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Environmental sources and sinks of alkyllead compounds

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Evidence is presented in favour of a natural environmental alkylation process as a source of atmospheric vapour-phase alkyllead. Several species of marine flora have been cultured under laboratory conditions with added doses of inorganic lead, and production of alkyllead, predominantly trimethyllead (Me_3Pb^+), has been measured. Atmospheric concentrations and ratios of alkyl and inorganic lead at urban, rural and remote sites suggest that differential decay and deposition processes for different species, together with an environmental alkylation source, may explain enhanced ratios of total alkyllead/total lead in maritime air masses.

Keywords: Alkyllead, bioalkylation, washout ratios, phytoplankton, marine algae

INTRODUCTION

Under natural environmental conditions it seems likely that lead compounds may undergo alkylation, by either biological or chemical processes, and numerous investigations have been made into the possible role of naturally occurring sediments and micro-organisms. Methylation of divalent inorganic lead (Pb^{2+}) is theoretically unlikely due to the difficulty, indicated by thermodynamic considerations, of the initial oxidative conversion of lead(II) to lead(IV).[1] Alkylation of organic lead(IV) compounds proceeds rapidly, however, although it is difficult to ascribe the process to purely biological or chemical pathways.[2–5] The presence of anthropogenically-sourced trialkyllead compounds in the environment could then account, by a dismutation process, for subsequent release of tetra-alkyllead compounds in laboratory incubations of sediments and other materials. This process would be less likely in remote unpolluted regions as the source of man-made trialkyllead would be less substantial.

Reisinger *et al.*[5] found no evidence for the biomethylation of inorganic lead, possibly due to an inadequate detection limit ($0{\cdot}09\ \mu g$ Pb cm^{-3} extract), although incubations with the organic salts Me_3PbOAc, Et_3PbOAc and Et_3PbCl produced Me_4Pb and Et_4Pb. These compounds can react with certain sulphur-containing compounds, as well as with free sulphide, with evolution of tetra-alkyllead via a disproportionation process; Jarvie *et al.*[2] suggested that organic trialkyllead salts can be converted to sulphides, with subsequent decomposition to form R_4Pb (Eqn [1]). They found that no Et_3MePb was produced after addition of Et_3PbCl to sediment, indicating that no direct methylation was taking place. Thompson and Crerar[6] found that incubation with marine sediments resulted in quantitative methylation of added Me_3PbOAc, possibly by partial or complete disproportionation, but only a very small apparent conversion of inorganic lead occurred. When a sterilised sediment sample was spiked with Me_3PbOAc and sodium sulphide (Na_2S), methylation was quantitative after 24 h, indicating the importance of the sulphide ion in assisting the disproportionation reactions of Me_3Pb^+. It was concluded that methylation of inorganic lead(II) was highly inefficient due to difficulty in oxidation of Pb(II) to Pb(IV); it may however be possible under aerobic conditions via reaction with the carbonium ion, CH_3^+. Craig,[4] investigating the methylation of Me_3PbOAc, found that Me_4Pb was released from sterilised and active sediments in equal quantities that could be explained by chemical disproportionation reactions, while Schmidt and Huber[3] measured Me_4Pb in concentrations higher than could be explained by redistribution reactions, after addition of Me_3PbCl to an anaerobic sample. In this case, the amount of Me_4Pb evolved from a biologically active sediment was much higher than that produced by a sterile sample. Jarvie *et al.*[7] attempted biomethylation using sediments and spiking with inorganic lead and synthetic monoalkyllead compounds. Only limited evolution of Me_4Pb was detected and this was ascribed to disproportionation of organolead compounds already present in the sediment, or to contamination.

$$\begin{aligned} 2R_3PbX + H_2S &\rightarrow (R_3Pb)_2S + 2HX \\ &\rightarrow R_4Pb + R_2PbS \end{aligned} \qquad [1]$$

In the present study, results of some laboratory investigations of lead bioalkylation processes are presented and placed into perspective with a discussion including the results obtained from atmospheric measurements and studies of chemical transformations and deposition pathways of lead compounds.[8-11]

Biomethylation has been attempted in aqueous cultures containing different types of marine algae, incubated under both aerobic and anaerobic conditions, and in yeast suspensions enriched with the methyl donor, *S*-adenosyl methionine. Cultures of marine phytoplankton *Emiliania huxleyi, Amphidinium carterae, Gyrodinium auroleum* and *Thalassiora eccentrica* were prepared in sterilised seawater with and without addition of inorganic lead. The marine macroalgae *Chaetomorpha aerea* and *Fucus spiralis* were incubated in seawater with and without added lead and under both aerobic and anaerobic conditions.

EXPERIMENTAL

Marine phytoplankton

Cultures of the four marine algae were obtained from the Marine Biological Association, Citadel Hill, Plymouth, UK.

A suitable culture medium was prepared as follows: 1 kg of coarsely sieved garden soil was autoclaved for 60 min at 5 psig (pounds per square inch gauge; 34 kPa) with 2 dm^3 of tapwater. A sufficient quantity of extract (200 cm^3) was then filtered through a Whatman no. 41 filter paper and sterilised by autoclave for 35 min at 15 psig (103 kPa). After 41 dm^3 of seawater had been filtered (Whatman no. 41), it was reduced to 95% with distilled water to allow for evaporation, and sterilised for 35 min at 15 psig (103 kPa). A sodium salt solution containing 20 g sodium nitrate ($NaNO_3$) and 0.8 g disodium hydrogenphosphate (Na_2HPO_4) in 100 cm^3 distilled water was made up and sterilised as before.

Three culture flasks were prepared for each phytoplankton, each containing 250 cm^3 seawater, 12.5 cm^3 soil extract, 0.25 cm^3 sodium salt solution, and 5 cm^3 of the organism as received. A 0.25 cm^3 aliquot of lead nitrate ($Pb(NO_3)_2$) solution (1 mg cm^{-3}) was added to two flasks to give an added lead(II) concentration of approximately 1 mg dm^{-3}. The flasks were maintained at 18 °C in diffuse daylight. One flask containing added lead for each organism was arranged so that volatile alkyllead compounds could be collected, using a continuous headspace displacement by activated-charcoal filtered air onto 0.5 g of Porapak Q contained in a 9 cm length of stainless-steel tubing.

The Porapak tubes were pre-cleaned in a thermal desorber (GN Concentrator) oven for 30 min at 200 °C before use. A blank determination was performed using a flask containing pure Milli-Q water. The air flow rate was maintained at 10 cm^3 min^{-1} to avoid breakthrough of alkyllead from the Porapak over the sampling period.

Analysis for alkyllead presence was performed after a 10-day incubation, using three methods: (A) derivatisation using propylmagnesium chloride; (B) direct determination of volatile compounds using cryogenic trap preconcentration; and (C) analysis of the Porapak tubes. The methods are described below.

(A) Each solution (200 cm^3) was extracted for 30 min on a mechanical shaker, using 10 cm^3 of 0.5 mol dm^{-3} sodium diethyldithiocarbamate (NaDDTC), 10g sodium chloride (NaCl) and 5 cm^3 hexane. The recovered hexane (~3 cm^3) was dried over anhydrous sodium sulphate (Na_2SO_4) and propylated using 0.5 cm^3 of 2.0 mol dm^{-3} propylmagnesium chloride (PrMgCl). After gentle shaking for 10 min, 5 cm^3 of 0.5 mol dm^{-3} sulphuric acid (H_2SO_4) was added (to destroy excess Grignard), the organic layer was removed and dried (Na_2SO_4), concentrated to 0.5 cm^3 by nitrogen evaporation and analysed by gas chromatography–atomic absorption spectrometry (GC AA) (50μl injections).[12,13]

(B) Each solution (50 cm^3) was removed to a 100 cm^3 serum bottle, capped with a rubber/aluminium septum and plumbed into the GN Concentrator–GC AA system using hollow needles. Helium was passed through the solution at 100 cm^3 min^{-1} for 5 min to allow collection of any analytes on the GN Concentrator liquid nitrogen-cooled cryogenic trap which was subsequently flash-heated to 150°C, flushing analyte into the GC AA detection system.

(C) The Porapak tubes were analysed for volatile alkyllead using the two-stage GN Concentrator thermal desorber.[14]

Marine macrophyte algae

Samples of two types of marine algae, *Chaetomorpha aerea*, a green, short-filament, semi-transparent variety, and *Fucus spiralis*, a brown, tough, bladder-forming variety, were collected from breakwaters close to Walton Pier, Essex, UK. Two experiments were performed: (I) using independent sub-sample incubations and (II) using sub-samples drawn from mass-incubation vessels at various time intervals. The experiments were carried out as described below.

(A) 23 g (wet weight) of each alga was washed thoroughly in Milli-Q water and transferred to ten 500 cm^3 flasks. Seawater (500 cm^3, filtered, Whatman no. 41) was added. Inorganic lead in the form of lead acetate ($PbOAc_2$) was supplied to flasks 1–6 so as to raise the inorganic lead concentration by 1 mg dm^{-3}, and to flasks 7 and 8 to increase lead(II) by 10 mg dm^{-3}. Flasks 9 and 10 contained background levels of lead(II). The necks of the flasks were plugged with cottonwool.

Analysis was performed after 3, 10, 17 and 60 days, the total sample being divided into two portions: (i) 400 cm^3 of solution only (no alga) transferred into a fresh, clean bottle, and (ii) 100 cm^3 of solution plus the 23 g of alga, in the original flask. Extraction of (i) was performed using 20 g NaCl, 30 cm^3 0.5 mol dm^{-3} NaDDTC and 10 cm^3 hexane, and carried out for 30 min on a mechanical shaker. The amount of hexane recovered was typically 50% (5 cm^3), and this was routinely concentrated to ~0.5 cm^3 prior to derivatisation using PrMgCl. Extraction of (ii) was carried out after homogenisation of the total sample for 2 min in a commercial blender: 10 g NaCl, 60 cm^3 of 0.5 mol dm^{-3} NaDDTC and 30 cm^3 hexane were used, the extraction being continued for 40 min. Recovery of hexane was ~60% (18 cm^3). Concentration was effected by volume reduction to 5%. Aliquots (50μL) were transferred to the GC AA system.

(B) Two large glass vessels were each filled with 10 dm^3 of filtered seawater and 440 g of washed brown macrophyte algae. Aerobic incubation was initiated in one vessel using an activated-charcoal filtered air supply passing through the solution, while the other vessel was subjected to an anaerobic environment by flushing with nitrogen followed by sealing. Lead acetate was added to each container to give an increased inorganic lead concentration of 0.5 mg dm^{-3}.

Samples (500 cm^3) of liquid were drawn from each vessel at regular intervals, extracted using 10 cm^3 of 0.5 mol dm^{-3} NaDDTC, 12.5 g NaCl and 3 cm^3 hexane, and examined for the presence of alkyllead using the propylation technique.

Yeast cultures

Preparation of an *S*-adenosyl methionine (*S*-AM)-rich yeast culture was achieved using the method of Schlenk and Depalma.[15] A culture medium was made up using phosphate (8 g KH_2PO_4, 4 g K_2HPO_4), 8 g trisodium citrate, 4 g magnesium chloride ($MgCl_2.6H_2O$), 0.24 g manganese sulphate ($MnSO_4.H_2O$), 0.8 g calcium chloride ($CaCl_2.6H_2O$), 0.4 g zinc sulphate ($ZnSO_4.7H_2O$), 8 g ammonium sulphate ($(NH_4)_2SO_4$), 60 g glucose and 3 g DL-methionine [$CH_3SCH_2CH_2CH(NH_2)COOH$]. The solution was made up to 4 dm^3 in a beaker with Milli-Q water and 50 g yeast (*Saccaromyces cerevisiae*) added. The beaker was covered with parafilm to prevent aerial contamination and aerated using an air supply filtered through activated charcoal and a 0.45 μm membrane filter. An additional charge of 30 g glucose was added after 18 h and the yeast harvested after 48 h incubation at ambient temperature. Separation from the nutrient medium was achieved by centrifugation at 2000 rpm for 15 min in 1 dm^3 batches. The supernatant solution was analysed for the presence of *S*-AM using a spectrophotometer scanning the UV spectrum from 200 to 300 nm. The expected *S*-AM peak was observed at 260 nm, preceded by a higher peak at 234 nm, probably due to the decomposition product methylthioadenosine. The yeast was removed to a refrigerator for storage.

Sub-culture media were prepared in 500 cm^3 flasks using a total volume of 250 cm^3 and a similar proportion of mineral supplement as described above. 15 ml of yeast and 5 g glucose were used per flask. Duplicate incubations were performed using added quantities of lead nitrate to concentrations of 1 mg dm^{-3} and 10 mg dm^{-3} Pb. A blank incubation was performed without any additional lead(II). In order to rupture the yeast cells and release *S*-AM, 50% of the flasks were subjected in advance to ultrasonic irradiation for 30 min. Any methyllead detected from these pre-sonicated flasks would indicate methylation via *S*-AM from a non-metabolic pathway. Disruption of cells after the incubation period and subsequent detection of methyllead would indicate alkyllead release from the cells. Alkyllead released via normal metabolic pathways would be indicated should it be detected in the non-disrupted flasks.

After incubation the flasks were sonicated where necessary, the contents centrifuged, and the supernatant extracted into 10 cm^3 hexane using 12.5 g sodium chloride and 12 g NaDDTC, over 30 min in a mechanical shaker. The hexane extract was dried over anhydrous sodium sulphate, then derivatised by the normal method using butylmagnesium chloride. The final extract was concentrated using nitrogen evaporation and analysed by GC AA.

The experiment was repeated using an *S*-AM-enriched yeast supplied by Sigma Chemical Co., Poole, Dorset, U.K., with aerobic and anaerobic incubations and omitting any pre-sonication stages previously described. Aerobic conditions were ensured by passing activated-charcoal filtered air through the culture solution; anaerobic conditions were ensured by using nitrogen gas. The purge gas was passed through Porapak Q tubes after leaving the culture vessels, in order to retain any Me_4Pb that might be produced. A flow rate of 10 cm^3 min^{-1} was used.

The cultures were analysed after 14 days, using propylmagnesium chloride as the derivatisation agent, after the addition of 20 cm^3 of 2 mol dm^{-3} sodium hydroxide and 10 min ultrasonic cell disruption.

RESULTS

Quantities of methyllead produced by the phytoplankton cultures are given in Table 1. *Emiliania hux-*

Table 1 Production of methyllead from cultures of phytoplankton (expressed as ng dm^{-3} of culture solution)

Culture[a]	Method A Me_4Pb	Me_3Pb^+	Me_2Pb^{2+}	Method B Me_4Pb	Method C Me_4Pb
1 *Emiliana huxleyi*	—[b]	—	—	5.1	—
2 *Thalassiora eccentrica*	—	—	—	—	—
3 *Amphidinium carterae*	—	—	—	—	—
4 *Gyrodinium auroleum*	—	6.4	13.3	13.2	—

[a] Cultures 2 and 3 can be considered experimental blanks.

[b] — indicates below detection limit.

Table 2 Production of trimethyllead species from macrophyte cultures

	3-day				10-day				17-day				60-day	
	Brown		Green		Brown		Green		Brown		Green		Brown	Green
Added lead(II) (mg dm^{-3})	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(i)	(ii)	(iii)	(iii)
0	22.9	0.25	10.5	0.06	27.5	0.09	—	0.20	22.0	0.38	26.7	3.3	N/A	N/A
1	N/A	N/A	N/A	N/A	41.7	0.006	6.7	—	N/A	2.9	35.0	2.2	8.7	1.0
10	N/A	N/A	N/A	N/A	57.2	0.36	11.0	—	38.0	2.2	23.5	3.3	N/A	N/A

Analysis by method A (see text).

Results expressed (i) as ng dm^{-3} in aqueous solution; (ii) as ng g^{-1} in algal tissue; (iii) as total ng/flask. N/A, not available.

Table 3 Production of alkyllead from macrophyte cultures (experiment II) expressed as ng dm^{-3}

Incubation period (days)		Me_3Pb^+	Me_2Pb^{2+}	$R_nPb^{(4-n)+}$[a]	Et_2Pb^{2+}
0	*A*[b]	—	—	—	—
	B[b]	—	—	—	—
3	*A*	—	—	—	—
	B	—	—	—	—
6	*A*	3.28	—	4.45	—
	B	5.92	—	—	—
9	*A*	2.32	—	6.80	4.00
	B	2.79	—	—	—
12	*A*	2.85	—	4.78	2.64
	B	1.91	—	—	—
16	*A*	10.85	4.95	10.43	5.50
	B	3.56	—	—	—
19	*A*	8.45	—	13.18	6.70
	B	11.28	—	—	—

Analysis by method A (see text). Added inorganic lead concentration was 0.5 mg dm^{-3}. Analysis of fresh alga show no trace of accumulated alkyllead. — indicates below detection limit.

[a] A lead-containing species is seen in the analysis, possibly $MePb^{3+}$ but more likely an analytical artefact. [b] *A*, aerobic culture; *B*, anaerobic culture.

leyi and *Gyrodinium auroleum* cultures evolved Me_4Pb at trace levels while Me_3Pb^+ and Me_2Pb^{2+} were also detected in the *Gyrodinium auroleum* solution.

Results from the macrophyte cultures (experiment A) are shown in Table 2. Only Me_3Pb^+ is listed as this was the predominant species evolved. Concentrations are given (i) in aqueous solution and (ii) in the algal tissue. For the 60-day analysis, the figures given are the total quantities in the sample bottle (500 cm^3 solution + 23 g alga). Analysis of seawater before incubation showed no trace of alkyllead. The results of experiment B (Table 3) indicate the presence of Me_3Pb^+ in all cultures after six days of incubation. The presence of $MePb^{3+}$ may be postulated in all aerobic samples after six days, although this has not been confirmed. Et_2Pb^{2+} was released in aerobic samples after nine days, possibly due to release of previously accumulated alkyllead although this seems unlikely as no trace was detected in anaerobic samples. Analysis of fresh algae collected at the same location showed no trace of accumulated alkyllead.

Production of alkyllead from the yeast cultures was much lower than from the marine algae. Traces of Me_3Pb^+ were observed in extracts from one of the blank flasks and one of the 1 mg dm^{-3} lead sonicated flasks. These correspond to Me_3Pb^+ concentrations of <4 ng dm^{-3} in the original solutions. A larger Me_3Pb^+ peak was observed from the other 1 mg dm^{-3} sonicated flask, corresponding to ~ 40 mg dm^{-3} Me_3Pb^+. Of the commercial *S*-AM-rich yeast cultures, 50% yielded traces of Me_3Pb^+ under both aerobic and anaerobic conditions but only with additional added inorganic lead. No trace of alkyllead was found in either the blank solutions or from the Porapak tubes.

DISCUSSION

The chemical cycle of lead compounds in the environment may be described in a simplified form by Eqn [2]:

$$R_4Pb \rightleftharpoons R_3Pb^+ \rightleftharpoons R_2Pb^{2+} \rightleftharpoons (RPb^{3+})^* \rightleftharpoons Pb^{2+} \qquad [2]$$

where ( )* denotes an unstable species.

The decomposition of tetra-alkyllead compounds may occur homogeneously in the gas phase by photolysis or reaction with ozone (O_3), triplet atomic oxygen $O(^3P)$ or hydroxyl radical (OH). Heterogeneous reactions on the surface of atmospheric particles may also play a minor role. The tetra-alkyllead compounds Me_4Pb and Et_4Pb are fairly stable under dark conditions but degrade rapidly in the presence of sunlight and photochemical oxidants. Rate constants of 8.0×10^5 ppm^{-1} h^{-1} and 70.2×10^5 ppm^{-1} h^{-1} respectively have been calculated for reaction with OH.[8] Reaction rate constants for OH–trialkyllead of 2.2×10^5 ppm^{-1} h^{-1} (trimethyllead) and 8.1×10^5 ppm^{-1} h^{-1} (triethyllead) have also been determined.[16] These are substantially lower than the corresponding R_4Pb–OH rate constants, indicating the relatively long atmospheric lifetime of these species, which may be transported some considerable distance from anthropogenic sources. Half-lives ($T_{1/2}$) of 5–10 h (Me_4Pb) and 0.6–2 h (Et_4Pb) during summer months and 17–34 h (Me_4Pb) and 2–8 h (Et_4Pb) during winter have been estimated[8] while $T_{1/2}$ for the breakdown products Me_3Pb^+ and Et_3Pb^+ of ~5 and 1.5 days respectively have also been determined.[16,17] These calculations are based on an annual mean ambient hydroxyl concentration of 1×10^6 OH cm^{-3}, which may in reality be appreciably variable,[18] causing some uncertainty in these half-life estimates. Assumptions are also made that reaction with hydroxyl is the main mechanism of removal, contributions from direct photolysis, reaction with ozone and deposition processes being relatively unimportant.

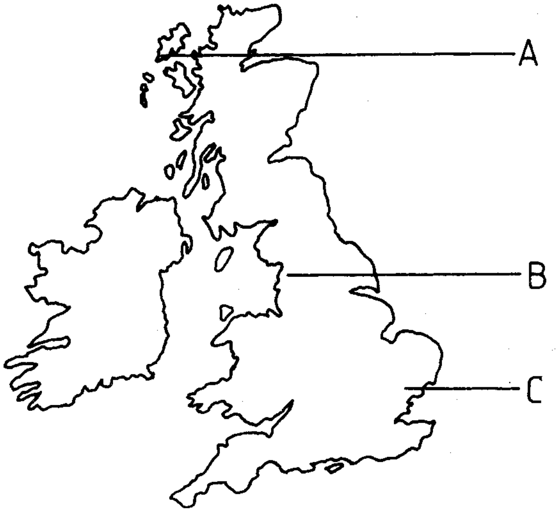

Figure 1 Map indicating sampling sites in the UK. A, Harris (Outer Hebrides); B, Lancaster; C, Colchester.

Harrison and Laxen[9] showed that the ratio of alkyllead to total lead in the atmosphere, in the absence of a local source, lies generally in the range 0.5–8.0%. It was also suggested that lifetimes of both inorganic lead aerosol and vapour-phase tetramethyllead were similar and of the order of several days, thus resulting in little expected change in the tetra-alkyllead/total lead ratio at remote rural sites distant from urban source areas. In practice, this was not found to be the case. A large number of air samples taken at rural sites were found to have unusually high ratios, up to a maximum of 33%, and an analysis of air mass trajectories revealed that these elevated ratios were associated with air that had passed over the open sea, and estuarine and coastal areas (see Fig. 1). Much lower ratios of ~2% were associated with air that had passed over urban areas to the south and south-east of the sampling sites, consistent with either negligible loss of any lead species, or similar rates of decomposition/deposition of alkyllead and rainout/washout/dry deposition of inorganic lead aerosol.

Hewitt and Harrison[10] further investigated the atmospheric chemistry of alkyllead compounds, and confirmed the presence of vapour-phase trialkyllead in the rural atmosphere. This is considerably more stable than tetra-alkyllead (R_4Pb) and may provide an additional explanation for elevated alkyllead/total lead ratios, which were found to be similar to those in the earlier study, with ratios of up to 43% for maritime air masses sampled in the Outer Hebrides (Fig. 1). Over one 24 h period, a change in wind direction from north-east to south resulted in an abrupt change in alkyllead/total lead ratios, from 9–43% to 4–6%, as anthropogenically-polluted air reached the sampling sites. On another occasion a change in wind direction from northerly to southerly resulted in a decrease in ratios from 17–50% to 5–17%. During easterly air flows (air from continental Europe), total alkyllead/total lead was ~3%, and R_4Pb/total Pb <1%, the former values being similar to those expected in urban air and emphasising the importance of vapour-phase ionic alkyllead species. If particulate lead aerosol is removed more rapidly by deposition processes during transportation, enhanced alkyllead/total lead ratios will arise. However, as less precipitation generally falls over sea than land, this may not provide an adequate explanation of the observed phenomena, as continental air masses may also experience substantial ageing.

Hewitt and Harrison[10] investigated the release of alkyllead from sediments incubated in the laboratory, and found that this occurred in approximately half of the samples, albeit with wide variability. Sterilization by autoclave followed by further incubation under sterile conditions resulted in cessation of alkyllead evolution. Typically, Me_4Pb alone was produced, although Et_4Pb was evolved for a brief period only in a few cases, probably due to traces present in the sediment initially, from pollution sources. When inorganic ^{210}Pb nitrate was added to the sediments, ^{210}Pb-labelled alkyllead was evolved after a 14-day initial period. The conversion efficiency for the process (activity of ^{210}Pb-labelled alkyllead emitted in 14 days/total ^{210}Pb activity in the sediment) was in the range of $(0.9-2.6) \times 10^{-7}$, a figure slightly higher than that calculated from the ratio of the mass of alkyllead evolved to total mass of lead in the sediment, indicating that added lead may be more readily available for conversion than that already complexed or adsorbed in the sediment. The observed R_4Pb release rates were found, when translated into a box model calculation, to be sufficient to account for concentrations of alkyllead measured in maritime air masses.

All species of alkyllead may be subject to deposition via washout and rainout processes, or to reaction with aerosol particles. Allen *et al.*[11] measured R_4Pb, R_3Pb^+ and R_2Pb^{2+} simultaneously in vapour and aerosol phases and in bulk deposition, at urban and semirural sites in south-east England (Colchester) (Fig. 1). Me_4Pb was found to be the predominant gas-phase species (0.7–10.9 ng Pb m^{-3} at the urban site; <0.14–11.0 ng Pb m^{-3} at the semirural site), while Me_3Pb^+ was also present at high concentrations (0.11–19.8 ng Pb m^{-3} urban; 0.11–2.1 ng Pb m^{-3} semirural). Ionic alkyllead compounds were also commonly found in aerosol samples although this only represented a minor fraction of total atmospheric organic lead. The high relative proportion of vapour-phase R_4Pb to gaseous R_3Pb^+ indicates the proximity of emission sources of alkyllead compounds in this region of the UK. The ratio of alkyl/inorganic lead was found to be in the range 1.3–26.9% at the urban site, and 0.6–20% at the semirural site.

Washout factors (i.e. ratio of concentration in rainwater (mg kg^{-1}) to concentration in air (mg kg^{-1})) for alkyllead and lead(II) were calculated to be in the range 8–79 and 93–633 respectively at the urban site and 30–104 and 24–1141 at the semirural site, implying a relative enrichment of alkyllead in an ageing air mass, as the alkyllead is less efficiently scavenged. It is likely, however, that washout ratios for alkyllead will increase as the air mass ages, assuming no further anthropogenic input, as tetra-alkyllead is converted to the more soluble trialkyl form. It may not, therefore, be feasible to utilise the data obtained in this study for the interpretation of measurements made elsewhere at a more remote site with entirely different meteorological characteristics. If a lower washout of alkyllead relative to inorganic lead(II) could be confirmed at a wider range of locations, an explanation could be presented for the increased alkyllead/total lead ratio in marine air masses.

Similar overall removal rates for organic and inorganic lead would indicate the need for an environmental source process to explain enhanced ratios. The experimental work reported in this paper indicates that marine algal flora may well provide this source, as significant releases of alkyllead have been measured under a variety of conditions. Although the evolution of Me_4Pb from the cultures has not been measured quantitatively, this may be explained by recent work which has revealed considerable difficulty in recovery, by headspace flushing techniques, of tetra-alkyllead added to this type of medium (<15%).[19] Given the appreciable rates of alkyllead breakdown reactions in water,[17] the observation of an apparent persistence, and indeed accumulation (Table 3), of alkyllead in these experiments is strongly indicative of continued alkyllead production over several weeks.

It is instructive to re-examine the data presented by Hewitt and Harrison,[10] who measured alkyllead and lead(II) aerosol in both easterly and westerly air masses at two rural sites in north-west England and at a remote site on the island of Harris in the Outer Hebrides. Mean total alkyllead concentrations at the rural sites were similar for both air mass trajectories (2.4 and 3.3 ng m^{-3} easterly, 2.9 and 2.8 ng m^{-3} westerly), while lead aerosol was present in much lower concentration in westerly air (mean 115 and 101 ng m^{-3} easterly, 56 and 24 ng m^{-3} westerly). Air reaching the Harris site was not expected to have received any recent anthropogenic injections of lead compounds, yet mean concentrations of total alkyllead were found to be 3.2 and 7.3 ng m^{-3} during two separate sampling periods. Corresponding lead aerosol concentrations were 16.4 and 16.5 ng m^{-3}. Thus alkyllead concentrations were higher and lead aerosol concentrations lower, at the remote island site as compared with both rural sites. This provides excellent evidence for the presence of a maritime source of volatile alkyllead, as Atlantic air masses reaching Harris will not have traversed any land surfaces, while similar air masses will cross either Ireland or south-west Scotland before reaching the rural north-west sites. Thus a dilution effect will reduce alkyllead concentrations in air reaching these sites from distant sources. Further evidence for this postulate is provided by mean total alkyllead concentrations measured on Harris, which were ~10 ng m^{-3} for northerly and westerly air masses, and ~5 ng m^{-3} for southerly and easterly air, while inorganic lead aerosol concentrations were higher in the latter case, giving total alkyllead/total lead ratios of ~30% and ~10% respectively. Tetra-alkyllead represented a small fraction of total vapour-phase alkyllead (<5%), and was undetected in many samples. As R_4Pb provided <25% of total vapour-phase alkyllead at the north-west England sites, and was the predominant species in the south-east England (Colchester) measurements, a pattern emerges whereby the R_4Pb/total alkyllead ratio decreases markedly with increasing distance from anthropogenic sources. (An unknown influence is the marked reduction in the alkyllead content of petrol marketed in the UK, from 0.4 to 0.15 g dm^{-3}, which occurred shortly prior to the Colchester measurements. This will clearly have influenced total atmospheric alkyllead concentrations, but is not expected to affect the ratio of R_4Pb/total alkyllead emitted by motor vehicles.)It is not unlikely that a maritime source of tetra-alkyllead will result in relatively high atmospheric vapour-phase trialkyllead concentrations, given the rapid decomposition of R_4Pb suggested earlier.

In the context of differential removal processes it is instructive to examine the case of atmospheric sulphur chemistry. Sulphur dioxide (SO_2) is analogous to trialkyllead in being a water-soluble gas with an atmospheric oxidation rate (by OH in dry air) of around 1% h^{-1}; the five-day half-life of trimethyllead corresponds to a 0.6% h^{-1} breakdown rate. Sulphur dioxide oxidation forms sulphate (SO_4^{2-}) as a fine aerosol directly analogous to inorganic lead aerosol.

Table 4 Calculated values of gas-phase alkyllead/total lead (%)

	Travel time (days)	Lead(II) lifetime, τ (days) 0.1	0.5	1	5	10	20	30
A	0	3.4	3.4	3.4	3.4	3.4	3.4	3.4
	1	99.7	11.5	4.6	2.1	1.9	1.8	1.8
	2	100	32.5	6.1	1.3	1.1	1.0	0.9
	5	100	96.0	14.2	0.3	0.2	0.1	0.1
	10	100	100	42.0	0	0	0	0
	20	100	100	94.3	0	0	0	0
B	0	3.4	3.4	3.4	3.4	3.4	3.4	3.4
	1	99.9	18.5	7.6	3.6	3.3	3.1	3.1
	2	100	59.3	16.5	3.8	3.2	2.9	2.8
	5	100	99.5	27.7	4.5	2.8	2.2	2.0
	10	100	100	99.5	6.1	2.3	1.4	1.2
	20	100	100	100	10.6	1.6	0.6	0.4
C	0	3.4	3.4	3.4	3.4	3.4	3.4	3.4
	1	99.9	19.6	8.2	3.9	3.5	3.3	3.3
	2	100	62.5	18.4	4.4	3.6	3.3	3.2
	5	100	99.8	78.7	6.3	3.9	3.1	2.8
	10	100	100	99.7	11.5	4.6	2.8	2.4
	20	100	100	100	31.9	6.1	2.3	1.7

A: $\tau_{1/2}$ (alkyllead) = 1 day (λ = 0.693).
B: $\tau_{1/2}$ (alkyllead) = 5 days (λ = 0.139).
C: $\tau_{1/2}$ (alkyllead) = 10 days (λ = 0.069).

For basis of calculation see Eqn [3] (text).

Transport of sulphur dioxide emissions from the UK across the North Sea to Scandinavia is observed to be associated with appreciable loss of sulphur dioxide by wet and dry deposition and oxidation, and receipt of sulphur in Scandinavia primarily as the longer-lived sulphate aerosol. This analogy suggests that inorganic lead aerosol will be the longer-lived atmospheric species and thus in the absence of an environmental source of alkyllead, the ratio of alkyllead to inorganic lead should decrease, rather than increase with transport time.

Theoretical calculations of the ratio total vapour-phase alkyllead/total lead were made (Table 4) utilising lifetimes (τ) for inorganic lead of from 0.1 to 30 days, half-lives ($\tau_{1/2}$) for vapour-phase alkyllead of 1, 5 and 10 days, and travel time from the emission source of up to 20 days. In this context, lifetime, τ, is defined by

$$\tau = A/F$$

where A = atmospheric burden of species (kg), and F = flux of species to and from atmosphere at steady state (kg s^{-1}). Half-lives are the conventionally defined period for removal of 50% of the reactant. Concentrations of the two species were then calculated using the relationship

$$C = C_0 e^{-\lambda t} \qquad [3]$$

(i.e. first-order kinetics), where C is concentration at time t, C_0 is initial concentration and λ is the first-order decay constant (= $1/\tau$).

For [lead(II)], $\lambda = 1/\tau$

for [total alkyllead], $\lambda = \dfrac{\ln 2}{\tau_{1/2}}$

Initial concentrations of 3 ng m^{-3} Pb (total alkyllead) and 85 ng m^{-3} (inorganic lead) were selected. These are median values measured at the Essex University site, and are representative of typical semirural air in this region.

The calculated data indicate that given an inorganic lead lifetime of five days or more, the ratio remains low unless a high $\tau_{1/2}$ for total alkyllead (10 days) is combined with considerable distance from source (20 days). This situation is unlikely. If, however, $\tau(Pb^{2+})$ is reduced to one day or less, elevated ratios are observed at travel times of only two days ($\tau_{1/2}$ [total alkyllead] = 5–10 days) for five days ($\tau_{1/2}$ [total alkyllead] = 1 day). Further reductions in assumed inorganic lead lifetime, in combination with extended distance from emission sources, cause extremely high ratios which clearly have minimal applicability to the natural environment. Given $\tau_{1/2}$ for [total alkyllead] of between five and ten days, relatively little change in ratio is seen at inorganic lead lifetimes over five days and at most transport intervals.

It appears from these calculations that elevated ratios would not be expected from calculations made using measured atmospheric lifetimes for the different species, unless these lifetimes are radically altered by, for example, unusual meteorological conditions. The previously estimated value for $\tau_{1/2}$ of Me_3Pb^+ of five days may be an overestimation as this relates to removal by homogeneous reactions only, and takes no account of washout, rainout and dry deposition processes. The lifetime of inorganic lead in marine air is not well quantified and is expected to be rather variable. If a value of 1–3 days is taken,[10] it is just possible that elevated ratios of alkyllead/total lead in maritime air may be explained by differential lifetimes of these species alone. This does not, however, explain the high absolute magnitude of alkyllead concentrations at the island site of Harris, which appear to be explicable only in terms of a maritime source of alkyllead.

CONCLUSION

Alkyllead species have been detected in media containing several types of living flora. It has, however, been difficult to confirm any progressive accumulation of these compounds, while chemical decomposition probably causes continual losses. It is also difficult to ascribe biomethylation specifically to either the yeast organism or the macrophytes unequivocally as these were not cultured under aseptic conditions and were thus subject to possible bacterial interferences. (The phytoplankton cultures were handled using sterile techniques.)

Clearly there is good additional evidence here for the environmental alkylation of lead, whether this be by chemical and/or biological pathways. The earlier work suggesting alkylation processes as a possible explanation for elevated organic/total lead ratios in clean maritime air masses should not be dismissed on the basis of prolonged vapour-phase trialkyllead lifetimes only. Indeed it is probable that both environmental alkylation and differential lifetimes are responsible for this observed phenomenon.

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