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Emission to air of volatile organotins from tributyltin contaminated harbour sediments

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An analytical method for determining the presence in air of volatile forms (e.g. chlorides) of tributyltin (TBT) and that of methylbutyltins $Me_nBu_{(4-n)}Sn$ ($n = 1$–3) was developed and used to establish whether dredged harbour sediments contaminated with TBT served as sources of air pollution with respect to organotin compounds. The method was based on active sampling of the air being analysed and sorption of analytes onto Poropak-N. Sorbed methylbutyltins were extracted with dichloromethane and analysed by gas chromatography using flame photometric detection. Other butyltins were converted into butyltin hydrides prior to analysis by gas chromatography. It was shown that TBT-contaminated sediments from Marsamxett Harbour, Malta, placed in 0.5 l chambers through which air was displaced by continuous pumping for 11 days released mainly methylbutyltins, with concentrations (as tin) reaching maximum 48 h mean values of 8.7 (Me_3BuSn), 22.1 (Me_2Bu_2Sn) and 93.0 ng m^{-3}($MeBu_3Sn$) being measured. Other volatile forms of TBT, dibutyltin and monobutyltin were detected in the headspace air, but very infrequently and at much lower tin concentrations (<2 ng m^{-3}). It was also shown that methylbutyltins dissolved in sea-water ([Sn] = 0.2 to 400 ng l^{-1}) were very difficult to exsolve from this medium, even on prolonged evaporation of the solutions using mechanical agitation and active ventilation. The results suggest that emission of methylbutyltins from contaminated sediments probably occurs only from the surface of the material. The environmental implications of these findings in the management of TBT-polluted harbour sediments are discussed. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: butyltin; volatile; analysis; sediments

INTRODUCTION

The impact of tributyltin (TBT) on the marine environment has been extensively studied in view of the widespread use of TBT compounds as biocides in antifouling marine paints and also in view of the pronounced ecotoxicity of TBT. On the other hand, butyltin compounds are assumed to be absent from the atmosphere because of their low volatility, and few investigations on their atmospheric abundance have been attempted.[1–5] Since organotins such as triphenyltin chloride are also used as wood preservatives (acaricides), timber houses could represent potential sources of airborne organotin pollution, especially for indoor air. To our knowledge the only published work on the occurrence of organotins in ambient outside air was that reported by Kuballa *et al.*[4] who failed, however, to detect any such compounds in the atmosphere.

It is known that TBT degrades in the marine environment by sequential dealkylation to produce dibutyltin (DBT), monobutyltin (MBT) and eventually 'inorganic tin(IV)', formally Sn^{4+}, which is non-toxic. Recent reports from our laboratory,[6,7] however, suggest that in addition to these compounds there are other organotins that form from TBT: these are fully alkylated methylbutyltins having compositions $MeBu_3Sn$, Me_2Bu_2Sn and Me_3BuSn (Me: methyl; Bu: butyl). These compounds, rarely mentioned in the literature,[8] are very probably produced by environmental methylation of TBT, DBT and MBT respectively. The *in vitro* conversion of TBT into $MeBu_3Sn$ in a harbour sediment is the subject of another study in our laboratory, and preliminary results have indeed shown this conversion to be possible.[9]

Tetraorganotins, unlike polar ionizable TBTX compounds (X: halogen, carboxylate, etc.), consist of neutral, non-ionizable molecules and are thus expected to be more

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volatile and to adsorb less strongly to mineral matter in sediments, although such compounds would still bind firmly to any sedimentary organic matter. It is thus possible that dredging operations of organotin-contaminated sediments could cause these compounds to mobilize into the atmosphere once the sediments are beached and exposed to open air. Indeed, the presence in Maltese harbour sediments[6] of, for example, Me_3BuSn at concentrations (as tin) in the range 0.01 to 9 μg g^{-1} suggests that such sediments could present a significant source of airborne toxic organotins, both as vapours and in aerosol forms. This paper presents and discusses results of experiments on the mobilization to the atmosphere of organotin compounds present in harbour sediments contaminated with TBT; it also describes tests on the tendency to evaporation of methylbutyltins in sea-water, since this has an effect on the evaporation efficiency of these compounds from wet sediments.

MATERIALS AND METHODS

The validation of the analytical method is discussed in detail by Vassallo,[10] and only a brief summary of the method is presented here. Methylbutyltins present in air were adsorbed onto Poropak-N (Waters Corp.) and back-extracted into dichloromethane (25 ml) containing 0.3% HCl, which solution, after concentration by nitrogen blow-down to 5 ml and spiking with tetrabutyltin as internal standard, was analysed by gas chromatography with flame photometric detection (GC-FPD). A Perkin Elmer Model 8000 gas chromatograph fitted with a 30 m long non-polar BP1 column (SGE) was employed. The detector, kept at 300 °C, was equipped with a 610 nm optical filter and the analyte solution (1 to 3 μl) was injected splitless through a Grob injector maintained at 210 °C. The temperature programme was as follows: 65 °C for 4 min then to 260 °C at 30 °C min^{-1}, with an isothermal hold for a further 4 min. The limit of detection in air for methylbutyltins, based on analysis of a 4 m^3 air sample, was 0.25 ng m^{-3}. It was established that, for amounts of analytes ranging between 1 and 100 ng (as tin), the recovery efficiency for methylbutyltins is >90%. Sorbent extracts were also analysed for the presence of any other volatile forms (e.g. chlorides) of TBT, DBT and MBT using the method of Swami and Narang,[5] which involves conversion of the sorbed butyltins into volatile butyl hydrides by ethanolic $NaBH_4$ prior to analysis by GC-FPD. It was found that the presence of humidity in the air sample did not affect the sorption efficiency of the sorbent for organotins. Also, charged cartridges were found not to lose analytes to a significant degree if stored at 10 °C for 14 days. Authentic methylbutyltins for use as standards were synthesized by the method of Maguire and Huneault.[11] Compound identities for the field samples were confirmed by GC–mass spectrometry (MS) (Shimadzu GC-17, QP5050).

Six harbour sediment samples, of mainly calcitic composition, silty texture and dark grey in colour, were collected in the autumn of 1997 from each of two yacht marinas in Marsamxett Harbour, Malta, namely Lazzaretto Creek and Msida Creek, using a grab sampler. Several sediments from these two areas were analysed previously in our laboratory and found[6] to contain an average TBT content (as tin) of 0.26 μg g^{-1} ($N = 3$, Lazzaretto; $N = 9$, Msida); individual TBT contents varied from 0.03 to 1.5 μg g^{-1}, and there was no statistically significant difference in TBT levels between sediments taken from the two creeks.

Wet sediment (175 g) from the top 3 cm layer was placed in each of 12 experimental 'chambers' made from 0.5 l polyethylene wash bottles; a 13th chamber not containing sediment constituted the blank. The sediment mass had a surface area of 90 cm^2 and was 1.5 cm thick. Air was blown over the top surface of the sediments in the chambers by an oil-free vacuum pump at a rate of 72 l h^{-1}, entering the chamber through a plug of activated charcoal and exiting from a cartridge of Poropak-N consisting of two columns of sorbent (150 and 50 mg, separated by 0.5 cm in a Pasteur pipette, the smaller back column to protect against analyte breakthrough). The sorbent cartridge was changed once every 2 days for a total period of 11 days and the cartridge contents analysed for both butyltins and methylbutyltins. Some of the extracts were also analysed qualitatively by GC with flame ionization detection (FID).

A separate set of experiments was designed to establish the evaporation efficiency of methylbutyltins from solution in sea-water under different physical conditions. Air was passed for 24 h at different rates (0.14 or 2.2 l min^{-1}) through a 25 ml Quickfit two-necked flask containing reconstituted sea-water (10 ml) spiked with methylbutyltin concentrations (as tin) ranging from 0.2 to 400 ng l^{-1} using four different arrangements: (a) bubbling air in the flask using a Pasteur pipette dipped into the solution; (b) same as (a) but with the pipette tip kept 3 mm above the solution surface to cause a rippling effect; (c) passing air through the flask without the pipette and stirring the solution with a magnetic follower; (d) same as in (c) but with the magnetic stirrer switched off. In each case, the air issuing from the flask was passed through Poropak-N and analysed for organotins as described earlier. In some cases, the water volume was reduced to about 2 ml at the end of the experiment.

RESULTS AND DISCUSSION

In the sediment evaporation experiments, the wet sediment samples showed signs of drying out during the first few hours, and all samples appeared dry on day 5. All air samples from the chambers, including the blank control, initially contained a naphthalene peak (identified by GC–MS), which had disappeared or decreased considerably in most cases by day 11. This peak did not interfere with the analysis of the organotins, since it had a very different retention time. The results of qualitative GC-FID analysis of the sorbed material from pumped headspace air showed that

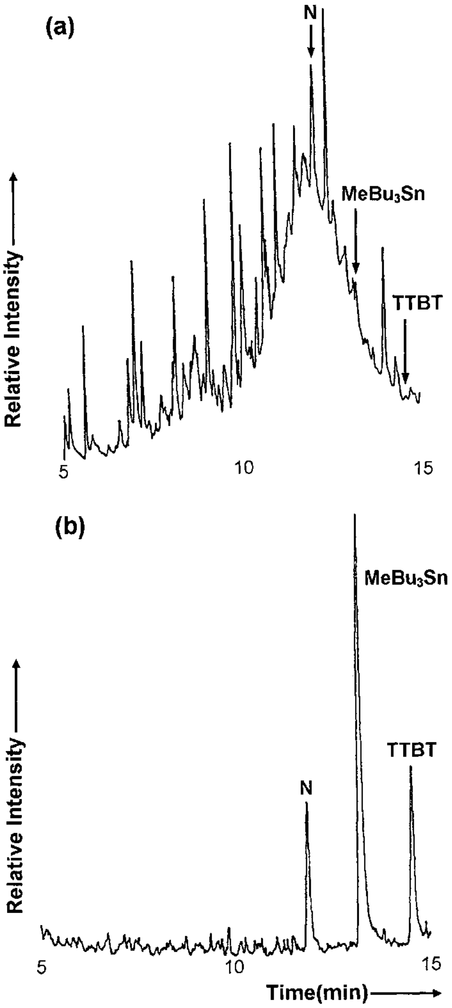

Figure 1. Gas chromatograms obtained from the same extract derived from pumped headspace air above Msida Creek sediment (day 11 of experiment) using (a) FID and (b) FPD. Peak labelled N is due to naphthalene (see text).

Table 1. Mass spectral data generated by low-resolution GC-MS showing main fragments for methylbutyltins and butyltin hydrides

Compound	Base peak	Other fragment ions
$\mathrm{Me_3BuSn}$	161–165: $[\mathrm{Me_3Sn}]^{+\cdot}$	203–211: $[\mathrm{Me_2BuSn}]^{+\cdot}$
		146–154: $[\mathrm{Me_2Sn}]^{+\cdot}$
		131–139: $[\mathrm{MeSn}]^{+\cdot}$
		116–124: $[\mathrm{Sn}]^{+\cdot}$
$\mathrm{Me_2Bu_2Sn}$	147–155: $[\mathrm{Me_2Sn}]^{+\cdot}$	245–253: $[\mathrm{MeBu_2Sn}]^{+\cdot}$
		203–211: $[\mathrm{Me_2BuSn}]^{+\cdot}$
		188–196: $[\mathrm{MeBuSn}]^{+\cdot}$
		173–181: $[\mathrm{BuSn}]^{+\cdot}$
		131–139: $[\mathrm{MeSn}]^{+\cdot}$
		116–124: $[\mathrm{Sn}]^{+\cdot}$
$\mathrm{MeBu_3Sn}$	188–196: $[\mathrm{MeBuSn}]^{+\cdot}$	287–295: $[\mathrm{Bu_3Sn}]^{+\cdot}$
		245–253: $[\mathrm{MeBu_2Sn}]^{+\cdot}$
		173–181: $[\mathrm{BuSn}]^{+\cdot}$
		131–139: $[\mathrm{MeSn}]^{+\cdot}$
		116–124: $[\mathrm{Sn}]^{+\cdot}$
$\mathrm{BuSnH_3}$	116–124: $[\mathrm{Sn}]^{+\cdot}$	173–181: $[\mathrm{BuSn}]^{+\cdot}$
$\mathrm{Bu_2SnH_2}$	174–182: $[\mathrm{BuSnH}]^{+\cdot}$	232–240: $[\mathrm{Bu_2SnH_2}]^{+\cdot}$
		116–124: $[\mathrm{Sn}]^{+\cdot}$
$\mathrm{Bu_3SnH}$	174–182: $[\mathrm{BuSnH}]^{+\cdot}$	288–296: $[\mathrm{Bu_3SnH}]^{+\cdot}$
		232–240: $[\mathrm{Bu_2SnH_2}]^{+\cdot}$
		116–124: $[\mathrm{Sn}]^{+\cdot}$

the samples were emitting mainly petroleum-like substances, characterized by a set of homologous peaks, and an unresolved complex mixture, and that the organotin compounds were very minor peaks in the FID chromatogram (Fig. 1). The identities of the peaks in the FPD chromatograms were determined by comparison with authentic standards and confirmed by GC–MS. Mass spectral data of the compounds $\mathrm{MeBu_3Sn}$, $\mathrm{Me_2Bu_2Sn}$ and $\mathrm{Me_3BuSn}$ as obtained by GC–MS analysis are given in Table 1, which also includes data for the butyltinhydrides. Figure 2 is the complete mass spectrum of the chromatographic peak corresponding to $\mathrm{MeBu_3Sn}$ found present in Msida Creek sediment on the day 11 of the experiment: the spectrum contains the highly characteristic tin isotope clusters and has a base 'peak' at 189–197 due to $[\mathrm{BuMeSn}]^{+\cdot}$. The mass spectra of all organotins obtained from the sediments were almost identical to the corresponding mass spectra generated from authentic standards.

Quantitative results are given graphically in Figs 3 and 4, where the 48 h mean concentrations of tetraorganotins and derivatized butyltins respectively released from the sediments to air are plotted against time. Table 2 shows the experimental design of the evaporation experiments from sea-water samples spiked with methylbutyltins. Only in the case of experiment number 4 (arrangement (a)) were any organotins actually recovered, with recovery efficiencies as follows ($N = 3$): $\mathrm{Me_3BuSn}$, 79 ± 19%; $\mathrm{Me_2Bu_2Sn}$, 111 ± 8%; $\mathrm{MeBu_3Sn}$, 112 ± 11%. In all other experiments, no organotins were detected in pumped headspace air above the sea-water.

Emission of any organotins from the sediments was below detection limit during the first 2–3 days of the experiment when the sediments were still visibly wet. Results obtained with the experiments described in Table 2 suggest that methylbutyltins are very difficult to exsolve from sea-water, and this could explain their efficient retention in the water-logged sediments. Once the sediments dry out, neutral methylbutyltins, but not the polar ionogenic TBT, DBT and MBT, evaporate off fairly readily. As Figure 4 shows, release to air of these butyltins, probably as aerosols, was sporadic and occurred at significantly lower concentration than tetraalkyltins. The evaporated butyltins are probably in the chloride form, although this could not be ascertained analytically by the present protocol.

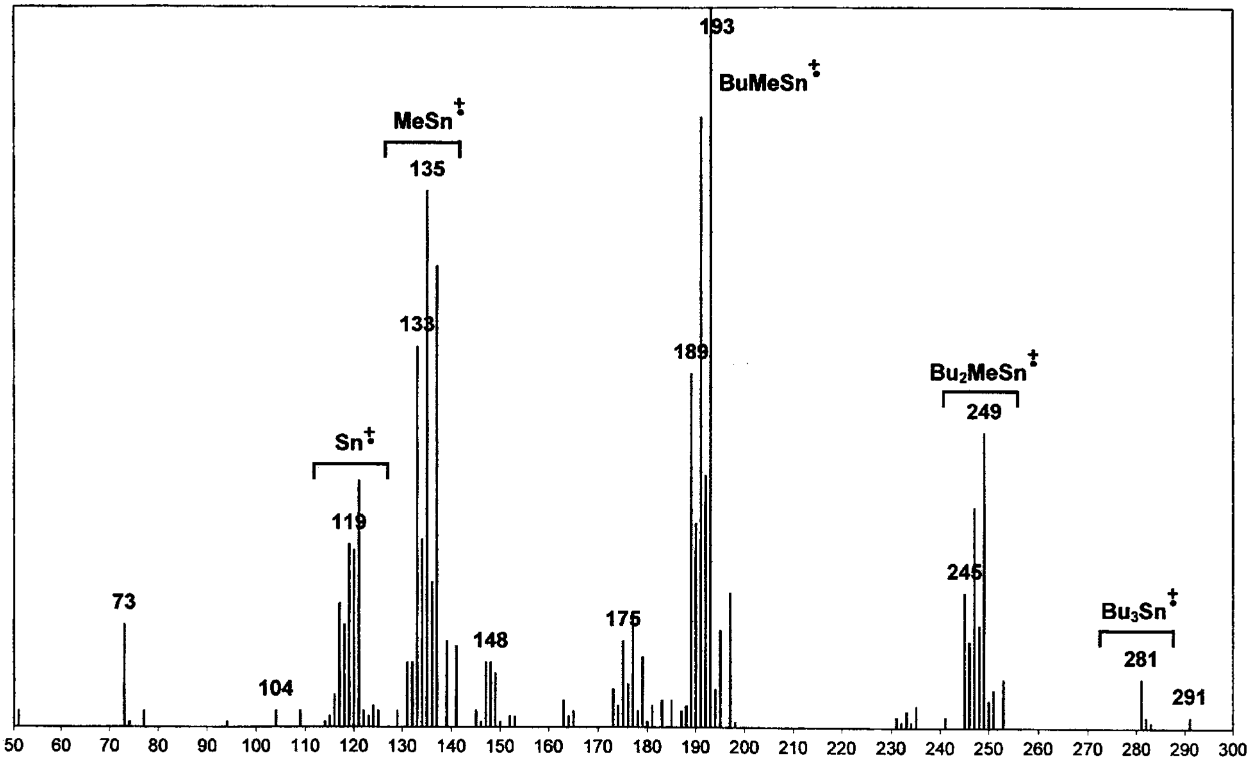

Figure 2. Low-resolution mass spectrum of methyltributyltin found present in pumped headspace air from Msida Creek sediment (day 11 of experiment).

The most abundant organotin in pumped headspace air from sediments was methyltributyltin, which is also the least volatile of the three methylbutyltins. These compounds have saturated vapour pressures that decrease with increasing molecular mass; at 25 °C, the measured values in our laboratory[9] were found to be: 0.4 ± 0.07 ($MeBu_3Sn$), 2.1 ± 0.2 (Me_2Bu_2Sn), 8.5 ± 0.7 Pa (Me_3BuSn). Besides volatility, there is the factor pertaining to the affinity of the molecules for the solid matrix of the sediment, an affinity that probably also increases with molecular size. Thus, one concludes that it is very likely that the predominance of methyltributyltin in the vapour phase must reflect a significantly higher abundance of this tetraorganotin in the sediment. It is not clear why Msida Creek sediments released significantly more methylbutyltins than Lazzaretto Creek sediments, since TBT levels in both creeks were ostensibly similar judging from previously analysed material. It may be that the sands sampled and analysed (3 years) previously were not fully representative of the sediments collected in 1997 and employed in this work, even though both sets of sedimentary material derived from similar environments.

The airborne concentrations of volatile organotins measured in this work may suggest that the TBT-contaminated sediments found in Marsamxett Harbour constitute a rather weak air pollution source that may be insufficient to produce concentration levels in the open air which are harmful to humans. The occupational exposure limit value for TBT compounds (as tin) in air is quoted[12] as 0.1 mg m^{-3}; if an ambient limit value is taken to be 1/40 of the occupational limit standard,[13] and assuming that TBT and methylbutyltins are equally toxic (TBT is expected to be more toxic than a tetraorganotin[14]), then a value of 2.5 μg m^{-3} is indicated. The highest concentrations of methylbutyltins measured in the headspace of the evaporation chamber were well below this value and subsisted for only a few days.

If we assume a bulk concentration (as tin) of tetraorganotin in the sediment of 0.1 μg g^{-1} based on previous results,[7] then 100 g of sediment, for example, would theoretically be able to provide 10 000 ng (as tin) of the substance by exhaustive evaporation. Organotin emissions generally peaked at days 7 to 9 and then decreased gradually to disappear below the detection limit; by extrapolation from the data, this event for methyltributyltin could occur around day 20. Assuming an average evaporated total organotin headspace concentration (as tin) of 20 ng m^{-3} (see Fig. 3), then the predicted total organotin emission from the sediment is (480 h) (0.072 m^3 h^{-1}) (20 ng m^{-3}) = 691 ng (as tin) per 100 g sediment. This value only represents about 7% of organotin present and potentially available, and might suggest that release from the

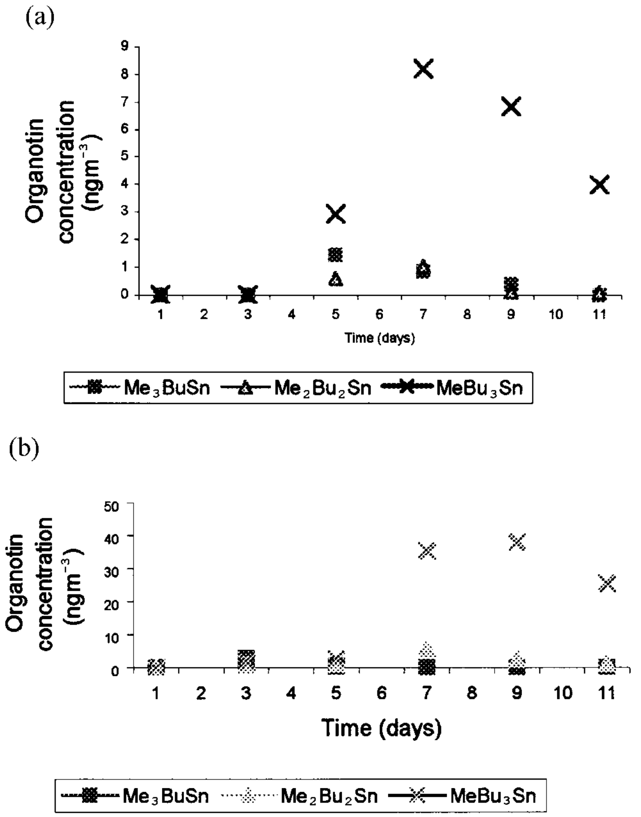

Figure 3. Mean 48 h concentrations (as tin) of tetraorganotins in pumped sediment headspace: (a) Lazzaretto Creek sediment; (b) Msida Creek sediment. Limit of detection: 0.25 ng m^{-3}.

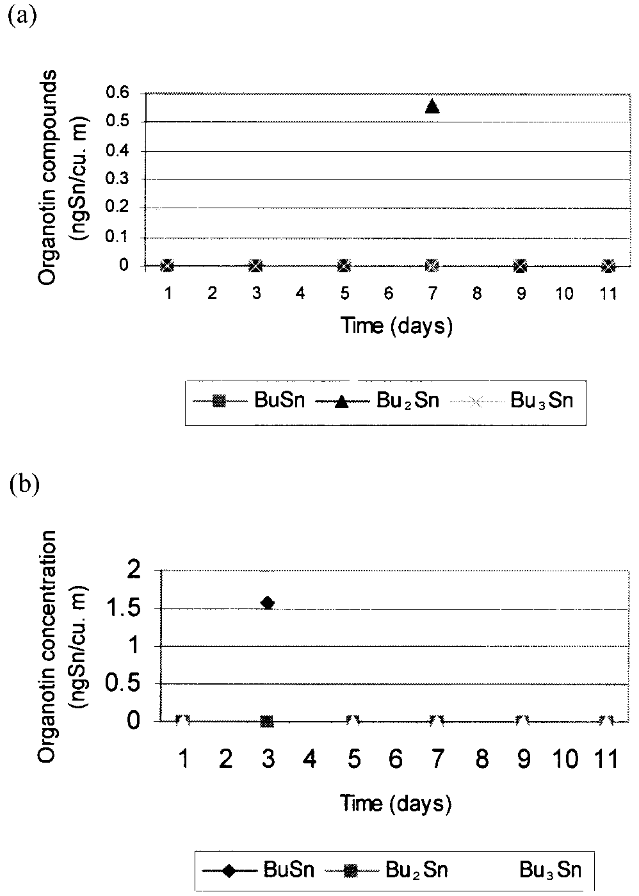

Figure 4. Mean 48 h concentrations (as tin) of derivatized TBT, OBT and MBT in pumped sediment headspace: (a) Lazzaretto Creek sediment; (b) Msida Creek sediment. Limit of detection same as for tetraorganotins.

sediment mass is probably restricted to the surface layer. These data suggest that beached sediments with an organotin contamination level similar to that of Msida Creek would emit a total of about 80 μgSn per square metre of exposed surface area. Moreover, the data also suggest that sediments could retain their load of volatile organotins until such time as the material is disturbed to expose fresh surfaces, when emissions of these vapours could resume. During the handling of dredged harbour sediments that are heavily polluted with TBT, situations could arise that might expose personnel working on site to some risk from volatile organotins; the magnitude of the risk is best evaluated by actual measurements on site for such air pollutants. Finally, the phenomenon may have ecotoxicological effects that would need to be addressed when taking decisions regarding management strategies for such sediments.

CONCLUSIONS

Marine sediments contaminated with TBT residues can host

Table 2. Experimental design of arrangement (a) for the evaporation of methylbutyltins from sea-water[a]

Experiment	Air flow (l min^{-1})	Organotin concentration (as tin) (ng l^{-1})	Final volume of evaporated sea-water (ml)
1	0.14	0.2	9.8
2	0.14	400	10
3	2.20	0.2	2.2
4[b]	2.20	400	2.4

[a] See Materials and Methods section. Arrangements (b)–(d) at air flow rates of 0.14 –2.20 l min^{-1} produced no detectable evaporated methylbutyltins

[b] Only in this experiment were methylbutyltins recovered by evaporation (see text).

methylbutyltins, presumably formed by environmental methylation of TBT and its debutylated metabolites. These substances are far more volatile than polar TBT, DBT and MBT, and would be released into the atmosphere from sediments that have been dredged up from the sea and allowed to dry on land. The preliminary results presented here suggest that the air pollution from such sediments is probably minor; however, more work is necessary to establish the extent of this problem, especially in situations where the vapours emitted can accumulate in some way, and also in regard to any ecological effects caused by any land uses to which the sediments may be applied.

REFERENCES

1. Zimmerli B and Zimmermann H. *Luft. Z. Anal. Chem.* 1980; **304**: 23.
2. Maguire RJ. *Appl. Organomet. Chem.* 1987; **1**: 475.
3. Kawata K, Minagawa M, Fujieda Y and Yasuhara A. *J. Chromatogr. A* 1993; **653**: 369.
4. Kuballa J, Wilken R, Jantzen E, Kwan KK and Chau YK. *Analyst* 1995; **120**: 667.
5. Swami K and Narang RS. *J. AOAC Int.* 1996; **79**(1): 170.
6. Vella AJ, Mintoff B, Axiak V, Agius D and Cassone R. *Toxicol. Environ. Chem.* 1998; **67**: 491.
7. Vella AJ, Mintoff B and Axiak V. *Sci. Total Environ.* 2000; **258**: 89.
8. Maguire RJ. *Environ. Sci. Technol.* 1984; **18**: 291.
9. Tabone Adami JP. *Methylation of tributyltin species in marine sediments*. M.Sc. Dissertation, Department of Chemistry, University of Malta, 2000.
10. Vassallo R. *Organotin compounds in the atmosphere*. M.Sc. Dissertation, Department of Chemistry, University of Malta, 1998.
11. Maguire RJ and Huneault H. *J. Chromatogr.* 1981; **209**: 458.
12. Meinema HA and Bulten EJ. Tin. In *Metals and their Compounds in the Environment – Occurrence, Analysis and Biological Relevance*, Marian E (ed.). VCH: Weinheim, Germany, 1990; 1243–1257.
13. Harrison R. *Pollution: Causes, Effects and Control*, 2nd edn. Royal Society of Chemistry: London, 1992.
14. Blunden SJ, Hobbs LA and Smith PJ. The environmental chemistry of organotin compounds. In *Environmental Chemistry*, Bowen HJM (ed.). Royal Society of Chemistry: London, 1984; 49–77.