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Concentrations, Phase Partitioning and Deposition of Specific Alkyl-lead Compounds in the Atmosphere

Yun Wang,[1] Alan B. Turnbull[1] and Roy M. Harrison[1]*
[1] Institute of Public and Environmental Health, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

Measurements of alkyl-lead compounds in air and rain at rural and urban sites in central England during 1996 are reported. Vapour, aerosol and rain concentrations of individual tetra-, tri- and di-alkyl-lead species have been determined simultaneously at both sites, along with inorganic lead aerosol. The results show the predominance of vapour-phase over particle-associated species, with tetramethyl-lead being the most prevalent vapour-phase compound, with concentrations of up to 5.8 ng Pb m^{-3}. Theoretical phase-partitioning coefficients for individual alkyl-lead compounds have been calculated and compared with measured values. Washout ratios for alkyl-lead compunds were found to be smaller than for inorganic lead. Atmospheric concentrations of both organic and inorganic lead appear to be falling, broadly in line with recent reductions in the use of alkyl-lead in gasoline. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

Atmospheric contamination by alkyl-lead compounds is known to arise from the use of tetra-alkyl-lead (R_4Pb) compounds as anti-knock gasoline additives. Released into the atmosphere with exhaust gases and by fuel evaporation, tetra-alkyl-lead compounds decompose to trialkyl-lead (R_3Pb^+) and dialkyl-lead (R_2Pb^{2+}) species, being finally converted to inorganic lead aerosol. Over recent years their use has declined appreciably in developed countries due to increased market penetration of unleaded gasoline, and limitations on permitted levels in leaded gasoline. Several studies have shown that these changes have led to a direct impact on airborne inorganic lead levels.[1–4] However, there is little information on corresponding changes in alkyl-lead concentrations in the atmosphere over the UK, although it is known that alkyl-lead can be more toxic to living organisms than inorganic lead, due to its greater solubility in fatty tissues.[5]

Tetra-alkyl-lead compounds, once released into the atmosphere, have typical half-lives of 2–7 h in summer and 10–34 h in winter,[6] with tetraethyl-lead known to be less stable than tetramethyl-lead. The ionic alkyl-lead species are more persistent, trimethyl-lead having a half-life of about five days. Half-lives of 126 h for vapour-phase Me_3Pb^+, 34 h for Et_3Pb^+, 41 h for Me_4Pb and 8 h for Et_4Pb have been predicted for reaction with hydroxyl radicals in the atmosphere.[7] Decomposition of airborne tetra-alkyl species by photolysis and reaction with hydroxyl radicals to form soluble and particle-bound ionic alkyl-lead (R_3Pb^+ and R_2Pb^{2+}) extends the atmospheric lifetime of organic lead, and allows for medium-range transport in the atmosphere. In addition, some of the ionic alkyl-lead species have greater persistence once deposited into the surface water and soil environment. Although removal processes can include particle and vapour-phase dry deposition, as well as wet deposition, many previous studies have suggested that wet deposition may be the most important removal mechanism for alkyl-lead pollutants from the atmosphere, and a major

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* Correspondence to: Roy M. Harrison.

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source of these species in surface waters.[8–10] Although tetra-alkyl species are the most abundant alkyl-lead compounds in the atmosphere, they are of low water solubility and exist essentially in the vapour phase. However, ionic alkyl species are more soluble and can be observed in the particulate phase, thus making them subject to greater potential washout by rain. Therefore, the environmental behaviour of these species can be predicted from their physical and chemical properties. Table 1 provides some of the more important of these parameters. The vapour pressure and solubility were established recently according to methods that have been published elsewhere.[11]

This study set out to measure current concentrations of atmospheric alkyl-lead and inorganic lead, and to further improve our understanding of the behaviour and fate of alkyl-lead compounds in the atmosphere. The concentrations of inorganic lead and of individual R_4Pb, R_3Pb^+ and R_2Pb^{2+} compounds have been measured in the vapour phase, particle-bound and in wet deposition. Two sampling sites were used, one in central Birmingham, the other in a rural location 40 km south-west of the city centre. Meteorological parameters were collected at each site with 15-min resolution. The measured concentrations are compared with those determined several years earlier at comparable sites with a view to evaluation of temporal trends. The data were also used to calculate phase-partitioning coefficients, which are then compared with those predicted by their respective physical and chemical properties.

ENVIRONMENTAL SAMPLING

Urban sampling was conducted at the University of Birmingham campus within the central area of the West Midlands conurbation but away from direct road-traffic influences (52° 27′N; 1° 56′W). The second site, 40 km south-west of Birmingham, was located in a rural environment with no significant nearby development (52° 16′N, 2° 14′W). Air sampling was conducted during the spring of 1996, with a few samples taken before this date. Rainwater samples were collected at the University of Birmingham site from January 1993 to April 1996.

Rainwater

Rainwater samples, including associated dry deposition, were collected using 12-in (30-cm) diameter glass funnels leading into 2.5-litre brown glass bottles. The funnels were exposed to the atmosphere for sufficient time to collect a minimum of one litre of rain. Samples were stored at 4 °C prior to analysis.

Vapour-phase tetra-alkyl-lead components

Vapour-phase R_4Pb compounds were collected by drawing air sequentially through two stainless-steel adsorption tubes [3.5 in × 1/4 in (8.9 cm × 0.6 cm i.d.)]. The first tube was packed with Tenax TA (0.4 g, 60–80-mesh); with Porapak QS (0.4 g, 50–80-mesh) in the subsequent tube. Prior to sampling, each tube was con-

Table 1. Selected physical and chemical properties of alkyl-lead compounds (20 °C)

Compound	Mol. wt	M.p. (°C)	Vapour pressure, P^0_L (Pa)[b]	Solubility, S^0_L (mol m^{-3})[c]	Henry's law constant[d] (Pa m^3 mol^{-1})
Me_4Pb	267.19	n.a.[a]	3458	7.24×10^{-2}	4.77×10^4
Et_4Pb	323.19	n.a.	34.6	1.21×10^{-3}	2.86×10^4
Me_3PbCl	287.69	190	19.8×10^{-2}	24×10^3	8.25×10^{-6}
Et_3PbCl	329.69	166	2.89×10^{-3}	1.59×10^3	1.83×10^{-6}

[a] n.a., not available.

[b] P^0_L, liquid vapour pressure for Et_4Pb and Me_4Pb and sub-cooled liquid vapour pressure for Me_3PbCl and Et_3PbCl.

[c] S^0_L, liquid solubility for Me_4Pb and Et_4Pb and sub-cooled liquid solubility for Me_3PbCl and Et_3PbCl.

[d] H, calculated as P^S_L/S^S_L.

ditioned for 2 h at 190 °C by gently passing purified nitrogen through. The tubes were then kept at −20 °C prior to sampling. Previous research has shown Tenax is most efficient for trapping less-volatile alkyl-lead compounds, whereas Porapak is preferred for the more volatile species.[12] To prevent decomposition of R_4Pb during sampling, ozone was removed from the airstream prior to the adsorption tubes by a short length of PTFE tubing packed with iron(II) sulphate [2 in × 1/4 in diam. (5.1 cm × 0.6 cm diam.)]. To remove airborne particles, a 47-mm cellulose acetate membrane filter (0.45 μm) was fitted to the inlet. A breakthrough volume of 600 litres at 20 °C was determined using this sampling method. In most cases a 24-h sampling period was employed corresponding to 500–600 litres. The exposed sample tubes were kept at −20 °C prior to analysis.

Vapour-phase ionic alkyl-lead components

The more-soluble ionic alkyl-lead vapour-phase species were sampled into a series of two Dreschel bottles at a flow rate of 0.8 1 min^{-1} for periods of 36 h, each bottle containing 150 ml distilled deionized water and 2 g NaCl (to mitigate the effect of freezing temperatures). Particles were removed using a cellulose acetate filter (0.45 μm) as for tetra-alkyl-lead. Following collection, the contents of the two Dreschel bottles were combined, and stored at 4 °C prior to analysis.

Particle-phase components

All particle-bound alkyl-lead components, and inorganic lead aerosol, were collected onto 10 in × 8 in (25.4 cm × 20.3 cm) PTFE-coated glass-fibre filters (Palflex Corp.) using a high-volume air sampler (Graseby Andersen) at a flow rate of 1.0 m^3 min^{-1} for 24 h.

ANALYTICAL TECHNIQUES

Gas-chromatographic procedures linked to atomic absorption spectroscopy (GC/AAS) have been developed over recent years which allow speciation of alkyl-lead compounds at the low analytical detection limits necessary for these environmental measurements.[8, 10–11] Data were generated for this report using a gas chromatograph (Perkin–Elmer F17) fitted with a glass column (1.2 mm × 6 mm) packed with 10% OV-101 on Chromosorb W (80–100-mesh) and interfaced to a Perkin–Elmer 2380 atomic absorption spectrometer using heated PTFE tubing (1.6 mm × 0.75 m at 180 °C). A detailed description of the installation and optimum operating conditions for this system have been described in a previous paper.[11] The performance of this method for alkyl-lead compounds in air and rainwater samples using the GC/AAS system are presented in Table 2, with further details for each sampling procedure below.

Vapour-phase tetra-alkyl-lead

The exposed Tenax and Porapak tubes were desorbed at 165 °C using helium at a flow rate of 140 ml min^{-1} for 10 min. The resulting products were cryogenically concentrated in a glass-lined stainless-steel tube immersed in liquid nitrogen. Finally, the steel tube was electrically flash-heated to 150 °C with the sample being introduced to the GC along with the carrier gas. A more detailed account of this method can be found elsewhere.[8]

Table 2. Detection limits and recoveries for alkyl-lead compounds in air and rainwater

Compound	Air (vapour) Limit of detection (ng Pb m^{-3})	Recovery (%)	Aerosol particles Limit of detection[a] (pg Pb m^{-3})	Recovery (%)	Rainwater Limit of detection[c] (ng Pb l^{-1})	Recovery (%)
Me_4Pb	0.10[a]	80	0.20	51	0.62	55
Et_4Pb	0.30[a]	60	0.41	88	1.00	60
Me_3Pb^+	0.15[b]	78	0.20	90	0.88	90
Et_3Pb^+	0.23[b]	70	0.48	94	1.38	87
Me_2Pb^{2+}	0.21[b]	66	0.35	80	1.25	85
Et_2Pb^{2+}	0.19[b]	50	0.55	87	1.10	97

[a] Based on 24-h sample. [b] Based on 36-h sample. [c] Based on 1-l sample.

Vapour-phase ionic alkyl-lead

The ionic alkyl-lead compounds were sampled into water (approx. 400 ml) and were liquid-extracted (twice) into hexane (10 ml + 10 ml) in the presence of NaCl and NaDDTC (sodium diethyldithiocarbamate, 0.25 M). Following concentration of the hexane extract to 0.5 ml under clean nitrogen, the alkyl-lead components were propylated using a Grignard reagent (propylmagnesium chloride, 0.3 ml), and finally injected (50μl) into the GC/AAS system. A detailed description of the procedures for measuring alkyl-lead compounds in aqueous samples can be found elsewhere.[11, 13]

Particle-bound alkyl-lead

After removal of a small section of the high-volume PTFE filter for inorganic lead determination (9 cm^2), the filter was mechanically shaken with water (500 ml) and hexane (10 ml). The hexane from the resulting emulsion was then separated by a combination of centrifugation and addition of anhydrous sodium sulphate. The final extract was reduced to 200 μl under clean nitrogen prior to injection into the GC/AAS system for determination of R_4Pb species. R_3Pb^+ and R_2Pb^{2+} species were determined in the remaining aqueous extract by the addition of EDTA (3 g), to mask the inorganic lead present, and the adjustment of the pH to 8.5 by the addition of ‘880’ ammonia solution. To this solution, NaCl (10 g) and NaDDTC (5 ml, 0.5 M) were then added, followed by two sequential liquid extractions into hexane (10 ml + 10 ml). The hexane fraction was concentrated under nitrogen to 0.5 ml before addition of the Grignard reagent (0.3 ml). After excess Grignard reagent had been removed by addition of sulphuric acid (3 ml, 0.5 M), this propylated hexane extract was injected (50 μl) into the GC/AAS system.

Inorganic lead

Total dissolved inorganic lead in rainwater samples was determined independently by filtering a small aliquot of the rain sample (50 ml) through a 0.45-μm cellulose acetate membrane with analysis by graphite furnace atomic absorption spectroscopy (GF/AAS). Some experiments were undertaken to determine the impact of assessing only the dissolved inorganic lead, which found more than 85% to be dissolved. This is supported by another study which showed that, in western Europe, lead in rainfall tends to be dissolved due to low pH values in rain.[14]

Particle-bound inorganic lead in the atmosphere was determined from a small section of the high-volume PTFE filter (9 cm^2). The filters were placed in acid-washed polypropylene screw-top bottles (60 ml), and then extracted into 25 ml of 10% nitric acid (Aristar) by shaking in a vertical reciprocator for 1 h prior to introduction into the GF/AAS.

Tetra-alkyl-lead in UK gasoline

To assess the proportion of different tetra-alkyl-lead species in gasoline (petrol), the content of six commercial leaded gasoline brands was determined. Analysis was achieved by simple dilution of the gasoline in hexane, with direct injection into the GC/AAS system as described earlier.

RESULTS AND DISCUSSION

Tetra-alkyl-lead distribution in gasoline samples

The gasoline samples were collected in early 1996 at six gasoline stations in the Birmingham area. The distribution of tetra-alkyl-lead found in these samples is presented in Table 3. On average, the leaded gasoline samples contained approximately 0.08 g l^{-1} of lead as R_4Pb compounds. Five species of R_4Pb were detected in three of the samples, with just two species being detected in the remaining three samples. It can be clearly seen in Table 3 that the overall most abundant lead compound added to these samples of gasoline was Et_4Pb.

Occurrence of alkyl-lead species in the atmosphere

A summary of the overall data in Tables 4 and 5 provides the mean (using zero for values below the detection limit), range and number of positive determinations for both sites. The results are illustrated in Figs. 1–4, where the total vapour- and particle-phase alkyl-lead concentrations are plotted separately for each site. It can be seen from these graphs that Me_4Pb is the predominant vapour-phase species at both sites, although other vapour-phase R_4Pb compounds are occa-

Table 3. Tetra-alkyl-lead distribution in commercial gasoline

Brand	Total R_4Pb (g Pb l^{-1})	Percentage of total alkyl-lead present Me_4Pb	Me_3EtPb	Me_2Et_2Pb	$MeEt_3Pb$	Et_4Pb
A	0.059	12.8	22	35.6	18.6	11
B	0.088	11.4	0	0	0	88.6
C	0.074	11.8	19.7	26.8	17.5	24.2
D	0.088	8.4	19.2	31.7	19.2	21.5
E	0.090	10.7	0	0	0	89.3
F	0.083	12	0	0	0	88

sionally observed. However, as noted above, the leaded gasoline samples analysed contained far more Et_4Pb than Me_4Pb. The predominance of Me_4Pb in the environment may be due to a number of factors. The vapour pressure of Me_4Pb is 100 times higher than Et_4Pb, leading to greater evaporative losses. In addition, the greater thermal stability of Me_4Pb may favour its passage through the combustion cycle intact.[15] It has been reported that the abundance of Me_4Pb in vehicle exhaust is more than five times as great as that of Et_4Pb,[16] although this would clearly be dependent upon the gasoline source. Further reports have clearly indicated that the rate of Et_4Pb breakdown in the atmosphere is greater than that of Me_4Pb.[7] The vapour-phase ionic R_3Pb^+ and R_2Pb^{2+} compounds measured in this study result both from direct vehicular emission[16] and atmospheric decomposition of R_4Pb species.[6] Although the R_4Pb species were never detected particle-bound, the less-volatile ionic alkyl-lead compounds, specifically Me_3Pb^+ and Et_2Pb^{2+}, were observed in all aerosol samples (Figs. 2 and 4).

The concentrations of organolead can be seen to vary considerably over the period of sampling and between the sites. The results in Tables 4 and 5 also include the alkyl-lead/total lead fraction (as percentage). Figure 5 correlates this percentage with inverse wind speed, and a regression analysis also showed a weak relationship between percentage alkyl-lead/inorganic lead and inverse temperature. At the urban site, lower wind speeds and lower temperatures are associated with higher relative alkyl-lead content. This is probably related to greater exhaust emission of alkyl-lead from choked vehicles on cold, still winter days. Alkyl-lead compounds are also more stable in the atmosphere under such conditions. Some studies have shown that reac-

Table 4. Atmospheric lead concentrations — urban site

	Vapour-phase measurements (ng Pb m^{-3})			Particle-phase measurements (pg Pb m^{-3})		
Lead	Mean (σ)	Range	Times detected (out of 17)	Mean (σ)	Range	Times detected (out of 17)
Me_4Pb	1.2 (1.7)	nd – 5.8[a]	14	—[b]	—	0
Me_3EtPb	0.1 (0.3)	nd – 1.0	2	—	—	0
Me_2Et_2Pb	—	—	0	—	—	0
Et_4Pb	0.17 (0.1)	nd – 0.40	2	—	—	0
Me_3Pb^+	0.23 (0.4)	nd – 2.0	9	7.0 (3.0)	2.4 – 11.2	17
Me_2EtPb^+	0.02 (0.1)	nd – 0.4	1	—	—	0
$MeEt_2Pb^+$	—	—	0	—	—	0
Et_3Pb^+	(0.02)(0.1)	nd – 0.23	2	1.6 (2.5)	nd – 8.3	4
Me_2Pb^{2+}	—	—	0	1.7 (1.9)	nd – 5.1	8
Et_2Pb^{2+}	0.42 (0.7)	nd – 5.4	8	20.8 (13)	nd – 45	15
Total alkyl-lead	2.1 (2.2)	nd – 8.9	16	30.8 (16)	3.0 – 58.9	17
Inorganic lead (ng m^{-3})				93 (52)	29 – 193	17
Percentage organic lead in total lead				2.0 (1.5)	0 – 5.8	

[a] nd, Not detected. — Below detection limit.

Table 5. Atmospheric lead concentrations — rural site

Lead species	Vapour-phase measurements (ng Pb m^{-3}) Mean (σ)	Range	Times detected (out of 11)	Particle phase measurements (pg Pb m^{-3}) Mean (σ)	Range	Times detected (out of 11)
Me_4Pb	1.3 (2.2)	nd – 7.5[a]	8	—	—	0
Me_3EtPb	0.02 (0.1)	nd – 0.16	1	—	—	0
Me_2Et_2Pb	—	—	0	—	—	0
Et_4Pb	0.19 (0.1)	nd – 0.3	3	—	—	0
Me_3Pb^+	0.12 (0.1)	nd – 2.2	4	8.4 (2.2)	2.4 – 12.7	11
Me_2EtPb^+	—	—	0	0.5 (0.8)	nd – 2.0	3
$MeEt_2Pb^+$	—	—	0	—	—	0
Et_3Pb^+	—	—	0	1.9 (2.9)	nd – 8.5	3
Me_2Pb^{2+}	—	—	0	1.3 (1.5)	nd – 4.2	4
Et_2Pb^{2+}	0.14 (0.1)	nd – 0.4	2	16 (12)	nd – 25	9
Total alkyl-lead	1.5 (2.4)	nd – 8.4	9	27.7 (16)	6.8 – 63	11
Inorganic lead (ng m^{-3})				49 (14.7)	27 – 75	11
Percentage organic lead in total lead				2.6 (3.4)	nd – 12.1	

[a] nd, not detected. —, Below detection limit.

tions of R_4Pb and R_3Pb^+ with hydroxyl radicals and ozone in the atmosphere are faster during summer than in winter.[7] It was observed that maximum solar radiation around midday induced a decrease in the ratio of alkyl-lead to inorganic lead.[17] Correlation of weather parameters with lead at the rural site were less clear than for central Birmingham, probably due to the variable air-mass trajectories and source strengths in this region, being away from urban emission.

Over recent years, the use of leaded gasoline has declined due to increasing environmental and

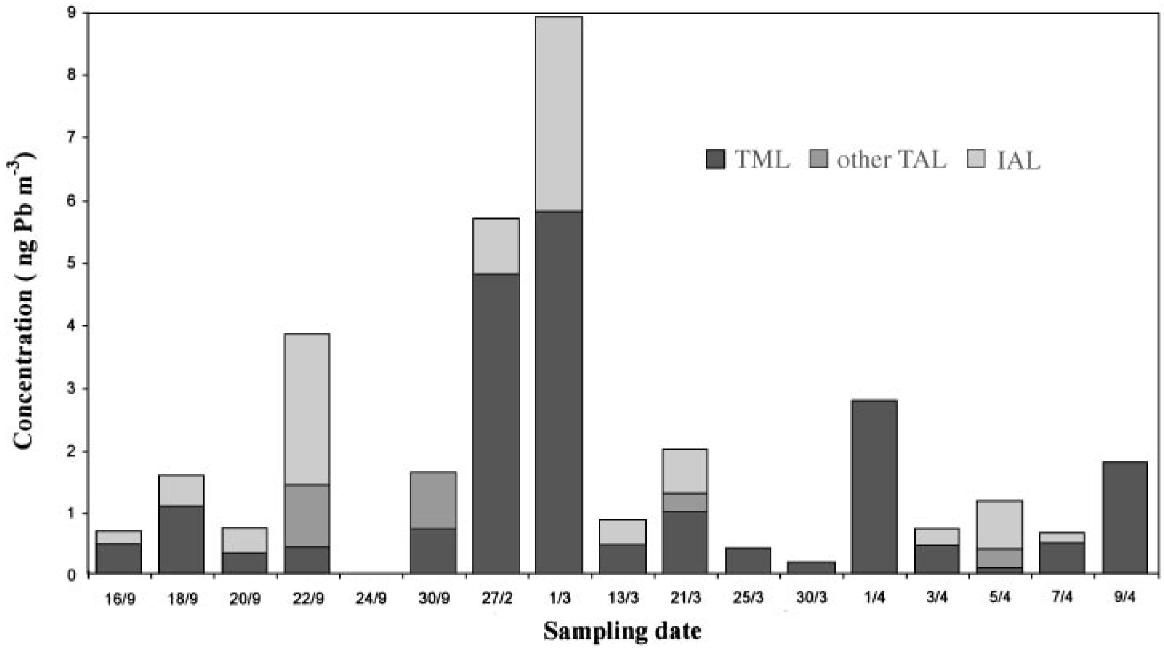

Figure 1 Vapour-phase alkyl-lead concentrations during 1995–1996 — urban site. TML, tetramethyl-lead; TAL, tetra-alkyl lead; IAL, ionic alkyl-lead.

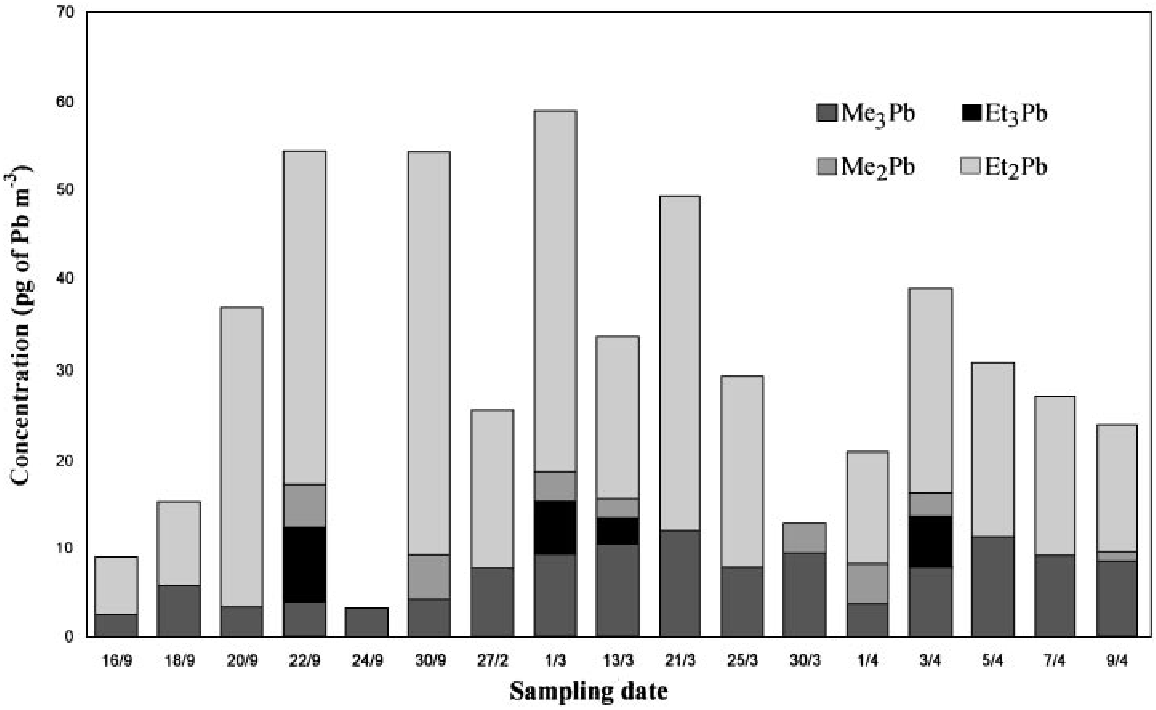

Figure 2 Particle-phase alkyl-lead during 1995–1996 — urban site.

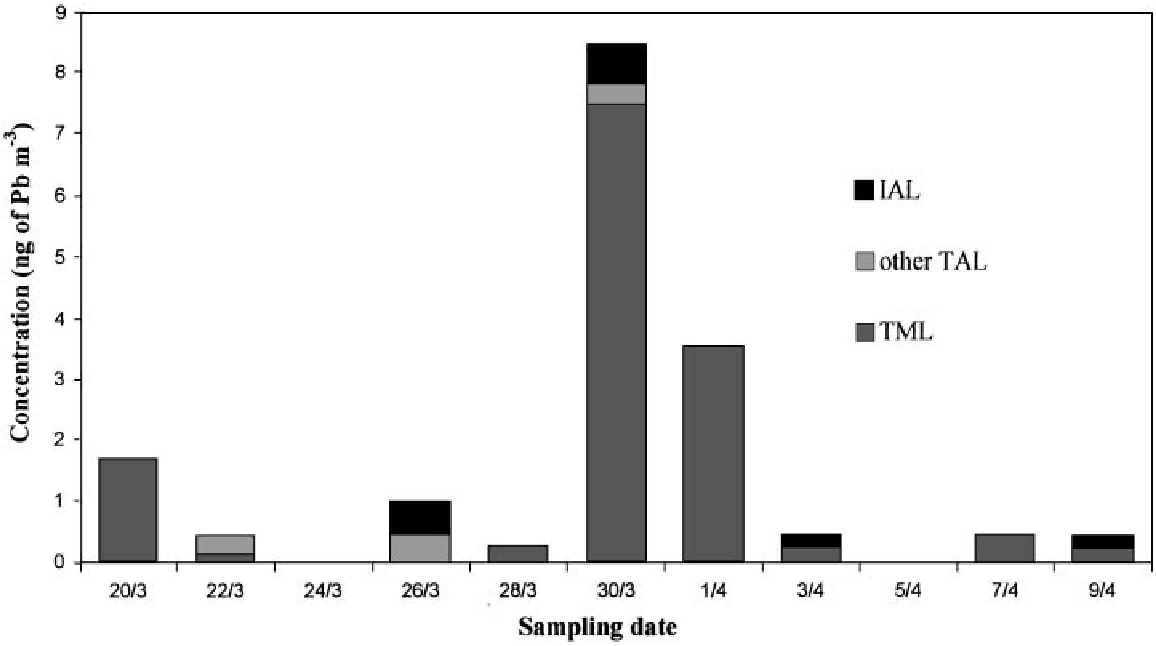

Figure 3 Vapour-phase alkyl-lead, Spring 1996 — rural site.

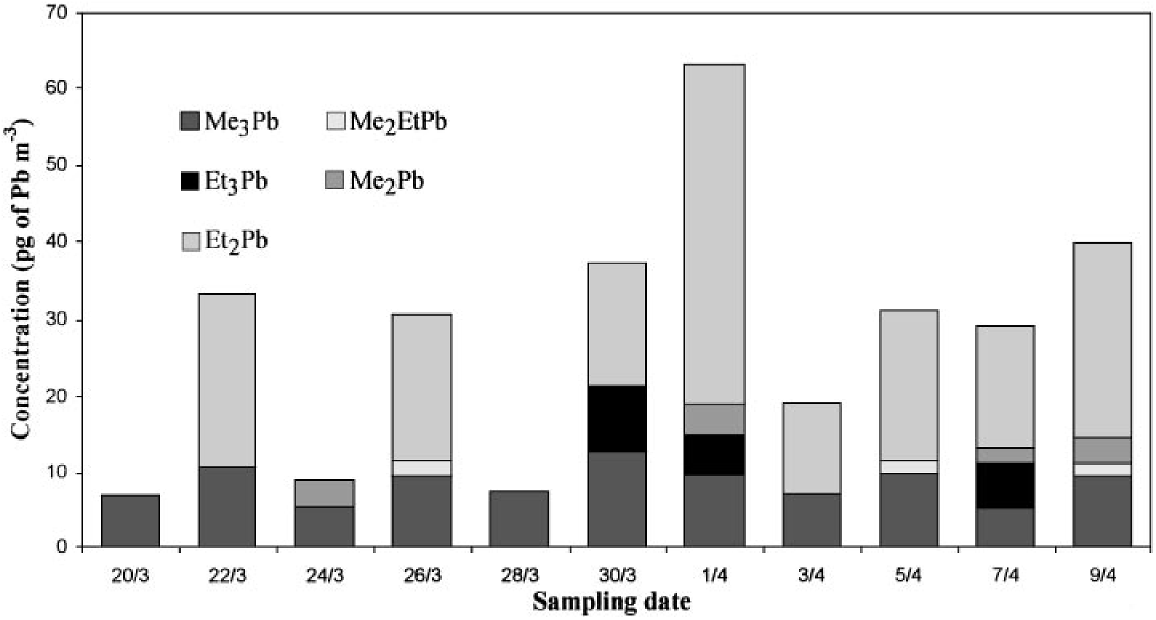

Figure 4 Aerosol alkyl-lead, spring 1996 — rural site.

health concerns. The annual lead emission figures from road vehicles in the UK between 1984 and 1996 are plotted in Fig. 6, together with some corresponding data on air levels of alkyl-lead and inorganic lead from UK sites. In calculating these emissions it has been assumed that only 70% of this lead in gasoline is emitted in exhaust products, the remainder being retained in engine oil and the exhaust system.[18] As can be seen in Fig. 6, a sharp drop in lead emissions occurred between 1985 and 1986. This was due to a change in the legal limit of lead in gasoline from 0.4 g l^{-1} to 0.15 g l^{-1} in January 1986. Although the air concentration data presented in Fig. 6 were obtained from different locations (Lancaster, 1984;[19] Colchester, 1985[20] and 1986;[8] Birmingham, 1996), it is clear that the reduction in total alkyl-lead and inorganic lead concentrations in the atmosphere is broadly in line with the reduction in use of alkyl-lead compounds in gasoline.

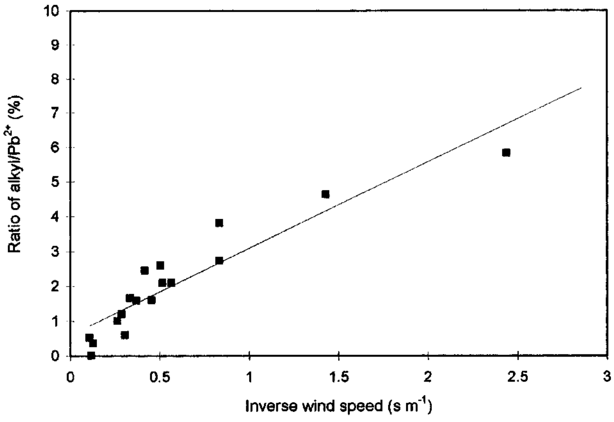

Figure 5 Correlation of alkyl-lead inorganic lead ratio (%) with inverse wind speed — urban site.

Phase partitioning in the atmosphere

As mentioned earlier, the phase partitioning of alkyl-lead compounds in the atmosphere is dependent upon their physical and chemical properties. For solid trialkyl-lead compounds, the sub-cooled liquid vapour pressure (P^0_L) and sub-cooled liquid solubility (S^0_L) are provided in Table 1 as they have been found to represent environmental behaviour more truly when applying theoretical equations.[21] The solid water solubility (S^0_S) and solid vapour pressure (P^0_S) of ionic alkyl-lead compounds has been measured in a previous study.[22] Associated sub-cooled liquid values were estimated using Eqn [1], where T_M and T are the melting point and ambient temperature (K) of different species, R is the gas constant (8.314 J mol^{-1} K^{-1}), and ΔS_F is the entropy of fusion (J mol^{-1} K^{-1}).[23] An average value of $\Delta S_F/R = 6.79$ is commonly used to define the entropy of fusion.[21]

$$\ln P^0_L/P^0_S \text{ or } S^0_L/S^0_S = \Delta S_F(T_M - T)/RT \quad [1]$$

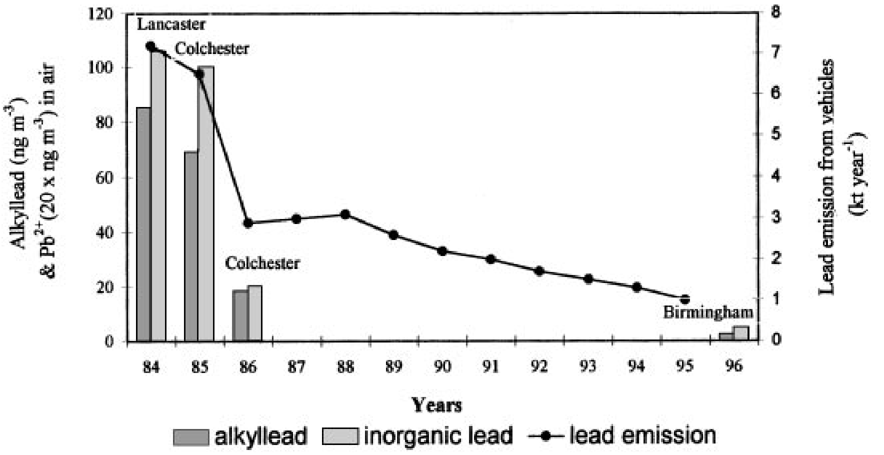

Figure 6 Total alkyl-lead and inorganic lead in air and annual lead emission.

The Henry's law constant (*H*) is also provided in Table 1; this can be considered as the ratio of the liquid or sub-cooled liquid vapour pressure to the liquid or sub-cooled liquid solubility. Because of the importance of these two parameters, the Henry's law constant is often used to explain and predict the partitioning behaviour of organic compounds in the environment.

An estimate of the true particle–vapour partition coefficients (*P*/*V*) of semi-volatile compounds in the atmosphere can be gained from the simultaneous measurement of the ratio of particle-bound (*F*) and gaseous (*A*) concentrations, referred to as the *F*/*A* ratio.[17] In this research, only Me_3Pb^+, Et_3Pb^+ and Et_2Pb^{2+} species could be detected in both atmospheric phases simultaneously to determine *F*/*A* ratios. The mean values of these measured *F*/*A* ratios are presented in Table 6. At the urban site, mean *F*/*A* ratios of 2.3% for Me_3Pb^+ (range 0.7–6.1%) and 5.3% for Et_2Pb^{2+} (range 1–10.5%) were obtained. Corresponding values at the rural site were 4.7% for Me_3Pb^+ (range 2.9–6.4%) and 5.1% for Et_2Pb^{2+} (range 3.9–6.3%). However, sampling artefacts associated with *F*/*A* measurements are known to affect this ratio either positively or negatively. In addition to artefacts such as decomposition on, or volatilization from, filter media, the quantity and composition of airborne particles is also known to influence true *P*/*V* partitioning. There have been extensive studies into these aspects of sampling airborne semi-volatile organic compounds which will depend upon component vapour pressure, ambient temperature, and general stability during sampling conditions.[24,25]

The fraction of alkyl-lead compounds bound to atmospheric particles can be calculated from a

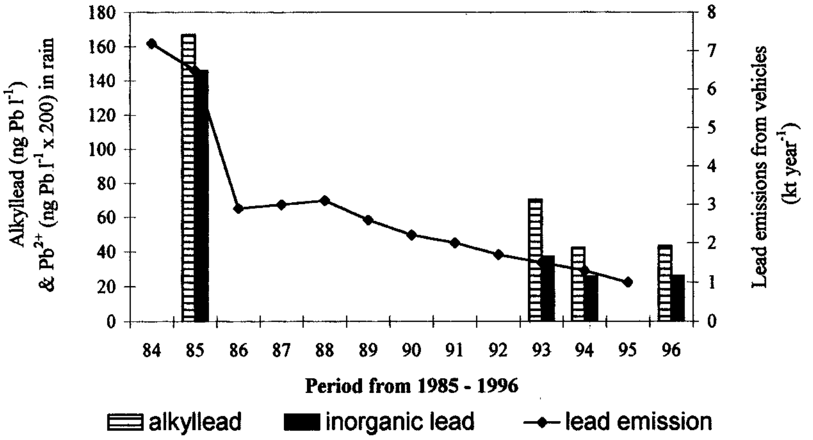

Figure 7 Annual alkyl-lead emission and measured rain concentration in the UK.

Table 6. Observed and predicted alkyl-lead species in vapour and particle phases

Lead species	Observed mean value Vapour phase (ng Pb m^{-3})	Predicted from Eq [2] Particle phase (pg Pb m^{-3})	Particle partitioning (%) Predicted	Observed[a]
Me_4Pb				
Urban	1.2	2×10^{-4}	2×10^{-5}	
Rural	1.3	7×10^{-5}	4×10^{-6}	
Et_4Pb				
Urban	0.17	3×10^{-3}	2×10^{-3}	
Rural	0.19	9×10^{-3}	5×10^{-4}	
	Particle phase (pg Pb m^{-3})	Vapour phase (ng Pb m^{-3})		
Me_3Pb^+				
Urban	7.0	2.4	0.3	2.3
Rural	8.4	9.2	0.1	4.7
Et_3Pb^+				
Urban	1.6	0.01	14	4.2
Rural	1.9	0.04	5	
Et_2Pb^{2+}				
Urban	21			5.3
Rural	16			5.1

[a] Observed particle partitioning is *A/F* ratio (%).

model proposed by Junge.[26] Equation [2] relates the adsorbed fraction (Φ) to the sub-cooled liquid vapour pressure (P^0_L, Pa) and the total aerosol surface area (S_T, cm ^{2} cm^{-3} air):

$$\Phi = c\,S_T/(P^0_L + c\,S_T) \qquad [2]$$

In Eqn [2] Junge assumed that $c = 1.7\times10^{-4}$ Pa cm and does not vary greatly among such semi-volatile organic compounds, and this value is applied here. The aerosol surface area (S_T) is known to vary greatly in ambient conditions, although guidelines have been suggested in the literature for the variation that can be expected.[27] Values for S_T used in the subsequent estimations were 1.1×10^{-5} cm^2 cm^{-3} for urban and 3.5×10^{-6} cm^2 cm^{-3} for rural environments. A measured value for aerosol surface area, generated at the University of Birmingham site from 18 October to 30 November 1995, was 6×10^{-6} cm^2 cm^{-3}, in good agreement with the data selected above.

In addition, to calculate Φ using Eqn [2], the vapour pressure needed to be adjusted for the average temperature of 5 °C during the sampling period. According to the temperature and vapour pressure regression equations proposed by Shapiro and Frey,[28] the tetraethyl-lead vapour pressure and triethyl-lead chloride sub-cooled liquid vapour pressures were found to change from 34.58 Pa to 9.58 Pa and 2.9×10^{-3} Pa to 1.2×10^{-3} Pa respectively between 20 and 5 °C. Therefore, the use of an overall adjustment factor of 3 for the change from 20 °C to the mean sampling temperature of 5 °C has been applied to the P^0_L values.

The calculated values for the percentage particle-bound character of alkyl-lead species according to Eqn [2] are presented in Table 6. According to the Φ values in Table 6, we can further estimate the equilibrium particle concentrations of R_4Pb from their measured gaseous concentrations, and the equilibrium gaseous concentrations of R_3Pb^+ from their measured particle concentrations. As can be seen in Table 6, volatile tetra-alkyl-lead species (Me_4Pb and Et_4Pb) are predicted to partition almost completely into the vapour phase, and hence could not be detected in any of the aerosol samples, being well below the limit of detection. However, less volatile ionic alkyl-lead species are observed adsorbed to atmospheric particles, and could easily be observed in all aerosol samples. As can also be seen in Table 6, the estimated proportion of Et_3Pb^+ in the vapour phase is roughly 50 times lower than that of Me_3Pb^+.

Wet deposition

The results for alkyl-lead compounds in rainwater from the two sampling sites are outlined in Table 7. The measurements include some dry deposition of alkyl-lead compounds on the funnel throughout the sampling period, and will lead to consequent overestimation of the alkyl-

Table 7. Concentrations of lead species measured in rain

Lead species	Urban site (ng Pb l^{-1}) Mean (σ)	Range	Times detected[a]	Rural site (ng Pb l^{-1}) Mean	Range	Times detected[b]
Me_3Pb^+	14.9 (8.4)	5–33	10	5.7	2–9	2
Me_2EtPb^+	0.5 (1.0)	nd–3[c]	2	—	—	0
$MeEt_2Pb^+$	0.3 (0.9)	nd – 3	1	–	–	0
Et_3Pb^+	14.4 (8.4)	5–34	10	13.5	12–15	2
Me_2Pb^{2+}	0.6 (1.8)	nd – 6	1	—	—	0
Et_2Pb^{2+}	13.3 (9.6)	6–40	10	4.3	nd – 9	1
Pb^{2+}	6,464 (5,786)	2100–22 670	10	3400	1600–5200	2
Fraction of organic lead (%)	0.9 (0.5)	0.3–2.1		0.9	0.4–1.5	

[a] Out of a total of 10 samples. [b] Out of a total of two samples. [c] nd, Not detected.

lead in wet deposition. As seen in Table 7, the predominant species were consistently Me_3Pb^+, Et_3Pb^+ and Et_2Pb^{2+}, which were detected in all rain samples collected in generally similar quantities. The relatively high amounts to Et_3Pb^+ in rain, irrespective of low airborne concentrations, can be explained by the greater solubility, and thus enhanced scavenging, of this species by rainfall. The consistently high values for Me_3Pb^+ in rain will reflect its longer lifetime in the atmosphere compared with other species, and the general airborne predominance of its precursor, tetramethyl-lead.[7] It can also be noted that the urban values were two to three times higher than that found at the rural site. Tetra-alkyl species in rain were always below the detection limit during this sampling campaign, confirming rain to be less important as a removal mechanism for these species. Monoalkyl-lead species (RPb^{3+}) were often identified in the chromatographic plots. Their presence, however, is considered to be due to a derivatization artefact associated with inorganic lead contamination within the Grignard reagent.[29] Therefore, the suspect RPb^{3+} species found in this study have been neglected.

Scavenging of alkyl-lead compounds into cloud droplets and into falling rain will be a combination of both vapour- and particle-phase removal. However, because of the low solubility of tetra-alkyl-lead, it would not be expected to find significant vapour-phase removal of these compounds in rain. In contrast, the more soluble and particle-bound ionic alkyl-lead will be subject to particle- as well as vapour-phase removal. Washout ratios for ionic alkyl-lead, total alkyl-lead and inorganic lead have been calculated using the measured data from both sides. These have been given in Table 8 as the ratio of concentration in rain (ng m^{-3}) to that in air (ng m^{-3}). Mean concentrations at each site from Tables 4, 5 and 7 were used to produce these values. These washout values are in good agreement with earlier research by Allen *et al.*,[8] which reported mean values of washout factors for total alkyl-lead and inorganic lead respectively of 3.2×10^4 and 2.5×10^5 at an urban site, and 5.4×10^4 and 2.8×10^5 at a semi-rural site. The average daily wet deposition rates for total alkyl-lead and dissolved inorganic lead during each sampling period have also been calculated and are presented for both sites in Table 9. The average wet deposition at the urban site was 1020 and 8.1 pg cm^{-2} day^{-1} for inorganic lead and total alkyl-lead respectively, with corresponding rural values of 760 and 3.6 pg cm^{-2} day^{-1}.

Observed concentrations of alkyl-lead and inorganic lead in rainwater collected at UK sites over a number of years have been collated. Table 10 summarizes the data obtained from Essex University and Birmingham University by taking the mean values for total alkyl-lead and inorganic lead in individual rainwater samples. In the case of the more recent data (1993 and later), volume-weighted concentrations have been calculated; this was not possible for the 1985 data as rainfall depth information was unavailable. The data are plotted in Fig. 7 alongside the trend in lead emission from leaded-gasoline use. It may be seen that inorganic lead in rain has fallen in

Table 8. Observed washout ratios

Lead species	Urban site	Rural site
Me_3Pb^+	6.5×10^4	4.4×10^4
Et_3Pb^+	7.0×10^5	6.8×10^5
Total alkyl-lead	2.2×10^4	1.6×10^4
Inorganic lead	6.9×10^5	7.0×10^5

Table 9. Wet deposition rates of alkyl-lead and inorganic lead in precipitation

Sample period	Rainfall (mm)	Rain concentration (ng Pb l^{-1}) Inorganic lead	Alkyl-lead	Deposition rate (pg cm^{-2} day^{-1}) Inorganic lead	Alkyl-lead
Urban					
8–21 Sept. 1995	47.8	3300	49	1110	17
21 Sept.–6 Oct. 1995	19.7	5282	38	740	6.7
6–25 Oct. 1995	24.7	2410	29	310	3.3
25 Oct.–14 Nov. 1995	39.5	6300	80	1240	17
14–30 Nov. 1995	27.8	8350	33	1450	6.7
22 Jan.–13 Feb. 1996	60.2	6990	38	1910	10
13–27 Feb. 1996	23.1	2100	25	350	3.3
27 Feb.–13 Mar. 1996	14.0	22670	76	2120	6.7
13–24 Mar. 1996	17.4	2012	43	320	6.7
24 Mar.–14 Apr. 1996	24.8	5230	29	680	3.3
Rural					
20–24 Mar. 1996	14.0	5230	23	1460	6.7
24 Mar.–8 Apr. 1996	4.3	1600	24	50	0.67

line with automotive lead emissions, whilst for alkyl-lead the decline has been slightly less. Data presented in an earlier study[11] indicated that alkyl-lead in rain had fallen by only half as much as the reduction in lead emissions from road traffic between 1985 and 1993. The larger dataset now available, together with the use of volume-weighted concentrations, indicates a decline in alkyl-lead only a little less than that of inorganic lead. Whilst this finding must still be viewed with some caution, it is possible that alkyl-lead emission from vehicles is not linearly related to alkyl-lead use in gasoline. The air concentration data shown in Fig. 6 do not, however, support this view. Taking air and rainwater data together, the decline in both alkyl-lead and inorganic lead in the atmosphere is broadly in line with declining use of lead in petrol.

CONCLUSION

The determination of alkyl-lead and inorganic lead in vapour, aerosol and rain samples has provided the current trends of these compounds in urban and rural air in central England. The results showed the predominance of vapour-phase over particle-bound species, with tetramethyl-lead being the most prevalent vapour-phase species. It was also found that at the urban site, lower windspeed and lower temperatures are associated with higher alkyl-lead relative to inorganic lead. The theoretical phase-partioning coefficients, predicted by their respective physical and chemical properties, suggested almost 100% of tetra-alkyl-lead existing in the vapour phase, and around 0.3% of trimethyl-lead and 14% of triethyl-lead bound on atmospheric particles. These estimated data fit quite well with the data from our field measurements. Washout of total alkyl-lead is less efficient than for inorganic lead. This is probably due to the predominant occurrence of alkyl-lead as gaseous R_4Pb, which leads to less effective scavenging than for aerosol inorganic lead. The observed concentrations of atmospheric alkyl-lead and inorganic lead showed that the reduction in both total alkyl-lead and inorganic lead concentrations in the atmosphere was broadly in line with the reduction in use of alkyl-lead compounds in gasoline, although the

Table 10. Concentrations of total alkyl-lead and inorganic lead in rain, 1985–1996

Location	Year	No. of samples	Alkyl-lead (ng l^{-1})	Pb^{2+} (ng l^{-1})	Reference
Essex University	1985	11	167	29,200	30
Birmingham University	1993	32	70.5	7420	This study
Essex University	1994	12	42.4	5140	This study
Birmingham University	1995–1996	17	43.2	5260	This study

concentration in rain show a larger relative decline for inorganic lead than for alkyl-lead.

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