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Adsorption characteristics of tributyltin on municipal solid waste compost

Daniel Said-Pullicino and Alfred J. Vella*

Department of Chemistry, University of Malta, Msida, Malta

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The sorption behaviour of tributyltin (TBT) from reconstituted seawater onto municipal solid waste (MSW) compost was investigated to give first insights into the equilibrium and kinetic behaviour of this process. The rate of adsorption, the influence of pH, and the adsorbate hydrophobicity on the partitioning process were investigated. Adsorption kinetics indicated an initial fast rate of adsorption of TBT followed by a slower rate. The similarity of Freundlich sorption and desorption coefficients for TBT showed that the sorption process is also reversible, similar to that for the adsorption of TBT onto marine sediments. It was found that the adsorption capacity for TBT onto compost was highest at pH 6.7, and for other organotins it increased with increasing adsorbate hydrophobicity, following the trend tripropyltin < TBT < tripentyltin. The use of washed MSW compost as a sorbent for the purification of TBT-contaminated wash waters as generated in large quantities during hull cleaning in dry docks is suggested as a mitigatory measure against pollution of the marine environment by TBT. Calculations suggest that modest amounts of compost will likely be required to treat the contaminated wastewaters generated from the Malta dry docks if a multiple batch system is adopted.

KEYWORDS: tributyltin; sorption; municipal solid waste compost; seawater; environment

INTRODUCTION

Tributyltin (TBT) has proved to be an extremely efficient and widely used marine biocide in antifouling paints. It reduces hull roughness, hence preventing drag, improves manoeuverability and speed per unit of fuel, and thus lowers environmental pollution by carbon dioxide and sulfur dioxide as well as increasing the time a vessel can be at sea.[1] However, the extreme toxicity of TBT to marine organisms has resulted in numerous adverse biological effects on non-target organisms, the best known of which are imposex in marine gastropods and shell deformation in oysters. TBT has been cited as the most toxic substance ever introduced deliberately into the marine environment,[2,3] and its widespread use has made TBT a contaminant of global concern resulting in an imminent total ban;[4] at the same time, there is growing interest in the biogeochemical cycling of what must be a considerable presence of environmental organotins derived from TBT.

In most European countries an Environmental Quality Standard (EQS) for tin of 2 ng l^{-1} for marine water samples is now implemented.[5] The EQS, defined as the maximum concentration of a pollutant in water allowed over a particular period or geographical area, is frequently exceeded in marinas and harbours around Malta and levels are sufficiently high to cause concern.[6]

The major point sources of TBT in coastal areas appear to be dry docks and other facilities where ship-building, repair and hull cleaning and repainting occur. We have investigated the possibility of cleaning up discharges and contaminants released from dry docks and ship-repair yards by the use of municipal solid waste (MSW) compost, which is a cheap and readily available adsorbent. Preliminary work carried out by Vassallo and Vella[7] has already shown that MSW compost can act as an effective solid-phase sorbent for the removal of TBT in solution. The major objectives of this study were to determine in greater detail the sorption behaviour of TBT onto MSW compost and to give first insights into the equilibrium and kinetic behaviour of this transfer process.

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*Correspondence to: Alfred J. Vella, Department of Chemistry, University of Malta, Msida, Malta, MSD 06.
E-mail: alfred.j.vella@um.edu.mt

MATERIALS AND METHODS

MSW compost

Compost was obtained from the Marsascala Waste Composting Plant, which is the only facility of its kind in Malta. The feedstock consisted of mechanically separated municipal solid waste with a minor component of 'green waste' in the form of garden waste from parks and civic amenity sites and excluded sewage sludge or other special wastes. The waste materials were composted by a 'windrow' technique involving an active phase in 'Eco Pod'® tarpaulins 60 m long and 1.5 m diameter for 12 weeks, followed by a maturation period of 8 weeks. A single batch of MSW compost was employed for all experiments. Obvious granules of glass, plastic, etc., comprising at least 12% by mass of the whole compost sample, were removed manually before use. The fresh compost had the following bulk composition (percentage by mass on a wet weight basis): 29.0% organic matter, of which 30% humic acids and 15% fulvic acids and non-humic substances, 9.2% acid-insoluble (clayey) matter, 12.5% inert materials (>4.0 mm) and 23.0% moisture content. The fresh compost was air dried, crushed to pass through a 2.8 mm sieve and thoroughly mixed prior to use. The IR spectrum of the compost was very similar to that for MSW compost from the same composting facility used in a previous study,[7] as well as for a city refuse compost from Yokohama, Japan,[8] 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}).

Analytical method

The method adopted for the analysis of organotins in aqueous solutions was similar to that described by Carlier-Pinasseau *et al*.[9] Determination required no pretreatment of the sample, except for buffering with an ethanoic acid–sodium ethanoate buffer (pH 4.6) and filtering through a 0.45 μm membrane filter. The procedure was based on a one-step simultaneous ethylation and extraction using sodium tetraethylborate reagent (200 μl of a 4% w/v solution) added directly to the aqueous phase (20 ml) in the presence of an iso-octane layer (2.0 ml): ethylated organotins, being tetrasubstituted molecular compounds, are rapidly and efficiently extracted into the non-polar solvent, which can then be easily separated from the aqueous system for analysis. Tripropyltin chloride (TPrTCl) was used as an internal standard. Direct extract analysis was performed using a Perkin Elmer Model 8000 capillary gas chromatograph equipped with a flame photometric detector (cGC-FPD). A 25 m fused silica, narrow bore, BP1 capillary column (SGE, Australia) was used. The tin detection limit was 0.4 ng injected in the column. A standard mixture containing tetrabutyltin (TTBT) and ethylated TBT, dibutyltin (DBT), monobutyltin (MBT) and TPrT was used daily to verify the quality of the gas chromatographic performance.

Interaction of TBT with dissolved organic matter

Although the Grignard derivatization used by Vassallo and Vella[7] was capable of alkylating all TBT in solution, irrespective of whether it was associated with soluble organic matter or not, no data were available on the ethylation efficiency of sodium tetraethylborate in the presence of dissolved organic matter (DOM). This issue was investigated as follows: deionized water and a series of solutions obtained through serial dilution of the DOM extract and having an organic carbon (OC) concentration between 0.0 and 0.6 mg ml^{-1} were each spiked with 400 ng (as tin) of TBT and TPrT (internal standard), stirred for 15 min and then analysed. TTBT (400 ng as tin) was utilized as a recovery standard, since this compound did not require derivatization and could be added to the iso-octane after the other organotins had been extracted from solution. All determinations were carried out in triplicate. DOM was extracted from MSW compost by shaking with deionized water (1 : 3 compost mass to solution volume ratio) for 16 h at room temperature under nitrogen. After centrifugation at 5000 *g* for 20 min, the supernatant was filtered first through a 0.7 μm GF/C glass microfibre filter and then through a 0.45 μm cellulose acetate membrane filter (Whatman, Springfield Mill, UK). Quite apart from the effect that DOM had on the analytical procedure for organotins (*vide infra*), it would still have been appropriate to establish sorption/desorption characteristics of compost washed free of DOM because it would otherwise have been difficult to control experimental conditions from a medium that would be releasing variable amounts of organic matter into solution.

Adsorption and desorption of TBT by washed compost

MSW compost was washed free of DOM as described by Vassallo and Vella.[7] The reduction of DOM in the leachate was monitored by measuring the reduction in UV–visible absorption over the range 200 to 900 nm. The final washed compost was air dried, gently crushed to pass through a 2.8 mm sieve and used throughout this work.

The rate of adsorption of TBT onto MSW compost was monitored as a function of time. Samples of washed compost (0.3 g dry weight (DW)) were accurately weighed in 30 ml centrifuge tubes and 25 ml of a 1025 μg l^{-1} solution of TBT in reconstituted seawater, containing 3 g l^{-1} of sodium azide as a biocide, were added. The tubes were equilibrated in the dark at constant room temperature. The TBT remaining in solution was determined in triplicate, by analysing the supernatant of the tubes at various time intervals from mixing.

The adsorption isotherm of TBT on washed compost was determined using the batch equilibrium method at 25 °C. Various solutions of TBT in reconstituted seawater (25 ml) with an initial concentration of 1025 μg l^{-1} (as tin) were equilibrated for 24 h, in the dark, with different amounts of washed compost, ranging from 0.1 to 0.5 g wet weight in Corex centrifuge tubes. Sodium azide (0.3 g) was also added as a biocide to prevent the degradation of TBT, as reported by Vassallo and Vella:[7] we established experimentally that, at the concentrations employed in this work, azide ions do not interfere with the ethylation of TBT. A small subsample of the compost was taken and used for moisture content determination. The equilibration of compost with reconstituted seawater in the absence of TBT was also carried out to permit correction for any leachable organotins possibly present in the compost itself, although no such correction was eventually found to be necessary. The pH of the samples during equilibration was similar to that for reconstituted seawater (pH 8). After equilibration the tubes were centrifuged at 5000 *g* for 30 min and 20 ml of the supernatants were spiked with TPrT and analysed for organotins. All analyses, including a blank to permit correction for the sorption of TBT to the tube walls and other losses, were carried out in duplicate. The amounts sorbed were calculated from the difference between the initial and equilibrium concentrations of TBT in solution and expressed on a dry weight basis. Adsorption isotherms were obtained by plotting the amount of TBT adsorbed against the equilibrium concentration.

The desorption isotherm was obtained by replacing the supernatant from the adsorption experiment with reconstituted seawater not containing TBT, and the equilibration, centrifugation and analyses steps repeated. Compost concentrations from the initial sorption equilibrations were used to calculate the initial amount of TBT available on the compost for desorption. The amounts of TBT remaining on the compost were calculated from the difference between the initial TBT available on the compost and equilibrium concentrations of TBT in solution.

Effect of pH on adsorption of TBT onto compost

Isotherms were obtained to describe the adsorption of TBT on washed compost at different pH values, using the batch equilibrium method at 25 °C. The pH of the initial solution of TBT in reconstituted seawater ($1025\ \mu g\ l^{-1}$ as tin) was adjusted to values between 2.5 and 7.5 using HCl after addition of sodium azide ($3\ g\ l^{-1}$). Equilibration and analysis was carried out as described above. Since the pH of the solutions could have changed slightly during equilibration with compost, the pH of the supernatants was determined accurately after equilibration. Aqueous equilibrium concentrations of TBT were measured and compost-sorbed concentrations were calculated from the difference between the initial and equilibrium concentrations of TBT in solution and expressed on a dry weight basis. Adsorption isotherms at different pH values were obtained by plotting the amount of TBT adsorbed against the equilibrium concentration.

Adsorption of organotins as a function of carbon chain length

The effect of increasing the carbon chain length of the alkyl substituents on the adsorption of organotin compounds onto compost was studied. The adsorption isotherm of TPrT and TPeT on washed compost was determined using the batch equilibrium method at 25 °C as described above. Solutions of TPrT and TPeT in reconstituted seawater were prepared containing initial tin concentrations of $800\ \mu g\ l^{-1}$ and $2000\ \mu g\ l^{-1}$ respectively and containing sodium azide ($3\ g\ l^{-1}$). TBT was used as an internal standard in these determinations, and all analyses, including a blank, were carried out in duplicate.

RESULTS AND DISCUSSION

Interaction of TBT with DOM

The results (Fig. 1) show that for TBT, and to a lesser extent TPrT, the presence of DOM in solution greatly reduces the amount of organotin that can be converted into the ethylated tetrasubstituted derivative by the analytical method. It appears that the [Organotin–DOM] complexes formed in the presence of DOM are not sufficiently labile to allow derivatization of organotins. This incomplete ethylation of organotin when in the presence of DOM would, therefore, result in positive errors if one were to attempt to determine the quantity of sorbed TBT from the difference between the initial and equilibrium concentrations in solution. The data in Fig. 1 shows that ethylation efficiency for TBT is lower than that for TPrT in the presence of equivalent amounts of DOM; this suggests that interaction of DOM with TBT is possibly greater because of the greater hydrophobic character resulting from the longer chain alkyl groups.

Similar results obtained by Vassallo and Vella[7] showed that soluble organic matter from compost interacted with TBT in solution, increasing its retention in the dissolved state. Since the presence of DOM in fresh compost would result in a lowering of the adsorption capacity for TBT, all experiments carried out in this work on the interaction of

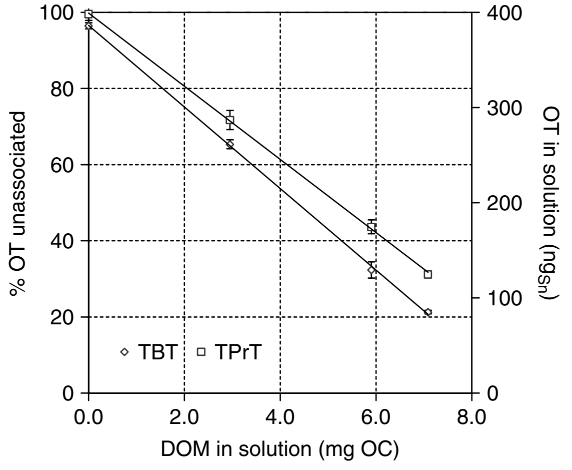

Figure 1. Association of TBT and TPrT with DOM in solution. Error bars represent SE.

TBT with compost were performed using compost samples previously washed free of DOM.

Adsorption and desorption of TBT by washed compost

The rate curve for the adsorption of TBT on washed compost (Fig. 2) shows that 95% of maximum adsorption was achieved within the first 30 min of equilibration and that adsorption reaches a state of equilibrium (~100% maximum adsorption) within 8 h. Therefore, a period of equilibration of 24 h was considered sufficient and was used in subsequent adsorption experiments.

TBT in seawater is an ionic species containing a permanent charge in addition to lipophilic groups. The binding of a polar molecule such as TBT may be a function of both its hydrophobicity, associated with the bulky butyl groups, and its polarity. For this reason, an attempt was made to fit the kinetic data to a one- and two-site binding hyperbola (Fig. 2). These hyperbolic equations describe the equilibrium binding of a substance to one or two kinds of binding sites as a function of time. Whereas the one-site binding hyperbola assumes a single type of interaction, the two-site binding hyperbola takes into account simultaneous interactions with two kinds of site having different affinities and different maximum adsorption capacities. The latter gave the best fit ($R^2 = 0.9459$), suggesting that adsorption of TBT onto compost could in fact involve fast cation exchange of TBT^+ species, as well as a slower adsorption of TBT^+ and TBT neutral species due to lipophilic attraction to the compost organic matter. This behaviour is similar to that observed by Hermosin *et al.*[10] in connection with the adsorption mechanism of monobutyltin onto phyllosilicate clay minerals, where the adsorption process was considered as occurring in two successive first-order steps.

The best fit for the adsorption and desorption isotherms of TBT on compost at a temperature of 25 °C and pH 7.8 was obtained by means of a non-linear regression adapted for the Freundlich equation (Fig. 3). The Freundlich equation is an empirical adsorption model that has been widely used in environmental chemistry. It can be expressed as

$$\frac{x}{m} = K_f C_e^n \tag{1}$$

where x/m is the amount of solute adsorbed (adsorbate) per unit mass of adsorbent, C_e is the equilibrium concentration of the solute in the bulk solution, K_f is the partition coefficient, and n is a constant. The results show clearly that adsorption of TBT onto MSW compost is a reversible process. Whereas normally the adsorption and desorption isotherms of TBT onto sediments give equal slopes, the desorption isotherm of TBT (as tin) from compost has a greater Freundlich sorption coefficient ($K_f = 3261 \pm 249\ \mu g^{1-n}\ ml^n\ g^{-1}$) than the respective adsorption isotherm ($K_f = 2099 \pm 302\ \mu g^{1-n}\ ml^n\ g^{-1}$). Desorption hysteresis was calculated as the ratio of Freundlich exponents for desorption to sorption, i.e. n_d/n_s (where subscripts d and s refer to desorption and sorption respectively). The smaller the hysteresis index, the higher the degree of hysteresis (i.e. the more difficult it is to desorb). The relatively high desorption hysteresis index (1.09 ± 0.06) shows that, although the K_f values are significantly different, the adsorption process is actually reversible. This discrepancy in K_f values could possibly be due to a small portion of TBT that is irreversibly bound to the compost or to slower kinetics associated with the process of TBT desorption from the solid matrix, such that the 24 h equilibration period was not actually sufficient for the desorption process to reach a state of equilibrium.

Both adsorption and desorption isotherms have Freundlich exponent n values (0.70 ± 0.04 and 0.76 ± 0.02 respectively)

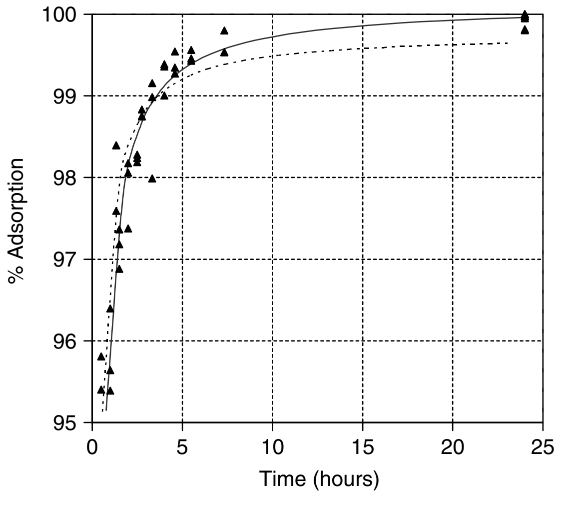

Figure 2. Rate curve for the adsorption reaction of TBT on compost, considering one- (dotted line) and two-site (whole line) binding hyperbolae.

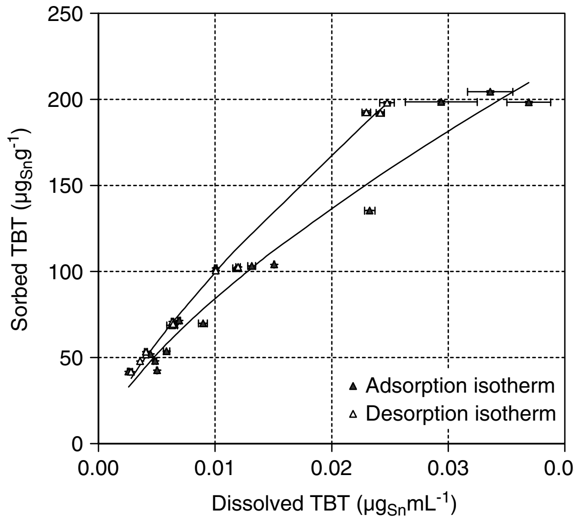

Figure 3. Adsorption and desorption isotherms of TBT on compost. Error bars represent SE.

that are significantly different from unity. The analysis of the n sorption coefficients indicates isotherm non-linearity ($n < 1$) and concentration-dependent TBT solid–solution distribution in both isotherms. The non-linear isotherms obtained indicate that the adsorbent (the compost) has a moderately lower affinity for the solute (TBT) at higher final concentrations. This is probably due to the heterogeneous composition and structure of compost substances, as well as to the diversity of adsorption mechanisms. Within the experimental concentration range used, no limiting adsorption was observed for TBT to the compost, implying that our samples had adsorbent surfaces that were never completely saturated by TBT.

Effect of pH on the adsorption of TBT onto compost

TBT in seawater is an ionic species containing a permanent charge in addition to hydrophobic groups. If the energy of adsorption is related to ionic interactions between TBT and compost, then the pH is expected to be one of the key experimental variables.

As illustrated in Fig. 4, the best fit for the isotherms was obtained by means of a non-linear regression adapted for the Freundlich equation. Clearly, sorption isotherms of TBT to compost at 25 °C were strongly pH dependent. Table 1 and Fig. 5 show the Freundlich adsorption coefficients obtained for each isotherm determined within the pH range 4.7 to 7.8, together with the respective r^2 for the non-linear regression. The results show a maximum adsorption at pH 6.7 with decreasing adsorption at lower or higher pH values. This is in good agreement with the general trends documented for organotin adsorption onto sediment particles[11] and mineral surfaces,[12] as well as for the association of triorganotin compounds with dissolved humic acids.[13] At the maximum adsorption (pH 6.7), K_f reached a value of 15.4×10^3 ml g^{-1}.

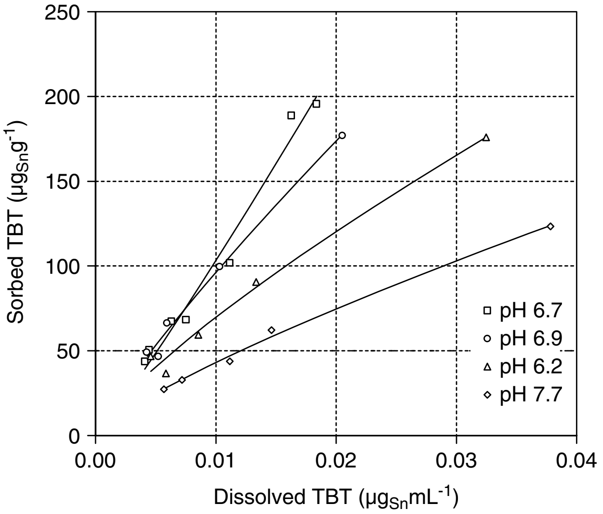

Figure 4. Adsorption isotherms of TBT on compost at pH values of 6.2, 6.7, 6.9 and 7.7. Error bars represent SE.

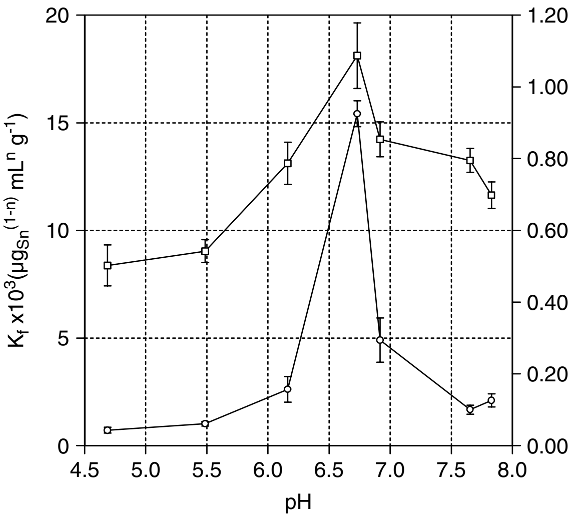

Figure 5. Variations of the Freundlich adsorption coefficients K_f (○) and n (□) for the adsorption of TBT to compost as a function of pH at a temperature of 25 °C. Error bars represent SE.

Table 1. The effect of pH on the adsorption of TBT onto compost at 25 °C

pH	K_f[a] (μg$^{(1-n)}$ ml^n g^{-1})	n[a]	r^2
4.7	717 ± 130	0.50 ± 0.06	0.9783
5.5	1012 ± 108	0.54 ± 0.03	0.9889
6.2[b]	2611 ± 592	0.79 ± 0.06	0.9861
6.7[b]	15 420 ± 600	1.09 ± 0.09	0.9768
6.9[b]	4898 ± 1024	0.85 ± 0.05	0.9914
7.7[b]	1672 ± 208	0.79 ± 0.03	0.9954
7.8	2099 ± 302	0.70 ± 0.04	0.9722

[a] Value ± SE.
[b] Respective adsorption isotherm plotted on Fig. 4.

These findings may be rationalized by considering the simultaneous action of two opposing effects influencing the sorption process: with increasing pH, the concentration of TBT$^+$ cations decreases through the formation of neutral TBTOH, which has a lower tendency to sorb, but the concentration of surface sites on the compost structure exhibiting negative charge increases (e.g. by formation of carboxylate and phenolate groups).

In aqueous solution, organotin compounds undergo pH-dependent hydrolysis. Cations are formed at pH < pK_a, and these monovalent organometallic cations behave as weak acids when hydrated. The pH-dependent dissociation reactions of TBT can be described formally as

$$\text{TBTCl} \rightleftharpoons \text{TBT}^+ + \text{Cl}^- \tag{2}$$

$$\text{H}_2\text{O} + \text{TBT}^+ \rightleftharpoons \text{TBT(OH)} + \text{H}^+ \tag{3}$$

Weidenhaupt *et al.*[12] reported a hydrolysis constant ($\mathrm{p}K_\mathrm{a}$) for TBT of 6.25. Hence, the dominant TBT species at $\mathrm{pH} < \mathrm{p}K_\mathrm{a} = 6.25$ is the cation, whereas at $\mathrm{pH} > 6.25$ the TBT is present as neutral TBTOH. Based on this $\mathrm{p}K_\mathrm{a}$ value, 26% of the TBT is cationic at pH 6.7. Besides pH, the dissociation reactions are also influenced by temperature, ionic composition and strength.

The positive monovalent TBT^+ ion is a Lewis acid, and tends to interact more easily with nitrogen and oxygen donors, particularly negatively charged ones, on the compost structure. Therefore, at low pH, the TBT species are mainly TBT^+ ions and the compost surface possesses less negative charge, if $\mathrm{pH} < \mathrm{pH}_\mathrm{zpc}$ (zero point of charge); hence, the adsorption of TBT^+ will be weakened as pH is lowered. When pH is increased, the OH^- ion becomes more abundant, the surface of the compost holds more negative charge, $\mathrm{pH} > \mathrm{pH}_\mathrm{zpc}$, and the adsorption of TBT^+ is increased until a point is reached (*c.* pH 6.7) at which TBT^+ initiates hydrolysis to form neutral complexes. Under these conditions electrostatic attraction is not the driving force and the key factor is the hydrophobic character of these compounds. Because this force is not so effective as electrostatic attraction the adsorption of TBT is reduced, although the negative charge of the solid phase continues to increase.

Figure 5 also shows a slight increase in the K_f at a pH above 7.7, which has not been reported to occur in sediments. This is probably a result of a change in the organic structure of the compost occurring at this higher pH. The slightly basic environment possibly leads to an unfolding of the compost aggregate structure, thus increasing the number of sites that could associate with TBT by hydrophobic interactions. This phenomenon could be a result of the deprotonation of weak acid functional groups (e.g. phenols) within the compost structure, which could bring about disruption of hydrogen bonding to open up previously aggregated humic structures. In fact, an eventual further increase in pH does result in the actual dissolution of most of the humic substances and leads to nearly complete solubilization of compost organic matter.

The n sorption coefficients (Table 1) indicate isotherm non-linearity ($n < 1$) and concentration-dependent TBT solid–solution distribution in some isotherms. Figure 5 also shows that the variation of n with pH follows a similar trend. Isotherms reach linearity ($n = 1$) at pH 6.7 but lose their linearity ($n < 1$) at higher and lower pH values. This variation demands a cautious interpretation of K_f values, since the units of the latter depend on n. The concentration-dependent sorption coefficients over the entire experimental TBT concentration range used (data not shown), calculated from K_f and n values as described by Chen *et al.*,[14] facilitate comparison between isotherms due to non-linearity.

Adsorption of organotins as a function of carbon chain length

The adsorption isotherms of various tri-substituted organotins (TOT^+) onto compost could give an indication of the effect that carbon chain length has on the adsorption process.

The hydrophobicity of TOT^+ increases with increasing carbon chain length within the series of monovalent, alkyl-substituted homologues, from TPrT to TPeT. In fact, the octanol/water partition coefficients K_ow of the neutral TOTOH species follow the order $\mathrm{TPrT} < \mathrm{TBT} < \mathrm{TPeT}$ with corresponding values for their $\log K_\mathrm{ow}$ being 2.1, 4.1, and 5.7 respectively.[12,15] The hydrophobic interaction between the neutral organotins in solution and the organic matter in compost is expected to increase with increasing hydrophobicity of the adsorbate, resulting in an increase in K_f along the series.

The Freundlich adsorption isotherm obtained for TPrT (mass of tin) on compost ($K_\mathrm{f} = 612 \pm 63\ \mu\mathrm{g}^{(1-n)}\ \mathrm{ml}^n\ \mathrm{g}^{-1}$ and $n = 0.88 \pm 0.06$) at a temperature of 25.0 °C and pH 7.8, shows a significantly lower affinity for compost with respect to TBT (mass of tin) ($K_\mathrm{f} = 2099 \pm 302\ \mu\mathrm{g}^{(1-n)}\ \mathrm{ml}^n\ \mathrm{g}^{-1}$) under the same experimental conditions. Since the large initial concentration of TPeT in solution required to be able to obtain an equilibrium concentration exceeded the low solubility of TPeT in reconstituted seawater, adsorption coefficients for TPeT could not be quantified experimentally. Nevertheless, since all the TPeT in solution prior to equilibration ($2000\ \mu\mathrm{g\ l}^{-1}$ as tin) was adsorbed by the same mass of compost used in the experiments with TPrT and TBT, this meant that the adsorption of TPeT was greater than that of TBT. Therefore, the adsorption of these three tri-substituted alkyl organotins onto compost followed the expected trend $\mathrm{TPrT} < \mathrm{TBT} < \mathrm{TPeT}$.

Modelling the processing of dockyard wastes using MSW compost

The adsorption characteristics of compost suggest that the substance, when washed free of soluble organic matter, could serve as a good adsorbent for TBT from dockyard wastewaters. It will be shown that treatment of TBT-contaminated wastewaters using compost could reduce the contamination level of the wastewater to a value that allows disposal to the sea without causing significant environmental impact.

The adsorption process for TBT on compost can be represented as

$$\mathrm{TBT}_\mathrm{aq} + \mathrm{C} \rightleftharpoons \mathrm{TBT}_\mathrm{c} \tag{4}$$

where C represents solid compost, TBT_aq the dissolved form of TBT, and TBT_c the sorbed material on compost. This equilibrium can be expressed in terms of the Freundlich equation as

$$K_\mathrm{f} = \frac{M_{\mathrm{TBT}_\mathrm{c}}}{W_\mathrm{c}} \left(\frac{V_\mathrm{aq}}{M_{\mathrm{TBT}_\mathrm{aq}}} \right)^n \tag{5}$$

where $M_{\mathrm{TBT_c}}$ (μg) is the mass of TBT adsorbed onto a mass W_c (g) of compost and $M_{\mathrm{TBT_{aq}}}$ (μg) is the mass of TBT in a volume V_{aq} (ml) of water at equilibrium. K_f and n are the Freundlich isotherm constants. If $M^0_{\mathrm{TBT_{aq}}}$ is taken to represent the initial mass of TBT present in the water prior to equilibration with the compost, then

$$M_{\mathrm{TBT_c}} = M^0_{\mathrm{TBT_{aq}}} - M_{\mathrm{TBT_{aq}}} \tag{6}$$

and since $M^0_{\mathrm{TBT_{aq}}} >> M_{\mathrm{TBT_{aq}}}$, Eqn (5) can be rewritten as

$$K_f = \frac{M^0_{\mathrm{TBT_{aq}}}}{W_c}\left(\frac{V_{aq}}{M_{\mathrm{TBT_{aq}}}}\right)^n \tag{7}$$

It is estimated[6] that, at the Malta dry docks, the high-pressure hosing of ships' hulls covered with TBT-containing antifouling paints in preparation for repainting generates about 600 t of wastewater per year, which delivers about 0.9 t of TBT into the marine environment, both in the dissolved and in solid form as dislodged TBT-containing particles. The solubility of TBT in water is often estimated at approximately 4 mg l^{-1}, but measurements of TBT concentrations very rarely exceed 1 mg l^{-1}.[2] Using Eqn (7) and considering an approximate maximum value for the adsorption coefficient $K_f = 1.5 \times 10^4$ ml g^{-1} and $n = 1$ (at pH 6.7), a mass of 20×10^6 kg of compost would be required theoretically to reduce the concentration of TBT in 600 t of wastewater exposed to washed compost, in a single batch operation, from 1 mg l^{-1} to 2 ng l^{-1} (the EQS).[5] For a multiple batch operation process using a given volume of wastewater V_{aq} and x compost batches each of equal weight W_c, it can be shown that

$$(M_{\mathrm{TBT_{aq}}})^n = M^0_{\mathrm{TBT_{aq}}}\left(\frac{(V_{aq})^n}{W_c K_f}\right)^x \tag{8}$$

Therefore, by substituting for $x = 10$ in Eqn (8), the mass of compost required in each batch to achieve overall reduction in aqueous TBT concentration to 2 ng l^{-1} is 148 kg so that the total mass of compost (xW_c) is 1485 kg.

In practice, achieving values for $x > 1$ is possible by passing wastewater through a column of compost where multiple equilibrations can be achieved along its length. The column can be considered as being divided into a number of 'theoretical plates', each one representing a single equilibrium step. Thus, the more theoretical plates, the greater the number of equilibrium steps x. The value for x for such a process is related to the flow rate of wastewater through the column of compost.

Like other adsorbents, the efficiency of compost is pH dependent, and a compost filter would have an efficiency that is variable but controllable. In practice, some wastewaters are derived essentially from seawater at a pH of approximately 8.2, whereas actual wash-down of a ship is usually carried out using fresh water at a pH that may be as low as 6. Many wastewaters are an unpredictable and constantly varying mixture of seawater and fresh water, so pH effluent control might be required to obtain maximum efficiency from compost.

The effective outcome of any pollution control by most of adsorption mechanisms is to transfer the pollutant from the contaminated matrix onto a sorbent, thus potentially creating a secondary problem of solid waste disposal. Transfer of the spent compost to soil has ecotoxicological implications, since such an action could give rise to organotin pollution of both aquatic and terrestrial systems. However, degradation of TBT into non-toxic products, which is likely to be accelerated by the presence of micro-organisms in soil and compounds derived from compost itself, might make this an interesting disposal prospect. Clearly, this aspect will still need to be investigated fully by field studies using soil–spent compost mixtures and would be the subject of further studies.

CONCLUSIONS

Although quantitative prediction of TBT sorption to a complex matrix like compost is very difficult, mainly due to the heterogeneity of the compost organic structure and our rather limited knowledge of organotin interactions with natural organic matter, the high organic content of MSW compost and its porous physical structure led us to anticipate that the material would serve as a good adsorbent for TBT in seawater. Not only have the current results confirmed the possibility of using compost as an adsorbent for the effective removal of TBT in solution, but they have also provided a deeper insight into the chemical processes involved in the partitioning of TBT between the solid and liquid phases.

The experimental determination of the kinetics of the sorption process, and that of isotherms of both adsorption and desorption, has shown that adsorption of TBT onto compost is a fast and reversible process, with a steady-state equilibrium being achieved within 8 h. This means that TBT, compost and water may easily approach equilibrium in well-mixed environments. The effect on the sorption process of pH and carbon chain length of the organotin compounds supports the hypothesis that both hydrophobic interactions and ionic complexation play a role in the partitioning process. The pH of the medium changes the speciation of TBT and also affects the surface charge of the solid phase. At a pH of about 6.7 the adsorption capacity is at a maximum, and at higher pH values the hydrophobic interaction becomes the driving force of adsorption, when butyltin compounds exist mainly as neutral hydroxides in the water phase. The adsorptive capacity also increases with increasing carbon chain length, and we have established that it follows the trend TPrT < TBT < TPeT.

The results dealing with the interaction of TBT with soluble organic matter have confirmed that DOM derived from compost is capable of complexing with organotin compounds in solution, thus favouring their retention in the aqueous phase. This phenomenon also reveals a limitation of the boroethylation technique for organotins in matrices rich in soluble organic matter.

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