APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 7, 623–633 (1993)

A study of the partitioning and sorptive behaviour of butyltins in the aquatic environment

P H Dowson , J M Bubb and J N Lester*
Environmental and Water Resource Engineering Section, Department of Civil Engineering, Imperial College of Science, Technology and Medicine, London SW7 2BU, UK

This study was designed to investigate the partitioning and sorptive behaviour of tributyltin (TBT), and its degradation products dibutyltin (DBT) and monobutyltin (MBT), in the aquatic environment. Factorial experiments were undertaken to determine the importance of pH and particulate matter concentration in the sorption of butyltin compounds to solid phases. Results indicate that in freshwaters MBT, and to a lesser extent TBT, will be partitioned towards the particulate phase, whereas DBT exhibits a 50:50 partitioning between particulate and solution phases. In estuarine waters, whilst MBT will almost exclusively sorb on to particulates, TBT will be predominantly in the solid-phase fractions but 10–30% may remain in solution. DBT, in contrast, is solubilized in estuarine waters. A more detailed investigation of TBT sorption and particulate matter concentration was undertaken using adsorption isotherms on different sediment types. The results from batch isotherm tests plotted according to the Freundlich adsorption model revealed that TBT adsorption varied with sediment type, increasing in the order sandy-silt < silty-sand < silty-clay. TBT sorption was found to be reversible, indicating that contaminated sediments may release TBT to overlying waters following sediment disturbance. Interstitial water partitioning studies indicate that TBT predominates in the particulate phase with partition coefficients for TBT higher than for DBT and MBT. The TBT partition coefficient in interstitial waters appears to be related to total organic carbon loadings.

Keywords: Antifouling paints, tributyltin (TBT), dibutyltin (DBT), monobutyltin (MBT), partitioning, sorption, desorption, isotherm, Environmental Quality Target, sediment, dredging

INTRODUCTION

The fate of xenobiotic compounds in the aquatic environment is closely linked to their partitioning between aqueous media and particulate matter. Organic pollutants can either be sorbed on to particulate matter or exist in solution. The two major phenomena that affect the distribution of metal species between dissolved and particulate phases are adsorption on to particulate matter and flocculation in which the species are trapped by newly formed particulate matter. Because the two mechanisms are not easily distinguishable, the term 'sorption' is usually used to describe the cumulative effect of both processes. Sorption is considered one of the most important processes responsible for reducing the concentration and toxicity of butyltin compounds in the water column and is also the principal pathway for tributyltin (TBT) accumulation in sediments.[1] Soluble pollutants are more mobile and available than particulate-associated pollutants and are consequently more likely to undergo bioaccumulation.[2] The determination of the sorptive behaviour of TBT is therefore necessary in order to understand its fate in freshwater and estuarine environments.[3]

Several researchers have shown that organotin compounds sorb to suspended particulate matter and to bottom sediment,[4–7] but few investigations have compared the sorptive behaviour of TBT under freshwater and estuarine conditions.[8] Association of TBT with suspended particulates is dependent on particulate matter concentration, salinity and the presence of natural organic chelating materials,[8–11] so distinct changes in the partitioning behaviour should be apparent between fresh and saline environments.

Experiments with unfiltered seawater from San Diego Bay, USA, containing low suspended particulate matter concentrations, showed that 6–11% of the added TBT sorbed to the particulate

---

[*] Author to whom correspondence should be addressed.

0268-2605/93/080623-11 $10.50

Received 4 June 1993
Accepted 27 July 1993

fraction.[4] Seligman and co-workers[12] found that the partition coefficient (K_p) values determined for TBT associated with suspended particulates approach 3×10^3 at concentrations of 5.8–6.7 mg dm^{-3} (as Sn); this agrees favourably with the work in Canadian waters.[13] Solid-phase partitioning has also been shown to increase in waters adjacent to yacht repair facilities,[12] where 22% of TBT was sorbed to suspended particulates, producing K_p values in the order of 4×10^3. This degree of particulate enrichment was attributed to suspended particulate paint. This implies that the partitioning and fate of TBT are also dependent upon geographical considerations, in addition to physicochemical parameters dictated by water chemistry.

Two types of experimental design have been utilized in this present study to elucidate the equilibrium and sorptive behaviour of butyltin compounds (including TBT) undergoing sediment–water transfer processes. Factorial experiments were employed to investigate the effect of pH and particulate matter upon the transfer of butyltin compounds from the soluble to the particulate phase in both freshwater and estuarine environments. In the latter case the influence of salinity was also assessed. Batch isotherm experiments were subsequently undertaken to elucidate the importance of particulate matter concentration and sediment type in TBT sorption. Desorption experiments provided information on the ability of sediments to release sorbed contaminants back to the water column following sediment disturbances due to dredging operations or other forms of physical agitation. Such remobilization of butyltins has important implications for biological uptake. Likewise, interstitial water/sediment partitioning studies provide information on the potential for butyltin uptake by benthic organisms.

MATERIALS AND METHODS

Factorial experiments

A factorial experimental design enables the simultaneous investigation of the individual and synergistic effects that a number of physicochemical parameters exert on the removal of butyltin compounds from the solution phase. The advantages and disadvantages of factorial experiments have been summarized[14] and their application to the study of methyltin sorption has been assessed.[6] Due to the complexity of environmental processes and interactions during river transport, this design is most appropriate. The use of the factorial design is, however, slightly limiting, in that it only reports data for the high and low points of each parameter range; it is therefore used as an exploratory tool to assess the significance of both single and multiple parameters which affect the removal of butyltin compounds at any confidence level.[11] Associations between these parameters can subsequently be investigated further using detailed batch isotherm studies.

The factorial experiments focused on three parameters which have been shown to be important in determining the partitioning of butyltins in fresh and estuarine waters. The pH of water determines the association and dissociation of functional groups (e.g. carboxyl groups) which affect the degree of adsorbance and solubility. Salinity was used as a reference scale to define estuarine processes, whilst an artificial sorbent, in the form of hydrous iron oxide (BDH Ltd, Dagenham, UK), was utilized to represent suspended particulate matter. Hydrous iron oxide is a major constituent of most riverine sediments and is an important binding and complexing agent. Lee[15] proposed that the hydrous metal oxides of iron and manganese are the principal control mechanisms for a number of heavy metals in sediments. The common occurrence of these oxides as coatings on particulate matter allows them to exert a chemical activity far in excess of their concentrations. Various concentrations of iron oxide were used in this present study as it is known to be a very important scavenger for heavy metals.[16]

Partitioning of butyltin compounds in freshwater river systems

Two parameters were used to investigate the partitioning of butyltin compounds in freshwater river systems: a pH range (6–8) representative of freshwater areas and a particulate matter concentration ranging from 10 to 1000 mg dm^{-3}. A large volume of freshwater was collected from the River Ore in Suffolk, UK, which from previous surveys has been found to be uncontaminated with organotin compounds.[17] Table 1 describes the average chemical parameters at this site and at Orford Haven (a saline water site) during the week of the sampling date. The water was filtered through 0.45 μm Whatman cellulose nitrate filters

(BDH Chemicals Ltd, Dagenham, UK) to remove all suspended matter. Water volumes of 200 cm^3 were placed in amber glass bottles (Fisons Ltd, Loughborough, UK) adjusted to the various pH ranges under study and loaded with hydrous iron oxide at the required concentrations. The pH was determined with an Orion 701A pH meter and Russell CE 72 combination pH electrode. Acidic solutions were obtained by adding 0.1 M hydrochloric acid and alkaline solutions by adding 0.1 M sodium carbonate.[11] Solutions were subsequently shaken for 12 h at 12 °C to equilibrate and the pH was rechecked and adjusted if necessary, although very little change in pH was found to occur over this 12 h equilibration period.

Butyltin chloride spikes (181 ng dm^{-3} (as Sn) for TBT, 97 ng dm^{-3} for DBT and 209 ng dm^{-3} for MBT) were subsequently introduced and the pH rechecked. The samples were shaken for a further 12 h. Butyltins have been shown to sorb rapidly to sediment from aqueous solution[5] so a 12 h period was considered sufficient for equilibrium attainment. Each sample was filtered through 0.45 μm nucleopore polycarbonate filters (Millipore Ltd, Watford, UK) and the filtrate collected in amber glass bottles and analysed. The adsorption of butyltin compounds on to polycarbonate filters has been found to be negligible.[9] One set of seven factorial experiments was performed in duplicate for TBT, DBT and MBT in the freshwater partitioning experiments, along with experimental blanks for each butyltin compound.

Table 1 Average chemical parameters for water utilized in factorial experiments

Parameter[a]	Snape Quay (freshwater site 1)	Orford Haven (saline site 2)
pH	7.95	7.93
Temperature (°C)	14.0	14.0
Conductivity (μS cm^1)	1825	48990
BOD (mg dm^3)	2.29	1.19
Chloride (mg dm^3)	372	19657
Ammonia (mg dm^3)	0.11	0.034
Salinity (ppt)	0.67	35.6
DO (field %)	94	92
DOC (mg C dm^3)	5.26	1.41

[a] Abbreviations: BOD, biological oxygen demand; DO, dissolved oxygen; DOC, dissolved organic carbon.

Table 2 Physical and chemical properties of sediments used for batch isotherm adsorption studies

Site and grid reference	Sed. composition (%)					
	Sand	Silt	Clay	TOC[a] (%)	pH	S^{2-} (mg kg^{-1})
Trowse Mill (243 068)	62.8	37.2	0	1.4	7.6	n.d.[b]
Rockland (340 053)	39.7	60.3	0	12.5	7.2	180
Cantley (384 033)	15.0	84.0	1.0	6.9	7.8	108

[a] TOC, total organic carbon. [b] n.d., not detectable.

TBT adsorption isotherm experiments

The sorption of tributyltin chloride by selected East Anglian sediments was studied using a batch isotherm technique similar to the concentration difference method.[8, 18] Solutions were analysed for TBT, DBT and MBT, to assure that degradation did not occur during the course of the experiments.

Freshwater sediments with varying sand, silt and clay composition were collected from different areas of the River Yare in Norfolk, UK. Table 2 describes the physical and chemical properties of the sediments. Water from the River Yare, uncontaminated by butyltins, was filtered through 0.45 μm cellulose nitrate filters to remove all suspended matter in the water and was stored in the dark at 12 °C. A tributyltin chloride spike was made up from a 10 mg dm^{-3} stock solution and added to filtered water to achieve a water column concentration of 3.6 μg dm^{-3} (as Sn). Water volumes of 200 cm^3 (containing 0.72 μg TBT as Sn) were placed in Teflon centrifuge bottles (BDH Ltd, Dagenham, UK). For each isotherm experiment, five different weighed amounts of sediment were used, ranging from 0 to 3 g dry weight equivalent. The bottles were shaken for 12 h at 12 °C in the dark. A sixth tube without sediment was also run with each batch to account for any TBT adsorption losses to the tube walls. After the 12 h equilibration period the tubes were centrifuged at 2000 g on an MSE-Hi-Spin centrifuge for 10 min. The supernatant was filtered through 0.45 μm nucleopore polycarbonate filters and analysed for TBT and its degradation products. Aqueous equilibrium concentrations of TBT were calculated and sorbed sediment concentrations were found by difference relative to TBT available (tube 6).[8]

Partitioning of butyltin compounds in estuarine river systems

Salinity measurements in this study were determined by titrating saline water with silver nitrate solution to obtain the chlorinity value of the water in parts per thousand (ppt). The salinity was then obtained by multiplying the chlorinity by 1.807 which gives the equivalent salinity value in parts per thousand.[19]

A large volume of estuarine water was collected from the saline reach of the River Ore at Orford Haven (this was at the top of the salinity range, i.e. 35 parts per thousand) and filtered through 0.45 μm filters to remove suspended matter. Dilutions of saline water were made with the freshwater obtained further upstream to give the salinity values of 5, 17.5 and 35 ppt. These solutions were loaded with hydrous iron oxide at the required concentrations (10 and 1000 mg dm^{-3}), equilibrated for 12 h at 12 °C, spiked with butyltin compounds and shaken for a further 12 h. Samples were filtered through 0.45 μm nucleopore polycarbonate filters and analysed for butyltin compounds. For the estuarine experiments, 12 factorial experiments were undertaken in duplicate for the three butyltin compounds (TBT, DBT and MBT), along with experimental blanks.

Background losses and decomposition

Adsorption of butyltin compounds to container walls was measured on random sample bottles by first rinsing the test bottles with 25 cm^3 of distilled water and shaking for 12 h with 100 cm^3 of 10% (v/v) Aristar nitric acid/deionized water.[11] The leaching solutions were analysed for butyltin compounds. Sorptive losses to container walls were less than 7% for all compounds. Minor degradation reactions for butyltin compounds occurred during the factorial experiments. MBT and DBT (less than 5% in both cases) occurred in TBT solutions; MBT (less than 4%) occurred in DBT solutions. Adsorptive losses of TBT to container walls in batch isotherm experiments were less than 3%. No degradation appeared to occur during these experiments.

Investigation into butyltin desorption from contaminated sediments

A number of contaminated sediments were utilized in the desorption experiments to determine if sediments act as permanent sinks for contaminants or if sediment disturbances can release butyltins back into the water column. Sediments, containing between 59 and 700 ng g^{-1} TBT (per 20 g wet wt), were collected from contaminated sites[17] and were mixed with 200 cm^3 of overlying water (previously identified as being uncontaminated[17]) in Teflon centrifuge bottles which were subsequently shaken for 12 h. All water was filtered through 0.45 μm cellulose nitrate filters before use, to remove suspended matter. Samples were stored in the dark at 12 °C. Each experiment was undertaken in triplicate using the same shaking and filtering procedure as described previously. Solutions were analysed for TBT, DBT and MBT and percentage desorption for each compound was calculated.

Butyltin partitioning between sediment and interstitial water

Partitioning studies were undertaken to give an insight into the distribution of butyltin compounds between solid and interstitial water-dissolved phases in the sediment compartment. Sediment samples were obtained from a number of East Anglian rivers and estuaries. The samples were subdivided and one set was extracted to determine total butyltin concentrations in the sediment.[20] The other subsamples were centrifuged at 6000g (MSE Hi-Spin centrifuge) at 20 °C for 20 min to separate interstitial water from the sediment. The centrifugate was filtered through 0.45 μm nucleopore polycarbonate filters an analysed for butyltin compounds.

Butyltin analysis

Organotins were speciated using the 'purge and trap' boiling-point separation method described by Dowson *et al.*[20] Organotin hydrides were cryogenically trapped using liquid nitrogen and separated on a simple chromatographic column packed with Chromosorb G.HP 80/100 mesh, coated with 10% OV-101. Hydride species were sequentially desorbed in relation to their specific boiling points after heating of the column (−196 to 200 °C). The hydrides were carried by a helium flow (140 $cm^3 min^{-1}$) with oxygen and hydrogen being introduced into the quartz cell as additive gases with respective flows of 20 $cm^3 min^{-1}$ and 500 $cm^3 min^{-1}$. Detection was performed by a Perkin–Elmer 1100 B atomic absorption spectrometer operating at a wavelength of 224.6 nm, using an electrothermally heated (900 °C) quartz

Table 3 Mean percentage removal of butyltin compounds from freshwaters under different environmental conditions

Experiment	PM (mg dm^{-3})	pH	Butyltin Removal (%) TBT	DBT	MBT
1	1000	8	69.5	66.5	100
2	10	8	68	34	92.5
3	1000	6	100	62	100
4	10	6	64.5	40.5	89
5	100	7	70.5	50.5	96.5
6	100	7	73	38	100
7	100	7	71	38	100
Mean value of centre points			71.5	42.2	98.8
Standard deviation of centre points			±3.6	±8.9	±2.9

PM, Particulate matter concentration.

furnace and a tin EDL lamp (Perkin–Elmer Ltd). Detection limits in water samples utilizing the above analytical system were approximately 3 ng dm^{-3} for TBT, 1 ng dm^{-3} for DBT and MBT. Detection limits in sediments were 3 ng g^{-1} for TBT, 1 ng g^{-1} for DBT and MBT.

RESULTS

Influence of pH and particulate matter concentrations on the partitioning behaviour of butyltin compounds

In factorial experiments when there are n parameters to consider, 2^n experiments are necessary to measure the effects of all combinations of parameters when testing at high and low levels. The $n+1$ centre point experiments (i.e. experiments 5–7 in the freshwater experiments listed in Table 3 and experiments 9–12 in the estuarine experiments listed in Table 5) detect any deviation from linearity in the experimental response and allow random error determination. Standard deviations, calculated from these centre points, display the degree of experimental variability.

Freshwater

The percentage removal of TBT, DBT and MBT from aqueous to the sediment phase under freshwater conditions at different pH values and particulate matter concentrations is given in Table 3. The results indicate different patterns of sorption for each butyltin compound as controlled by the physicochemical environment, but in general terms TBT exhibited a tendency toward solid-phase partitioning, accounting for between 65 and 100% of the TBT available, whilst DBT displayed a much lower level of sorption (34–67%) and MBT was almost completely sorbed to particulate matter in all experiments (89–100%).

The partitioning of TBT in freshwater samples was dictated by both pH and particulate matter concentration (Table 3). At low pH (6.0), TBT sorption was enhanced by increased suspended matter; increasing from 65 to 100% as the total suspended solid concentration increased from 10 to 1000 mg dm^{-3}. At higher water pH, TBT removal was independent of particulate matter concentration. Sorption of DBT appeared to be influenced more by particulate matter concentration than by water pH. Removal of DBT was about 40% at low particulate matter concentrations (10 mg dm^{-3}) but increased to approx. 62% at 1000 mg dm^{-3} suspended matter, irrespective of pH. MBT revealed a very strong affinity for hydrous iron oxide which was independent of pH. Sorption of MBT was enhanced by increased suspended matter, increasing from 90 to 100% as the total suspended solid concentration increased from 10 to 1000 mg dm^{-3} respectively, but generally MBT displayed a strong affinity for solid-phase partitioning at all particulate matter concentrations between pH 6 and pH 8.

Batch isotherm experiments were subsequently undertaken to elucidate further the behaviour of butyltin sorption by the use of natural particulate matter rather than a model substrate in freshwater sediments. In order to compare the different adsorptive capacities of the sediment types under study and to allow a direct comparison of TBT adsorptive properties with other compounds, the Freundlich adsorption model was used. The aqueous and sorbed equilibrium data from each experiment are displayed in Table 4. Aqueous and sorbed equilibrium data were then logged and plotted by linear regression according to the linearized form of the Freundlich equation:

$$\log q_e = \log K + 1/n \log C_e \qquad [1]$$

where n and K are Freundlich constants; q_e is the amount of TBT adsorbed per unit mass of sediment (μg g^{-1}) and C_e is the aqueous residual concentration of TBT (mg dm^{-3}).

Freundlich adsorption isotherms for TBT on sandy-silt, silty-sand and silty-clay sediments are illustrated in Fig. 1. All experiments produced linear isotherms. The isotherms illustrate that the

Table 4 TBT sorption isotherm data for freshwater sediments[a]

Sediment type	Suspended dry wt (g)	Dissolved TBT (μg)	Sorbed TBT (μg)	Sorbed TBT (%)	K_p
Silty-clay (Cantley)	0.319	0.209 ± 0.018	0.511 ± 0.018	70.97 ± 1.4	1464 ± 136
	0.638	0.112 ± 0.018	0.606 ± 0.018	84.17 ± 2.0	1677 ± 265
	0.957	0.047 ± 0.005	0.671 ± 0.005	93.19 ± 0.9	2929 ± 414
	1.276	0.022 ± 0.005	0.698 ± 0.005	96.94 ± 0.8	4973 ± 1643
	1.595	0.016 ± 0.002	0.704 ± 0.002	97.78 ± 0.5	4900 ± 1765
Silty-sand (Rockland)	0.370	0.251 ± 0.004	0.469 ± 0.004	65.14 ± 2.2	960 ± 97
	0.740	0.136 ± 0.005	0.584 ± 0.005	81.11 ± 0.77	1096 ± 57
	1.110	0.060 ± 0.002	0.660 ± 0.002	91.67 ± 1.25	1863 ± 335
	1.480	0.041 ± 0.001	0.679 ± 0.001	94.30 ± 1.30	2195 ± 605
	1.850	0.029 ± 0.001	0.691 ± 0.001	95.97 ± 0.96	2493 ± 760
Sandy-silt (Trowse)	0.626	0.313 ± 0.007	0.405 ± 0.007	56.25 ± 1.34	400 ± 5
	1.252	0.197 ± 0.008	0.523 ± 0.008	72.69 ± 1.06	398 ± 40
	1.878	0.104 ± 0.007	0.616 ± 0.007	85.56 ± 0.77	607 ± 55
	2.504	0.057 ± 0.005	0.663 ± 0.005	92.08 ± 0.64	883 ± 76
	3.130	0.046 ± 0.003	0.674 ± 0.003	93.57 ± 0.63	896 ± 75

[a] All analyses were performed in triplicate.

finer-grained silty-clay sediment exhibited a larger capacity for TBT adsorption than silty-sands. In all three cases an increase in particulate matter concentration led to an increase in TBT removal. However, the percentage TBT removal from the dissolved phase at equivalent concentrations is considerably lower in the isotherm experiments than in both the freshwater and estuarine factorial studies conducted with iron oxide as a model substrate.

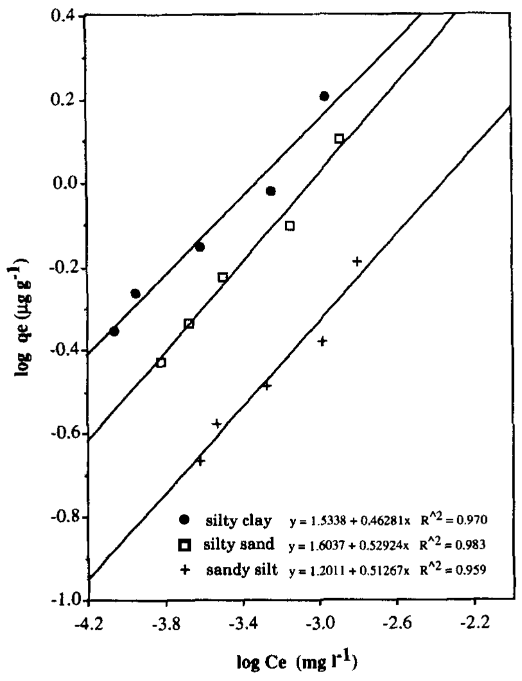

Figure 1 TBT adsorption isotherms.

Estuarine waters

The relationships between pH, particulate matter concentration and salinity and their respective influences on butyltin partitioning are illustrated in Table 5 for a simulated estuarine river system environment. The estuarine experiments revealed different patterns of adsorption for each butyltin compound. Removal ranged from 67 to 100% for TBT and 15 to 47% for DBT, whilst MBT was almost completely removed in all experiments (71–100%).

The partitioning experiments undertaken in estuarine samples revealed that the sorption of TBT was dictated, to some degree, by salinity but not by pH. An increase in salinity caused a slight increase in TBT adsorption (>16%) in experiments where pH was low (6.0), irrespective of particulate matter concentration. However, at high pH (8.0), no significant increase in adsorption occurred as particulate matter concentration increased. Dibutyltin, on the other hand, appeared to be influenced more by pH than by either particulate matter concentration or salinity, with the greatest adsorption (47%) occurring at a lower pH (6.0) and high salinity. An increase in particulate matter concentration at pH 6.0 resulted in a 13% increase in DBT sorption. Monobutyltin displayed a very strong affinity for particulate matter which was independent

Table 5 Mean percentage removal of butyltin compounds from estuarine waters under different environmental conditions

Experiment	pH	Particulate matter concn (mg dm^{-3})	Salinity (ppt)	Butylin removal (%)		
				TBT	DBT	MBT
1	8	1000	35	72	20	100
2	8	1000	5	75	25	100
3	8	10	35	80	15	100
4	8	10	5	76	18	71
5	6	1000	35	100	47	100
6	6	1000	5	84	35	100
7	6	10	35	89	34	100
8	6	10	5	67	38	100
9	7	100	17.5	80	25	100
10	7	100	17.5	76	29	100
11	7	100	17.5	70	32	100
12	7	100	17.5	83	35	100
Mean value of centre points				77.3	30.3	97.8
Standard deviation of centre points				±5.6	±4.3	±8.4

of pH and salinity. In all but one experiment, MBT was completely sorbed on to the particulates regardless of the suspended matter concentration or any other factorial combinations. The only experiment to display <100% sorption of MBT was at high pH, low particulate matter concentration and low salinity (experiment 4).

Butyltin desorption from contaminated sediments

Table 6 illustrates the total butyltin concentration (μg) in 20 g of sediment and the resulting percentage butyltin desorption to the overlying water after a 12 h shaking period. Results indicate desorption of butyltins, to varying degrees, in all five contaminated sediments. Desorption of DBT predominated at three out of five sites, accounting for between 1.4 and 6% of the DBT available, whilst MBT desorption was most predominant at the remaining two sites, accounting for between 0.8 and 2.5%. The general order of desorption was DBT>MBT>TBT, indicating that TBT is most strongly bound and DBT the least strongly bound to sediments. Although this only amounts to a TBT release of <1% from contaminated sediments, it resulted in TBT water concentrations between 30 and 170 ng dm^{-3}, which may still be significant.

Butyltin partitioning between sediment and interstitial water

Butyltin partition coefficients (K_p) between sediment and interstitial water were calculated from Eqn [2]. Partition coefficients are displayed in Table 7 along with the total organic carbon and percentage grain size distribution values. All sediment K_p values were derived from dry weight concentrations.

Table 6 Availability and % desorption of butyltin compounds in sediment

Location[a]	Available butyltin in sediment (μg)				Butyltin desorption (%)		
	Total butyltin	TBT	DBT	MBT	TBT	DBT	MBT
Robertson's Boatyard (F)	5.90	2.30	3.00	0.62	0.57	1.30	2.43
Tidemill Marina (F)	1.90	1.01	0.62	0.27	0.85	6.08	0.81
Woolverstone Marina (E)	1.30	0.71	0.32	0.26	0.85	5.86	2.31
Titchmarsh Marina (E)	5.40	2.70	1.30	1.40	0.70	1.43	0.79
Tollesbury Marina (E)	9.80	6.10	3.20	0.44	0.56	0.74	1.63

[a] (F), freshwater site; (E), estuarine site.

Table 7 Butyltin partition coefficients (K_p) in sediment and interstitial water

Location[a]	Sed composition (%) Sand	Silt	Clay	TOC[b] (%)	Partition coefficients (K_p) TBT	DBT	MBT
Fishers Dyke (F)	13	60	27	7.4	4.55×10^4	1.49×10^3	9.15×10^2
Brundall Marina (F)	17	56	28	9.8	5.55×10^3	5.71×10^3	9.47×10^2
Hickling Broad (F)	82	18	0	0.9	1.48×10^3	4.32×10^2	1.71×10^2
Oulton Broad (F)	11	70	19	4.1	2.24×10^3	4.07×10^3	2.56×10^2
Robertsons Boatyard (F)	23	65	12	3.3	2.89×10^3	2.70×10^3	2.17×10^3
Whisstocks Boatyard (F)	26	58	16	3.3	1.62×10^3	1.36×10^3	2.25×10^3
Tidemill Marina (F)	44	52	4	3.3	2.87×10^3	1.15×10^3	3.80×10^3
Woolverstone Marina (E)	29	57	14	3.4	1.59×10^3	1.06×10^3	1.26×10^3
Titchmarsh Marina (E)	27	66	7	3.7	6.20×10^3	2.50×10^3	4.43×10^3
Tollesbury Marina (E)	28	64	8	3.3	6.69×10^3	3.00×10^3	3.99×10^3

[a] (F), (E), as in Table 6. [b] TOC, total organic carbon.

$$K_p = \frac{\text{Butyltin concentration in sediment } (\mu\text{g kg}^{-1})}{\text{Butyltin concentration in interstitial water } (\mu\text{g dm}^{-3})} \quad [2]$$

From Table 7 it can be seen that the partition coefficient values for TBT, DBT and MBT fall within the range 1.71×10^2–4.55×10^4 with TBT values in the order of 10^3 except for Fishers Dyke. Values for K_p are generally in the order TBT > MBT > DBT, although in certain cases e.g. Oulton Broad and Brundall Marina, DBT had the highest K_p value. In order to investigate the possible relationships between butyltin partitioning and organic matter content, Spearman's rank correlation analysis was undertaken using the Statview II software package. Paired observations between sediment TOC and TBT gave significant correlation ($r^2 = 0.88$ at the 99.5% confidence level). However, this relationship was probably heavily influenced by the data point from Fisher's Dyke. Slightly less significant relationships were observed for DBT ($r^2 = 0.77$ at the 95% confidence level). No statistically significant relationship was observed between MBT and TOC at any confidence level. Similarly, no significant relationship was observed between K_p values and the percentages of sand, silt and clay at any confidence level.

DISCUSSION

The removal of butyltin compounds from the soluble to the particulate phase in both the freshwater and estuarine experiments could be stimulated by various processes. Leaching experiments demonstrated that there were no major losses of TBT, DBT and MBT due to adsorption on to container walls, so it can therefore be assumed that sorption on to particulate matter was the removal mechanism responsible for the reduction in soluble water column concentrations. The degree of sorption is generally influenced by the surface area available for contaminant binding, the presence of other organic and inorganic compounds competing for those adsorption sites and the structure and charge of butyltin compounds in the water.[11]

The partitioning experiments undertaken in freshwater samples highlighted the importance of particulate matter concentration in dictating the sorption characteristics of TBT and its degradation products, but this appeared only to be statistically significant at a low pH (6.0). Tributyltin generally exhibited a tendency toward solid-phase partitioning, accounting for between 65 and 100% of the TBT available, whilst DBT displayed a much lower level of sorption (34–67%) and MBT was almost completely sorbed to particulate matter in all experiments (89–100%). Batch isotherm experiments utilizing natural sediment for TBT sorption studies, however, revealed that an increase in particulate matter results in increased TBT sorption in all sediment types. Results obtained for the relationship between pH and adsorption were not as clear as those discussed for particulate matter and no statistically significant relationships were apparent between pH and any of the butyltin compounds. The effect of different particulate matter loadings and pH in estuarine waters revealed different trends from those conducted in freshwater. A definite trend was revealed for DBT, where a decrease in removal occurred with increasing pH. Tributyltin exhibits a similar behaviour to DBT but the results are statistically less significant, whilst no significant conclusions can be drawn from the MBT experiments.

The order of affinity of the butyltins for iron oxide sorption (MBT>TBT>DBT) may be attributed to differences in the chemistry of these compounds. The hydrophobicity of alkyltin compounds increases with an increasing number of carbon atoms and the number of alkyl groups bonded to the tin. The observed mixed adsorption trend for butyltin compounds results from tributyltin adsorption favoured by hydrophobicity and monobutyltin adsorption favoured by polarity. It has been suggested that the polarity of the buytlins could be an important factor influencing sorptive behaviour, with the more polar MBT being more strongly attracted to the dissolved phase.[11] However, in the freshwater factorial experiments presented here, MBT was almost totally associated with the particulate phase; this appears to contradict Randall and Weber's findings, although their experiments were undertaken under estuarine and not freshwater conditions. The general trend for metal ions in aqueous media is an increase in metal removal with increasing pH induced through enhanced competition for the negatively charged sites on the particulate matter at lower pH by H^+ ions.[21] A decrease in adsorption at lower pH values would therefore occur. The butyltins do not appear, however, to adhere to this rule as no statistically significant relationships were apparent between pH and any of the butyltin compounds. This implies that other factors are responsible for the sorptive behaviour of butyltins.

A major factor to consider which may be responsible for the different sorptive behaviour of TBT between the factorial and isotherm experiments is the different nature and age of adsorbent used. The factorial experiments utilized hydrous iron oxide (which contains no organic carbon) as an artificial sorbent which may not be such a good model for determining butyltin sorption because of its high sorptive capacity relative to natural sediments. Additionally, ageing of the precipitate reduces the sorptive capacity of the iron oxide as a result of molecular rearrangements which improve the crystallinity of the precipitate.[6] The hydrous iron oxide precipitate used in the factorial studies, however, was aged for only one week; this could have had a major effect on the ability of these precipitates to interact with heavy metals and other chemical contaminants,[19] and could explain why the hydrous iron oxide displayed a greater sorptive capacity for butyltins than the natural sediment used in the isotherm experiments. The difference in sorption between sediment types may be explained by the significantly greater surface area and more active sites for adsorption of TBT by sediments with a higher proportion of fine-grained silt and clay particles. Silts and clays contain charged minerals such as montmorillonite which impart a negative charge, thus attracting cationic species, whilst also being enriched in organic matter; the combined effect increases the degree of sorption. Sands, in contrast, are composed of neutrally charged minerals such as quartz and feldspar[21] and have a lower specific surface area and organic carbon content which reduce their binding capacity.

The estuarine partitioning experiments assessed the additional effect of salinity upon butyltin removal from solution and did not reveal any significant salting-out effects for TBT at pH 8 (environmental pH) at 5 to 35 ppt. Results at pH 7 were similar, indicating little change in TBT sorption with changing salinity. A decrease in DBT sorption was, however, apparent with increasing salinities, whilst salinity appeared not to influence the sorptive behaviour of MBT. Significant salting-out effects for TBT have been reported[10,11] which has been attributed to the lower solubility of TBT at higher chloride concentrations. Other work has shown that TBT sorption coefficients decreased with increasing salinity and varied by a factor of 2 over the salinity range.[8] The strongly linear decrease of the TBT sorption coefficient with increasing salinity observed by Unger *et al.*[8] may result from ion-exchange competition of seawater cations with sorbed TBT species, or from changes in the nature of TBT species in solution due to formation of chloro-TBT complexes. At high salinities less adsorption is expected, because of competition of chloride ions with the particulate matter for the butyltin species and competition of sodium ions with the butyltin compound for carboxylate sites on the particulate matter. Thus Na^+ partially neutralizes—COO^- groups of organic acids bound to the particulate matter, leading to a less negative particulate matter charge.[6] This explanation could be valid for DBT, where sorption appears to decrease with increasing salinity, but in the case of TBT an increase in salinity does not seem to enhance adsorption significantly. Changes in the salinity effect over the estuarine range cannot be inferred from the results obtained in this study because the factorial design only reports data for the high and low ends of the salinity range (i.e. 5 and 35 ppt) confirming the findings of Randall and Weber for DBT and TBT.[11] In view of the contradictory data, further studies on the effects of salinity on partitioning are desirable.

Butyltin partitioning work reported by other authors[8,11] utilizes artificial seawater devoid of organic compounds and complexing agents which are known to be important for contaminant binding,[21] whereas in all the experiments undertaken in this study natural freshwater and estuarine water have been used. It is possible that adsorption differences between artificial and natural waters may be considerable. Natural freshwaters and estuarine waters contain dissolved organic compounds such as humic and fulvic acids that may associate in some unknown manner with butyltin species in solution. It is therefore possible that butyltin adsorption may be specific to the particular estuary considered and adsorption characteristics should be determined for each individual river system.[8]

Desorption studies revealed that butyltin binding is reversible, with TBT, DBT and MBT all desorbing to differing degrees. The general order of desorption was DBT > MBT > TBT, indicating that TBT is the most strongly bound and DBT the least strongly bound to sediments. In these studies desorption of DBT predominated at three out of five sites, accounting for between 1.4 and 6% of the DBT available, whilst MBT desorption predominated at the remaining two sites, accounting for between 0.8 and 2.5%. Although only 1% of the TBT was released from contaminated sediments, this may be significant, releasing between 30 and 170 ng dm^{-3} to the overlying water, which is well in excess of the EQT limit for fresh and estuarine waters.[22] Dredging activities have been undertaken during the past few years at all sites utilized in this study and TBT water column concentrations have been found to be of the same order of magnitude as those derived in the desorption experiments.[23] *In situ* mesocosm studies undertaken at the sediment–water interface also indicate a potential for DBT desorption from the sediment.[24] The desorption process is probably dependent on the degree of sediment disturbance and the time lag since sediment disturbance occurred. Sorption of butyltin compounds back on to particulate matter would also occur and should be taken into account when estimating butyltin concentrations in the water column resulting from desorption.

The partitioning of butyltin compounds between sediment and interstitial water is important in determining bioavailability, as dissolved TBT present in the interstitial water is directly available to benthic organisms. Tributyltin appeared to be principally associated with the particulate phase. At Robertson's Boatyard, for example, particulate and dissolved TBT concentrations were 202 ng g^{-1} and 70 ng dm^{-3} respectively. This can be accounted for by the hydrophobic nature of TBT, which displays a higher affinity for particulate interactions than the more polar DBT and MBT. The partition coefficients for TBT ranged from 1.07×10^2 to 4.55×10^4, which is in general agreement with other published work.[8,11,24] Sediment TOC appeared to be an important control upon TBT partitioning, with the highest partition coefficients coinciding with high organic loadings, but more data is needed incorporating a wider range of TOC values in sediments to confirm these findings. This would indicate that the binding capacity of TBT increases in highly organic sediments. There appears to be no systematic relationship between the partition coefficients of TBT, DBT and MBT in freshwater or estuarine sediments, but in general MBT appeared to show slightly less affinity for the particulate phase in freshwater sediments, compared with DBT and TBT. However, in estuarine sediments (Woolverstone, Titchmarsh and Tollesbury), MBT partition coefficients were higher than for DBT. This indicates that the more polar MBT has a higher affinity than DBT for the particulate phase in saline areas. In all cases, significant amounts of TBT are potentially available for uptake by benthic organisms.

CONCLUSIONS

The partitioning and sorptive behaviour of butyltin compounds is dictated by a number of physicochemical parameters in the aquatic environment. In freshwaters MBT, and to a lesser extent TBT, will be present mainly in the adsorbed phase, whereas DBT will be present in significant amounts in both the dissolved phase and on the particulate matter. TBT sorption is also dependent on sediment type, with finer-grained clay and silt-type sediments being more receptive to

TBT adsorption than larger-grained sands. In estuarine waters MBT will almost exclusively adsorb on to particulates; TBT will be present predominantly in the solid-phase sections but 10–30% could be retained in solution. DBT, in contrast, is solubilized in estuarine waters. The order of adsorption to particulate matter for butyltins is MBT>TBT>DBT. However, these adsorption characteristics probably differ between catchments and should be determined for each individual river system. Interstitial water partitioning studies indicate that TBT predominates in the particulate phase. Partition coefficients in sediments appeared to be weakly related to total organic carbon loadings, with the highest partition coefficients coinciding with high organic carbon content. However, TOC alone is not a good predictor of TBT sorption. Tributyltin sorption was found to be reversible in freshwater and estuarine environments, indicating that contaminated sediments may release TBT, and to a greater extent DBT, to overlying waters in the UK east coast estuaries studied following sediment disturbance.

Acknowledgements This work was carried out under contract to the National Rivers Authority (formerly Anglian Water), who gave approval for publication. One of the authors (PD) is grateful to The Science and Engineering Research Council for the award of a Postgraduate Studentship. Additionally we thank Simeon Jones for undertaking TOC analysis and Dr Steve Lambert for his help and comments with this manuscript.

REFERENCES

1. De Mora, S J, King, N G and Miller, M C *Environ. Technol.*, 1989, 10: 901
2. Knezovich, J P and Harrison, F L *Water, Air Soil Pollut.*, 1987, 32: 233
3. Clark, E A, Sterritt, R M and Lester, J N *Environ. Sci. Technol.*, 1988, 22: 600
4. Seligman, P F, Grovhoug, J G, Valkirs, A O, Stang, P M, Fransham, R, Stallard, M O, Davidson, B and Lee, R F *Appl. Organomet. Chem.*, 1989, 3: 31
5. Dooley, C A and Homer, V Naval Ocean Systems Technical Report No. 917, US Navy, San Diego, CA, 1983
6. Donard, O F X and Weber, J *Environ. Sci. Technol.*, 1985, 19: 1104
7. Laughlin, R B, Guard, H E and Coleman, W M *Environ. Sci. Technol.*, 1986, 20: 201
8. Unger, M A, MacIntyre, W G and Huggett, R J *Environ. Toxicol. Chem.*, 1988, 9: 907
9. Valkirs, A O, Stallard, M O and Seligman, P F Butyltin partitioning in marine waters. In: *Proc. Oceans '87 Organotin Symposium,* vol 4, IEEE Service Center, Piscataway, NJ, 1987, pp 1375–1379
10. Harris, J R W and Cleary, J J Particle–water partitioning and organotin dispersal in an estuary. In: *Proc. Oceans '87 Organotin Symposium,* vol 4, IEEE Service Center, Piscataway, NJ, 1987, pp 1370–1374
11. Randall, L and Weber, J H *Sci. Total. Environ.*, 1986, 57: 191
12. Valkirs, A O, Seligman, P F and Lee, R F Butyltin partitioning in marine waters and sediments. In: *Proc. Oceans '86 Organotin Symposium,* vol 4, IEEE Service Center, Piscataway, NJ, 1986, pp 1165–1170
13. Maguire, R J and Tkacz, J *J. Agric. Food Chem.*, 1985, 33: 947
14. Box, G E P, Hunter, W G and Hunter, J S *Statistics for Experiments*, John Wiley and Sons, New York, 1978
15. Lee, G F Role of hydrous metal oxides in the transport of heavy metals in the environment. In: *Proc. Int. Conf. Heavy Metals in the Aquatic Environment,* Krendell, P A (ed), Pergamon, Oxford, 1975, pp 137–149
16. Salomons, W and Förstner, U *Metals in the Hydrocycle*, Springer-Verlag, New York, 1984
17. Dowson, P H, Bubb, J M and Lester, J N *Mar. Pollut. Bull.*, 1992 24: 492
18. MacIntyre, W G and deFur, P O *Chemosphere*, 1985, 14: 103
19. Stumm, W and Morgan, J J *Aquatic Chemistry*, 2nd edn, John Wiley and Sons, USA, 1981
20. Dowson, P H, Pershke, D, Bubb, J M and Lester, J N *Environ. Pollut.*, 1992, 76: 259
21. Förstner, U and Wittmann, G T W *Metal Pollution in the Aquatic Environment*. Springer-Verlag, New York 1981
22. Zabel T F, Seager, J and Oakley S D (eds) Proposed environmental quality standards for List II substances in water (organotins), TR 255, Water Research Centre (WRC), Medmenham, UK, 1988
23. Dowson, P H, Bubb, J M and Lester, J N *Mar. Pollut. Bull.*, 1993, 26: 487
24. Stang, P M and Seligman, P F *In situ* adsorption and desorption and butyltin compounds from Pearl Harbour, Hawaii, sediment. In: *Proc. Oceans '87 Organotin Symposium*, vol 4, IEEE Service Center, Piscataway, NJ, 1987, pp 1386–1391