Pb tracer (<sup>208</sup>Pb/<sup>206</sup>Pb ~ 14 000) and processed through chemistry. Pb concentrations of 14 aerosol samples ranged from 6.1 to 33 µg g<sup>-1</sup>. Chemistry plus MC-ICP-MS blanks ranged from 0.25–0.86 ng, with total Pb from the full analytical procedure, which is mainly from the filter material, ranging from 3–9 ng. This was sufficiently small (<5% of total Pb) compared to the total aerosol Pb analysed so that correction for Pb blank was not required for the solution-mode data.

#### Laser ablation mode

Samples were ablated using a New Wave Research Microprobe II, 266 nm Nd:YAG laser system coupled to the MC-ICP-MS using the standard volume (30 cm<sup>3</sup>) ablation cell. Particulate introduction directly into the plasma while avoiding ablating

fibres from the filters was achieved using a low-fluence, dynamic ablation protocol. Laser power was reduced to levels far less than where the laser would ablate the quartz fibres and a 100–400 µm diameter beam was rastered over the filter surface. The laser was operated at 10 Hz and focussed on the filter surface. Laser power and rastering speed were adjusted to provide adequate ion-beam size. <sup>208</sup>Pb saturation of the Faraday cup amplifier was avoided in all instances, and <sup>204</sup>Pb ion beams were at least several 10's of millivolts to ensure good counting statistics. A small test area on each filter was ablated so that optimal running conditions were achieved. Almost all particles along the ablation path were dislodged from the filter surface with no attendant damage to the quartz fibres, and were transported directly to the ICP torch in a high-purity argon carrier gas. The affect of the laser on the aerosol particles was not studied in detail but the larger particles were clearly observed being dislodged from the filter rather than vaporised, although the fate of the smallest particles is not known. 50–100 static multicollection ratios were collected in blocks of 25 ratios, with baselines measured at half-mass positions. As with the solution-mode analyses, mass bias correction was made by measuring <sup>205</sup>Tl/<sup>203</sup>Tl of natural Tl aspirated in 2% HNO<sub>3</sub> through the desolvating nebuliser, and in turn, passed through the ablation cell where it mixed with the laser-liberated PM<sub>10</sub>, similar to the protocol used for LA-ICP zircon geochronology.<sup>28</sup> This mass bias correction only accounts for isotope fractionation occurring in the ICP source and not at the point of ablation. As there is no established PM<sub>10</sub> standard material with certified isotope composition, fractionation arising from processes other than within the plasma could not be assessed. However, because laser fluence parameters were adjusted to simply dislodge the particles rather than ablate them, mass fractionation arising at the point of ablation is considered insignificant. Following the solution-mode protocol, instrument accuracy and precision was monitored by running ≥6 analyses of Tl-spiked NIST 981 common Pb solution both at the start and end of the analytical sessions, aspirated as above, as well as additional analyses to bracket filter analyses. During the course of analyses both the P54 and Axiom had a sensitivity of *ca.* 100 V ppm<sup>-1</sup> Pb. Potential blank contribution to the overall filter deposit composition was investigated by rastering the laser beam over the surface of the heat-treated unexposed filters and monitoring the resulting Pb ion current. Total Pb ion currents <10<sup>-14</sup> A were obtained for blank filters, compared to total sample ion currents of >5 × 10<sup>-11</sup> A. These results were indistinguishable from the on-peak baselines originating from the carrier gas alone. It is concluded that for the fluence used, negligible Pb was extracted from the interstitial spaces between the fibres and the fibre surfaces.

## Results and discussion

The filter data are summarized in Table 1, and plotted in Fig. 1 and 2. Uncertainties given in Table 1 are propagated from the internal run precisions (2 std. dev.) and the overall uncertainty of NBS 981 for the analytical session.

The solution-mode data span a considerable range in <sup>206</sup>Pb/<sup>204</sup>Pb–<sup>208</sup>Pb/<sup>204</sup>Pb space, outlining an approximately linear trend. Data from different sampling periods plot in distinct fields: 1998 and 1999 data plot in distinct clusters, with

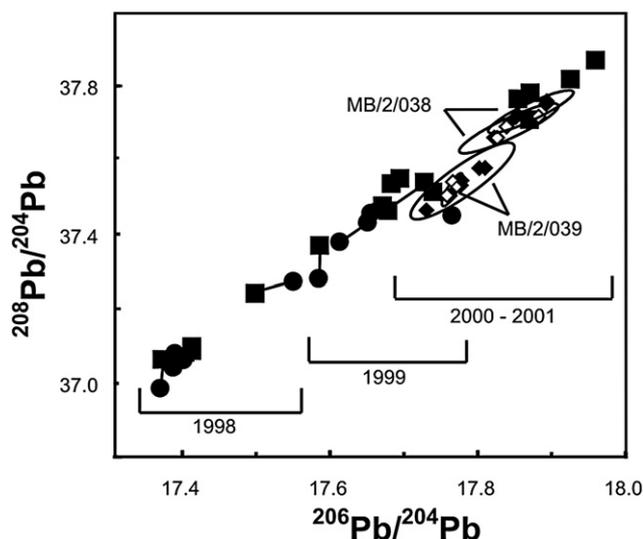
**Table 1** Pb isotope compositions of UK aerosols 1998–2001<sup>a</sup>

Sample	Mode	<sup>206</sup> Pb/ <sup>204</sup> Pb (±2σ %)	<sup>208</sup> Pb/ <sup>204</sup> Pb (±2σ %)	<sup>207</sup> Pb/ <sup>204</sup> Pb (±2σ %)	<sup>208</sup> Pb/ <sup>207</sup> Pb (±2σ %)	<sup>206</sup> Pb/ <sup>207</sup> Pb (±2σ %)	Pb/ppm	Pb from petrol (%) <sup>d</sup>
1998–2001 Filter data								
KCL 016 E (2/12/98)	Sol. <sup>c</sup>	17.498 ± 0.02	37.249 ± 0.03	15.562 ± 0.04	2.3936 ± 0.01	1.1245 ± 0.02		
	LA <sup>c</sup>	17.550 ± 0.02	37.281 ± 0.09	15.556 ± 0.02	2.397 ± 0.08	1.1276 ± 0.01		
KCL 018 E (6/12/98)	Sol. <sup>b</sup>	17.3722 ± 0.004	37.071 ± 0.007	15.5576 ± 0.005	2.3828 ± 0.006	1.1166 ± 0.002		
	LA <sup>c</sup>	17.370 ± 0.05	36.99 ± 0.22	15.541 ± 0.04	2.380 ± 0.20	1.1172 ± 0.07		
KCL 021 SW (12/12/98)	Sol. <sup>b</sup>	17.3896 ± 0.005	37.074 ± 0.02	15.563 ± 0.008	2.3821 ± 0.003	1.1173 ± 0.002		
	LA <sup>c</sup>	17.39 ± 0.10	37.045 ± 0.01	15.545 ± 0.03	2.3828 ± 0.04	1.118 ± 0.14		
KCL 024 WNW (18/12/98)	Sol. <sup>b</sup>	17.4128 ± 0.005	37.1055 ± 0.02	15.5625 ± 0.008	2.3843 ± 0.003	1.1188 ± 0.002		
	LA <sup>c</sup>	17.390 ± 0.04	37.088 ± 0.05	15.568 ± 0.02	2.3820 ± 0.02	1.1169 ± 0.04		
KCL 027 W (24/12/98)	Sol. <sup>b</sup>	17.4127 ± 0.005	37.095 ± 0.02	15.564 ± 0.009	2.3834 ± 0.003	1.1187 ± 0.002		
	LA <sup>c</sup>	17.401 ± 0.04	37.070 ± 0.02	15.563 ± 0.02	2.3823 ± 0.02	1.1182 ± 0.003		
KCL 029 W (28/12/98)	Sol. <sup>b</sup>	17.408 ± 0.04	37.082 ± 0.02	15.566 ± 0.008	2.3823 ± 0.002	1.1183 ± 0.002		
	LA <sup>c</sup>	17.387 ± 0.04	37.050 ± 0.04	15.561 ± 0.07	2.3811 ± 0.007	1.1174 ± 0.03		
KCL 195 NW (2/12/99)	Sol. <sup>b</sup>	17.6709 ± 0.005	37.484 ± 0.02	15.568 ± 0.008	2.4077 ± 0.002	1.1350 ± 0.002	19	
	LA <sup>c</sup>	17.646 ± 0.05	37.437 ± 0.08	15.549 ± 0.04	2.4075 ± 0.02	1.135 ± 0.10		
KCL 197 W (6/12/99)	Sol. <sup>b</sup>	17.7275 ± 0.006	37.548 ± 0.02	15.572 ± 0.009	2.4113 ± 0.004	1.1384 ± 0.002	13	
	LA <sup>c</sup>	17.765 ± 0.05	37.459 ± 0.02	15.557 ± 0.01	2.4080 ± 0.009	1.1357 ± 0.05		
KCL 201 N (14/12/99)	Sol. <sup>b</sup>	17.6645 ± 0.005	37.475 ± 0.009	15.5631 ± 0.005	2.4079 ± 0.004	1.1350 ± 0.002	9.6	
	LA <sup>c</sup>	17.655 ± 0.03	37.464 ± 0.04	15.559 ± 0.04	2.4083 ± 0.04	1.1351 ± 0.07		
KCL 203 N (18/12/99)	Sol. <sup>b</sup>	17.5855 ± 0.005	37.378 ± 0.008	15.5607 ± 0.004	2.4020 ± 0.003	1.1301 ± 0.002	5.7	
	LA <sup>c</sup>	17.55 ± 0.13	37.334 ± 0.05	15.561 ± 0.01	2.399 ± 0.09	1.128 ± 0.14		
KCL 206 SW (24/12/99)	Sol. <sup>b</sup>	17.7390 ± 0.006	37.521 ± 0.008	15.5766 ± 0.005	2.4088 ± 0.003	1.1388 ± 0.002	6.3	
	LA <sup>c</sup>	17.65 ± 0.30	37.42 ± 0.30	15.56 ± 0.24	2.4048 ± 0.02	1.135 ± 0.17		
KCL 209 W (30/12/99)	Sol. <sup>b</sup>	17.678 ± 0.03	37.471 ± 0.01	15.5679 ± 0.005	2.4070 ± 0.005	1.1355 ± 0.002	23	
	LA <sup>c</sup>	17.650 ± 0.04	37.440 ± 0.09	15.551 ± 0.05	2.4081 ± 0.04	1.1353 ± 0.08		
MB/2/01 W (9/12/00)	Sol. <sup>b</sup>	17.925 ± 0.04	37.825 ± 0.03	15.577 ± 0.03	2.4282 ± 0.05	1.1507 ± 0.05	19	20
MB/2/02 SW (12/12/00)	Sol. <sup>b</sup>	17.871 ± 0.04	37.788 ± 0.03	15.577 ± 0.03	2.4260 ± 0.05	1.1473 ± 0.05	29	30
MB/2/04 SSW (18/12/00)	Sol. <sup>b</sup>	17.694 ± 0.01	37.558 ± 0.03	15.584 ± 0.03	2.4099 ± 0.01	1.1354 ± 0.02	23	63
MB/2/05 SE (22/12/00)	Sol. <sup>b</sup>	17.870 ± 0.01	37.716 ± 0.03	15.596 ± 0.03	2.4182 ± 0.01	1.1457 ± 0.02	24	30
MB/2/06 N (29/12/00)	Sol. <sup>b</sup>	17.679 ± 0.01	37.538 ± 0.03	15.565 ± 0.03	2.4117 ± 0.01	1.1358 ± 0.02	11	66
MB/2/042 E (25/9/01)	Sol. <sup>b</sup>	17.683 ± 0.02	37.544 ± 0.03	15.560 ± 0.02	2.4129 ± 0.01	1.1365 ± 0.01	25	66
MB/2/045 SW (25/10/01)	Sol. <sup>b</sup>	17.959 ± 0.02	37.877 ± 0.03	15.585 ± 0.02	2.4304 ± 0.01	1.1524 ± 0.01	14	13
MB/2/046 NW (31/10/01)	Sol. <sup>b</sup>	17.854 ± 0.02	37.772 ± 0.03	15.582 ± 0.02	2.4241 ± 0.01	1.1458 ± 0.01	23	33
<b>LA reproducibility tests</b>								
MB/2/038/ session A	LA <sup>b</sup>	17.891 ± 0.03	37.766 ± 0.02	15.577 ± 0.01	2.4245 ± 0.03	1.1485 ± 0.02		
	LA <sup>b</sup>	17.892 ± 0.04	37.758 ± 0.02	15.574 ± 0.01	2.4247 ± 0.05	1.1486 ± 0.04		
	LA <sup>b</sup>	17.848 ± 0.04	37.716 ± 0.03	15.571 ± 0.01	2.4216 ± 0.04	1.1459 ± 0.03		
	LA <sup>b</sup>	17.854 ± 0.02	37.732 ± 0.02	15.575 ± 0.01	2.4220 ± 0.03	1.1465 ± 0.02		
	LA <sup>b</sup>	17.851 ± 0.05	37.723 ± 0.03	15.577 ± 0.01	2.4224 ± 0.05	1.1462 ± 0.05		
Session A average ± 2SD%		<b>17.87 ± 0.25</b>	<b>37.74 ± 0.12</b>	<b>15.58 ± 0.03</b>	<b>2.423 ± 0.12</b>	<b>1.147 ± 0.23</b>		31
MB/2/038/ session B	LA <sup>b</sup>	17.822 ± 0.05	37.668 ± 0.04	15.561 ± 0.04	2.4194 ± 0.06	1.1441 ± 0.04		
	LA <sup>b</sup>	17.826 ± 0.05	37.667 ± 0.04	15.557 ± 0.02	2.4195 ± 0.04	1.1451 ± 0.04		
	LA <sup>b</sup>	17.882 ± 0.05	37.725 ± 0.03	15.564 ± 0.02	2.5250 ± 0.04	1.1488 ± 0.04		
	LA <sup>b</sup>	17.839 ± 0.06	37.697 ± 0.03	15.567 ± 0.02	2.4204 ± 0.04	1.1456 ± 0.05		
Session B average ± 2SD%		<b>17.86 ± 0.20</b>	<b>37.71 ± 0.19</b>	<b>15.57 ± 0.11</b>	<b>2.422 ± 0.13</b>	<b>1.147 ± 0.15</b>		35
MB/2/039/ session A	LA <sup>b</sup>	17.730 ± 0.03	37.472 ± 0.03	15.577 ± 0.02	2.4065 ± 0.02	1.1389 ± 0.02		
	LA <sup>b</sup>	17.810 ± 0.03	37.586 ± 0.02	15.589 ± 0.02	2.4115 ± 0.03	1.1424 ± 0.02		
	LA <sup>b</sup>	17.768 ± 0.03	37.525 ± 0.02	15.589 ± 0.02	2.4078 ± 0.03	1.1399 ± 0.02		
	LA <sup>b</sup>	17.802 ± 0.03	37.585 ± 0.02	15.593 ± 0.01	2.4100 ± 0.03	1.1415 ± 0.03		
	LA <sup>b</sup>	17.777 ± 0.04	37.540 ± 0.03	15.588 ± 0.02	2.4083 ± 0.04	1.1405 ± 0.03		
	LA <sup>b</sup>	17.778 ± 0.03	37.552 ± 0.02	15.590 ± 0.02	2.4091 ± 0.03	1.1406 ± 0.02		
Session A average ± 2SD%		<b>17.78 ± 0.32</b>	<b>37.54 ± 0.23</b>	<b>15.59 ± 0.07</b>	<b>2.409 ± 0.15</b>	<b>1.141 ± 0.21</b>		48
MB/2/039/ session B	LA <sup>b</sup>	17.766 ± 0.06	37.548 ± 0.03	15.590 ± 0.02	2.4077 ± 0.06	1.1393 ± 0.05		
	LA <sup>b</sup>	17.771 ± 0.03	37.535 ± 0.02	15.587 ± 0.01	2.4085 ± 0.03	1.1405 ± 0.02		
	LA <sup>b</sup>	17.762 ± 0.02	37.511 ± 0.02	15.583 ± 0.02	2.4069 ± 0.02	1.1397 ± 0.02		
	LA <sup>b</sup>	17.758 ± 0.03	37.512 ± 0.03	15.584 ± 0.02	2.4073 ± 0.03	1.1399 ± 0.02		
Session B average ± 2SD%		<b>17.76 ± 0.06</b>	<b>37.53 ± 0.10</b>	<b>15.59 ± 0.04</b>	<b>2.408 ± 0.06</b>	<b>1.140 ± 0.09</b>		50

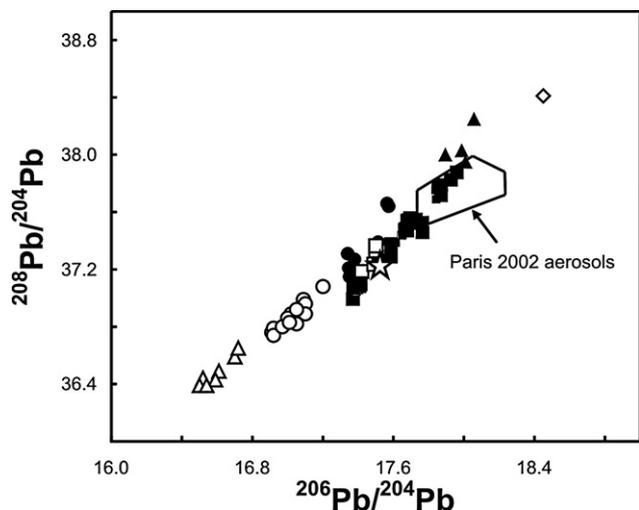
<sup>a</sup> Archive sample number, average wind direction, sampling date. <sup>b</sup> Single analysis (±2SE). <sup>c</sup> Replicate analysis (±2SD). <sup>d</sup> Calculated from measured <sup>206</sup>Pb/<sup>204</sup>Pb and data and equations from Monna *et al.*<sup>17</sup> and data from Roy *et al.*<sup>31</sup>

progressively higher <sup>206</sup>Pb/<sup>204</sup>Pb–<sup>208</sup>Pb/<sup>204</sup>Pb (*i.e.* relatively non-radiogenic to more radiogenic compositions) over time. The one exception is KCL 016 (12/12/1998) which plots close to the 1999

data field and far from the otherwise tight data cluster for 1998. It was noted that the prevailing wind direction during the KCL 016 sample period was significantly different than that for the



**Fig. 1**  $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{208}\text{Pb}/^{204}\text{Pb}$  plot of 1998–2002 London  $\text{PM}_{10}$  compositions. Filled squares are solution-mode MC-ICP-MS data, filled circles are LA-MC-ICP-MS data. LA data for the two analytical sessions for filters MB/2/038 – 039 are shown in diamonds (open and filled symbols distinguish data collected during two separate analytical sessions). Error ellipses for these two samples represent 2 SD uncertainties for each session calculated from the replicate analyses. Brackets highlight the range in  $^{206}\text{Pb}/^{204}\text{Pb}$  for different sample periods.



**Fig. 2**  $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{208}\text{Pb}/^{204}\text{Pb}$  plot comparing data from this study with historical UK data and petrol compositions<sup>24,31,32</sup> (open triangles lead petrol, white star unleaded petrol, open diamond UK pre-industrial, black triangles industrial: aerosols; open circles Southampton 1994–1995, black circles urban London 1995–1996, open squares Oxford 1998, black squares Marylebone Road London 1998–2001 (this study).

other 1998 samples which may have affected the relative contributions of the different  $\text{PM}_{10}$  sources. In contrast, 2000–2001 data overlap.

Laser ablation data were obtained for 1998–1999 filters and two filters from 2001. Whereas chemical preparation removed sample matrix for the solution-mode samples and facilitated

comparable running conditions with the NBS 981 standard, matrix matching of standards with laser ablation samples was not possible. As a result, accuracy and reproducibility could only be determined in a less-direct fashion.

Reproducibility was estimated from replicate analyses of two complete filters (*i.e.* not aliquoted for other analytical purposes). The two filters (MB/2/038 and 039) were rastered over a range of areas varying in dimension from  $\sim 0.1 \text{ cm} \times 0.8 \text{ cm}$  up to  $2.2 \text{ cm} \times 4.0 \text{ cm}$ . Both filters were analysed under identical instrument operating conditions and the data are summarized in Table 1. Within-run analytical uncertainties of individual analyses for all isotope ratios were on the order of  $\pm 0.01$  to  $0.06\%$  (2SE). Average isotope ratio uncertainties for the replicate filter analyses obtained during a single session were on the order of  $\pm \sim 0.3\%$  (2SD), interpreted here as a reasonable estimate of the overall reproducibility, accounting for both instrumental variations and within-filter heterogeneity. Agreement of the filter data from the two separate analytical sessions was on the order of  $0.1\%$  or better.

Accuracy was explored by comparing laser ablation and solution-mode data on the same filters when permitted by sample availability. In all cases the isotope ratios of each sample analysed in both modes agree to better than  $\pm 0.3\%$ , the external reproducibility estimated by the replicate analyses above. We would conclude that the laser ablation data are accurate to within the level of discernment afforded by the estimated external reproducibility and that mass fractionation during analysis was adequately corrected for by TI-normalization. Overall, the LA-mode data outline the same trend as the solution-mode data (Fig. 1), and despite being less precise, the temporal evolution of Pb isotope compositions could have been determined in the absence of solution-mode data.

In this study, the blank/sample ratios obtained by laser ablation were  $\sim 0.1\%$ , significantly lower than for solution mode. This decreased blank effect could be usefully exploited in studies where steps cannot be taken to optimize the filters for solution mode, *e.g.* examining archived filters, or filter analysis by facilities lacking clean chemistry laboratories. As sample throughput is relatively high, laser ablation sampling could also lend itself to reconnaissance or epidemiological studies across large urbanized areas, particularly those that are heavily polluted with high Pb concentrations in the airborne particulates.

Fig. 2 illustrates the Marylebone Road aerosol isotope compositions in the context of UK urban sites sampled between 1994 and 1998. The 1994–1995 aerosol compositions of Monna *et al.*<sup>17</sup> provide baseline data pre-dating the final period of leaded petrol phasing-out and are plotted with their compilations of the Pb isotope compositions of leaded petrol, pre-industrial natural Pb, and estimates of “industrial” Pb based upon French sources. The data show a mixing trend in  $^{206}\text{Pb}/^{204}\text{Pb}$ – $\text{Pb}/^{204}\text{Pb}$  space with aerosol Pb from various locations (London, Southampton) recording non-radiogenic Pb compositions of petrol-derived emissions and more radiogenic industrial contributions. 1994–1995 aerosol Pb isotope composition was strongly controlled by petrol contributions, with sample site Pb composition dependant upon proximity to roads with high traffic densities, wind direction (hence potential dilution of traffic sources) and time of sampling (weekend *vs.* weekday variation in traffic densities). Of interest is the large spread of isotope compositions exhibited by

the suburban London sample site, which is significantly more radiogenic than other sites.

UK aerosol Pb isotopic composition had been relatively constant in the ~20 years prior to 1998 leading to the prediction, based on North American data trends, that phasing out leaded petrol should be reflected in a shift in isotopic composition.<sup>14</sup> Such an evolution of aerosol Pb compositions over time is indeed revealed by the data from this study, 1998 Oxford data, and 1994–1995 data.<sup>14,24</sup> London 1998 and Oxford 1998 compositions are very similar, presumably reflecting a similar balance between traffic-derived Pb and that from other sources. London 1999 data are sufficiently different from the 1998 data to show that phasing out of leaded petrol was well advanced in 1999. The 2000–2001 data crucially document the final effect of totally removing leaded petrol from the UK environment. It is noteworthy that while the 1998 and 1999 data do not overlap, the 2000 and 2001 data completely overlap, and partly overlap with 1999. The similarity of the 2000 and 2001 data suggest stabilisation of Pb sources in London by this time, with these aerosol compositions approaching but not meeting with the fields of “industrial” or background geological sources. This situation could result from a number of factors: [1] recycling of Pb originating from leaded petrol additives residual within the urban environment; [2] presence of a second-order traffic-related Pb source; or [3] a local London “industrial” isotope signature distinct from the industrial signatures documented in the literature. While [1] and [3] cannot be discounted, research in other urban areas points to [2] as the most probable scenario. Unleaded petrol is known to contain Pb while diesel and its combustion products have very low Pb concentrations.<sup>31,32</sup> Furthermore, data from Shanghai and Paris indicate that vehicles burning unleaded petrol are still contributing to the overall Pb budget in high traffic areas, albeit reduced from petrol’s former prominence.<sup>32,33</sup> In the light of these observations, it is highly probable that petrol combustion in London is still an important PM<sub>10</sub> Pb source, and as such, is still a useful tracer of traffic PM<sub>10</sub> contributions in general, although the industrial Pb isotope compositions and scale of Pb recycling is not yet characterised for the London environment. Mixing calculations using French industrial Pb compositions,<sup>17</sup> the Pb composition of unleaded petrol,<sup>31</sup> and PM<sub>10</sub> data from this study indicate that 2000–2001 unleaded petrol-related contributions mainly ranges from 26 to 56% (extremes at 13% and 66%) of the Marylebone roadside Pb budget (Table 1).

Phasing out leaded petrol elsewhere in Western Europe, in cases pre-dating phasing out in the UK, resulted in parallel aerosol Pb isotope evolution towards more radiogenic compositions up to the time of complete elimination of leaded petrol. This evolution is well characterised for PM<sub>10</sub> in France,<sup>15–17,32</sup> and the similarity of the London data to measurements from Paris is particularly striking (Fig. 2). Such a convergence of isotope compositions indicates very similar primary controls on the isotope composition of pollution sources. In addition, Paris and London now share similar proportions of traffic-related Pb in the total aerosol budget (*c.f.* traffic related Pb 30–50% of total Pb for Paris aerosols<sup>32</sup>) and the increased variability of aerosol composition on a day to day basis.<sup>15,32</sup>

The reduction in Pb compositional differences between UK aerosol sources, coupled with continuing reduction of Pb levels in

the environment will inevitably result in previously subordinate sources of Pb having a greater impact on the aerosol Pb budget. In many places such sources are not yet well studied but will need characterisation in order to understand isotopically variable and complex local environments. It is also likely that distal transport of Pb from relatively high-Pb environments will increasingly impact on the local UK Pb aerosol composition, following the trend observed in Germany,<sup>14</sup> where long-term Pb reduction in the environment has made it possible to observe the affects of Russian and Eastern European Pb. At the same time it will be progressively more challenging with the sampling protocols used here to analyse all of the Pb isotopes on samples collected over ≤24 h periods, a desirable timescale for considering the affects of local meteorological conditions and disparate Pb sources. Multicollector Faraday measurements are presently capable of satisfying the analytical constraints given the high sensitivity of state of the art MC-ICP-MS, but in future multiple ion counting capability now available for the latest generation MC-ICP-MS instruments, or high sensitivity SF-ICP-MS with ion counting detectors, may be required to study short timescale aerosol compositional variations.

## Conclusions

Pb isotope compositions for London UK PM<sub>10</sub> atmospheric particulates were measured by solution-mode MC-ICP-MS for samples collected at intervals between 1998 and 2001, and show a dramatic shift to increasingly radiogenic compositions over time. This relates directly to the final phasing out of leaded petrol in the UK. The similarity of 2000 and 2001 data suggest that the Pb isotope composition in London had stabilised, providing a useful baseline for continuing UK PM<sub>10</sub> monitoring studies through the 21<sup>st</sup> century.

The observed Pb isotope evolution trend parallels that of other regions that phased out leaded petrol, with 2000–2001 London and 2002 Paris aerosol isotope compositions being particularly similar. In London, traffic-related Pb contributions to PM<sub>10</sub> are still important, but other Pb sources are becoming increasingly prominent. Continuing UK PM<sub>10</sub> Pb isotope investigation is warranted as there are contributing factors that either are poorly quantified or subject to change. Accurate source apportionment between traffic-related and other local and distal Pb sources is currently precluded and it is a prerequisite that better constraints on the local anthropogenic sources are obtained, as this will facilitate distal source assessment.

Lastly, a pilot investigation of LA-MC-ICP-MS showed that although the level of precision achieved does not match that of the more established techniques, the data are sufficiently accurate and precise to show the main Pb isotope trends in our study area. Some advantages of the method include low Pb blank and by-passing of chemical separation of Pb, which could facilitate aerosol studies in analytical facilities lacking the clean laboratory conditions or where reconnaissance level data is required.

## References

- 1 J. O. Nriagu and J. M. Pacyna, *Nature*, 1988, **333**, 134–139; J. O. Nriagu, *Sci. Total Environ.*, 1992, **92**, 13–28.
- 2 UK National Air Quality Information Archive; [http://www.airquality.co.uk/archive/data\\_and\\_statistics.php](http://www.airquality.co.uk/archive/data_and_statistics.php).

- 3 World Health Organization Regional Office for Europe, Air quality Guidelines for Europe, 2nd edn, WHO Regional Publications, *European Series*, 91, 2000; World Health Organization, Health Aspects of Air Pollution, results from the WHO project, *Systematic Review of Health Aspects of Air Pollution in Europe*, Geneva, 2004.
- 4 J. Carignan, A. Simonetti and C. Gariépy, *Atmos. Environ.*, 2002, **36**, 3759–3766.
- 5 M. Murozumi, T. J. Chow and C. C. Patterson, *Geochim. Cosmochim. Acta*, 1969, **33**, 1247–1294.
- 6 E. A. Crecelius and D. Z. Piper, *Environ. Sci. Technol.*, 1973, **7**, 1053–1055.
- 7 D. N. Edgington and J. A. Robbins, *Environ. Sci. Technol.*, 1976, **10**, 266–274.
- 8 K. K. Bertine and E. D. Goldberg, *Environ. Sci. Technol.*, 1977, **11**, 297–299.
- 9 C. F. Boutron, J. P. Candelone and S. Hong, *Geochim. Cosmochim. Acta*, 1994, **58**, 3217–3225.
- 10 K. J. R. Rosman, W. Chisholm, C. F. Boutron, J. P. Candelone and C. C. Patterson, *Geophys. Res. Lett.*, 1994, **21**, 2669–2677.
- 11 M. I. Hornberger, S. N. Luoma, A. van Green, C. Fuller and R. Anima, *Mar. Chem.*, 1999, **64**, 39–55.
- 12 W. Shotyk, D. Weiss, P. G. Appleby, A. K. Cheburkin, R. Frei, M. Gloor, J. D. Kramers, S. Reese and O. Van Der Knaap, *Science*, 1998, **281**, 1635–1640.
- 13 M. Schwikowski, C. Barbante, T. Doering, H. W. Gaeggeler, C. Boultron, U. Schotterer, L. Tobler, K. Van de Velde, C. Ferrari, G. Cozzi, K. Rosman and P. Cescon, *Environ. Sci. Technol.*, 2004, **38**, 957–964.
- 14 A. Bollhöfer, W. Chisholm and K. J. R. Rosman, *Anal. Chim. Acta*, 1999, **390**, 227–235; A. Bollhöfer and K. J. R. Rosman, *Geochim. Cosmochim. Acta*, 2000, **64**, 3251–3262; A. Bollhöfer and K. J. R. Rosman, *Geochim. Cosmochim. Acta*, 2001, **65**, 1727–1740; A. Bollhöfer and K. J. R. Rosman, *Geochim. Cosmochim. Acta*, 2002, **66**, 1375–1386.
- 15 K. Deboudt, P. Flament, D. Weiss, J.-P. Mennessier and P. Maquinghen, *Sci. Total Environ.*, 1999, **236**, 57–74; T. Moreno, W. Gibbons, T. Jones and R. Richards, *Atmos. Environ.*, 2003, **37**, 4265–4276.
- 16 A. Veron, P. Flament, M. L. Bertho, L. Alleman, R. Flegal and B. Hamelin, *Atmos. Environ.*, 1999, **33**, 3377–3388.
- 17 F. Monna, J. Lancelot, I. W. Coiudace, A. B. Cundy and J. T. Lewis, *Environ. Sci. Technol.*, 1997, **31**, 2277–2286.
- 18 D. W. Dockery, C. A. Pope, X. P. Xu, J. D. Spengler, J. H. Ware, M. E. Fay, B. G. Ferris and F. E. Speizer, *New Engl. J. Med.*, 1993, **329**, 1753–1759.
- 19 C. A. Pope, M. J. Thun, M. M. Namboodiri, D. W. Dockery, J. S. Evans, F. E. Speizer and C. W. Heath, *Am. J. Respir. Crit. Care Med.*, 1995, **151**, 669–674.
- 20 F. Laden, L. M. Neas, D. W. Dockery and J. Schwartz, *Environ. Health Perspect.*, 2000, **108**, 941–947.
- 21 R. A. Goyer, *Environ. Health Perspect.*, 1990, **86**, 177–181.
- 22 D. C. Rice, *Environ. Health Perspect.*, 1996, **104**(suppl. 2), 337–351.
- 23 T. Moreno, W. Gibbons, T. Jones and R. Richards, *Atmos. Environ.*, 2003, **37**, 4265–4276.
- 24 B. Sitzmann, M. Kendall, J. Watt and I. Williams, *Sci. Total Environ.*, 1999, **241**, 63–73.
- 25 J. Zhou, PhD thesis, University of London, 1997.
- 26 W. M. White, F. Alarède and P. Telouk, *Chem. Geol.*, 2000, **167**, 257–270.
- 27 H. P. Longerich, B. J. Fryer and D. F. Strong, *Spectrochim. Acta, Part B*, 1987, **42**, 39–48.
- 28 M. S. A. Horstwood, G. L. Foster, R. R. Parrish, S. R. Noble and G. M. Nowell, *J. Anal. At. Spectrom.*, 2003, **18**, 837–846.
- 29 M. F. Thirlwall, *Chem. Geol.*, 2002, **184**, 255–279.
- 30 A. Bouvier, J. Blichert-Toft, F. Moynier, J. D. Vervoort and F. Albarède, *Geochim. Cosmochim. Acta*, 2007, **71**, 1583–1604.
- 31 S. Roy, PhD thesis, Université Paris 7-IPGP, 1996.
- 32 D. Widory, S. Roy, Y. Le Moullec, G. Goupil, A. Cocherie and C. Guerrot, *Atmos. Environ.*, 2004, **38**, 953–961.
- 33 J. Zheng, M. Tan, Y. Shibata, A. Tanaka, Y. Li, G. Zhang, Y. Zhang and Z. Shan, *Atmos. Environ.*, 2004, **38**, 1191–1200.