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Methylation of inorganic lead by Tamar Estuary (UK) sediments

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Tetramethyllead (TML) has been produced from inorganic lead salts using biologically active sediments and waters from the Tamar Estuary, S.W. England. The TML production was a two-stage process involving an initial lag phase of about 100 hours followed by the exponential appearance of TML, which amounted to about 0.03% of total added lead. The methylation process is discussed in the context of lead transport in estuaries

Keywords: Lead methylation, inorganic lead, estuarine sediments, coupled gas chromatography–atomic absorption spectrophotometry (GC AA)

INTRODUCTION

The major organolead molecules present in the environment are the tetraalkyllead (TAL) compounds and their di- and tri-alkyl decomposition products.[1] Elevated levels of TAL compounds have two possible sources, either (i) anthropogenic petroleum inputs and/or (ii) environmental methylation of natural lead compounds. While the former is well established, the latter is the subject of some controversy in the literature. Several papers report the production of TML from trimethyllead acetate under environmental conditions.[2–5] Claims have been made that the methylation of this compound is biologically mediated. However, Craig[4] has concluded that it is not necessary to invoke biological mechanisms for the production of TML from trimethyllead acetate, since chemical disproportionation and/or dismutation could be equally important.

Apart from studies on trimethyllead acetate there are relatively few studies of the environmental methylation of inorganic lead salts,[3,5,6] possibly because of the analytical difficulties of the detection of small amounts of TML. In an interesting experiment, Hewitt[8] overcame the analytical problem by using radioactive lead (^{210}Pb) but he found that the production of TML depended on the source of the intertidal sediments. Thus there is a need to confirm the existence of the methylation of inorganic lead compounds in estuaries, which receive a significant pollutant lead input.

In this work, incubation experiments and abiotic controls were carried out on sediments from the Tamar Estuary, S.W. England. Sediments from this estuary are biologically active and have been shown to convert a maximum of 8% inorganic arsenic to dimethylarsenic species.[9] There is clearly the potential in these sediments for methylation and the analytical constraints for organolead compounds have been overcome through the development of a sensitive analytical technique.[10,11]

EXPERIMENTAL

Modelling procedure

The sediments were collected from the low-salinity region of the Tamar Estuary, along with freshwater which was filtered (passing 0.45 μm membrane filters) prior to use. The bulk chemical properties of the sediments were determined by established methods,[12] which gave total particulate lead (by HF digest) of 158 $\mu g\,g^{-1}$, acetic acid available lead of 33 $\mu g\,g^{-1}$ and a carbon content of 4.8%. The porewaters surrounding these sediments had a sulphide content of 0.26 $mg\,g^{-1}$, a dissolved inorganic lead concentration of 18 $\mu g\,dm^{-3}$ and no dissolved TML was detected. The sediments were examined by optical microscopy which showed the presence of the microorganisms *Genus bacillus* and *Pseudomonas*.

Suspensions were prepared in 150 cm^3 flasks containing 10 g of sediment, 50 cm^3 of filtered freshwater, and a nutrient mix (0.5% Nutrient Broth I; 0.1% D-glucose; 0.1% yeast extract).

Inorganic lead salts were added to give a concentration of 10 mg Pb dm^{-3} and the flasks were sealed. The suspensions were then incubated at 30°C with a light flux, in the spectral range 400–700 nm, of 3×10^{15} quanta cm^{-2} s^{-1}, for up to 500 h. Evolved head-space gases were analysed at various intervals by withdrawing 1 cm^3 of gas from the flasks using a gastight syringe. All the experiments were carried out in duplicate.

Sterile estuarine waters, sediments, nutrients and lead spikes were prepared by undertaking three separate autoclaving exposures each of 30 min duration. The sterility of the materials was tested using streaks on nutrient agar and soil extract agar samples.[4]

Analytical method

The evolved head-space gases were analysed using a sensitive coupled gas chromatography–atomic absorption spectrophotometric system (GC AA) which has been described in detail elsewhere.[10,11] The TML detection limit was 14 pg with a relative standard deviation of 1.3% at the 500 pg level. The total and available lead levels were determined by graphite furnace atomic absorption spectrometry, the sulphide content by an ion-selective electrode and the carbon by the measurement of loss on ignition.[11,12]

Results and discussion

In the sterile controls carried out using the reagents and added lead, no detectable levels of TML were observed following full incubation runs in duplicate. However, in the biologically active sediment systems, TML was produced from $Pb(NO_3)_2$, $PbCl_2$ and $Pb(OAc)_2$, as shown in Fig. 1. The results showed that the production of TML in each case followed an initial delay period lasting 80–150 h. The production of TML reached a maximum after a period of 300–400 h and the yield of TML was 0.005% for $Pb(OAc)_2$, 0.026% for $Pb(NO_3)_2$ and 0.028% for $PbCl_2$. The yield for $Pb(NO_3)_2$ is in good agreement with the value of 0.026% obtained by Thompson and Crerar[7] for marine sediments incubated at 15°C with 5 mg $Pb(NO_3)_2$ dm^{-3} for 600 h. In addition, the fact that $Pb(OAc)_2$ is such a poor methylation substrate suggests that any possibility of lead methylation being due to the

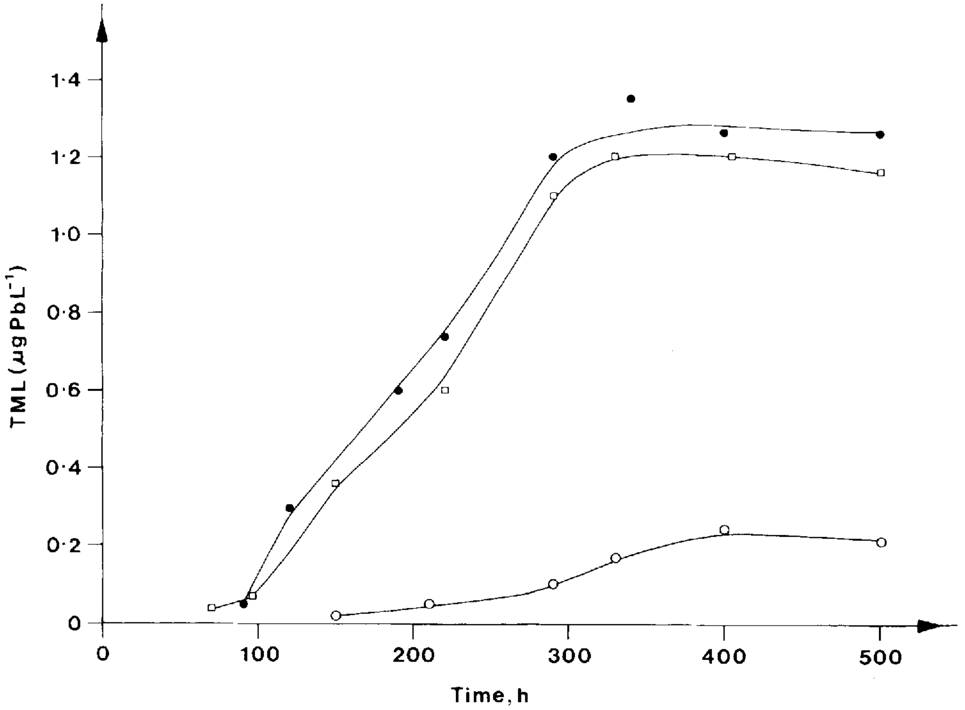

Figure 1 The time-dependent appearance of TML (μg Pb dm^{-3}) in sediments from three inorganic lead sources: ●, $Pb(NO_3)_2$; □, $PbCl_2$; ○, $Pb(OAc)_2$.

methyl group originating from an acetate moiety (as may occur in mercury methylation[1]) is not occurring for $PbCl_2$ and $Pb(NO_3)_2$.

The conversions observed here are 100-fold less than those observed for equivalent $(CH_3)_3PbOAc$ systems with Tamar sediments.[11] The smaller yields of TML from lead(II) salts compared with lead(IV) is thought to be due to two mechanistic factors. Firstly, the oxidation of lead(II) to lead(IV) is thermodynamically difficult. It is thought that the reaction can occur by an oxidative addition of carbocation (CH_3^+)[6,13] followed by dismutation of transient $(CH_3)Pb^{3+}$ to form partially and possibly full methylated species. Secondly, if sulphide is present in the system, then inorganic lead will produce lead sulphide (PbS) which will be unreactive. The implication of the results is that there is a two-stage reaction where the first stage is the slow formation of the $(CH_3)Pb^{3+}$ intermediate followed by a more rapid methylation, through dismutation. In fact, much of the TML formation from $(CH_3)_3PbOAc$ could arise from dismutation of that species.

The sediment used in the above experiments was collected in October (water temperature 14°C). Also, a second series of sediment samples was collected to study the effect of temperature; these were collected in March (water temperature 6°C). No detectable levels of TML were produced from these later sediments. This strongly suggests that different microorganisms were present in these later, essentially winter, sediments, compared with the summer sediments studied above. Clearly such variations may, in part, account for the variety of results obtained by different workers.

The time-dependent appearance of TML in the summer sediments is exponential (see Fig. 1) and it can be interpreted in terms of an overall first-order reaction. The first-order plots are shown in Fig. 2 for the $Pb(NO_3)_2$ and $PbCl_2$ results. The rate constants are $3 \times 10^{-3} h^{-1}$ for $Pb(NO_3)_2$ and $3.7 \times 10^{-3} h^{-1}$ for $PbCl_2$. The half-lives for the production of TML are in the range 190–220 h, following the delay period of about 100 h. The significance of these timescales is that they greatly exceed the residence times of freshwater in estuaries but they are short compared with sediment residence times, which for the Tamar is about 1.4 years.[14] Thus, if inorganic lead is injected into the very low-salinity region of estuaries (as a consequence, for example, of acid mine drainage), then that proportion of the metal adsorbed on to particles and committed to the sediments could undergo methylation. The fact

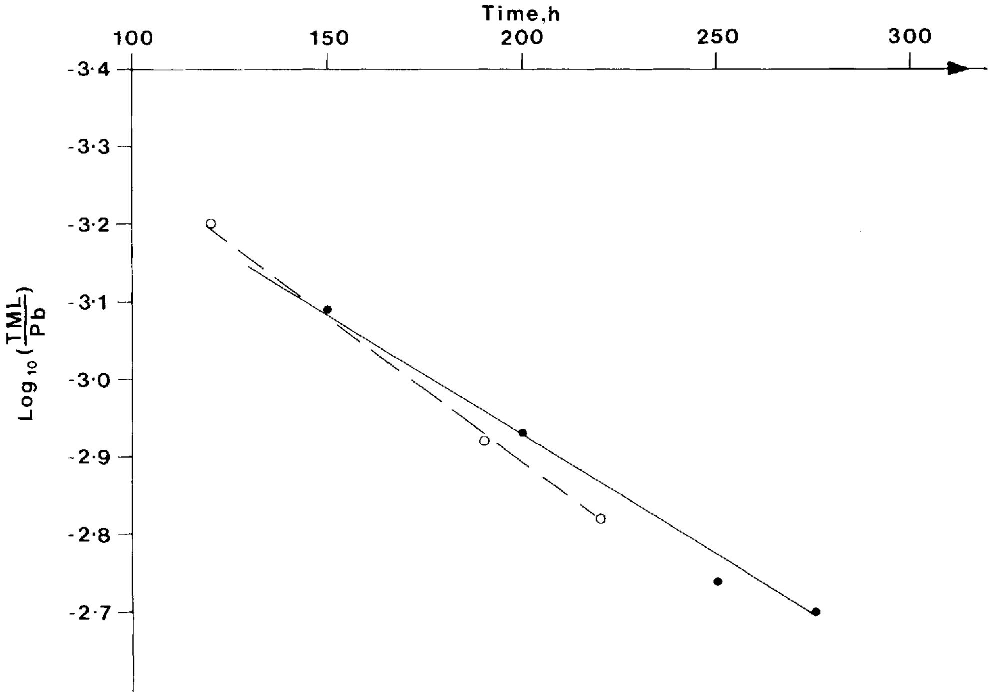

Figure 2 First-order plots for the appearance of TML from sediments containing: ●, $Pb(NO_3)_2$; ○, $PbCl_2$.

that TML has not been observed in Tamar waters, despite extensive surveys,[11] points to the fact that it has a short lifetime, being inherently unstable and volatile.

While the yields of TML from estuarine sediments are low, even under favourable conditions, they may represent an important transport mechanism for lead in the estuarine environment. This is because of the volatility of TML.[15-17] Lead converted to TML may be rapidly volatilized to the atmosphere in the summer months and, while photolytic decomposition may also be rapid,[15,18] the aerosol of lead species may be transported some distance from the source.

This work also illustrates the value of a highly sensitive and selective GC AA system which has allowed the study of lead methylation in sediments amended with only trace levels of inorganic lead. The use of head-space gas sampling has the advantage of minimal disturbance of the model system or the lead speciation. Such non-intrusive sampling is recommended for any similar studies.

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