APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 7, 567–575 (1993)

# Assessment of recent trends in concentrations of alkyl-lead compounds in rainwater

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

**Concentrations of tetra-, tri and di-alkyl-lead compounds in rain have been measured at rural and urban sites in England. The measurements are compared with similar data collected in the early 1980s, prior to a 72% reduction in the emission of lead from combustion of leaded petrol. Whilst concentrations of inorganic lead have fallen broadly in line with emissions of automotive lead, alkyl-lead concentrations in rain have fallen by only 50% or less, and thus the ratio of alkyl-lead to inorganic lead in rain has increased appreciably. The reason for this phenomenon is unclear. The data suggest that lead in rainwater would fall to approximately 2 μg dm$^{-3}$ if automotive lead emissions fell to zero.**

**Keywords: alkyl-lead, rainwater, gas chromatography/atomic absorption spectroscopy, temporal trends**

## INTRODUCTION

Tetra-alkyl-lead (TAL) additives have been used in petrol (gasoline) since the 1930s as an inexpensive means of improving the octane rating. However, in recent years, in both North America and Europe there have been legislative actions which have curtailed their use. In the UK there have been two major factors contributing to reduced emissions of lead from petrol vehicles. Firstly, the permitted maximum level of lead in petrol was reduced from 0.40 g dm$^{-3}$ to 0.15 g dm$^{-3}$ at the end of 1985. More recently, fiscal incentives have led to increased use of unleaded fuel. According to official government statistics, total lead emissions from petrol-engined road vehicles were 8.0 kt in 1975, 6.5 kt in 1985 and reduced to 1.8 kt in 1992.[1] Further market penetration of unleaded petrol has occurred since that time. Current emissions thus represent about 23% of the 1975 emissions and 28% of their 1985 level. Whilst concentrations of inorganic lead in air have broadly followed in this trend, there is no information from which to evaluate trends in alkyl-lead concentrations in the atmosphere.

It has been estimated that around 1% of the tetraethyl- and tetramethyl-lead added to petrol is released into the environment by car exhaust gases and by evaporation,[2] compared with about 70% emitted as inorganic lead particles. These volatile $R_4Pb$ species exist primarily in the vapour phase in the atmosphere and have half-lives in the region of a few hours. They are progressively broken down by hydroxyl radicals in the atmosphere to a variety of trialkyl and dialkyl species ($R_3Pb^+$, $R_2Pb^{2+}$) of which the trialkyl species predominate, with estimated half-lives of five days.[3] Monoalkyl-lead exists only as a transient intermediate in the breakdown to inorganic lead, the final product of alkyl-lead emissions. Due to their relative persistence and greater water solubility, trialkyls are accepted to be the major organolead species in rain, and this route is considered to be the most important removal process for atmospheric organic lead. Rainwater has been monitored in the past and provides a useful comparison of changes to the organic lead burden in the atmosphere. The high-altitude source of alkyl-lead in rainwater reduces the spatial variability inherent in the sampling of these compounds in other media, can can give an indication of the changes in mean atmospheric values over longer periods of time.

Clearly, the reduction in emission of tetra-alkyl-lead (TAL) should lead to a decrease in environmental levels of alkyl-lead species and in their ratio to inorganic lead, unless all sources of inorganic lead have diminished to the same degree. Other research has shown that the reduction of lead levels in petrol in the past has had a rapid influence on total atmospheric lead concentrations.[4–7] Inorganic lead in UK air has

* Author to whom correspondence should be addressed.

0268–2605/93/070567–09 $09.50


*Received 30 June 1993*
*Accepted 20 August 1993*

diminished appreciably in concentration since 1985.[1] In this paper, data for alkyl-lead species detected in rain during 1992/1993 are presented and compared with other data reported during the last decade.

Techniques for species-specific determination of alkyl-lead by hyphenated GC AA (coupled gas chromatography–atomic absorption spectroscopy) have been developed over recent years to allow the low analytical detection limits necessary for environmental levels, in the region of a few nanograms per litre ($dm^3$) in water.[8–10] An altered atomization-cell design is reported here which provides a more reliable and robust system for the introduction of the chromatographically separated alkyl-lead species into the AA light path.

## EXPERIMENTAL

### Sampling

Following earlier work by Harrison and co-workers,[2] bulk deposition (including wet and dry deposition) samples were collected by open-topped glass funnels. Two funnels positioned in parallel above 2.5 $dm^3$ brown bottles were sited near the University of Birmingham, approximately three miles (5 km) from the centre of Birmingham (population, one million). The University is in a generally suburban district with some industrial installations. A second site was chosen in a small, semi-rural South Suffolk village (Stoke by Nayland), which is approximately 10 miles (16 km) from the nearest towns (Colchester, Ipswich and Sudbury) and five miles (8 km) from any main roads. Sampling was also undertaken on the University of Essex library roof, a semi-urban site, to correspond with earlier data collected at this site in 1985. The samplers were exposed for sufficient time to collect a minimum of 1.0 $dm^3$ of precipitation.

### Extraction

Earlier work[11] has shown that tetra-alkyl-lead species adsorb onto glass sampling vessels and that, to detect these species, initial hexane extraction must take place within the original sampling vessel, with no prior filtration. Sub-samples of 1 $dm^3$ of rainwater were extracted into 30 $cm^3$ hexane in the sampling vessel by mechanical shaking (30 min, repeated once) after addition of NaCl (50 g) and sodium diethyldithiocarbamate (NaDDTC) (5 $cm^3$, 0.5 mol $dm^{-3}$). The combined hexane extracts were dried over anhydrous sodium sulphate ($Na_2SO_4$) and transferred to 25 $cm^3$ conical flasks. The extract was reduced under a nitrogen stream to near-dryness. Propyl magnesium chloride (Grignard reagent) was added and the flask shaken gently for 8 min. To the propylated extract, hexane (0.5 $cm^3$) and sulphuric acid (10 $cm^3$, 0.5 mol $dm^{-3}$) were added and, after a further gentle shaking, the contents were transferred to a small separating funnel. The hexane was removed, dried over $Na_2SO_4$ and stored at −20 °C prior to analysis. Propylation of the ionic alkyl-lead to the volatile tetra-alkyl form allows for separation by gas chromatography. A small number of rainwater samples from the Birmingham and Suffolk sites were filtered through 0.45 μm cellulose acetate filters prior to extraction. It has been shown that ionic alkyl-lead species exist entirely in solution and are not influenced by filtration, but tetra-alkyl-lead species adsorb onto suspended solids and would not be recovered from rainwater after filtration.[11]

### Analysis

Separation of the alkyl-lead species was achieved by GC using a glass column (1.2 m × 6 mm o.d. × 3 mm i.d.) packed with 10% OV-101 on Chromosorb W (80–100 mesh). The injection temperature was set at 150 °C and an oven temperature programme of 80–180 °C (20 °C $min^{-1}$) was used. An injection volume of 25 μl was found satisfactory throughout the analysis. The transfer line from the GC to the AA was constructed of PTFE tubing (0.75 m × 1.6 mm i.d.) and was kept at 140 °C. This transfer line required regular cleaning to prevent losses through adsorption of the alkyl-lead species to the tubing walls. The atomization cell in the light path of the AA was constructed from silica tubing (16 cm × 1.5 cm o.d.) which was held inside an electrothermal heating mantle. The whole assembly was packed with high-temperature ceramic wool and encased in a Ceramit 10 (Ceramic Substrates Ltd, Newport, UK) machinable ceramic material, with slots to allow sample delivery. The outer surface temperature of the cell was below 100 °C, allowing for safer working conditions. The system was capable of withstanding temperatures in excess of 1000 °C. The electrothermal mantle required a 24 V, 40 A supply from an industrial transformer, which was in turn optimized by a voltage con-

troller on the 240 V supply. A thermocouple was used to set the 240 V voltage feed so that a stable temperature of 950 °C was achieved inside the central silica tube. The new cell has proved a very much more reliable design than previous systems using heating wire wrapped around silica cells in a firebrick.[12]

Recoveries of four species were determined directly by spiking laboratory water at a level of 100 ng $dm^{-3}$. Recoveries, in triplicate, were for trimethyl-lead 90%, triethyl-lead 87%, dimethyl-lead 73% and diethyl-lead 97%. Limits of detection of between 0.6 and 2 ng $dm^{-3}$ as lead in rainwater were achieved for a sample of rainwater. For other species, sensitivity ratios were derived from qualitative standards. Recoveries of the volatile tetra-alkyl species were much lower because of the evaporation steps during extraction, and were between 50 and 60%. None of the results given below has been corrected for recovery.

Total dissolved inorganic lead in rainwater samples was determined independently by graphite furnace AA (GF AA). Samples were prefiltered through 0.45 μm cellulose acetate filters, as in earlier work in our laboratory.[2,3]

## RESULTS AND DISCUSSION

The results from the rainwater samples collected at the three sites are presented in Tables 1–3. Eleven species were quantified; monoalkylated species were not qualified and are presented as $RPb^{3+}$. It is not expected to find the monoalkylated compounds in samples from the environment, due to their instability; however, other workers have also found these species in rain,[10,13,14] and it has been suggested that their presence may be due to an artefact of the analytical procedure.[15]

The predominant species were consistently triethyl- and diethyl-lead, which were detected in all samples with a maximum concentration of 207 ng $dm^{-3}$ at the Birmingham site during February 1993. Trimethyl- and dimethyl-lead concentrations were around 30% of the ethyl analogues and were detected in most, but not all, samples.

Some TAL species were detected, and total $R_4Pb$ levels reached 32 ng $dm^{-3}$ in the sample exposed throughout February 1993. It may be possible that TAL are scavenged by rain (washout), but such dissolved species would be expected to decompose rapidly in rainwater while in the sampling container. The possibility of unquantifiable dry deposition onto funnel surfaces during dry periods could enhance levels, though this was thought unlikely because of the low adsorption of TAL to atmospheric aerosols,[2] and also photochemical degradation while the sampler was exposed. In samples filtered prior to extraction, no TAL species were detected. Other studies have also detected the occasional presence of TAL in rain at broadly similar concentrations,[3] although generally studies report levels as below detection limits.

The values at Birmingham University were around twice the levels found at the rural site in Suffolk. The few samples available from the Essex University library roof show levels between those found in Birmingham and those in Suffolk. The higher levels of triethyl- and diethyl-lead, found in all samples might simply be explained by the predominance of tetraethyl-lead as the major petrol additive. However, other workers have found ionic methyl-lead levels much higher than corresponding ethyl-lead ones during the summer months, possibly because of the enhanced photodegradation of the ethyl species.[16] Radojevic and Harrison[3] also found more trimethyl-lead than triethyl-lead in summer sampling of rainwater in 1985. Winter samples from the same research showed a reversal of this trend, with triethyl-lead levels greater than trimethyl-lead. Therefore, the season of sampling may be the most significant parameter determining the ratio of methylated to ethylated species, although this hypothesis is not well supported by our recent data.

Table 4 summarizes data obtained from a number of sites since 1984 by taking the mean of detections of trialkyl-lead, dialkyl-lead, total alkyl-lead and inorganic lead in individual samples. The ratio of organic lead to inorganic lead for each data set was calculated by taking the mean of individual ratios, using totals of all alkyl-lead species. There are inherent problems in comparing data from different sites due to differences in local weather patterns and the relative impact of traffic for the specific area. Comparing levels at the same site from different years to some degree normalizes these problems. Only the data from Essex University were collected at identical locations, and to date a limited number of samples means interpretations should be viewed with some caution. However, many of the data listed in Table 4 have been averaged over long periods

**Table 1** Alkyl-lead species (ng $dm^{-3}$) and inorganic lead (μg $dm^{-3}$) detected in rain at rural Suffolk site

| Period | $Me_4Pb$ | $Me_3EtPb$ | $Me_2Et_2Pb$ | $Et_4Pb$ | $Me_3Pb^+$ | $Me_2EtPb^+$ | $MeEt_2Pb$ | $Et_3Pb^+$ | $Me_2Pb^{2+}$ | $Et_2Pb^{2+}$ | $RPb^{3+}$ | $Pb^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 24–29 Nov. 1992[a] | —[b] | — | — | — | 5 | — | — | 8 | — | 3 | — | 4.1 |
| 29 Nov.–7 Dec. 1992[a] | — | — | — | — | 4 | — | — | 16 | — | 12 | — | 3.9 |
| 9–20 Dec. 1992[a] | — | — | — | — | 8 | 9 | — | 36 | 8 | 29 | — | 5.7 |
| 20 Dec. 1992–15 Jan. 1993[a] | — | — | — | — | 5 | 3 | — | 43 | — | 32 | 2 | 2.1 |
| 15 Jan–27 Feb. 1993 | — | — | — | — | 13 | 7 | — | 34 | — | 21 | 3 | 3.6 |
| 27 Feb.–3 Apr. 1993 | — | — | — | — | 6 | 1 | 8 | 16 | — | 14 | — | 2.2 |
| 3–15 Apr. 1993 | — | — | — | — | 6 | 4 | — | 9 | — | 10 | — | 1.7 |
| 22–26 Apr. 1993 | — | — | — | — | 4 | — | — | 7 | 9 | 18 | — | 2.1 |
| 26 Apr.–20 May 1993 | — | 5 | — | — | — | — | 4 | 4 | 2 | 13 | 2 | — |
| Times detected | — | 1 | — | — | 8 | 5 | 2 | 9 | 3 | 9 | 3 | 8 |
| Range | — | 0–5 | — | — | 4–13 | 0–9 | 0–8 | 0–43 | 0–9 | 3–32 | 0–3 | 0–5.7 |
| Mean | — | 0.6 | — | — | 5.7 | 2.7 | 1.3 | 19.2 | 2.1 | 16.9 | 0.7 | 2.8 |
| SD | — | 1.6 | — | — | 3.3 | 3.2 | 2.8 | 14.6 | 3.7 | 9.2 | 1 | 1.7 |

[a] Samples filtered through 0.45 μm cellulose acetate filters. [b] Below detection limit.

**Table 2** Alkyl-lead concentrations (ng $dm^{-3}$) and inorganic lead (μg $dm^{-3}$) in rain collected at Essex University

| Period | $Me_4Pb$ | $Me_3EtPb$ | $Me_2Et_2Pb$ | $Et_4Pb$ | $Me_3Pb^+$ | $Me_2EtPb^+$ | $MeEt_2Pb$ | $Et_3Pb^+$ | $Me_2Pb^{2+}$ | $Et_2Pb^{2+}$ | $RPb^{3+}$ | $Pb^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12–27 May 1993 | —[a] | — | — | — | 13 | 7 | — | 4 | 6 | 17 | 7 | 1.9 |
| 20 May–4 Jun 1993 | — | 5 | — | — | 9 | — | — | 8 | 6 | 29 | 9 | 2.3 |
| 27 May–4 Jun 1993 | — | — | — | — | 19 | 8 | — | 11 | 10 | 26 | — | 2.8 |
| Times detected | 0 | 1 | 0 | 0 | 3 | 2 | 0 | 3 | 3 | 3 | 2 | 3 |
| Range | — | 0–5 | — | — | 9–19 | 0–8 | — | 4–11 | 6–10 | 17–29 | 0–9 | 1.9–2.8 |
| Mean | — | 1.7 | — | — | 13.7 | 5 | — | 7.7 | 7.3 | 24 | 5.3 | 2.3 |
| SD | — | 2.4 | — | — | 5 | 4.4 | — | 3.5 | 2.3 | 6.2 | 4.7 | 0.4 |

[a] —, Below detection limit.

**Table 3** Alkyl-lead species (ng $dm^{-3}$) and inorganic lead (μg $dm^{-3}$) detected in rain at Birmingham University

| Period | $Me_4Pb$ | $Me_3Et_2Pb$ | $Me_2Et_2Pb$ | $Et_4Pb$ | $Me_3Pb^+$ | $Me_2EtPb^+$ | $MeEt_2Pb$ | $Et_3Pb^+$ | $Me_2Pb^{2+}$ | $Et_2Pb^{2+}$ | $RPb^{3+}$ | $Pb^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 18–25 Nov. 1992[a] | —[b] | — | — | — | 4 | 10 | — | 12 | — | 13 | — | 6.1 |
| 25–30 Nov. 1992[a] | — | — | — | — | 3 | — | — | 13 | — | 11 | — | 3.7 |
| 30 Nov.–3 Dec. 1992[a] | — | — | — | — | 4 | — | — | 15 | — | 15 | — | 4.5 |
| 3–14 Dec. 1992[a] | — | — | — | — | 25 | 17 | — | 87 | 15 | 84 | — | 10.1 |
| 14–22 Dec. 1992 | 3 | 4 | 2 | — | 12 | 10 | — | 17 | 18 | 45 | — | 8.8 |
| 22 Dec. 1992–11 Jan. 1993 | 1 | 2 | 2 | 3 | 8 | 10 | — | 27 | 10 | 28 | — | 15.1 |
| 11–15 Jan. 1993 | — | — | — | — | 3 | — | — | 8 | — | 7 | — | 3.2 |
| 15–25 Jan. 1993 | 1 | 1 | — | — | 5 | 10 | — | 17 | 21 | 12 | — | 8.2 |
| 25 Jan.–1 Mar. 1993 | — | 6 | 14 | 12 | 49 | 30 | 36 | 207 | 25 | 141 | 61 | 39.8 |
| 22 Mar.–4 Apr. 1993 | — | — | — | — | 4 | — | — | 13 | — | 12 | — | 3.9 |
| 4–14 Apr. 1993 | — | — | — | — | 5 | — | 5 | 17 | — | 14 | — | 12.2 |
| 14 Apr.–17 May 1993 | — | — | — | — | 15 | 5 | 8 | 15 | 6 | 15 | 13 | 6.8 |
| 17 May–27 May 1993 | — | 1 | — | — | 25 | 12 | 11 | 110 | 15 | 70 | — | 7 |
| 27 May–1 Jun. 1993 | — | 5 | — | — | 6 | — | 3 | 9 | 5 | 27 | 7 | 3.1 |
| *Times detected* | 3 | 6 | 3 | 2 | 14 | 8 | 5 | 14 | 8 | 14 | 3 | 14 |
| Range | 0–3 | 0–6 | 0–14 | 0–12 | 3–49 | 0–30 | 0–36 | 8–207 | 0–25 | 7–141 | 0–61 | 3.1–39.8 |
| Mean | 0.4 | 1.4 | 1.3 | 1.1 | 12 | 7.4 | 4.5 | 40.5 | 8.2 | 35.3 | 5.8 | 9.5 |
| SD | 0.8 | 2.1 | 3.6 | 3.2 | 13.1 | 8.7 | 9.7 | 57 | 9 | 38.4 | 16.3 | 9.5 |

[a] Samples filtered through 0.45 μm cellulose acetate filters. [b] —, Below detection limit.

**Table 4** Reported values for alkyl-lead and inorganic lead from various studies over the last 10 years

| Location[a] | Year | No. of samples | $R_3Pb^+$ (ng $dm^{-3}$) | $R_2Pb^{2+}$ (ng $dm^{-3}$) | Total alkyl-lead | Inorganic lead (ng $dm^{-3}$) | Organic to inorganic ratio (%) | Reference |
|---|---|---|---|---|---|---|---|---|
| Antwerp (U) | 1984 | 12 | 93 | 86 | na[b] | na | 0.1 | 14 |
| Lancaster (SR) | 1984 | 8 | 164 | 0 | 164 | 40 100 | 0.9 | 3 |
| Essex University (SU) | 1985 | 11 | 51 | 106 | 167 | 29 200 | 0.7 | 3 |
| Colchester (U) | 1986 | 3 | 72 | 46 | 139 | 31 000 | 0.4 | 3 |
| University of Antwerp (SU) | 1986 | 37 | 30 | 20 | na | 31 060 | 0.2 | 16 |
| Rural Suffolk (SR) | 1993 | 12 | 28.9 | 19 | 49.2 | 3183 | 1.8 | This paper |
| Birmingham University (U) | 1993 | 14 | 64 | 43.5 | 118 | 9418 | 1.2 | This paper |
| Essex University (SU) | 1993 | 3 | 26.3 | 31.3 | 65 | 2310 | 2.9 | This paper |

[a] Abbreviations. U, urban; SU, semi-urban; SR, semi-rural. [b] na, Not available.

and use of total $R_3Pb^+$ and $R_2Pb^{2+}$ values removes the possible seasonal variability in the ratio of the methyl to ethyl levels that is suggested by Van Cleuvenbergen *et al.*[16]

The two sets of data from Essex University indicate that alkyl-lead levels have dropped by more than 50%. The earlier data from Essex were collected over a full year, whereas the current data were collected during late spring. Further data from Essex University covering the winter period should be collected if changes in levels are to be demonstrated more persuasively. Data from urban Colchester in 1986 and Birmingham in 1993 do not show a significant change, but the differences in local sources make such comparisons difficult. The limited data do, however, indicate that atmospheric alkyl-lead concentrations are in decline, but not to the degree which might have been expected considering the reductions in emission rates of the TAL additives. In contrast with this, inorganic lead measured at Essex University in 1993 was 10% of the level measured in 1985. Similar reductions can be inferred by values from Birmingham and Suffolk. These reductions are not reflected in the organolead concentrations; therefore organic/inorganic lead ratios increased over the period covered by Table 4. The reduction in inorganic lead concentrations is in proportion with the reduction in usage of alkyl-lead compounds. Figure 1 shows the changes in inorganic lead and total alkyl-lead at the sites identified in Table 4.

As mentioned in the Introduction, alkyl-lead usage diminished sharply between 1985 and 1992, with a decrease in total automotive emissions of lead amounting to 72%. Lead from vehicular sources is expected to be much the dominant contributor to lead-in-air. The fall in inorganic lead content in rain is broadly in line with this, but alkyl-lead concentrations have fallen only by about 50%, taking data from the same, or comparable, sites. The question must be considered

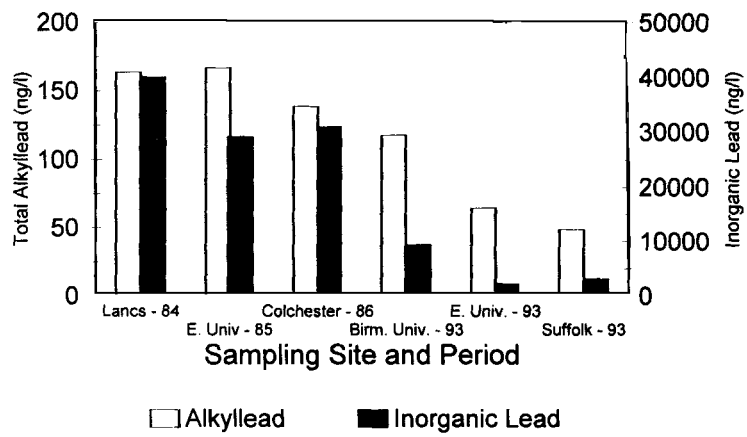


**Figure 1** Comparison of lead concentrations at various sites since 1984.

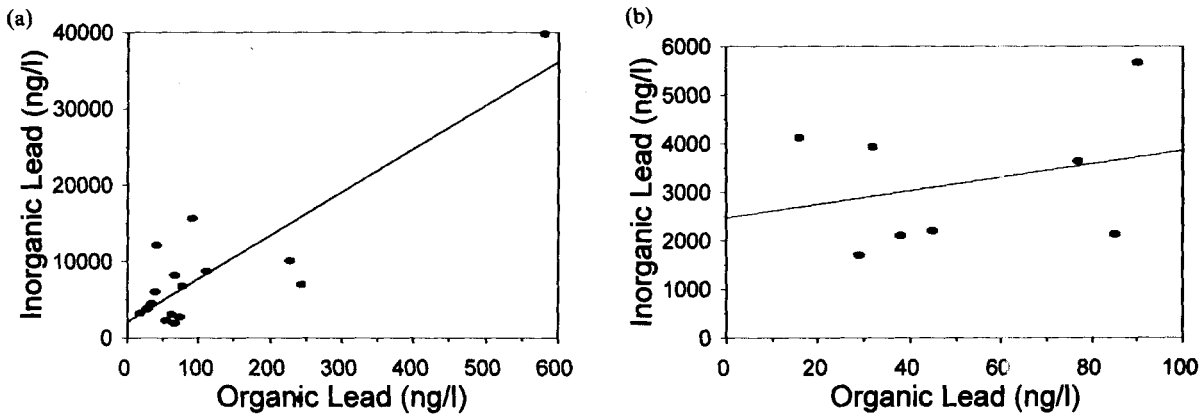


**Figure 2** Correlation of organic with inorganic lead at Colchester and Birmingham (a) and semi-rural Suffolk (b).

as to whether analytical procedures have changed so as to affect the data. The work has been carried out by the same research groups, using the same techniques and this, therefore, appears improbable. In recent work, the purity of analytical standards has been rigorously examined and found to be >95%. If the standards used in the earlier work had been of substantially lower purity, this would lead to an overestimation of concentrations which would not explain the phenomenon of an increased alkyl/inorganic lead ratio. Concentrations of particulate inorganic lead in air in the UK have fallen broadly in line with emission of lead from motor vehicles,[1] and our rainwater data for inorganic lead appear consistent with this trend. It is unclear why concentrations of alkyl-lead appear not to have fallen by the same proportion. This may simply be that emissions of alkyl-lead compounds are not linearly related to the concentrations in petrol. It should, however, be remembered that the main components of alkyl-lead in rain are trialkyl- and dialkyl-lead formed in the atmosphere from primary tetraalkyl-lead emissions; it is possible (although unlikely) that this system is non-linear. This tentative finding warrants more detailed investigation.

Correlations between alkyl-lead and inorganic lead are illustrated in Fig. 2. The relationship is good from combined data from Essex and Birmingham Universities ($r^2 = 0.76$), indicative of a common vehicular source in both locations. There was no correlation at the Suffolk site ($r^2 = 0.08$), which illustrates how strong source profiles may be lost as air masses move from city areas into rural districts. The $y$-intercept from linear regression in both cases illustrated in Fig. 2 gave similar values for residual inorganic lead: 2070 ng $dm^{-3}$ for the urban sites and 2470 ng $dm^{-3}$ for rural Suffolk. This presumably represents the inorganic lead in rain from non-automotive sources.

## SUMMARY

Alkyl-lead levels in rainwater show a declining tendency in samples taken at a number of sites over the last ten years. The degree of decrease appears less than would be expected from lower emissions of these compounds. Much lower inorganic lead levels have not been reflected in correspondingly lower alkyl-lead levels in Essex, where comparable data from the last decade exist. It appears that the proportion of alkyl-lead relative to inorganic lead in rain has approximately doubled since 1985, although the reason for this is unclear, as inorganic lead concentrations have fallen in proportion to alkyl-lead used in petrol. Regression analysis suggests that non-automotive lead in rain amounts to approximately 2 μg $dm^{-3}$.

## REFERENCES

1. Department of the Environment *Digest of Environmental Protection and Water Statistics*, No. 15 (1992), HMSO, London, 1993
2. Allen, A G, Radojevic, M and Harrison, R M *Environ. Sci. Technol.*, 1988, 22: 517
3. Radojevic, M and Harrison, R M *Atmos. Environ.*, 1987, 21: 2403
4. Robock, E, Georgii, H W and Muller, J J *Atmos. Environ.* 1987, 14: 89

5. Pattenden, N J and Branson, J R *Atmos. Environ.*, 1987, 21: 2481
6. Jenson, R A and Laxen, D P H *Sci. Tot. Environ.*, 1987, 59: 1
7. Page, R A, Cawse, P A and Baker, S J *Sci. Tot. Environ.*, 1988, 68: 71
8. Radojevic, M In: *Environmental Analysis using Chromatography Interfaced with Atomic Spectroscopy*, Harrison, R M and Rapsomanikis, S (eds), Ellis Horwood, Chichester, 1989, pp 223–257
9. Chau, Y K, Wong, P T S and Kramer, O *Analyt. Chim. Acta*, 1983, 146: 211
10. Chakraborti, D, De Jonghe, W R A, Van Mol, W E, Van Cleuvenbergen, R J A and Adams, F C *Analyt. Chem.*, 1984, 56: 2692
11. Harrison, R M and Radojevic, M *Environ. Technol. Lett.*, 1985, 6: 129
12. Forsyth, D S and Marshall, W D *Analyt. Chem.*, 1985, 57: 1299
13. Van Cleuvenbergen, R J A, Chakraborti, D, Van Mol, W and Adams, F C *Int. Conf. Heavy Metals in the Environment 1985*, CEP Consultants, Edinburgh, 1985, Pp 153–155
14. Van Cleuvenbergen, R J A, Chakraborti, D and Adams, F C *Environ. Sci. Technol.*, 1986, 6: 589
15. Van Cleuvenbergen, R J A, Chakraborti, D and Adams, F C *Analyt. Chim. Acta*, 1984, 182: 239
16. Van Cleuvenbergen, R J A and Adams, F C *Environ. Sci. Technol.* 1992, 26: 1354