

# Pb Isotopic Composition of Airborne Particulate Material from France and the Southern United Kingdom: Implications for Pb Pollution Sources in Urban Areas

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Pb isotopic studies of airborne particulate matter, incinerator ash, and gasoline have been carried out to determine sources of Pb pollution in urban areas from France and the southern United Kingdom.  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios in gasoline range from 1.061 to 1.094 (average values are 1.084 for France and 1.067 for the U.K.) while for industrially-derived Pb,  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios vary from 1.143 to 1.155. Natural Pb is more radiogenic and literature values for pre-industrial sediments give  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of 1.19–1.20 in France and 1.17–1.19 in the U.K. The measured Pb isotopic signature of airborne particulate matter reflects the relative importance of each of these sources, and samples taken from urban areas close to traffic in France and the U.K. show  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios that vary widely from 1.085 to 1.158. While alkyl-lead additives in gasoline are typically still the dominant source of Pb in urban particulate matter, the relative importance of gasoline-derived Pb has decreased, and as a result other sources (industrial and natural) can be identified using isotopic studies. This is a consequence of recent EU environmental legislation that significantly limits concentrations of Pb in gasoline and the increased market penetration of unleaded gasoline. In addition, at a given location, the Pb isotopic composition of particulate matter can vary considerably due to temporal variations in sources (i.e., variations in traffic density) and with wind direction.

## Introduction

Investigative studies of lead isotope compositions are well-established in geochemistry and geochronology and are increasingly used in environmental science (see the Clair C. Patterson Special Issue, *Geochim. Cosmochim. Acta* **1994**, *58*). While Pb concentration measurements may provide useful information about potential enrichments of this element, the sources of this Pb will often be ambiguous. To resolve this

uncertainty, Pb isotope ratios are studied. Pb has four stable isotopes:  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ , and  $^{208}\text{Pb}$ . The last three are radiogenic isotopes and are produced by the radioactive decay of  $^{238}\text{U}$ ,  $^{235}\text{U}$ , and  $^{232}\text{Th}$  respectively ( $^{204}\text{Pb}$  is non-radiogenic). Each lead ore deposit has its own characteristic Pb isotopic composition, depending on its age (strictly the time that the lead separated from its source rocks) and on its conditions of genesis (1). The isotopic composition of Pb in environmental materials is thus dependent on the ore bodies from which it was derived. In the environment, Pb isotopic ratios reflect the mixing of local/natural Pb with anthropogenic inputs, and mixing processes can be quantified if each source of lead has a distinctive isotopic composition. This principle has been used in a variety of media to determine anthropogenic Pb sources, for example, in freshwater (2–5), in sediments (6–11), and in aerosols (12–19). In France and the U.K., and in western Europe as a whole, the Pb currently used in anthropogenic processes is derived from foreign sources (ore bodies) that commonly have distinctly different isotopic compositions from the local/natural Pb present in rocks and soils. The isotopic signature of this anthropogenic lead is subject to economic factors (commodity, prices) and consequently may change with time according to the origin of the Pb ores used. It is thus essential to make frequent isotopic measurements to maintain a reliable database of anthropogenic Pb for a particular cultural region. Where investigations of environmental fluxes of Pb over a long period are made (i.e., in sedimentary or ice cores), it is clear that a good knowledge of the isotopic character of anthropogenic Pb is required if reliable historical pollution reconstructions are to be carried out. Studies of Pb in the United States are well established and varied, and the subject has a long history (8, 20–23). However, the European perspective is not so well established, and fewer data are available.

In this study, recently acquired isotopic data for pollution sources in France and the U.K. are presented, with measurements of airborne particulate matter collected from urban areas. The data provide a better understanding of local variability in Pb sources and show the relative importance of natural and anthropogenic Pb sources in urban air at a number of differing sites. The changing contributions of gasoline-derived Pb to the overall anthropogenic input of lead, due to changes in the use of unleaded petrol over the last 20 years, is also discussed.

## Methodology

**Sampling.** Airborne particulate matter was sampled in 12 French cities and two cities in the U.K. Where possible, sampling was carried out using a PPA60 (France) or TEOM (U.K.) instrument (Amiens, Caen, Le Havre, Lille, Paris, Montpellier, Strasbourg, Toulouse, and London). These devices have a multidirectional head that removes airborne particulate matter above  $10\ \mu\text{m}$  and aspirates the ambient air at a fixed-flow rate of  $25\ \text{L}\ \text{mn}^{-1}$  (PPA60) or  $13\ \text{L}\ \text{mn}^{-1}$  (TEOM). Samples were collected over 24 h on cellulose–nitrate membrane filters (porosity, 0.8; total diameter, 47 mm; exposed diameter, 33 mm). For other cities, where this equipment was not available, particulate matter was sampled using FILTROMAT equipment over a 24-h period at a fixed-flow rate of  $100\ \text{L}\ \text{h}^{-1}$  (Bar-le-Duc, Clermont Ferrand, Nantes, and Nice) or using precleaned  $0.2\text{-}\mu\text{m}$  PTFE membrane filters attached to a diaphragm pump (Southampton sites). Samples from Southampton were collected over periods ranging from 7 to 10 days and so represent a time-integrated measurement. In addition, five ash samples were removed from electrostatic filters from a French urban incinerator, and 16 leaded gasoline samples were collected in both countries into precleaned glass vials directly from the pump.

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**Chemical and Isotopic Analysis. (A) TIMS Analysis.** Analyses of French and United Kingdom (London) samples were performed using TIMS at Montpellier. Sample preparation was carried out under Class 100 laminar air flow clean benches in a clean room. Almost all the particulate matter was removed from the filters by ultrasonic agitation in 5 mL of deionized water with the help of a PTFE spatula. Filters were agitated for 2 min only to avoid partial decomposition of the filter, which may introduce a significant blank contribution. Acid digestion of the matrix was avoided for the same reason. The 100% removal of particulate material from the filter is not essential (as the above method of removal is unlikely to be particle size selective), and so the Pb isotopic composition of the material extracted is likely to be representative of the entire sample (Pb isotopic composition is independent of the amount of Pb extracted). After the removal of the filter, the water mixture containing the collected particulate matter was evaporated to dryness, and the residue was digested in 2 mL of high-purity aqua regia at 90 °C for 24 h. For the incinerator ashes, a few milligrams was digested in a PTFE beaker with a mixture of distilled HF, HNO<sub>3</sub>, and HCl heated at 90 °C for 1 week. For gasoline, 5 μL was slowly evaporated at 20 °C, and the residue was digested following the same procedure. The solutions were then evaporated, and 200 μL of 0.5 N HBr was added.

Pb separation was achieved using Bio-Rad AG1-X4 anion exchange resin following the conventional technique (5, 24): loading of the sample in 0.5 N HBr, washing twice with 1 mL of 0.5 N HBr, and a final elution of Pb with 0.5 mL of 6 N HCl. This operation was repeated to purify the sample and to ensure a stable thermal emission during measurements. Pb was loaded on a single Re filament using the silica gel/phosphoric acid method (25). Measurements of Pb isotopic ratios were carried out by thermal ionization mass spectrometry (TIMS) on a VG SECTOR mass spectrometer equipped with five Faraday cups using simultaneous multicollection in static mode. Regular measurements of the Pb standard, NIST 981, allowed the correction of the data for mass fractionation (1.35 ± 0.05 ‰ per amu). Analytical precision was found to be better than 1‰ for <sup>206</sup>Pb/<sup>204</sup>Pb, <sup>207</sup>Pb/<sup>204</sup>Pb, and <sup>208</sup>Pb/<sup>204</sup>Pb ratios and better than 0.2‰ for <sup>206</sup>Pb/<sup>207</sup>Pb and <sup>208</sup>Pb/<sup>206</sup>Pb ratios. Blank measurements, determined using a <sup>207</sup>Pb spike, show that Pb added during the analytical procedure by the operator is less than 0.25% of the Pb concentration in the samples and thus does not require correction. Duplicates of three aerosol samples (Le Havre, Lille, and Paris) show good reproducibility and confirm the significance of the analytical data.

**(B) ICP-MS Measurements.** Isotopic analyses of Southampton airborne particulate samples and of U.K. gasoline were performed at Southampton using a VG PlasmaQuad 2+ ICP-MS. This instrument has a very high sensitivity and produces a count rate of approximately 5.10<sup>5</sup> cps/ppb for Pb. Pb was preconcentrated in a similar manner to that described above, and the details are given in ref 11. MilliQ+ water and PRIMAR acids (Fisher) were used during all chemical manipulations. NIST 981 was used to monitor accuracy and to correct for mass fractionation, and procedural blanks were run to determine possible contamination from reagents and general handling. The only notable interference in ICP-MS measurements is the <sup>204</sup>Hg isobaric overlap on <sup>204</sup>Pb that is readily corrected for by monitoring <sup>200</sup>Hg. Analytical precision was generally better than 1% for <sup>206</sup>Pb/<sup>204</sup>Pb, <sup>207</sup>Pb/<sup>204</sup>Pb, and <sup>208</sup>Pb/<sup>204</sup>Pb ratios and better than 8‰ for <sup>206</sup>Pb/<sup>207</sup>Pb and <sup>208</sup>Pb/<sup>206</sup>Pb ratios.

## Results

Geochemists prefer conventionally to use Pb isotopic ratios incorporating <sup>204</sup>Pb due to the mathematical simplification of using a non-radiogenic isotope. However, environmental scientists tend to use <sup>206</sup>Pb/<sup>204</sup>Pb vs <sup>206</sup>Pb/<sup>207</sup>Pb or <sup>206</sup>Pb/<sup>207</sup>Pb

vs <sup>208</sup>Pb/<sup>206</sup>Pb because of their better analytical precision. Here we use <sup>206</sup>Pb/<sup>207</sup>Pb vs <sup>208</sup>Pb/<sup>206</sup>Pb for comparability with recent studies obtained using ICP-MS and also present conventional <sup>206</sup>Pb/<sup>204</sup>Pb vs <sup>208</sup>Pb/<sup>204</sup>Pb diagrams.

The environmental materials analyzed in the present study have distinct lead isotopic signatures (Tables 1 and 2). Gasolines possess the least radiogenic isotopic signatures, and Pb isotopic ratios show little regional variation. In France, <sup>206</sup>Pb/<sup>207</sup>Pb ratios range from 1.069 to 1.094 (average: 1.084 ± 0.009 at 1σ) whereas in the U.K. slightly lower values are found: <sup>206</sup>Pb/<sup>207</sup>Pb ratios ranging between 1.059 and 1.079 (average: 1.067 ± 0.007). Ashes from the French urban incinerator gave much higher (more radiogenic) <sup>206</sup>Pb/<sup>207</sup>Pb ratios ranging from 1.143 to 1.154 (average: 1.149 ± 0.005), similar to values for liquid urban wastes from Southern France (5) (average <sup>206</sup>Pb/<sup>207</sup>Pb = 1.157 ± 0.007, 1σ). The greatest variations in isotopic composition occurred in urban airborne particulate matter (sampled in nine French cities and two U.K. cities during the period November 1994–January 1996) that had <sup>206</sup>Pb/<sup>207</sup>Pb ratios between 1.085 and 1.158. Both regional and temporal variations in the Pb isotopic composition of urban airborne particulate matter were obvious. At a national scale, <sup>206</sup>Pb/<sup>207</sup>Pb ratios varied between 1.100 at Nantes and 1.145 at Toulouse, while locally two different sites in the same city, examined during the same day, show very distinct isotopic signatures: 1.104 (Toulouse station 6) and 1.145 (Toulouse station 12) (Table 1). In addition, substantial temporal variations were observed at west London (Teddington), where the Pb isotopic composition of airborne particles was monitored daily over two periods of approximately 1 week each in November 1995 and in January 1996. Here, the <sup>206</sup>Pb/<sup>207</sup>Pb ratios varied between 1.114 and 1.127 during the November 1995 sampling period and between 1.124 and 1.158 during the January 1996 sampling period (Table 2). For each period, the more radiogenic values are observed during the weekend or when the wind is from a SE direction (authors preliminary unpublished data). If the integrated sampling time is longer, as at Southampton (3–7 days), these variations are less clear. The regional and temporal variability in Pb isotopic composition reflects local variations in the relative importance of gasoline, industrial, and natural Pb sources and is discussed in the following sections.

## Discussion

**Isotopic Characterization of Pb Sources. (A) Pb from Gasoline.** Despite direct pump sampling of several different gasoline suppliers (Esso, Total, Agip, etc.), the range of measured <sup>206</sup>Pb/<sup>207</sup>Pb ratios is rather small for each country and so represents a relatively homogeneous source. The values are the lowest ever reported for French and U.K. gasoline: the average <sup>206</sup>Pb/<sup>207</sup>Pb ratio for French samples is 1.084 ± 0.009 (1σ), while the average for U.K. samples is 1.067 ± 0.007. In France and the U.K., the Octel Co. (Associated Octel in the U.K.) is the main producer of tetraethyl and tetramethyl lead (TEL-TML) added to fuels as an anti-knock compound. This company supplies nearly 80% of the Pb alkyls used in the refineries of both countries. Production of TEL-TMLs from U.S. companies has totally ceased due to national legislative requirements. Most of the Pb currently used in TEL-TML production is derived from the Precambrian Pb-Zn ore deposits of Australia and Canada, with minor contributions from Morocco and other sources [Octel Co., France (1995) and Associated Octel, U.K., personal communication, (1996)]. Pb from Australian and Canadian ores are characterized by low radiogenic signatures; the 1600–1700 Ma Broken Hill (New South Wales) and Mount Isa (Queensland) Pb ores show <sup>206</sup>Pb/<sup>207</sup>Pb ratios in the range 1.03–1.04 (1). The Mesozoic Pb-Zn province from Morocco shows a much more radiogenic <sup>206</sup>Pb/<sup>207</sup>Pb ratio of approximately 1.16–1.17. A mixing of 80% Australian Pb with

TABLE 1. Pb Isotopic Composition of Airborne Particulate Matter, Gasoline, and Incinerator Ashes in France

location/(station)	organization	date	characteristics	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
Airborne Particulate Matter								
Amiens	ASQAP	Sep 1, 1995	urban	17.276 ± 0.006	15.552 ± 0.006	37.10 ± 0.02	1.1108 ± 0.0001	2.1476 ± 0.0003
Bar-le-duc	AIRLOR	Sep 1, 1995		17.543 ± 0.005	15.553 ± 0.005	37.38 ± 0.01	1.1279 ± 0.0001	2.1309 ± 0.0003
Caen	ESPAC	Sep 7, 1995		17.329 ± 0.011	15.535 ± 0.010	37.15 ± 0.03	1.1155 ± 0.0001	2.1440 ± 0.0003
		Sep 8, 1995		17.350 ± 0.008	15.548 ± 0.008	37.19 ± 0.02	1.1158 ± 0.0001	2.1438 ± 0.0003
		Sep 1, 1995		17.448 ± 0.011	15.553 ± 0.011	37.28 ± 0.03	1.1219 ± 0.0001	2.1366 ± 0.0003
Clermont-Ferrand	AMPAC	Aug 14, 1995		17.236 ± 0.004	15.536 ± 0.005	37.09 ± 0.01	1.1094 ± 0.0001	2.1517 ± 0.0003
Le Havre	AIR NORMAND			17.248 ± 0.005	15.552 ± 0.005	37.09 ± 0.02	1.1091 ± 0.0001	2.1508 ± 0.0003
duplicate	AREMA LRT	Sep 1, 1995		17.288 ± 0.009	15.544 ± 0.009	37.16 ± 0.02	1.1123 ± 0.0001	2.1492 ± 0.0003
Lille				17.285 ± 0.005	15.540 ± 0.006	37.11 ± 0.02	1.1124 ± 0.0001	2.1469 ± 0.0003
duplicate	Préfecture de Police	Sep 13, 1995		17.425 ± 0.005	15.542 ± 0.005	37.26 ± 0.02	1.1212 ± 0.0002	2.1386 ± 0.0004
Paris				17.448 ± 0.011	15.553 ± 0.011	37.28 ± 0.03	1.1219 ± 0.0001	2.1366 ± 0.0003
duplicate								
Montpellier								
station 1	AMPADI	Jan 27, 1995		17.453 ± 0.007	15.567 ± 0.007	37.28 ± 0.02	1.1211 ± 0.0001	2.1361 ± 0.0003
station 4		Jan 29, 1995		17.382 ± 0.004	15.577 ± 0.005	37.23 ± 0.01	1.1159 ± 0.0001	2.1421 ± 0.0003
station 1		Jan 29, 1995		17.401 ± 0.007	15.564 ± 0.007	37.24 ± 0.02	1.1181 ± 0.0001	2.1402 ± 0.0003
station 1		Sep 7, 1995		17.202 ± 0.005	15.543 ± 0.005	37.05 ± 0.02	1.1068 ± 0.0001	2.1539 ± 0.0003
Nantes	LOIRESTU/AIR	Sep 7, 1995		17.084 ± 0.005	15.519 ± 0.005	36.91 ± 0.01	1.1008 ± 0.0001	2.1603 ± 0.0003
Nice	QUALIT'AIRO6	Sep 21, 1995		17.445 ± 0.005	15.547 ± 0.005	37.27 ± 0.02	1.1221 ± 0.0001	2.1363 ± 0.0003
Strasbourg	ASPA	Sep 1, 1995		17.566 ± 0.018	15.490 ± 0.016	37.31 ± 0.04	1.1342 ± 0.0002	2.1236 ± 0.0004
		Sep 4, 1995		17.611 ± 0.006	15.558 ± 0.006	37.42 ± 0.02	1.1319 ± 0.0001	2.1250 ± 0.0003
Toulouse								
station 6	ORAMIP	Sep 7, 1995	urban/smelter	17.139 ± 0.013	15.522 ± 0.013	36.96 ± 0.03	1.1042 ± 0.0001	2.1563 ± 0.0004
station 12		Sep 7, 1995		17.892 ± 0.004	15.622 ± 0.004	37.90 ± 0.01	1.1453 ± 0.0001	2.1184 ± 0.0004
Gasolines								
ELF	Leaded gasoline	Oct 1995	pump	16.564 ± 0.005	15.490 ± 0.005	36.41 ± 0.02	1.0693 ± 0.0001	2.1980 ± 0.0004
Leclerc Supermarket				16.759 ± 0.004	15.510 ± 0.005	36.59 ± 0.02	1.0806 ± 0.0001	2.1832 ± 0.0004
Monoprix Supermarket				17.014 ± 0.003	15.549 ± 0.004	36.95 ± 0.01	1.0942 ± 0.0001	2.1719 ± 0.0004
total		Nov 1995		16.996 ± 0.007	15.534 ± 0.007	36.89 ± 0.02	1.0942 ± 0.0001	2.1705 ± 0.0003
Esso		Dec 1995		16.679 ± 0.005	15.511 ± 0.005	36.53 ± 0.01	1.0753 ± 0.0001	2.1904 ± 0.0003
AGIP				16.897 ± 0.006	15.534 ± 0.006	36.80 ± 0.02	1.0878 ± 0.0001	2.1777 ± 0.0003
BP				16.641 ± 0.007	15.499 ± 0.008	36.47 ± 0.02	1.0736 ± 0.0001	2.1914 ± 0.0004
Shell				16.837 ± 0.006	15.510 ± 0.006	36.70 ± 0.02	1.0856 ± 0.0001	2.1796 ± 0.0003
Carrefour Supermarket				17.068 ± 0.004	15.597 ± 0.005	37.09 ± 0.02	1.0943 ± 0.0001	2.1728 ± 0.0004
Industrial Pb								
urban incinerator	CIVOM Sete	Sep 30, 1993	ashes	17.894 ± 0.004	15.661 ± 0.005	38.00 ± 0.01	1.1427 ± 0.0001	2.1236 ± 0.0003
		Oct 29, 1993		18.057 ± 0.007	15.698 ± 0.007	38.25 ± 0.02	1.1501 ± 0.0002	2.1183 ± 0.0007
		Dec 03, 1993		17.987 ± 0.003	15.634 ± 0.004	38.03 ± 0.01	1.1504 ± 0.0001	2.1143 ± 0.0003
		Jan 06, 1994		18.009 ± 0.003	15.595 ± 0.010	37.95 ± 0.01	1.1547 ± 0.0001	2.1070 ± 0.0002

TABLE 2. Pb Isotopic Composition of Airborne Particulate Matter and Gasoline in the U.K.

location	date	characteristics	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$		
Portsmouth (Southampton)	Nov 10, 1994	city suburb	Airborne Particulate Matter						
	Jan 8, 1995		17.05 ± 0.05		36.92 ± 0.05	1.105 ± 0.002	2.165 ± 0.003		
	Nov 28, 1994		17.05 ± 0.05		36.92 ± 0.05	1.102 ± 0.002	2.165 ± 0.003		
	Oct 21, 1994		17.20 ± 0.05		37.08 ± 0.05	1.111 ± 0.002	2.155 ± 0.003		
	Oct 20, 1994		16.91 ± 0.05		36.76 ± 0.05	1.089 ± 0.003	2.175 ± 0.003		
	Oct 28, 1994		16.92 ± 0.05		36.79 ± 0.05	1.096 ± 0.003	2.174 ± 0.003		
	Nov 18, 1994		17.02 ± 0.05		36.89 ± 0.05	1.098 ± 0.003	2.167 ± 0.003		
	Nov 5, 1994		16.92 ± 0.05		36.74 ± 0.05	1.098 ± 0.003	2.172 ± 0.003		
	Nov 25, 1994		17.09 ± 0.05		36.99 ± 0.05	1.098 ± 0.003	2.165 ± 0.003		
	Dec 10, 1994		17.02 ± 0.05		36.86 ± 0.05	1.101 ± 0.003	2.166 ± 0.003		
	Dec 17, 1994		17.10 ± 0.05		36.96 ± 0.05	1.101 ± 0.003	2.161 ± 0.003		
	Dec 3, 1994		17.00 ± 0.05		36.86 ± 0.05	1.101 ± 0.003	2.168 ± 0.003		
	Dec 27, 1994		17.05 ± 0.05		36.82 ± 0.05	1.102 ± 0.003	2.160 ± 0.003		
	Dec 23, 1994		16.97 ± 0.05		36.80 ± 0.05	1.103 ± 0.003	2.169 ± 0.003		
	Dec 30, 1994		17.01 ± 0.05		36.83 ± 0.05	1.104 ± 0.003	2.165 ± 0.003		
London (Teddington)	Sat Nov 4, 1995	urban		15.602 ± 0.005	36.89 ± 0.05	1.106 ± 0.003	2.157 ± 0.003		
	Sun Nov 5, 1995		17.564 ± 0.004		37.66 ± 0.01	1.1257 ± 0.0001	2.1440 ± 0.0003		
	Mon Nov 6, 1995		17.573 ± 0.003		37.64 ± 0.01	1.1273 ± 0.0001	2.1418 ± 0.0003		
	Wed Nov 8, 1995		17.341 ± 0.003		37.31 ± 0.01	1.1143 ± 0.0001	2.1513 ± 0.0003		
	Thu Nov 9, 1995		17.347 ± 0.003		37.21 ± 0.01	1.1159 ± 0.0001	2.1449 ± 0.0003		
	Fri Nov 10, 1995		17.351 ± 0.007		37.15 ± 0.02	1.1168 ± 0.0001	2.1409 ± 0.0003		
	Thu Jan 18, 1996		17.379 ± 0.007		37.27 ± 0.02	1.1163 ± 0.0001	2.1444 ± 0.0003		
	Fri Jan 19, 1996		17.513 ± 0.006		37.39 ± 0.02	1.1244 ± 0.0001	2.1347 ± 0.0003		
	Sat Jan 20, 1996		17.522 ± 0.010		37.43 ± 0.03	1.1241 ± 0.0002	2.1360 ± 0.0004		
	Sun Jan 21, 1996		17.790 ± 0.003		37.69 ± 0.01	1.1403 ± 0.0001	2.1187 ± 0.0003		
	Mon Jan 22, 1996		18.074 ± 0.007		37.95 ± 0.02	1.1582 ± 0.0001	2.0993 ± 0.0003		
			18.032 ± 0.007		37.86 ± 0.02	1.1557 ± 0.0001	2.0997 ± 0.0003		
	Texaco (Southampton)		Nov-Dec 1994	leadged 4* gasoline	Gasolines				
					16.61 ± 0.05		36.49 ± 0.05	1.059 ± 0.003	2.197 ± 0.003
					16.52 ± 0.05		36.44 ± 0.05	1.061 ± 0.003	2.196 ± 0.003
16.50 ± 0.05					36.39 ± 0.05	1.062 ± 0.003	2.197 ± 0.003		
16.59 ± 0.05					36.43 ± 0.05	1.066 ± 0.003	2.195 ± 0.003		
16.54 ± 0.05					36.39 ± 0.05	1.068 ± 0.003	2.191 ± 0.003		
16.70 ± 0.05					36.59 ± 0.05	1.076 ± 0.003	2.189 ± 0.003		
Shell (Southampton)		16.72 ± 0.05		36.65 ± 0.05	1.079 ± 0.003	2.186 ± 0.003			

20% of Moroccan Pb gives a ratio of 1.06. This calculated value is comparable with the mean of  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio measured today in French gasoline ( $1.084 \pm 0.009$ ;  $1\sigma$ ). In the U.K. in the late 1980s, Associated Octel used a mixture of Australian and Canadian ores in the approximate proportion 70:30 giving a  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of 1.076 (26) similar to the mean currently measured. The virtual monopoly for alkyl-lead additives held by the Octel Co., in both France and the U.K., implies a signature that is relatively homogeneous regardless of gasoline supplier. However, it should be noted that U.K. additives may not be exactly identical to those recipes used in France since the Octel Co. operates independently in both countries and may therefore purchase Pb from different sources.

**(B) Pb from Industrial Emissions.** It is difficult to precisely define the isotopic signature of an overall industrial Pb source because of the multiplicity of existing emissions. In addition, the Pb used by U.K. and French industry is dominantly imported since all indigenous Pb–Zn mineral deposits have been worked out in both countries. In the case of gasoline, it is possible to characterize a general Pb isotopic signature due to the effective market monopoly of the Octel Co., but it is obviously not possible to follow the same approach for industrial emissions. While it is likely that industrial emissions have a widely varying Pb isotopic composition (as shown by several workers), Mukai et al. (16) and Hamester et al. (19) have shown that the Pb isotopic composition of fly ashes from refuse incinerators can be used as a useful indicator of industrial Pb sources. All Pb-containing products are burned and mixed, and the lead isotope ratios are averaged to provide a representative “industrial Pb” signature. Data for the urban incinerator at Sète give  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios varying from 1.143 to 1.155 (Table 1). The range may be due to slight variation in the nature of burned products. Identical ratios have been recently found for the same kind of samples from Germany  $\sim 1.142$ – $1.159$  (19) and in Japan 1.15 (16). These values are comparable to those previously found in liquid urban waste ( $\sim 1.147$ – $1.160$ ) in southern France (5) and are much more radiogenic than those from gasoline. The application of the Student's *t*-test indicates that the differences between Pb from gasoline and industrial Pb are significant at greater than the 99.9% level. The imports thus are likely to include younger Pb ores (which are more radiogenic) than those from Australia. It is interesting to note that this range also corresponds to the world average of the main Pb ore deposits.

**(C) Natural Pb Derived from Rocks and Soils.** In France,  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios ranging from 1.193 to 1.200 were measured in pre-industrial sediments sampled in the Thau basin (southern France) and dated at more than 200 yr BP (27). Almost the same values were observed (1.197–1.210) in the pre-industrial sediments of the Seine, Loire, Gironde, and Rhône Rivers (3). This ratio is likely to be typical throughout France because most of the natural Pb is derived from Variscan continental crust (granite and metamorphic rocks) and from Mesozoic and Cenozoic sediments. This Pb has a  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio ranging from 1.18 to 1.20 (28). A remote contribution due to dust transport from North Africa and the Sahara may also occur, although the isotopic composition of these aerosols does not differ significantly from the local/natural Pb. Aerosols from Senegal and a sample from the Matmata loess (southern Tunisia) exhibit  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of 1.193 and 1.198, respectively (18, 29). Due to the lack of isotopic variation between these natural Pb sources, they will simply be considered as French natural lead.

In the U.K., the situation is very similar, however, with slightly less radiogenic ratios as shown by the studies of Hamilton and Clifton (7), Croudace and Cundy (11), and Sugden et al. (15). Pre-industrial sediments from Swansea Bay, Southampton Water, and central Scotland analyzed in these studies gave  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios between 1.17 and 1.19.

**Origin of Pb in Airborne Particulate Matter from Urban Areas.** In many previous studies, the Pb isotopic composition of urban particulate material, sampled in zones exposed to heavy vehicle traffic, has been considered to be dominated by automotive exhaust emissions. However, since the Pb isotopic composition of airborne particles in both countries shows a wide range of  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios (1.085–1.158), they cannot be due entirely to automotive emissions because measured gasolines range from 1.059 to 1.094. Plotted on  $^{206}\text{Pb}/^{207}\text{Pb}$  vs  $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  vs  $^{208}\text{Pb}/^{204}\text{Pb}$  diagrams, the points fall between the gasoline and the industrial domains (Figure 1). It is clear that the Pb from gasoline is an indisputable source since the Pb isotopic compositions of the urban aerosols cannot be explained by simple binary mixing between natural Pb and industrial Pb alone. In addition, the contribution of natural Pb cannot be excluded because the observed signatures can be reconstructed by three end member as well as two end member mixing. For these reasons, it is impossible to calculate the contribution of each component precisely. To do this, an examination of local influences such as the proximity of industries, traffic density, wind direction, and long-term monitoring of Pb isotopes would be required. Such calculations, though possible, are of limited use because they require generalizations to describe the behavior of the Pb at a given site based on only a few samples. Estimations of the gasoline component that avoid the problem of a ternary mixing solution can be made by initially considering binary mixing of gasoline and industrial Pb using the following conventional mixing equation:

$$X_1 = \frac{(^{206}\text{Pb}/^{204}\text{Pb})_{\text{SAMP}} - (^{206}\text{Pb}/^{204}\text{Pb})_{\text{IND}}}{(^{206}\text{Pb}/^{204}\text{Pb})_{\text{G}} - (^{206}\text{Pb}/^{204}\text{Pb})_{\text{IND}}} \quad (1)$$

where  $X_1$  is the percentage contribution of gasoline;  $(^{206}\text{Pb}/^{204}\text{Pb})_{\text{G}}$ ,  $(^{206}\text{Pb}/^{204}\text{Pb})_{\text{IND}}$ , and  $(^{206}\text{Pb}/^{204}\text{Pb})_{\text{SAMP}}$  are the isotopic signatures of the gasoline and industrial end-members and of the airborne particulate sample, respectively. This equation uses the  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio, but similar equations can be developed for the other isotope ratios.

Furthermore, binary mixing between gasoline and the more radiogenic natural Pb component gives the following equation:

$$X_2 = \frac{(^{206}\text{Pb}/^{204}\text{Pb})_{\text{SAMP}} - (^{206}\text{Pb}/^{204}\text{Pb})_{\text{NAT}}}{(^{206}\text{Pb}/^{204}\text{Pb})_{\text{G}} - (^{206}\text{Pb}/^{204}\text{Pb})_{\text{NAT}}} \quad (2)$$

where  $X_2$  represents the contribution of gasoline in this mixing model and  $(^{206}\text{Pb}/^{204}\text{Pb})_{\text{NAT}}$  is the isotopic composition of pre-industrial sediments. The average isotopic compositions of each end member used for the mixing models are shown in Table 3. Although the isotopic composition of the industrial end member has not yet been empirically defined for the southern U.K., a French signature is assumed to be reasonable.

Some differences occur between the  $^{206}\text{Pb}/^{207}\text{Pb}$ – $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{208}\text{Pb}/^{204}\text{Pb}$  graphs (Figure 1): particularly for gasoline values near the lower part of the  $^{206}\text{Pb}/^{207}\text{Pb}$ – $^{208}\text{Pb}/^{206}\text{Pb}$  couple and for U.K. particulate material. This is explained by the fact that samples having different  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  ratios can have a similar  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio, which is also true for all other ratios that do not include the  $^{204}\text{Pb}$  isotope. To reduce this effect,  $X_1$  and  $X_2$  are calculated by averaging the results obtained with each ratio. The range between  $X_1$  and  $X_2$  is a measure of the uncertainty on the estimate of the percentage contribution of gasoline-derived Pb when considering mixing between gasoline, industrial, and natural Pb.

As described below, the isotopic composition of gasoline-derived Pb has shown significant changes over the last 30 years. The models used here assume that resuspension of

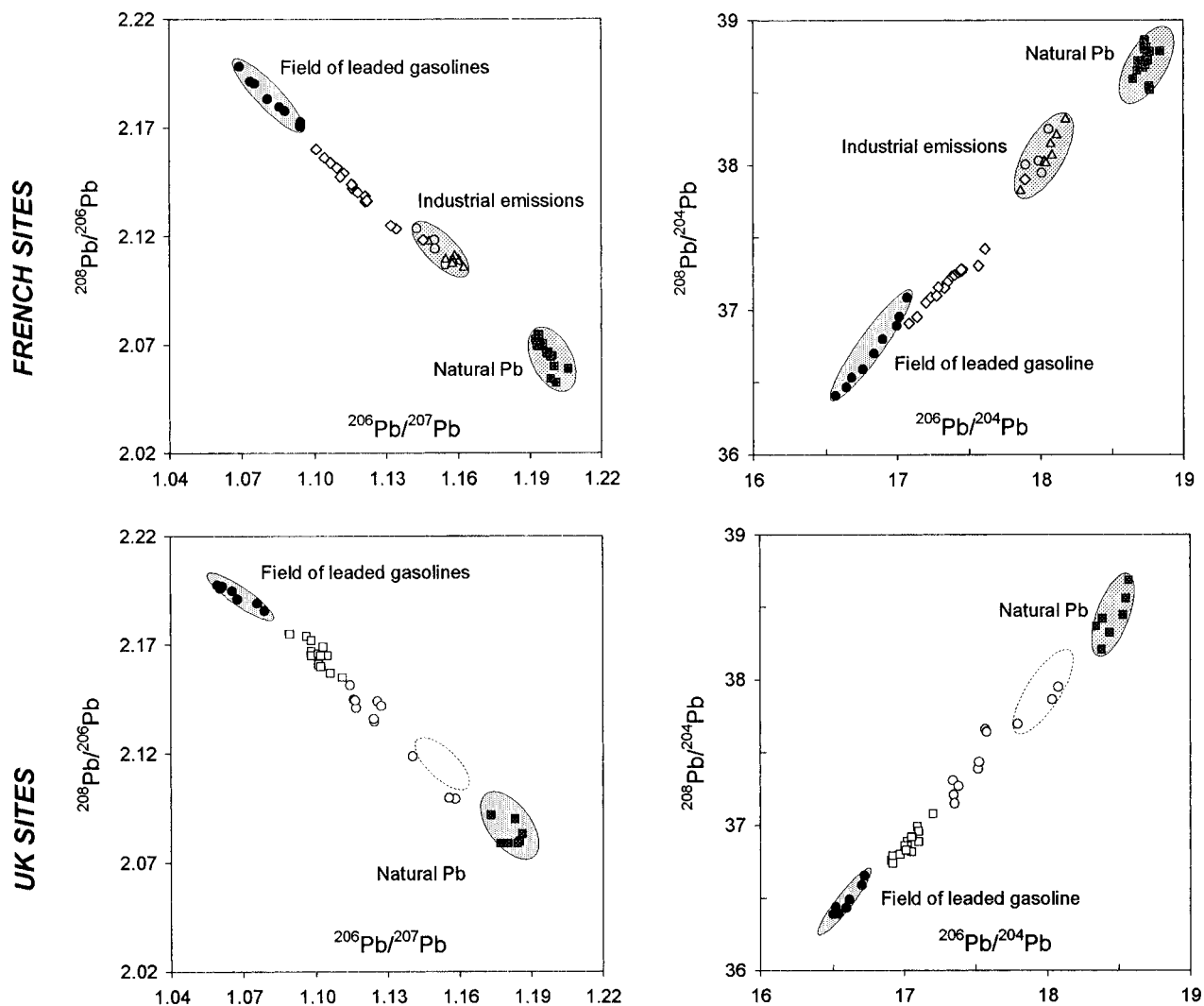


FIGURE 1.  $^{208}\text{Pb}/^{206}\text{Pb}$  vs  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  vs  $^{206}\text{Pb}/^{204}\text{Pb}$  in environmental samples from France and the U.K. (●) leaded gasoline, (gray circles) ashes from urban incinerator, (△) liquid urban waste (5), (■) pre-industrial sediment (3, 5, 7, 26), (◇) airborne particulate matter from French urban areas, (○) airborne particulate matter from London, (□) airborne particulate matter from Southampton.

TABLE 3. Average Isotopic Composition of Gasoline-Derived, Industrial, and Local/Natural Pb in France and the U.K.<sup>a</sup>

	<i>n</i>	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
End Members in France					
gasoline	9	16.83	36.71	1.084	2.182
industrial emissions	13	18.03	38.07	1.155	2.112
pre-early industrial sediments	16	18.73	38.72	1.197	2.066
End Members in U.K.					
gasoline	7	16.60	36.48	1.067	2.193
industrial emissions	<i>b</i>	18.03	38.07	1.155	2.112
pre-early industrial sediments	7	18.45	38.41	1.184	2.082

<sup>a</sup> *n*, number of samples. <sup>b</sup> Isotopic composition of the 'industrial' end member in the U.K. is assumed to be the same as in France.

"old" gasoline-derived Pb into the urban atmosphere has an insignificant impact on the gasoline end member. Several studies have shown that contaminants introduced into urban areas (i.e.,  $^{137}\text{Cs}$ ) have relatively low residence time in urban dusts, with half-lives usually less than 1 year (30, 31). That part of the Pb emitted in the 1960s and 1970s that has not been removed from urban areas by rainfall is likely to be present in a form not readily amenable to resuspension (e.g., in soils). Consequently, in the vicinity of dense automotive traffic, the contribution of old gasoline-derived Pb is likely to be relatively small.

**Origin of Pb in French Airborne Particulate Matter.** It is apparent that if the isotopic signature of airborne particulate

matter is similar to that of gasoline, the uncertainty (range between  $X_1$  and  $X_2$ ) is slight, i.e., for Nantes (Figure 2). By contrast, if the isotopic signature approaches industrial values, as found for station 12 of Toulouse, the contribution from gasoline is poorly constrained. In spite of this sometimes poor discrimination, samples can be divided into three groups. For Nantes, Toulouse station 6, Montpellier, and Le Havre, measurements show that 70–80% of Pb is derived from gasoline combustion, decreasing to 40–70% for Clermont-Ferrand, Paris, Amiens, Strasbourg, Lille, Caen, and Bar-le-Duc. Finally, a gasoline Pb contribution ranging from 10 to 40% is calculated for airborne particulate matter collected from Toulouse station 12. Figure 3 shows the change in

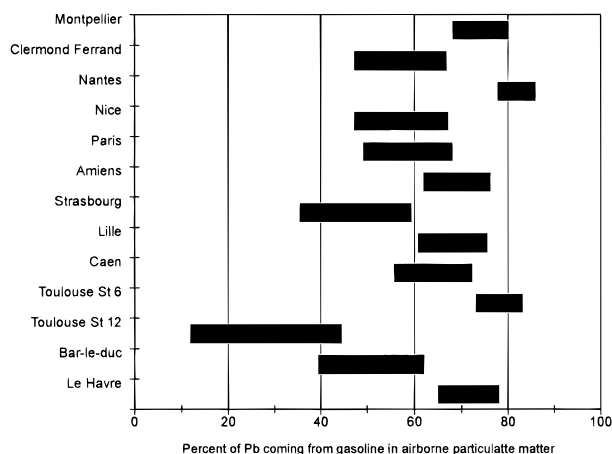


FIGURE 2. Calculated percentage contribution of gasoline-derived Pb to total airborne particulate Pb in urban areas from France.

airborne Pb concentration over time at the various French sites used in this study, since 1984. At most sites examined, the airborne Pb concentration has greatly decreased due to EU (European Union) legislation that has imposed reductions on the amount of Pb added to gasoline (0.15 g/L at present, compared with 0.65 g/L in the period 1965–1975, Associated Octel, personal communication) and on permitted Pb emissions and also the increasing use of unleaded gasoline. Pb concentrations shown in Figure 3 are generally much lower than the upper limit fixed by the EU of  $2 \mu\text{g}/\text{m}^3$  Pb as an annual average. Only Toulouse station 12 has not seen a general Pb decrease. This station, located in the center of the city, is close to a lead smelter used for battery recycling. This factory is a significant Pb polluter with an average emission rate of  $0.2 \text{ kg day}^{-1}$  (1993 value). The influence of an industrial input is evident at station 12, and only ~10% of the total Pb at this site is derived from gasoline combustion based on calculations using eq 1; the natural component is relatively insignificant. The other sampling site at Toulouse

(station 6), located 4 km from station 12, is exposed to very dense vehicle traffic and shows a relatively high airborne Pb concentration when compared to the other French cities. Here, the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio (1.104) indicates that, on the day sampled, the contribution from industrial activities was negligible, highlighting the dominantly local impact of the smelter. At Strasbourg, a rather radiogenic signature has also been found. This cannot be explained by a more radiogenic contribution from German gasolines because these have approximately the same Pb isotopic composition as French gasoline (19). Moreover, it is notable that in recent years more than 90% of German gasoline used is unleaded as compared with 50% and 40% for the U.K. and France, respectively (Associated Octel, personal communication). A more likely explanation is that sampling of material at Strasbourg was carried out in a zone that is now traffic-free, which explains why the Pb content and the gasoline contribution are so low.

**Origin of Pb in U.K. Airborne Particulate Matter. (A) Teddington, West London.** Airborne particulate samples collected from the Teddington area of west London show a large range in Pb isotopic ratios (Figure 4). This short-term variability is likely to be a result of varying wind direction and traffic densities. The major road in this area is to the west of the sampling site, and the least radiogenic values are found when the wind is from the west. Under SE winds, which cross areas of low traffic density, the most radiogenic data are found. The data confirm that Pb isotopic composition is also a function of traffic density since more radiogenic values are measured at the weekends. During weekend periods, traffic density is substantially lower than on weekdays when considerable congestion occurs due to commuter traffic. Even during days with higher traffic density, the contribution of Pb derived from gasoline does not exceed ~60% (Figure 4).

**(B) Southampton.** Samples in Southampton were collected using a low-volume air sampler over several days, and therefore the data represent generalized values and cannot be used to evaluate short-term effects. Air particles were

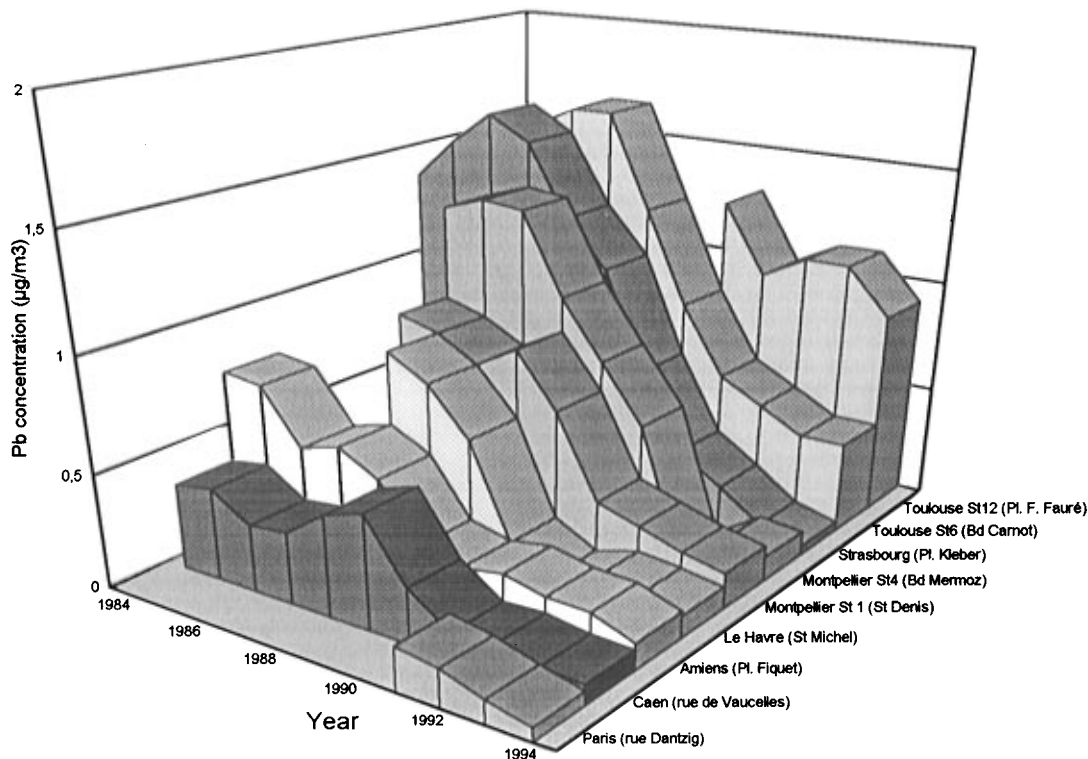


FIGURE 3. Temporal change in Pb concentration in urban air at various French sites (data from ORAMIP, ASPA, AMPADI, AIRNORMAND, ASQAP, ADEME, and LCPP, personal communication, 1995).

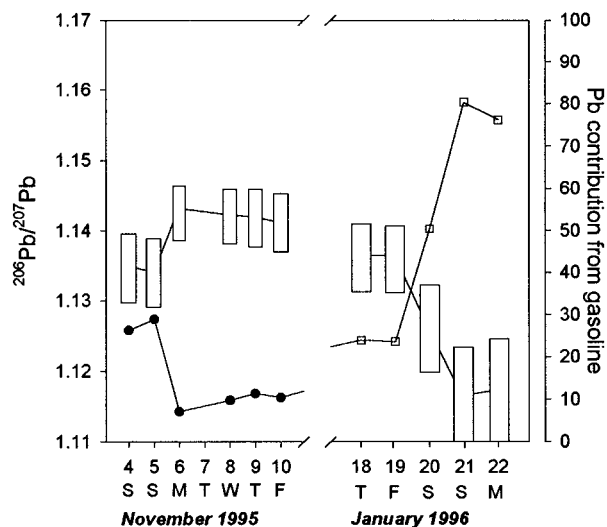


FIGURE 4. Evolution of  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios in airborne particulate matter collected at London (Teddington) in November 1995 (●) and January 1996 (□). The boxes represent the calculated contribution of Pb from gasoline (from eqs 1 and 2).

collected from a busy city center site and also from a suburb of the city (Portsmouth) that is also exposed to appreciable traffic. The former sampling site was by the main road while the latter was a garden site. The results show that gasoline-derived Pb makes a major contribution to particulate Pb in both areas: 61–84% of Pb is derived from gasoline combustion at the city center site and 56–74% at the Portsmouth suburban site.

These results confirm that gasoline is the main source of Pb in most French and in southern U.K. urban areas. However, following environmental legislation restricting concentrations of Pb in gasoline and the increased market penetration of unleaded gasoline, other sources of Pb can now be identified using isotopic studies and are likely to become increasingly evident.

**Evolution of Pb Isotopic Signatures in Environmental Materials.** The results from this study can be used to extend the existing database that describes the changing isotopic composition of anthropogenic Pb with time (Figure 5). This type of information is indispensable in historical reconstruction of Pb pollution sources in sediment and ice-core records or other environments (32–35). Table 4 summarizes the published data since 1965. In France, Chow et al. (22) measured a  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio of 1.162–1.163 in gasoline directly whereas many other workers have obtained data indirectly through the sampling of aerosols. These later workers considered that their results were more or less representative of automotive emissions. In 1975, grass sampled in the vicinity of a Parisian highway gave a ratio of 1.128 while in 1981 filtered aerosols taken in a car park near Paris were measured at 1.101 (2, 3). During the same period, Flament (36) found a similar ratio of 1.093 for aerosols collected along a highway in northern France. Monna et al. (5) reported slightly higher values of 1.109–1.111 for airborne particulate matter sampled in 1987, a few meters from heavy traffic in Montpellier. Finally, in 1988 Grousset et al. (29) collected aerosols from Lyon that had  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of 1.096. In the U.K., the available data are more limited. Hamilton and Clifton (7) reported  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of 1.126 and 1.105 in 1968 and 1971, respectively, measured in airborne particles from London and 1.134 in airborne particulate matter from Cardiff in 1968. More recently, Sugden et al. (15) found  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios ranging from 1.056 to 1.093 in Edinburgh over the period 1989–1991. The trends in the U.K. and France show a significant decrease in the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio during

TABLE 4. Previously Published Pb Isotopic Compositions of Environmental Samples from France and the U.K.

ref	method	year	sampling	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
22	TIMS	1966	gasoline	France				
22	TIMS	1966	gasoline	18.25			1.162	2.113
2	TIMS	1975	grass sample	18.24			1.163	2.113
2, 3	TIMS	Dec 1981	aerosols car park		15.56 ± 0.05		1.128	
3	TIMS	1984	aerosol/highway	16.99	15.54		1.101 ± 0.001	2.170
5	TIMS	Sep 1987	urban air/filter	17.385 ± 0.044	15.663 ± 0.039		1.1093 ± 0.0004	
5	TIMS	Sep 1987	urban air/filter	17.270 ± 0.003	15.556 ± 0.004		1.1102 ± 0.0001	
5	TIMS	Sep 1987	urban air/filter	17.332 ± 0.029	15.603 ± 0.027		1.1108 ± 0.0003	
29	ICP-MS	1988	car parking	16.749 ± 0.111	15.280 ± 0.086		1.096 ± 0.0003	2.102
7	TIMS	1968	air particles	U.K.				
7	TIMS	1968	air particles	17.66			1.134	2.155
7	TIMS	1971	air particles	17.45			1.126	2.141
15	ICP-MS	1989–1991	urban air/filter	17.32			1.105	
								1.056–1.093



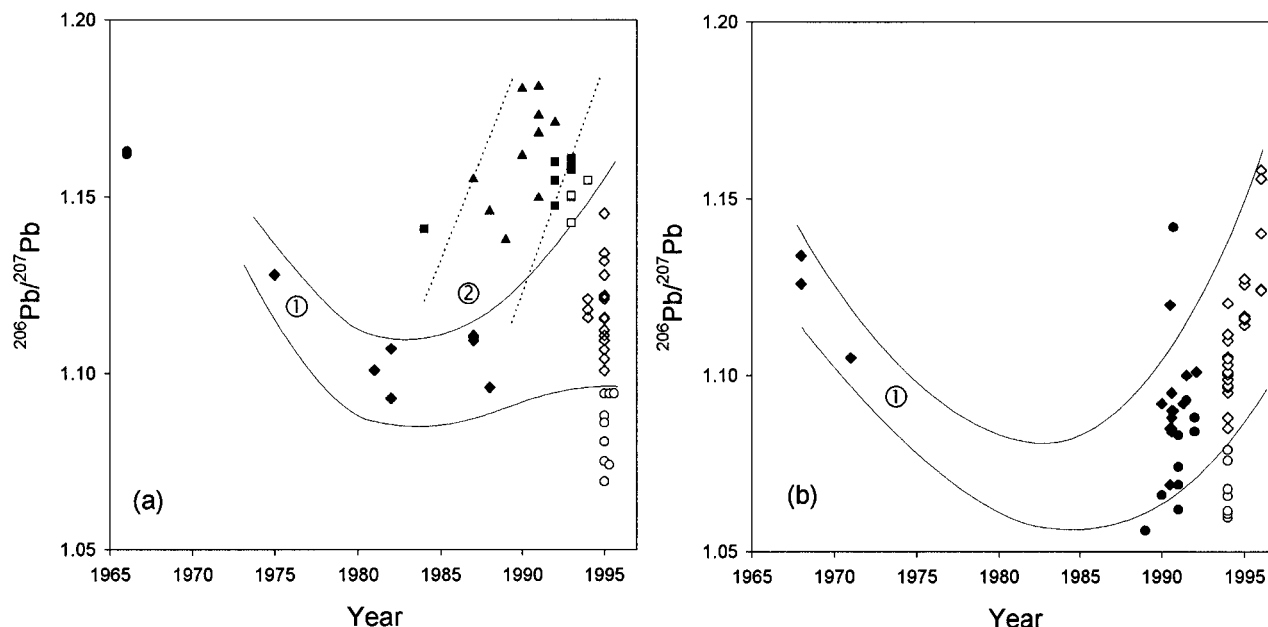


FIGURE 5. Change in  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio since 1965 for potential sources of Pb and airborne particulate matter in France (a) and the U.K. (b). Closed symbols, data from literature (see Table 4 for references); open symbols, this study: (○) gasoline, (□) industrial emissions. Field 1 represents the isotopic evolution of samples collected in urban areas (◇), and field 2 represents the isotopic evolution of aerosols collected in French mountains (△) (18).

1965–1980, which could be interpreted as a growing use of Australian lead. However, as mentioned above for both countries, modern urban aerosols have an isotopic signature that is always more radiogenic than those of gasoline, and so it is uncertain that the Pb isotopic ratios obtained in the past for aerosols perfectly reflect those in gasoline. Consequently, all results obtained using indirect sampling can only be considered as the upper limit of the gasoline component since other contributions cannot be excluded.

Concerning industrial Pb, there are few direct measurements available. In 1984, Petit measured  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios close to 1.141 in the atmosphere at various industrial sites of northern France (3), and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios between 1.147 and 1.161 have been measured in liquid urban waste (5). This kind of sampling allows a general assessment of the isotopic composition of industrially derived Pb, although values obtained may be slightly low due to mixing with gasoline-derived Pb. However, such values are in agreement with the range found from ashes from urban incinerators: 1.143–1.155. Although the database is preliminary, the isotopic signature seems to have remained rather constant over the last decade, but there are insufficient data available prior to the 1980s.

Grousset et al. (18) have shown a decrease of Pb content and a corresponding increase in  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios in French mountain aerosols since 1985 (see Figure 5), which was attributed to the decreasing input of Pb from automobile emissions. In urban areas, the same phenomenon is often noted, but to a lesser extent due to proximity to the sources of Pb pollution. In the urban environment, Pb derived from other sources (industrial and natural) has increased in relative terms and can no longer be neglected when assigning a characteristic anthropogenic Pb signature. Hence, even where Pb isotopes can be successfully applied in environmental studies, great care must be taken to define the isotopic character of all individual sources of Pb with representative sampling programs. Additionally, it is desirable that such isotopic monitoring is carried out frequently to provide a better database showing variations with time so that evolutionary changes in the Pb pollution record can be understood.

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