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Sorption of tributyltin in seawater by municipal solid waste compost

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The use of municipal solid waste (MSW) compost as a sorbent for tributyltin (TBT) in seawater was investigated. TBT-contaminated seawater, both artificially prepared and that collected from Msida Creek yacht marina (Malta), was allowed to percolate through untreated and water-washed columns of compost and then analysed for organotins using gas chromatography-flame photometric detection. About 90% of dissolved TBT ranging in concentration from about 800 to 8000 $ng_{Sn}l^{-1}$ was sorbed by treating 500 ml solutions with 100 g untreated compost. On the other hand, no detectable breakthrough of TBT was observed from compost that had previously been washed by water to remove soluble organic matter. Breakthrough of TBT from unwashed compost is thought to be due to formation of complexes between the soluble organic matter in compost and aquated TBT, which renders the organotin more hydrophilic. The use of washed MSW compost as sorbent for the purification of TBT-contaminated waters generated in large quantity during hull-cleaning activities in drydocks is suggested as a mitigatory measure against the impact of TBT on the coastal marine environment. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: tributyltin; sorption; compost; seawater; environment

The biocidal properties of tributyltin (TBT) and its use in antifouling marine paints have led to the release of this substance in marine environments. TBT, which has been cited as the most toxic substance ever introduced deliberately into the marine environment,[1] is also toxic to non-target organisms. Imposex in marine gastropods and shell deformation in oysters are the best known effects resulting from TBT contamination, and laboratory experiments and field observations suggest that adverse biological effects occur at concentrations below those detectable, so that a no-observed effect level (NOEL) has yet to be demonstrated.[2] A previously suggested[3] NOEL of 2 $ng_{TBT}\ l^{-1}$ (0.8 $ng_{Sn}\ l^{-1}$) is often exceeded in locations near ship-repairing and shipbuilding dockyards.

The lipophilic character and poor water solubility of TBT are such that, when the substance is introduced into water, partitioning will occur, with the organotin preferentially adsorbing onto particles. Reports from different authors using various conditions suggest that between 10 and 95% of TBT introduced into water is removed by sorption onto particles and remains strongly adsorbed to the solid matrix.[4] Several studies have shown that tributyltin compounds sorb onto sediments. TBT concentrations in aquatic sediments have generally been found to be approximately 5×10^2 to 1×10^4 times the overlying water column values.[5] Unger *et al.*[6] reported sorption coefficients ($[TBT]_{sed}/[TBT]_{water}$) ranging between 10^3 and 10^4 l kg^{-1} for Chesapeake Bay; values for Toronto Harbour sediments[7] range between 3.5×10^3 and 6.4×10^4 l kg^{-1} and for Detroit River sediments[8] between 3.3×10^2 and 1.9×10^4 l kg^{-1}. TBT also binds onto soils of various types. Fent and Muller found that organotins in municipal sewage were primarily associated with suspended solids and that these compounds transferred from sewage water to sludge in the process of sewage treatment.[9]

In this paper, we present results on a study of the sorption of TBT in seawater by municipal solid waste (MSW) compost. The hypothesis that we set out to test was whether MSW compost could provide an effective method for purifying TBT-contaminated waters (as generated in large quantities in activities related to ship-repair and maintenance as practiced in drydocks in Malta). The marine environment in coastal zones proximate to drydocking facilities is known locally, as elsewhere, to be a 'hot spot' of TBT pollution[10] and a

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remediation technique using a cheap, readily available material, if successful, could help significantly reduce the environmental impact of the ship repair and maintenance industry with respect to TBT pollution.

MATERIALS AND METHODS

MSW compost

The compost was obtained from the Marsascala Waste Composting Plant, which is the only facility of its kind in Malta. The feedstock is unsegregated municipal solid waste with a minor component of green waste and excludes sewage sludge or other special wastes. The method used was the windrow technique with a composting period of 150 days. A single batch of MSW compost was employed for all experiments. The compost had the following bulk composition (percent by mass): organic matter (36%), acid-insoluble (clayey) matter (6%), limestone and glass granules (23%) and humidity (35%). Obvious granules of glass, plastic, etc. were removed manually from the compost sample before use. The infra-red spectrum of the compost was very similar to that for city refuse compost from Yokohama, Japan,[11] and contains the following absorption bands indicative of groups typical of humic materials: aliphatic and aromatic C—H bonds (2900 cm^{-1} and 900–650 cm^{-1} respectively), carboxylic (1700–1600; 1500–1400 cm^{-1}) and alcoholic and/or phenolic OH groups (3500–3300; 1100–1000 cm^{-1}).

Work in our laboratory[12] has shown that the sorption capacity of the compost determined by digestion in aqua regia and analysis for copper(II) (used as index ion) is 447 ± 27 meq kg^{-1}, which is similar to that for compost from Japan,[13] and of which only a small fraction (8 meq kg^{-1}) is readily available by exchange with sodium(I).

Before sorption experiments onto the compost could be performed, it was established that the compost itself did not leach organotins. Leachate from the compost using artificial seawater (prepared by dissolving the required salts in deionized water) was analysed and verified to be free of organotin compounds.

Analytical method

The analytical procedure for organotins was based on that of Waldock *et al.*[14] and modified as described below. The aqueous sample (500 ml) was treated with 5 ml concentrated HCl and spiked with tripentyltin chloride (as recovery standard) and the solution extracted with 100 ml dichloromethane (DCM) containing 0.0125% tropolone. The DCM layer was taken to near dryness under nitrogen and the extract taken up in hexane and treated with excess 2 M propylmagnesium bromide (prepared in house) under nitrogen. The propylated derivatives were purified by elution from silica gel using hexane. Tetrabutyltin (Bu_4Sn) was used as internal standard; the risk of formation of this species from TBT by disproportionation was considered and it was thought to be insignificant in view of preliminary results obtained on tripentyltin, which, on standing in the compost leachate for 24 h, showed exclusive degradation into di- and mono-pentyl derivatives. Since tripentyltin was employed as a recovery standard, it was added to the aqueous samples just prior to extraction to avoid problems caused by its own decomposition. Analysis for organotins was by gas chromatography (GC) (Perkin Elmer Model 8000) with a flame photometric detector and a 25 m narrow bore BP1 capillary column (SGE, Australia). The tin detection limit was 0.1 ng injected in the column. A standard mixture containing propylated TBT, dibutyltin (DBT), monobutyltin (MBT) and Bu_4Sn was used daily to verify the quality of the gas chromatographic performance.

Leaching experiments

Artificial seawater samples (500 ml), pH 8.0 ± 0.2, were spiked with 2.0 or 4.0 μg of tin as bis(tributyltin)oxide (TBTO). These concentrations fall well within the solubility limit of TBTO, which ranges from 0.4 to 40 mg_{Sn} l^{-1} depending on temperature and pH.[15] Several samples were prepared for each TBTO concentration. Each spiked artificial seawater sample was then allowed to percolate dropwise through a 100 g compost column prepared by packing ground compost in 250 ml separatory funnels. Except for the removal of grit and glass granules, the MSW compost was used as obtained. Leachate from the compost filter bed was centrifuged for 15 min (at 3000 rpm) and the supernatant filtered under suction through a slow, fine-pored filter paper (Whatman no. 42). The leachate was then analysed for organotins as described above.

A similar sorption experiment was also carried out using real seawater taken from Msida Creek, Malta, a major yacht marina known to be contaminated with organotins.

A second set of experiments was carried out to study the effect of removing soluble organic matter in the compost on its sorption characteristics towards butyltins. Compost columns (100 g) were washed almost free of soluble organic matter by treating with a sufficient volume of organotin-free water until the characteristic deep red–brown colour of the leachate turned to a persistent pale yellow colour. The washed compost was then treated with 500 ml of artificial seawater spiked with TBTO at 4.00 μg_{Sn} l^{-1} and analysed as described above.

Stability of TBT in leachate solution

Since during the period between collection of leachate and solvent extraction of organotin for GC analysis (from 5 to 24 h) significant TBT degradation was suspected to have occurred (in view of probable microbiological activity in the organic-rich medium and possible photodegradation — the experiments were conducted in diffused light available in the laboratory and solutions were stored in the dark pending extraction), control experiments were performed to assess this as follows. Two 500 ml samples of each of the following mixtures were prepared: deionized water, artificial seawater,

Table 1. Analysis of leachate following percolation of 500 ml artificial seawater spiked with 2 μg of tin (samples 1–9) and 4 μg of tin (samples 10 and 11) as TBTO through a 100 g compost column

Sample no.	[MBT] ($ng_{Sn}\ l^{-1}$)	[DBT] ($ng_{Sn}\ l^{-1}$)	[TBT] ($ng_{Sn}\ l^{-1}$)	Σ [Sn_{TBT}] ($ng_{Sn}\ l^{-1}$)	% Σ [Sn_{TBT}] breakthrough	% Σ [Sn_{TBT}] retained on compost
1	318	n.d.	166	484	12.1	87.9
2	n.d.	138	386	524	13.2	86.8
3	224	126	n.d.	350	8.8	91.2
4	n.d.	n.d.	492	492	12.4	87.6
5	n.d.	n.d.	174	174	4.4	95.6
6	104	52	290	446	11.3	88.7
7	240	n.d.	104	344	8.7	91.3
8	100	n.d.	312	432	10.4	89.6
9	142	72	178	392	9.9	90.1
Average (1–9)					10.1	89.9
10	128	86	406	620	7.8	92.2
11	150	112	412	674	8.5	91.5
Average (10 and 11)					8.1	91.9

n.d.: not detected, i.e. $<5\ ng_{Sn}\ l^{-1}$.

and artificial seawater that had been leached through unwashed compost and filtered. Each solution was spiked with 2.00 μg of tin as TBTO and allowed to stand under the same conditions for 24 h and then analysed for organotins.

RESULTS

Sorption by unwashed compost

Gravity filtration through the compost bed of the 500 ml aliquots took approximately 30 min, but centrifugation and further filtration through filter paper added another 45 to 60 min of residence time of the organotins in aqueous solution before extraction for analysis.

Leachate from unwashed compost using artificial seawater produced, in addition to peaks from the internal (Bu_4Sn) and recovery (Pe_3PrSn) standards, another peak identified as tetrapropyltin (Pr_4Sn), which originates from inorganic tin(IV) in the compost. This probably derives from tin-containing residues in municipal waste, e.g. particles from tin-coated steel cans.

Generally, leachates from spiked artificial seawater contained inorganic tin(IV) and smaller peaks due to TBT, DBT and MBT. The presence of DBT and MBT indicated that degradation of TBT had occurred either during the percolation experiment or later, as the solution was standing prior to extraction (*vide infra*). Inorganic tin was largely attributable to that already present in the compost and, to a lesser extent, to degradation from TBT. The total amount of organotin that leached through the compost column, $\sum Sn_{TBT}$, was taken as the sum of all organotin forms, i.e.

$$\sum[Sn_{TBT}] = [Sn_{TBT}] + [Sn_{DBT}] + [Sn_{MBT}]$$

This equation ignores the contribution of any TBT-derived tin(IV) that could not be obtained directly due to the background presence of compost-derived tin(IV). However, using control experiments, it was estimated that less than about 5% of TBT degraded to tin(IV) and so the error involved is small. Total organotin breakthrough from the column (as $\%\Sigma$ [Sn_{TBT}]), expressed as a percentage of the amount of TBT added, is shown in Table 1. Samples 1 to 9

Table 2. Analysis of leachate following percolation of 500 ml contaminated seawater collected from Msida Creek through a 100 g compost column

Sample no.	[MBT] ($ng_{Sn}\ l^{-1}$)	[DBT] ($ng_{Sn}\ l^{-1}$)	[TBT] ($ng_{Sn}\ l^{-1}$)	Σ Sn_{OT} ($ng_{Sn}\ l^{-1}$)	% Σ Sn_{OT} breakthrough	% Σ Sn_{OT} retained on compost
12	n.d.	n.d.	58	58	5.2	94.8
13	n.d.	n.d.	94	94	8.4	91.6
Average					6.8	93.2

n.d. = not detected, i.e. $<5\ ng_{Sn}\ l^{-1}$.

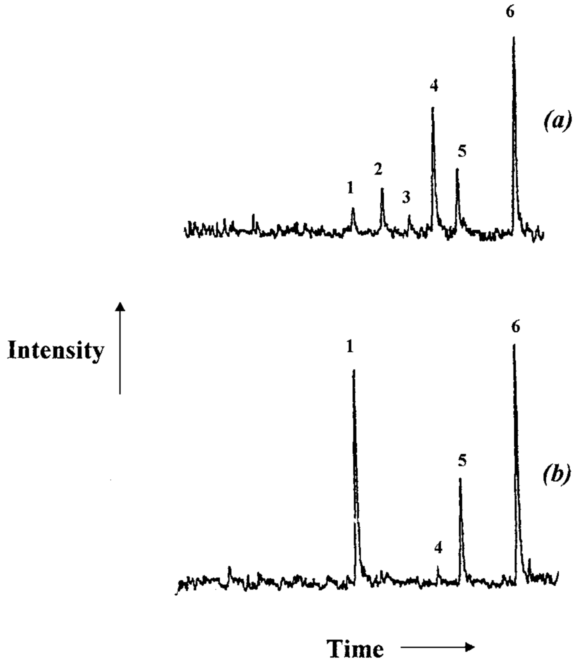

Figure 1. Gas chromatograms of extract from Marina Creek seawater (a) prior to sorption through compost and (b) after sorption through unwashed compost. Key to peak identification: (1) inorganic tin; (2) MBT; (3) DBT; (4) TBT; (5) tetrabutyltin (internal standard); (6) tripentyltin (recovery standard).

refer to the 2.00 μg of tin spike/500 ml water, whereas samples 10 and 11 refer to the 4.0 μg of tin spikes. In Table 2 the samples refer to contaminated seawater from Msida Creek. Gas chromatographic analysis (Figure 1) showed the seawater to contain 766 $\mathrm{ng_{Sn}\,l^{-1}}$, 104 $\mathrm{ng_{Sn}\,l^{-1}}$ and 254 $\mathrm{ng_{Sn}\,l^{-1}}$ of TBT, DBT and MBT respectively.

From Table 1, an average value for the percentage TBT retained on compost was 90% and 92% for artificial seawater of concentration 4 $\mathrm{\mu g_{Sn}\,l^{-1}}$ and 8 $\mathrm{\mu g_{Sn}\,l^{-1}}$ respectively. For contaminated seawater the percentage retention value for organotins, $\%\Sigma\ [\mathrm{Sn_{OT}}]$, expressed as $\Sigma\ [\mathrm{Sn_{OT}}]/\Sigma\ [\mathrm{Sn_{OT}}]^{\circ}$ (where $\Sigma\ [\mathrm{Sn_{OT}}]^{\circ}$ refers to the total concentration of organotins originally present in seawater and $\Sigma\ [\mathrm{Sn_{OT}}]$ refers to organotins in leachate), was 93%; here, DBT and MBT were completely retained by the compost bed. This data cannot be used to estimate sorption coefficients for TBT on compost, since the contact time with the filter bed was deliberately designed to be short and thus not conducive to equilibration. Indeed, the objective was to establish whether effective sorption onto the filter bed could be realized under flow-through conditions, which were completed as rapidly as possible.

Adsorption by washed compost

The sorption experiment was repeated using a column of compost that had previously been washed almost free of soluble organic matter as described above. When artificial seawater spiked with 4 $\mathrm{\mu g_{Sn}\,l^{-1}}$ were filtered through 100 g washed compost columns, no butyltins were detected in any of the leachates.

Decomposition of TBT in leachate

The degree of degradation of TBT using spiking experiments and wait times of 24 h was studied for the following media: deionized water, artificial seawater and compost leachate. Degradation of TBT into DBT and MBT was observed to occur in all media tested, but the rate of degradation was significantly different in the three media. The extent of degradation of TBT after 24 h was found to be as follows: 3% (deionized water), 6% (artificial seawater) and 13% (compost leachate). Aerobic microbiological oxidation, expected to be preponderant in compost leachate, is probably mainly responsible for the much faster degradation of TBT in this medium. If the kinetics of decomposition are assumed to be first order, then these results suggest a half life of about 5 days for TBT in compost leachate; this is comparable to the half life of 6 to 7 days in estuarine waters.[4] Thus, it would appear that the DBT and MBT found to be present in the leachate from unwashed compost probably derive from degradation of TBT in the leachate occuring during standing of the solution prior to extraction for GC analysis.

DISCUSSION

The nominal cation formed in solution from ionogenic TBT compounds has important hydrophobic content and a potential positive charge that is dependent on pH and the activity of anionic species co-present in solution. In addition, the cation exchange capacity, complexation properties and hydrophobic nature of a solid matrix in contact with dissolved TBT will also influence the extent and sorption characteristics of that matrix towards TBT. In seawater, at pH 8, in addition to $\mathrm{Bu_3SnCl}$, the species $\mathrm{Bu_3SnOH}$ would also be expected to be present, since the pH is higher than the hydrolysis constant ($\mathrm{p}K_{\mathrm{hydrolysis}} = 6.71$) for the hydroxo complex.[16] Such species could only take part in hydrophobic mechanisms with the sorbent.

The organic content of MSW compost is very high and its physical structure is rather porous, so that it was anticipated that the material would constitute an excellent matrix for sorption of TBT from seawater. Gonzalez-Prieto *et al.*[17] showed that the organic matter in compost from urban refuse consists mainly of cellulose and hemicellulose (32–52%), lignin (22–35%) and water-soluble compounds (15–30%) with a minor amount of lipids (4–6%). Thus, it would also be expected that compost produces in solution a significant amount of soluble humic matter that could bind to TBT, thus rendering it more hydrophilic. The association of TBT with dissolved humic acids in natural freshwaters over the pH range 3 to 9 has recently been found to be dominated by binding of $\mathrm{Bu_3Sn^{+}}$ to carboxylate and phenolate ligands and also by hydrophobic interactions.[18] Formation of humates of the type Bu_3SnR (where R denotes anions from soluble organic matter) favours retention of TBT in solution and would explain why sorption by unwashed compost of TBT is only about 90% efficient. When MSW compost is washed almost free of its soluble organic matter, the resultant matrix has been shown here to allow practically complete transfer of TBT from the aqueous to the solid phase presumably by reactions such as:

$$Bu_3SnOH + COMH = COMBu_3Sn + H_2O \qquad (1)$$
$$Bu_3SnOH + COMH = Bu_3SnOH \cdot COMH \qquad (2)$$

where COMH represents the organic matrix in compost. The interactions of TBT with this matrix are again expected to involve complexation reactions with carboxylate and phenolate groups [Eqn. (1)] as well as hydrophobic sorption [Eqn. (2)]. Silicate impurities in compost could also provide additional cation exchange sites, although the abundance of these materials in the MSW compost is minimal.

The fact that leaching of inorganic tin from compost persists even after prolonged washing suggests that tin(IV) is probably present as some insoluble phase (e.g. SnO_2), from which minute quantities continue to be mobilized in a form that, contrary to organotins, has little affinity for compost.

The results from this work suggest a new use for MSW compost: namely, that compost beds could be employed to filter TBT-contaminated waters such as are generated in large quantities during ship-repair and maintenance. The high-pressure hosing of ships' hulls covered with TBT-containing antifouling paints in preparation for repainting involves the mobilization of significant amounts of TBT in the wash water, both in the dissolved form and as dislodged TBT-containing particles. It is estimated that, at the Malta drydocks, this operation generates about 600 t of waste water per year, which delivers about 0.9 t of TBT into the marine environment.[10] The coastal environment in harbours and marinas around Malta is known to be significantly contaminated with TBT, and biological effects deriving from this contamination have recently been described.[19]

TBT sorbed on solid compost may also be expected to decay quickly, mainly as a result of aerobic biotic oxidation similar to that for dissolved TBT in compost leachate. This is anticipated by analogy with observed degradation rates in estuarine sediments under oxic conditions, where the lifetime of TBT is similar to that for dissolved TBT in the same environment.[4] Since degradation of TBT by debutylation ultimately generates inorganic tin, the compost bed would, in practice, act both as a filter for TBT and also as a medium for its detoxification.

MSW compost also contains other sorbed heavy metals, notably zinc, lead and copper in the medium to high parts per million range, especially if prepared from mixed urban refuse rather than from source-segregated household waste.[20] However, only a very small fraction of these metal ions is readily mobilized by cation exchange.[12] Breakthrough could, however, be facilitated if changes in the molecular structure of compost had taken place on prolonged use of the filter bed, and even the retention capacity for organotins could then be affected. Clearly, this is an issue that needs to be addressed by further work, preferably on a pilot-scale model of the compost filter bed.

MSW compost is potentially a ubiquitous material, although, in fact, composting rates of municipal waste do not exceed 1% in several countries (with some notable exceptions, e.g. Spain and Portugal, where rates as high as 10–13% are reported), and then the product is only employed as a soil improver in agriculture and for landscaping.[20] The application of compost to waste-water purification would not only address the adverse effects of TBT on the marine environment, but it would also add value to the compost as a waste recycling product. Providing additional applications for MSW compost would encourage further the composting option in the management of municipal solid waste, and this is a desireable objective.

CONCLUSIONS

The use of MSW compost as a solid phase sorbent for the effective removal of TBT in solution has been demonstrated. The soluble organic matter in compost provides ligand species in solution that bind to TBT and help retain it in the dissolved state, so that when untreated compost is used as sorbent, only about 90% reductions in TBT concentration are achieved. If the soluble organic matter in compost is first removed by washing with water, then TBT retention on compost is practically complete for contact times between solution and solid sorbent of about half an hour. The application of MSW compost as a sorbent for TBT would not only be a relatively cheap remedy for combating TBT pollution by treatment of drydocks waste waters at source, but it would also make composting of urban refuse a more attractive waste management strategy by providing a novel additional use for the compost.

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