J. Mar. Biol. Ass. U.K. (2003), **83**, 11–22
Printed in the United Kingdom

Organotin compounds in Mersey and Thames Estuaries a decade after UK TBT legislation

H. Harino*, S.C.M. O'Hara†, G.R. Burt†, B.S. Chesman†, N.D. Pope‡ and W.J. Langston†

*Osaka City Institute of Public Health and Environmental Sciences, Tohjo-cho, 8-34, Tennoji-ku, Osaka, 543-0026, Japan.
†Marine Biological Association, Citadel Hill, Plymouth, PL1 2PB. ‡Plymouth Marine Laboratory, Citadel Hill, Plymouth, PL1 2PB.
*Corresponding author, e-mail: j-harino@kawachi.zaq.ne.jp

Organotin (OT) compounds were determined in surface sediments and mussels *Mytilus edulis* from two major estuaries of the UK, the Mersey and the Thames, approximately one decade after legislation banning the use of tributyltin (TBT) compounds on small boats. Tributyltin concentrations in Mersey sediments ranged from 0.007–0.173 μg (as Sn) g^{-1} dry wt, increasing from the most upstream site, Fiddlers Ferry, towards the middle section of the estuary, and were highest at Stanlow, perhaps indicative of sources from the Manchester Ship Canal (MSC). A further peak in TBT concentrations occurred at New Brighton, opposite Liverpool Docks. Tributyltin was the predominant butyltin (BT) species in sediments (approximately 50%). Despite the fact that BTs represented only 4% of the total (HNO_3-extractable) tin in sediments there was a linear relationship between these two tin compartments. Furthermore, BTs in mussels were correlative with total extractable tin in sediment, though in contrast to sediments, 85% of the total tin in mussels was made up of BTs, the most predominant of which was TBT. Concentrations of TBT in mussels increased from 0.058 μg Sn g^{-1} dry wt at the mouth of the estuary to 0.214 μg Sn g^{-1} dry wt at their upstream limit, close to the entrance to the MSC (Eastham). Triphenyltin (TPT) compounds were detected in only one sediment sample (New Brighton, 0.359 μg Sn g^{-1} dry wt) and one mussel population (Egremont, 0.022 μg Sn g^{-1} dry wt). Tributyltin concentrations in sediments from the Thames Estuary were marginally lower (0.002–0.078 μg Sn g^{-1} dry wt) than those found in the Mersey: highest concentrations were present in the upper estuary and decreased seaward. Again BTs contributed only a small percentage (<1% mean) towards the total tin loading in Thames sediments, but represented most of the tin burden (80%) in mussels. In contrast to sediments, TBT levels in mussels from the Thames Estuary were slightly higher than the Mersey (concentrations ranged from 0.100 μg Sn g^{-1} dry wt at the mouth to 0.302 μg Sn g^{-1} dry wt upstream) suggesting that TBT bioavailability is disproportionately higher in the Thames. Phenyltins were not detected in Thames samples.

INTRODUCTION

Organotin (OT) compounds have been widely used as biocides, stabilizers in vinyl chloride, wood preservatives and fungicides. In particular, tributyltin (TBT) compounds have proved to be extremely effective biocides in antifouling paints. Unfortunately, however, TBT released from such antifouling paints caused adverse effects to non-target organisms—one of the first manifestations, in the 1970s being the shell deformity of oysters *Crassostrea gigas* (Laughlin & Linden, 1985). Since then, environmental contamination by OTs has been of concern world-wide and effects of these compounds on aquatic organisms have been extensively studied. Acute toxicity of TBT was initially described in the $\mu g\,l^{-1}$ range (e.g. Uren, 1983), though shell anomalies in oysters and other subtle sub-lethal impacts, including imposex in gastropoda (Bryan et al., 1986), were subsequently shown to occur at concentrations of $1\,ng\,l^{-1}$ or less. During the mid-1980s, surveys of OTs in marinas and estuaries indicated that concentrations of 100 ng TBT l^{-1}, and sometimes higher, were not uncommon (Maguire et al., 1982; Langston et al., 1987).

These and similar observations prompted the introduction in 1987 of UK legislation to eliminate products containing triorganotin compounds from use on vessels less than 25 m in length, and from fish-farming equipment. In order to protect aquatic organisms an environmental quality standard (EQS) for TBT was set at $2\,ng\,l^{-1}$ in seawater. Following legislation, a number of papers have been published reporting environmental improvements in relation to temporal trends in OTs (Waite et al., 1991; Waldock et al., 1999; Rees et al., 1999). However these are limited in number and it is recognized that not all sites are recovering at the same rate. Reductions in TBT loadings can sometimes be delayed by the persistence of OTs in benthic sediments (Langston & Pope, 1995; Langston, 1995), an issue which causes considerable technical, environmental and economic difficulty for the management of dredge spoils in estuaries. Concentrations in sediments close to dockyards, marinas, and hull cleaning facilities have previously been reported in the range 0.1–1 $\mu g\,g^{-1}$ (dry wt) and, occasionally, higher. There is need for broader surveillance of the marine environment to assess such reservoirs, and hence, to contribute to the debate

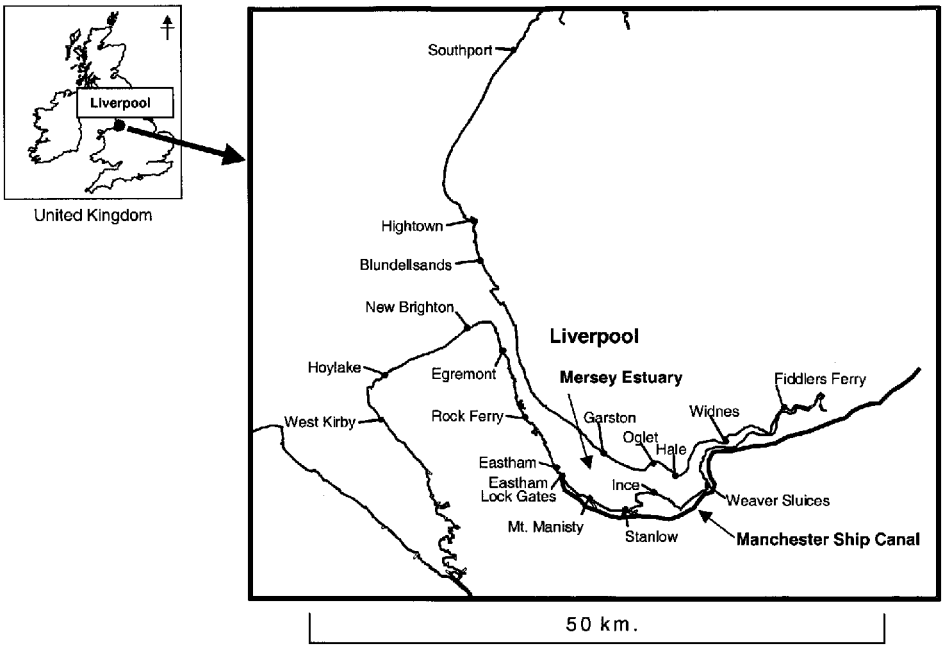

Figure 1. Sampling sites in the Mersey Estuary.

concerning the International Marine Organization's proposal to initiate a complete ban on organotin antifoulants scheduled to commence in 2003 (subsequently adopted as the International Convention on the Control of Harmful Anti-fouling Systems on Ships).

The Mersey and Thames are two of the most important estuaries in the UK. The Mersey Estuary receives drainage from a highly urbanized and industrialized catchment in north-west England, and, historically, has been contaminated by a wide variety of inorganic and organic chemicals (see, for example, Langston, 1986; Thomas et al., 1999). The Thames Estuary also has a legacy of contamination from a wide variety of sources, including a significant component from the large number of sewage treatment works present in the Greater London catchment (Environment Agency, 1997). Though they are no longer the major ports they were during the last century, commercial shipping is still a significant feature of the approaches to both estuaries.

In this paper, the distribution and status of butyltin (BT) as TBT, dibutyltin, (DBT), or monobutyltin, (MBT) and

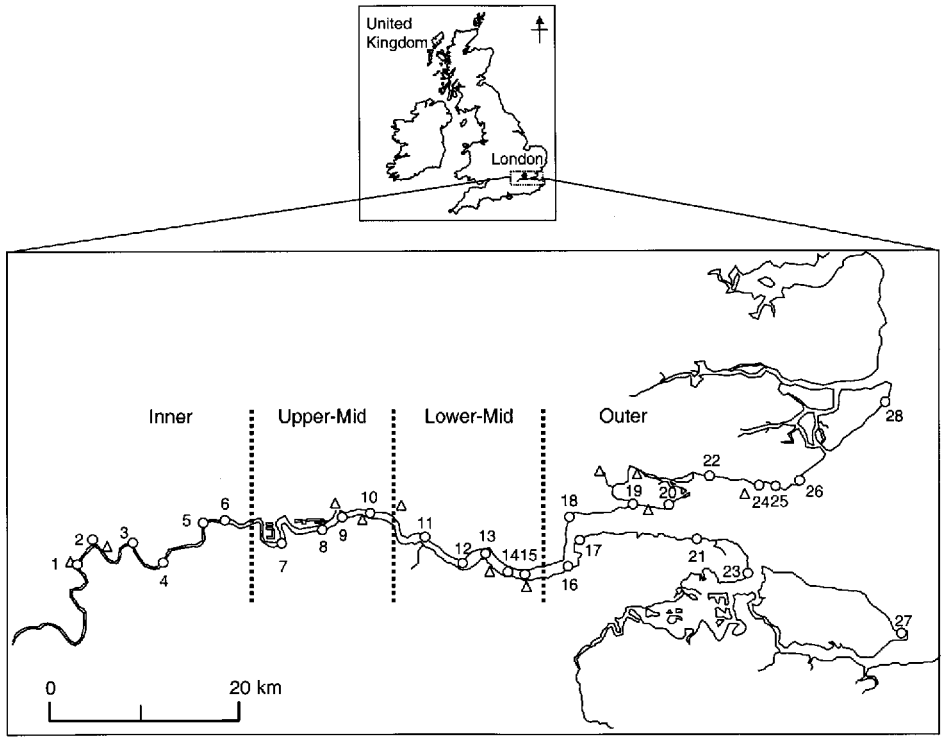

Figure 2. Sampling sites in the Thames Estuary: ○, sampling location; △, sewage treatment works.

https://doi.org/10.1017/S0025315403006738h Published online by Cambridge University Press

Table 1. *Recovery of organotins from sediment and mussel* Mytilus edulis *tissue spiked with standards.*

	Sample weight (g)	OT spike (μg)	% Recovery: means (and standard deviations)					
			MBT	DBT	TBT	MPT	DPT	TPT
sediment	2	1	103 (2.1)	114 (7.2)	74 (7.0)	88 (13.0)	119 (10.0)	120 (7.2)
mussel	0.2	0.1	80 (2.3)	82 (4.9)	79 (15.0)	55 (9.4)	120 (13.0)	89 (13.0)

OT, organotin compounds; MBT, monobutyltin; DBT, dibutyltin; TBT, tributyltin; MPT, monophenyltin; DPT, diphenyltin; TPT, triphenyltin.

phenyltin (PT) as triphenyltin (TPT), diphenyltin (DPT), or monophenyltin (MPT) residues in sediment and mussels from the Mersey and Thames Estuaries are described, based on material collected during a number of surveys made between 1995–1999, approximately one decade after initial TBT legislation.

MATERIALS AND METHODS

Sampling

The Mersey Estuary, north-west England (Figure 1), has a catchment area of ~5000 km^2 and encompasses much of the major industrial conurbation of western Lancashire as well as a number of smaller centres in Cheshire and Merseyside. Liquid wastes from textile, tanning, metal processing, chemical and petrochemical industries are discharged directly or indirectly (e.g. via the Manchester Ship Canal (MSC)) into the Mersey. The MSC runs alongside the estuary between Runcorn and Eastham, and water exchange between the two water bodies takes place at several locations including (intermittently) during locking operations (at Eastham) and, more extensively, at Weaver Sluices (Figure 1). For the current study, inter-tidal surface sediment samples, taken in May 1997 from 18 sites along the length of the Mersey Estuary (from Fiddlers Ferry, upstream, to the open coast at Southport) were analysed for organotins. At each site, sub-samples from three to four intertidal areas of approximately 1 m^2 were combined. Mussel (*Mytulis edulis*) samples collected during May 1995 from a smaller subset of sites—from Southport to Eastham (their upstream limit of distribution)—were also investigated for organotins.

The Thames Estuary, is the dominant estuary in south-east England (Figure 2) and has a catchment area (9900 km^2) almost double that of the Mersey, and an average flow of 82 m^3 s^{-1} though this can be highly variable (9–210 m^3 s^{-1}) depending on rainfall and abstraction. There are many water treatment works which discharge to the estuary, including the major plants at Mogden (near Kew), Crossness and Beckton. There are also inputs from storm water run-off and various industrial effluents, dockyards and marinas, sited along the watercourse. Sampling of sediments took place during July 1997 at sites between the tidal limit at Richmond, seawards to the outer estuary at Foulness on the northern bank and Shell Ness to the south. Mussels were collected, in November 1999, from several of the outer estuary sites, as far as their upstream limit of distribution at Canvey Island.

All samples were transported back to the laboratory in cold boxes. Sediment samples (~1 kg) were wet sieved and

Table 2. *Organotin compounds*[a] *(μg Sn g^{-1} dry wt) in sediment (<100 μm fraction) from the Mersey Estuary, 1997.*

Site	Distance* (km)	MBT	DBT	TBT
Fiddler's Ferry	0	0.016	0.009	0.007
Widnes	7	0.024	0.012	0.015
Weaver Sluices	10	0.026	0.024	0.023
Hale	11	0.011	0.005	0.009
Ince	12	0.021	0.018	0.019
Oglet	16	0.022	0.019	0.029
Stanlow	17.5	0.058	0.063	0.173
Mt Manisty	20	0.030	0.018	0.046
Garston	21.5	0.024	0.013	0.044
Eastham Lock Gates	23	0.021	0.008	0.026
Eastham	23.5	0.036	0.012	0.040
Rock Ferry	28.5	0.013	0.009	0.019
Egremont	34.5	0.019	0.014	0.035
New Brighton	39.5	0.080	0.065	0.123
Blundellsands	41.5	0.002	0.018	0.046
Hightown	45.5	0.021	0.009	0.025
Hoylake	48	0.009	0.002	0.012
Southport	60	0.016	0.005	0.012

[a], Phenyltin compounds were below the limits of detection, except at New Brighton, where TPT was detected (0.359 g Sn g^{-1} dry wt).
*, Distance (km) from Fiddler's Ferry, the most upstream site.

Table 3. *Organotin compounds*[a] *(μg Sn g^{-1}dry wt) in mussel* Mytilus edulis *from the Mersey Estuary, 1995.*

Site	Distance* (km)	MBT	DBT	TBT
Eastham Lock Gates	23	0.091	0.144	0.214
Egremont	34.5	0.046	0.047	0.112
New Brighton	39.5	0.042	0.032	0.060
Blundellsands	41.5	0.059	0.063	0.114
West Kirby	50	0.017	0.024	0.046
Southport	60	0.027	0.038	0.058

[a], Phenyltin compounds were below the limits of detection, except the sample from Egremont, where TPT was detected (0.022 g Sn g^{-1} dry wt). *, Distance downstream of Fiddlers Ferry.

https://doi.org/10.1017/S0025315403006738h Published online by Cambridge University Press

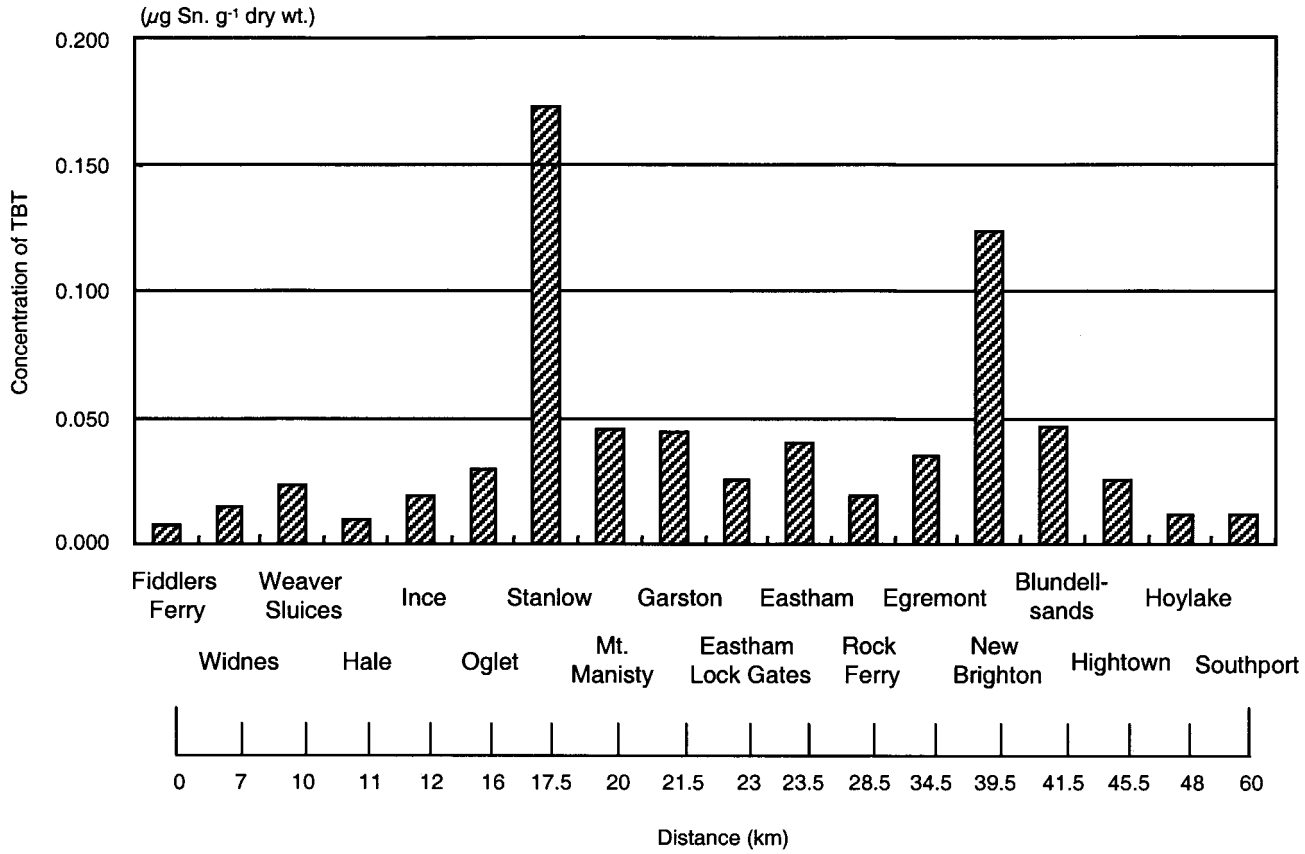

Figure 3. Concentration of TBT in sediment (<100 μm fraction) from the Mersey Estuary, 1997.

the <100 μm fraction stored at −20°C prior to analysis. Mussels were allowed to depurate in clean seawater (<1 ng l^{-1} TBT) for 48 h in order to purge potentially contaminating particulate material from the digestive tract. All soft tissues were removed from the shell and pooled samples (N=10) either lyophilized, ground in a pestle and mortar (with liquid nitrogen) and stored dry at room temperature, or stored frozen at −20°C, prior to analysis.

Analytical procedure

The method used for the determination of BTs and PTs in sediment and *M. edulis* was based on that of Harino et al.

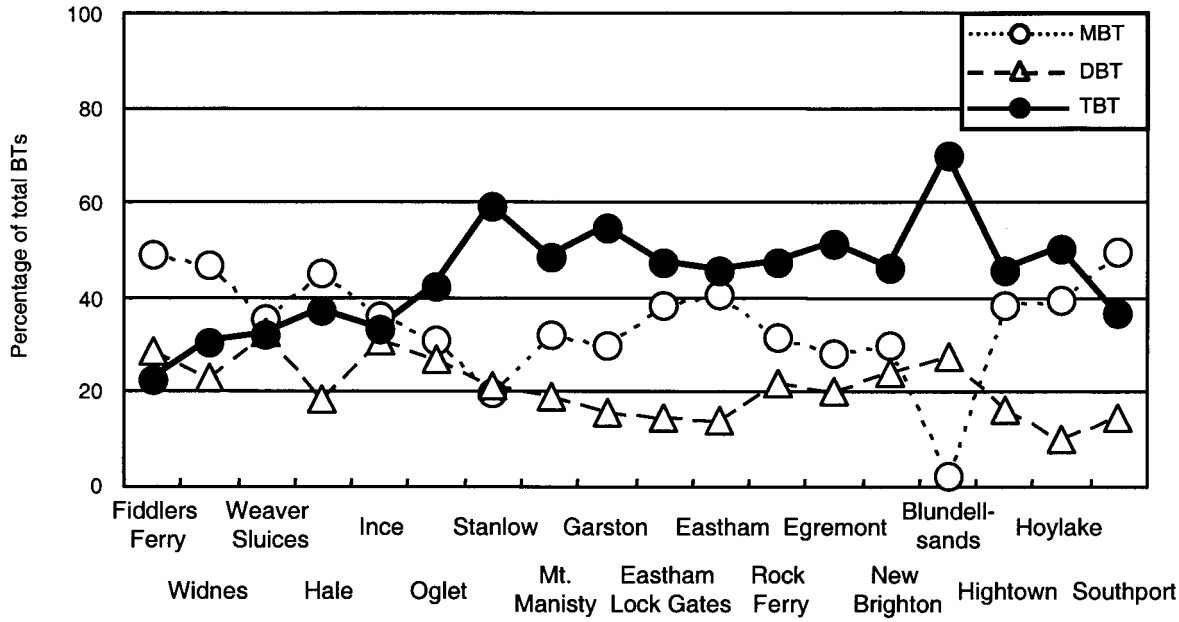

Figure 4. Composition of butyltins in sediment from the Mersey Estuary, 1997. ○, MBT; △, DBT; ●, TBT.

https://doi.org/10.1017/S0025315403006738h Published online by Cambridge University Press

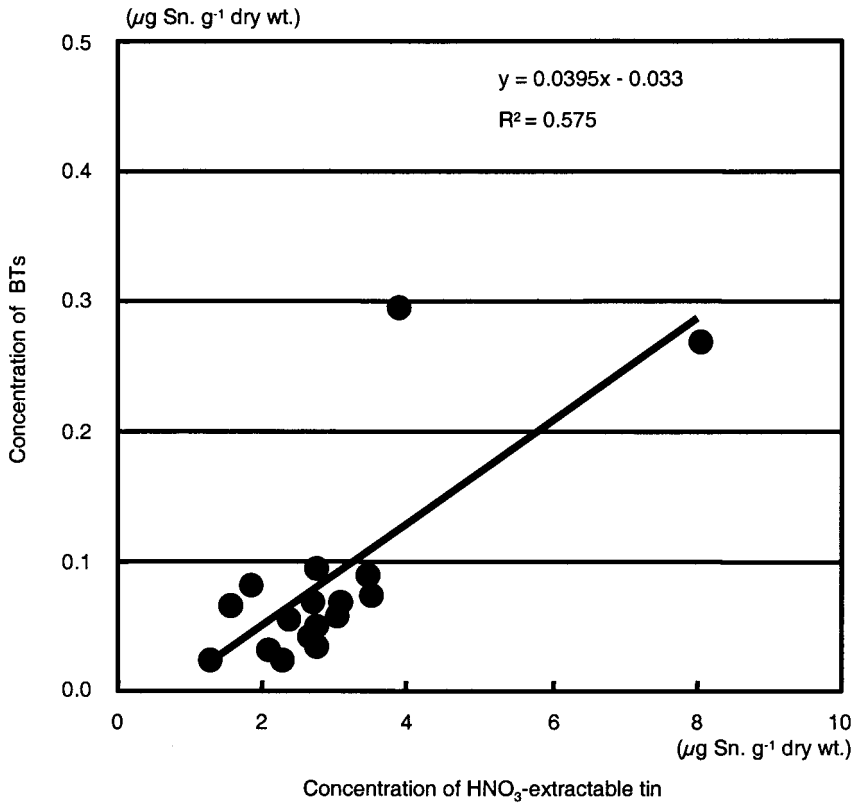

Figure 5. Relationship between butyltins and HNO_3-extractable tin in sediments, Mersey Estuary, 1997.

(1992) with some modifications. Briefly, four grams of wet sediment or biological sample were extracted or homogenized, respectively, with 10 ml of acetone following the addition of 5 ml of 1N HCl. After centrifugation for 5 min, the supernatant was removed and the procedure repeated. Combined supernatants were added to 100 ml of 25% NaCl solution and the OTs were extracted twice with 10 ml of 0.1% tropolone in benzene solution. With the sediment samples, co-extracted inorganic sulphur was washed from the analytes in the organic layer with an aqueous mixture comprising, 1 ml of 3.3% tetrabutylammonium hydrogensulphate and 10 ml of 16% sodium sulphite. This sulphur-removing step was not required with biological extracts. Sulphur-free organic layers from all sample types were dried with anhydrous Na_2SO_4 and concentrated to 1 ml. Each extract concentrate was mixed with 2 ml of n-propyl-Grignard reagent (2M propylmagnesium chloride in diethyl ether solution, Aldrich) and allowed to stand at room temperature (to form propyl-derivatized OTs) for 30 min. Excess Grignard reagent was destroyed with the addition of 5 ml of 1N H_2SO_4. Forty ml of distilled water was added to each mixture and the OTs extracted twice

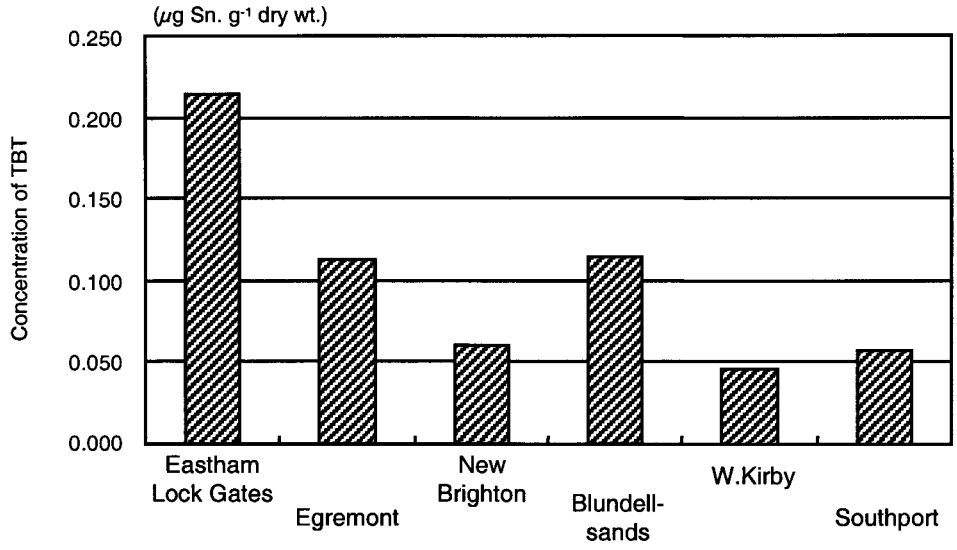

Figure 6. Concentration of TBT in mussels *Mytilus edulis* from the Mersey Estuary, 1995.

https://doi.org/10.1017/S0025315403006738h Published online by Cambridge University Press

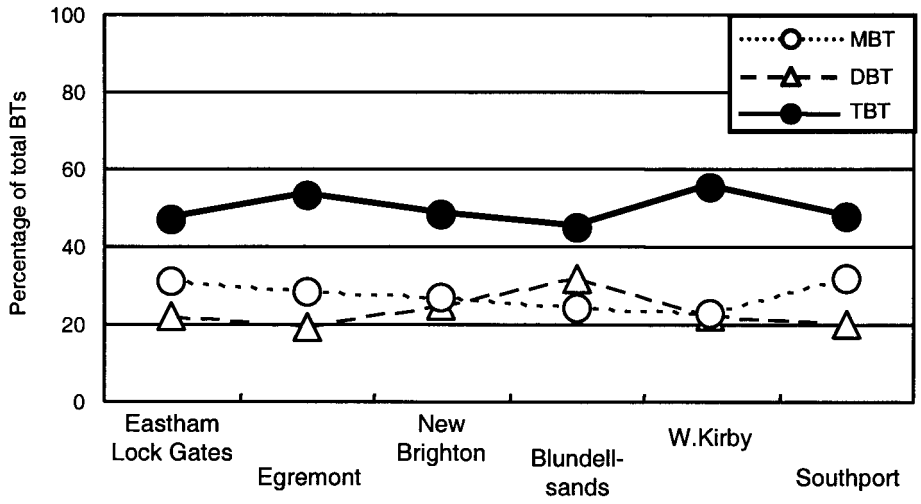

Figure 7. Composition of butyltins in mussels *Mytilus edulis* from the Mersey Estuary, 1995. ○, MBT; △, DBT; ●, TBT.

with 10 ml of 10% benzene in hexane solution. Combined extracts containing propylated OTs were dried with anhydrous Na_2SO_4, concentrated to 1 ml with a rotary evaporator, and hexane added to produce a final volume of 5 ml. These mixtures were passed through Sep-pak® Florisil® cartridges (Waters) and OTs eluted with 10 ml 10% benzene in hexane. Derivatized and purified extracts were then concentrated to 0.5 ml and organotin compounds were determined using a Varian Star 3400 C_X gas chromatograph equipped with a flame photometric detector (FPD) and a 590 nm cut-off interference filter. The separation was carried out on a 30 m (J & W Scientific) 0.53 mm ID column coated with 1.5 μm film DB-5 liquid phase. Column oven temperature programme: 50°C for 1 min, increased to 100°C at 15°C/min and to 290°C at 5°C/min and held for 7.5 min to allow elution of TPT. Injector and detector were both maintained at 290°C. Nitrogen was used as the carrier gas at a flow-rate of 7.0 ml/min. The flow-rates of air 1, air 2 and hydrogen for the dual-flame FPD detector were 80, 170 and 170 ml/min, respectively. On-column injection (5 μl) was employed.

All OT concentrations are reported as μg Sn g^{-1} dry wt. Recoveries and relative standard deviations (RSD) of analytes subjected to the complete analytical procedure

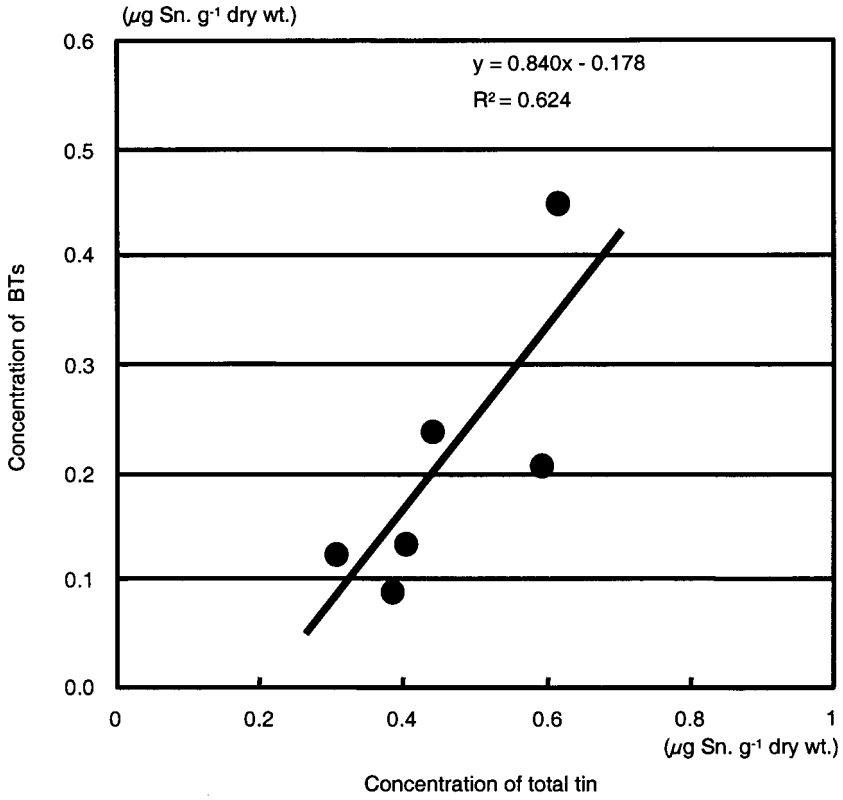

Figure 8. Relationship between butyltins and total tin in mussels *Mytilus edulis* from the Mersey Estuary, 1995.

https://doi.org/10.1017/S0025315403006738h Published online by Cambridge University Press

Table 4. *Organotin compounds*[a] *(μg Sn g^{-1} dry wt) in sediment (<100 μm fraction) from the Thames Estuary, 1997.*

Site number*	Location	MBT	DBT	TBT
1	Richmond	0.073	0.045	0.078
2	Kew Bridge	0.016	0.007	0.019
3	Hammersmith	0.042	0.125	0.027
4	Cadogan Pier	0.079	0.057	0.050
5	South Bank	0.034	0.030	0.041
6	London Bridge	0.027	0.038	0.049
7	Greenwich	0.031	0.028	0.030
8	Woolwich	0.016	0.017	0.022
9	Beckton	0.035	0.033	0.039
10	Crossness	0.019	0.021	0.022
11	Purfleet	0.022	0.021	0.025
12	West Thurrock	0.014	0.009	0.011
13	Grays	0.036	0.016	0.029
14	Tilbury	0.006	0.008	0.011
15	Gravesend	0.011	0.009	0.010
16	Coalhouse Fort	0.005	0.004	0.007
17	Lower Hope Point	0.025	0.004	0.023
18	Mucking	0.028	0.020	0.020
19	Hole Haven	0.004	0.002	0.003
20	Canvey Island	0.003	0.002	0.004
21	Allhallows	0.006	0.006	0.006
23	Grain Flats	0.006	0.009	0.006
24	Westcliff-on-sea	0.015	0.030	0.016
25	Thorpe Bay	0.004	0.003	0.004
26	Shoeburyness	0.002	0.002	0.006
27	Shell Ness	0.004	0.003	0.006
28	Foulness	0.003	0.002	0.002

[a], Phenyltin compounds were below the limits of detection.
*, Site numbers refer to locations in Figure 2.

are shown in Table 1. When 1 μg of each of the OTs was added to 2 g of sediment, recoveries and RSD of OTs were in the range of 74–120% and 2.1–13%, respectively. When 0.1 μg each of the OTs was added to 0.2 g of mussel, recoveries and RSD of OTs ranged between 55–120% and 2.3–15%, respectively.

The detection limits for BTs and PTs in sediment, corresponding to a signal-to-noise ratio of three, were of the order of 0.002 μg g^{-1} dry wt. The corresponding detection limits of BTs, DPT and TPT in mussel were also 0.002 μg g^{-1} dry wt and that of MPT was 0.004 μg g^{-1} dry wt.

RESULTS

Organotins in the Mersey Estuary

Organotin concentrations in sediment from the Mersey Estuary are shown in Table 2. Concentration ranges for MBT, DBT and TBT were 0.002–0.080, 0.002–0.065 and 0.007–0.173 μg g^{-1} dry wt, respectively. The only phenyltin detectable was TPT, present at 0.359 μg g^{-1} dry wt in the sediment sample from New Brighton (perhaps due to the presence of paint particles originating from nearby docks). Concentration ranges of MBT, DBT and TBT in mussel, *Mytilus edulis*, from sites along the Mersey Estuary were 0.017–0.091, 0.024–0.144 and 0.046–0.214 μg g^{-1} dry wt, respectively (Table 3). Only one of the mussel samples from the Mersey contained any detectable PT. Triphenyltin was present at a relatively low level (0.022 μg g^{-1} dry wt) in the population sampled at Egremont.

The spatial distribution of TBTs in surface sediments along the length of the Mersey Estuary is shown in Figure 3. In the upper estuary, TBT concentrations increased, generally, from Fiddlers Ferry (fresh water) downstream, implying that the estuary, rather than the River Mersey itself, may be the origin and reservoir of most of the particulate contamination. The highest concentration of TBT in sediment was that at Stanlow (0.173 μg g^{-1} dry wt). This site is adjacent to the MSC, near the mouth of the River Gowy. In the mid- to lower-estuary, between Mt Manisty and Egremont, TBT concentrations were in the range of 0.019–0.046 μg g^{-1} dry wt, showing little variation. At the mouth of the estuary a further potential 'hotspot' is indicated by the high TBT concentration in sediment from New Brighton (0.123 μg g^{-1} dry wt). Thereafter, concentrations declined with distance from the Mersey Estuary, along the shoreline of Liverpool Bay: lowest values were encountered at Southport to the north and Hoylake to the west.

The composition of different butyltin species in Mersey sediments, expressed as a percentage of total BT, is depicted for the length of the tideway in Figure 4. Monobutyltin was the predominant species at the head of the estuary, but proportions decreased, gradually, downstream between Fiddlers Ferry and Stanlow. In contrast, in this upper section of the estuary, the proportion of TBT increased, toward Stanlow (60%), and thereafter remained the dominant species except at the most seaward station (Southport). The high TBT contribution at Blundellsands (70%), and low proportion of MBT, suggests the influence of paint particles from nearby docks at Liverpool. No clear patterns were observed for DBT, other than perhaps a trend towards slightly lower proportions at the more seaward sites.

Concentrations of BTs (ΣMBT, DBT, TBT) are compared with those of 'total' (concentrated HNO_3-extractable) tin in Figure 5. The latter determinations involved microwave-assisted digestion of sediments in pressurized vessels, followed by analysis by hydride-generation atomic absorption spectrophotometry (HGAAS), and formed part of a separate study on metals in the Mersey (see Pope et al., 1998). The comparison between BTs and HNO_3-extractable tin reveals a reasonable linear relationship (R^2=0.575). The slope of the linear regression was 0.040 indicating that BT concentrations were equivalent to approximately 4% of the HNO_3-extractable tin. It should be noted, however, that HNO_3 may not extract all metals completely and may not be a true total (though any remaining metal is unlikely to be bioavailable). Notably, Sn present as cassiterite (SnO_2), is not soluble in concentrated HNO_3: comparisons with more rigorous techniques (fusion with ammonium iodide) indicate that for Mersey sediment 67 ±9% Sn is present as this highly inert, mineralized form. Irrespectively, it is clear that BTs represent only a minor proportion of the tin content of these sediments.

The spatial distribution of TBT in *M. edulis* collected from the Mersey between Eastham Locks and Southport is shown in Figure 6. Tributyltin concentrations in these mussels decreased in the direction of the open sea, as anticipated from the sediment data. The proportions of

https://doi.org/10.1017/S0025315403006738h Published online by Cambridge University Press

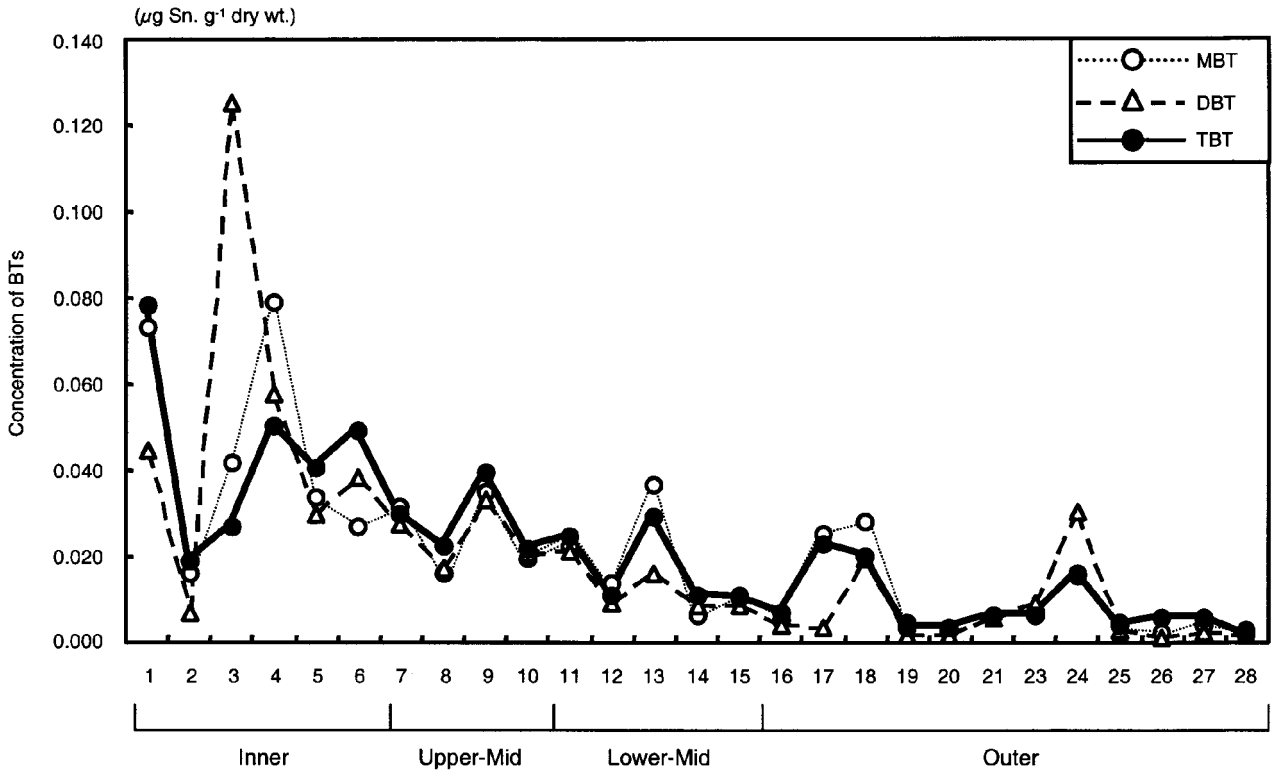

Figure 9. Concentration of butyltins in sediment (<100 μm fraction) from the Thames Estuary, 1997. ○, MBT; △, DBT; ●, TBT.

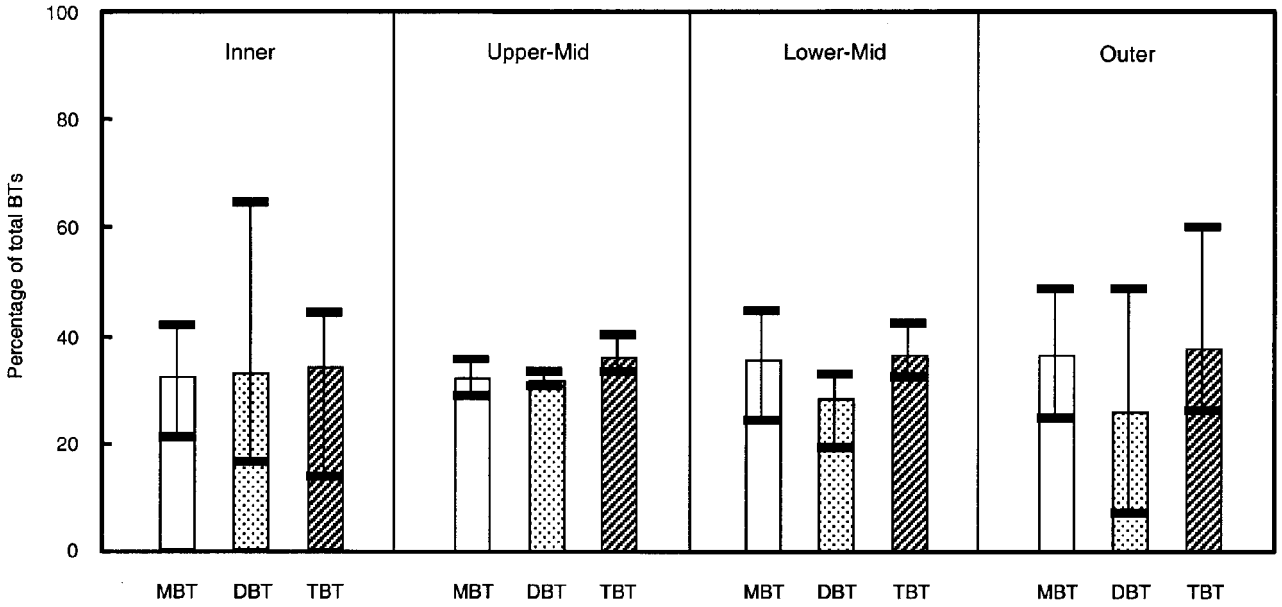

Figure 10. Composition of butyltins (means and ranges, expressed as percentages) in sediment from the Thames Estuary, 1997 (for location of zonal divisions see Figure 2).

various BT species in mussel are shown in Figure 7 and reveal a reasonably constant composition irrespective of location and total body burden: for MBT, DBT and TBT these proportions were 19–32%, 23–32% and 45–55%, respectively.

The relationship between BT concentration (ΣMBT, DBT, TBT) and total tin in mussel (determined by HGAAS, following microwave digestion of freeze-dried tissue; see Pope et al., 1996) was relatively strong (R^2=0.624) and the slope of the linear regression line was 0.840 (Figure 8). This implies that the major proportion of total tin in mussel (~84%) comprised BTs.

Organotins in the Thames Estuary

Butyltin concentrations in sediment from the Thames Estuary are listed in Table 4. Monobutyltin, DBT and TBT concentration ranges were 0.002–0.079, 0.002–0.125 and 0.002–0.078 μg g^{-1} dry wt, respectively.

https://doi.org/10.1017/S0025315403006738h Published online by Cambridge University Press

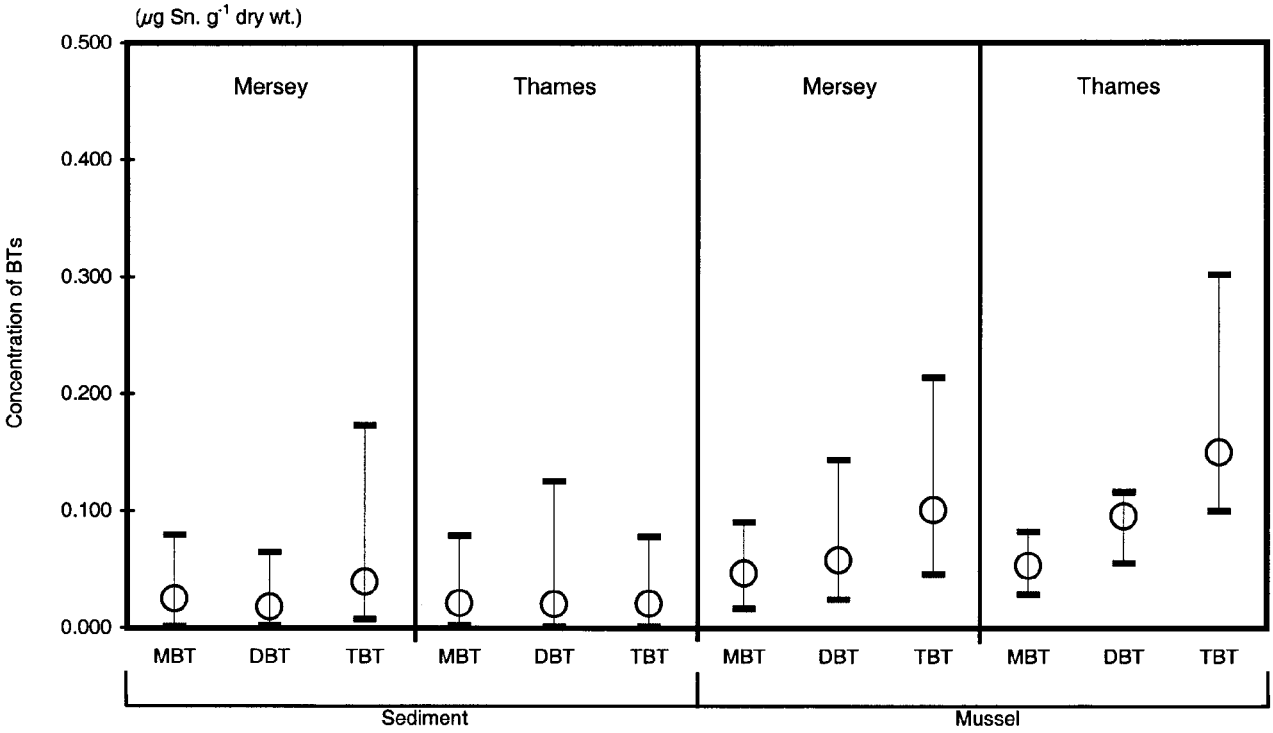

Figure 11. Comparison of butyltin concentrations (means and ranges) in sediments and mussels (*Mytilus edulis*) of the Mersey and Thames Estuaries.

Table 5. *Organotin compounds*[a] *(μg Sn g^{-1} dry wt) in mussel* Mytilus edulis *from the Thames Estuary, 1999.*

Site number*	Location	MBT	DBT	TBT
20	Canvey Island	0.033	0.083	0.126
21	Allhallows	0.053	0.098	0.101
22	Westcliff-on-sea	0.083	0.116	0.182
23	Grain Flats	0.060	0.110	0.302
25	Thorpe Bay	0.041	0.109	0.101
26	Shoeburyness	0.074	0.098	0.137
27	Shell Ness	0.029	0.055	0.100

[a], Phenyltin compounds were below the limits of detection.
*, Site numbers refer to locations in Figure 2.

The spatial distribution of BTs in sediment along the length of the Thames tideway (in 1997) is shown in Figure 9 (see Figure 2 for site locations). Concentrations of each of the BTs decreased in a seaward direction overall, though this was not a straightforward relationship with distance. As indicated in Figure 9 there may be a fair degree of heterogeneity even between adjacent sites. To help summarize and compare the data, sites were divided into four zones according to their salinity regimes: 'Inner estuary' sites, between Richmond and London Bridge (sites 1–6, Figure 2), were fresh-, or slightly brackish-water (0.14–1.96 practical salinity units (psu)); 'Upper-Mid estuary' (sites 7–10), between Greenwich and Crossness, were low salinity (4.47–11.7 psu); 'Lower-Mid estuary' sites (11–15), between Purfleet and Gravesend, were intermediate salinity (13.95–19.23 psu); 'Outer Estuary' sites between Coalhouse Fort and Foulness (sites 16–28) were typified by relatively high salinities (21.1–31.6 psu). Expressed on this salinity zonation basis, the decrease in BT concentrations from inner to the outer estuary was statistically significant ($P<0.05$; analysis of variance, Tukey's HSD test).

Relative proportions of BTs found in sediments within each of these zones are depicted (as means and ranges) in Figure 10. Ratios of MBT: DBT: TBT were very similar at the 'Inner' and 'Upper-Mid' estuary sites. However average proportions of DBT appear to decrease relative to the other BTs at 'Lower-Mid' and 'Outer' Thames sites. As in Mersey samples the sum of BTs represented a minor fraction (<1% mean) of the total tin in Thames sediments.

Butyltin concentrations in Thames mussels are shown in Table 5. Concentration ranges for MBT, DBT and TBT were 0.029–0.083, 0.055–0.116 and 0.1–0.302 μg g^{-1} dry wt, respectively. Butyltins constituted 80% of the total tin burden in Thames mussels (mean, all populations)—a similar proportion to that observed in Mersey mussels. Triphenyltin and other PTs were below the limits of detection in all samples from the Thames (mussels and sediments).

DISCUSSION

The Mersey and Thames Estuaries are among the largest, and economically, most important tidal waters in the UK. Traditionally, they have been regarded as examples of some of the most polluted estuaries in Europe, based largely on historic or anecdotal evidence, collated before the benefits of water quality improvement measures have had a chance to take effect. Unfortunately, recent information on the sources, distribution and behaviour of specific contaminants is sparse, hence the need for the current investigations on OTs. Such studies are essential to provide basic data on the ranges and concentrations of TBT and related compounds in these major estuaries—to re-evaluate their

https://doi.org/10.1017/S0025315403006738h Published online by Cambridge University Press

pollution status—and to assist in more general environmental fate predictions.

The Mersey still retains its reputation as an industrial estuary. Though its position as a major trading port has been in decline over the last two decades, shipping continues to utilize docks at Liverpool, Garston, Birkenhead and the MSC. Because OTs may still be used to protect commercial and naval vessels from fouling it is important to determine the current status of OT contamination, and the potential impact of inputs. Tributyltin concentrations in surface sediment collected from the Mersey Estuary ranged between 0.007–0.173 $\mu g\,g^{-1}$ dry wt. To put these results in to perspective with contemporary data elsewhere in the world, TBTs were present from 0.01–2.1 $\mu g\,g^{-1}$ dry wt in an industrial area of Japan (Harino et al., 1998), and from 0.004–4.5 $\mu g\,g^{-1}$ dry wt in Thailand (Kan-Atireklap, et al., 1997), whilst an average TBT value of approximately 0.5 $\mu g\,g^{-1}$ dry wt was reported for marine sediments in Hong Kong Harbour areas (Ko, 1995). Marina sediments from the Netherlands contained TBT in the range 0.006–0.52 $\mu g\,g^{-1}$ dry wt (Stab et al., 1996). Judging from these findings, TBTs in sediment from the Mersey Estuary do not appear to be exceptional for industrial sites, globally. Within the UK they appear to be fairly representative; for example, in the mid 1990s, TBT concentrations typically ranged from 0.026–0.181 $\mu g\,g^{-1}$ dry wt at most sites around Southampton Water and 0.002–0.119 $\mu g\,g^{-1}$ dry wt in Poole Harbour (Langston et al., 1997). Occasionally, however, concentrations close to docks and repair facilities may exceed this upper limit.

Triphenyltin was detected in only one sediment (New Brighton) and one mussel sample (Egremont), both close to the mouth of the Mersey. This is interesting because TPT is not thought to have been used as a component of antifouling paints applied in the UK. Its origins are uncertain but its presence here signifies, possibly, the influence of paint particles from overseas fleets. Similarly, whilst TPTs are not commonly reported in European marine habitats they have nevertheless been detected in some molluscs (e.g. *Mytilus galloprovincialis*, *Tapes decusata* and *Thais haemastoma*) and in red mullet *Mullus barbatus* from Spanish (Catalan) Mediterranean sites (Morcillo et al., 1997). Whilst antifouling paints are a likely source, origins associated with the use of TPT as a pesticide and fungicide during the last 30 years are also feasible (Langston, 1995; Kannan & Lee, 1996). Recently, for example, we have determined TPT residues in eels *Anguilla anguilla* from the Weston Canal (part of the MSC complex, near Warrington) which seem unlikely to have originated from antifouling applications (Harino et al., 2002). In view of the recognized toxicity of these triorganotins further research into their origins seems warranted.

The TBT concentrations in mussels *Mytilus edulis* from the Mersey Estuary ranged from 0.046–0.214 $\mu g\,g^{-1}$ dry wt Again this appears to be unremarkable by global standards. Values in mussels (*Mytilus galloprovincialis*) from three harbours on the Catalan coast, Masnou, Barcelona and St Carles, averaged 3.516, 0.461 and 0.067 $\mu g\,g^{-1}$ dry wt, respectively (Morcillo et al., 1997), whilst in freshwater mussels from the Netherlands, TBT concentrations of a similar range (0.18–2.5 $\mu g\,g^{-1}$ dry wt) have been reported (Stab et al., 1996).

In the axial profile of TBT concentrations in Mersey sediments significant peaks were observed at Stanlow and New Brighton (Figure 3). The presence of high concentrations of TBT at Stanlow may, as indicated, be due to the influence of water from the MSC and also the River Gowy, which drains land where substantial petrochemical industry facilities are sited. The TBT peak at the New Brighton site probably originates from settlement of enriched particles (including paint chips) which are transported from nearby docks. The fact that proportions of TBT were highest in the mid- and lower-estuary, and lowest upstream (Figure 4), also seems to infer that localized sources to the estuary (such as shipping and, possibly, wastes introduced via the MSC) are of more significance than riverine inputs from the Mersey.

The trend in TBT bioaccumulation in *M. edulis* further confirms the importance of estuarine sources, in that TBT concentrations decrease from the upstream limit of occurrence of mussels at Eastham, towards the open sea. As indicated earlier, water from the MSC and the Mersey Estuary are allowed to mix during locking operations at Eastham Lock. The presence of relatively high levels of TBT in mussels at this site is a further indicator that discharges of TBT from the MSC are a major influence on the estuary.

The composition of butyltins in mussels appears to vary little between locations along the Mersey. Tributyltin is the predominant species and represents approximately 50% of the total BT burden. Dibutyltin and MBT represent 27 and 23%, respectively. This ratio reflects the net product between uptake and metabolism of TBT in mussels: the relatively high proportion of the parent compound implies a significant influence from continuing inputs, albeit at relatively low levels. The strong correlation between total tin and BT concentrations in Mersey mussels is accounted for by the fact that the latter represent 85% of total tin burden. In contrast, BTs comprise only 4% of the HNO_3-extractable tin in Mersey sediments (and $<1\%$ in Thames sediments): this demonstrates the remarkably selective bioaccumulation of BTs, relative to inorganic Sn.

Tributyltin concentrations in sediment from the Thames Estuary (0.002–0.078 $\mu g\,g^{-1}$ dry wt) cover a slightly lower range than those in the Mersey, whilst DBT (and MBT) concentrations were broadly comparable in sediments from the two waterways (Figure 11). Despite the overall lower levels in Thames sediments, TBT concentrations in *M. edulis* (mean and maximum) exceed those in Mersey mussels by approximately 30% implying that bioavailability of TBT could be higher in the Thames.

Tributyltin concentrations in Thames sediments generally decreased in a seaward direction. There are major sewage treatment works and storm water run-off inputs to the inner- and mid-estuary which appear to be more significant sources of OTs than the dock areas located lower down the estuary. Furthermore, the ratio of DBT to total BTs is higher in the inner- and mid-Thames, suggesting discharges of DBT may also originate from sewage treatment works.

Clearly the factors which characterize the distribution of OTs in Mersey and Thames Estuaries are different and may reflect the different sources of contamination. It appears that the MSC and docks are a major influence on OT concentrations in the Mersey Estuary whilst inputs via sewage treatment works are likely to affect distributions in the Thames Estuary. Interestingly, these differences

also appear to influence bioavailability to filter-feeding molluscs. Although evidence is currently lacking, it is possible to suggest possible reasons for this phenomenon. Potentially, the high suspended solids load in the Thames Estuary (frequently of the order of 0.5 g l^{-1}) could render particle-associated contaminants such as TBT more readily-available for uptake in filter feeders such as mussels. Additionally, the disproportionate accumulation of TBT in Thames mussels could reflect enhanced assimilation due to the presence of sewage bi-products. Comparable enhancement of metal bioavailability has been attributed, for example, to the presence of bacterial exopolymers which appear to make sediment-bound forms more 'palatable' to filter feeders (Bryan & Langston, 1992).

CONCLUSIONS

Almost a decade after the prohibition of TBT paint on vessels less than 25 m in length (essentially the leisure fleet), TBT residues remain widespread in sediments from the Mersey and Thames Estuaries, and are typical of the concentration range found at many estuarine sites across the UK, and further afield. However, these concentrations are perhaps an order of magnitude lower than the worst-case values observed at the most contaminated locations (usually close to dockyards and marinas). Thus, chronic contamination of sediments appears to be an extensive feature in major industrialized estuaries and seems likely to persist for the foreseeable future. The main source of TBT in the Mersey is probably from docks and the MSC, whilst sewage treatment works appear to be a substantial source of TBT (and perhaps DBT) in the Thames. Triphenyltin was only detected in the occasional sample from the Mersey Estuary.

The data on OTs in sediment and mussels presented here should prove valuable as baseline information to assess the local benefits and time-scales for improvement following adoption of the International Convention on the Control of Harmful Anti-fouling Systems on Ships. They may help to establish, for example, the extent to which sediments from these estuaries remain reservoirs for OTs, and what the consequences will be for the management of dredging operations and disposal of spoils. More intensive studies would be useful in order to clarify the current status of OT contamination in these areas, and to establish the prognosis for recovery. In particular, sampling around potential sources (sewage treatment works; MSC; docks), including coring, might help to quantify their contributions to overall estuarine loadings. Mechanisms behind the apparent increased bioavailability of organotins in Thames mussels, and other biota, should also be investigated further.

REFERENCES

Bryan, G.W., Gibbs, P.E., Hummerstone, L.G. & Burt, G.R., 1986. The decline of the gastropod *Nucella lapillus* around south-west England: evidence for the effect of tributyltin from anti-fouling paints. *Journal of the Marine Biological Association of the United Kingdom*, **66**, 611–640.

Bryan, G.W. & Langston, W.J., 1992. Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: a review. *Environmental Pollution*, **76**, 89–131.

Environment Agency, 1997. *The water quality of the tidal Thames*. Environment Agency.

Harino, H., Fukushima, M. & Tanaka, M., 1992. Simultaneous determination of butyltin and phenyltin compounds in the aquatic environment by gas chromatography. *Analytica Chimica Acta*, **264**, 91–96.

Harino, H., Fukushima, M., Yamamoto, Y., Kawai, S. & Miyazaki, N., 1998. Organotin compounds in water, sediment, and biological samples from the Port of Osaka, Japan. *Archives of Environmental Contamination and Toxicology*, **35**, 558–564.

Harino, H., O'Hara, S.C.M., Burt, G.R., Pope, N.D., Chesman, B.S. & Langston, W.J., 2002. Butyltin and phenyltin compounds in eels (*Anguilla anguilla*). *Journal of the Marine Biological Association of the United Kingdom*, **82**, 893–901.

Kan-Atireklap, S., Tanabe, S. & Sanguansin, J., 1997, Contamination by butyltin compounds in sediments from Thailand. *Marine Pollution Bulletin*, **34**, 894–899.

Kannan, K. & Lee, K.R., 1996. Triphenyltin and its degradation products in foliage and soils from sprayed pecan orchards and in fish from adjacent ponds. *Environment Toxicology and Chemistry*, **15**, 1492–1499.

Ko, M.M.C., Bradley, G.C., Neller, A.H. & Broom, M.J., 1995. Tributyltin contamination of marine sediments of Hong Kong. *Marine Pollution Bulletin*, **31**, 249–253.

Langston, W.J., 1986. Metals in sediments and benthic organisms in the Mersey Estuary. *Estuarine, Coastal and Shelf Science*, **23**, 239–261.

Langston, W.J., 1995. Tributyltin in the marine environment: a review of past and present risks. *Pesticide Outlook*, **6**(6), 18–24.

Langston, W.J., Burt, G.R. & Mingjiang, Z., 1987. Tin and organotin in water, sediments, and benthic organisms of Poole Harbour. *Marine Pollution Bulletin*, **18**, 634–639.

Langston, W.J. et al., 1997. *Risk assesment of organotin antifoulings on key benthic organisms of European coastal habitats (BOATS) Final Report. MAS2-CT94-0099*: 247 pp.

Langston, W.J., Gibbs, P.E., Pascoe, P.L., Chesman, B.S., Burt, G.R., Pope, N.D. & McEvoy, J., 2000. Tributyltin (TBT) impact in the Thames Estuary. *Thames Estuary Water Quality Series*, **1**, 1–67. [Environment Agency.]

Langston, W.J. & Pope, N.D., 1995. Determinants of TBT adsorption and desorption in estuarine sediments. *Marine Pollution Bulletin*, **31**, 32–43.

Laughlin, Jr, R.B. & Linden, O., 1987. Tributyltin—contemporary environmental issues, *AMBIO*, **16**, 252–256.

Maguire, R.J., Chau, Y.K., Bengert, G.A., Hale, E.J., Wong, P.T.S. & Kramer, O., 1982. Occurrence of organotin compounds in Ontario lakes and rivers. *Environmental Science and Technology*, **16**, 698–702.

Morcillo, Y., Borghi, V. & Porte, C., 1997. Survey of organotin compounds in the western Mediterranean using molluscs and fish as sentinel organisms. *Archives of Environmental Contamination and Toxicology*, **32**, 198–203.

Pope, N.D., Langston, W.J., Burt, G.R. & Chesman, B.S., 1998. A survey of trace metals in biota of the Mersey Estuary—1995. *Plymouth Marine Laboratory Miscellaneous Publications*, **113**, 1–122.

Pope, N.D., Langston, W.J., Burt, G.R. & McEvoy, J., 1996. A survey of trace metals in biota of the Mersey Estuary—1995. *Plymouth Marine Laboratory Miscellaneous Publications*, **81**, 1–158.

Rees, H.L., Waldock, R., Matthiessen, P. & Pendle, M.A., 1999. Surveys of the epibenthos of the Crouch Estuary (UK) in relation to TBT contamination. *Journal of the Marine Biological Association of the United Kingdom*, **79**, 209–223.

Stab, J.A., Trass, T.P., Stroomberg, G., Kesteren, J. van, Leonards, P., Hattum, B. van & Brinkman, U.A., 1996. Determination of organotin compounds in the foodweb of a shallow freshwater lake in the Netherlands. *Archives of Environmantal Contamination and Toxicology*, **31**, 319–328.

Thomas, K.V., Benstead, R.E., Thain, J.E. & Waldock, M.J., 1999. Toxicity characterization of organic contaminants in industrialized UK estuaries and coastal waters. *Marine Pollution Bulletin*, **38**, 925–932.

Uren, S.C., 1983. Acute toxicity of bis(tri-butyltin) oxide to a marine copepod. *Marine Pollution Bulletin*, **14**, 303–306.

Waite, M.E., Waldock, M.J., Thain, J.E., Smith, D.J. & Milton, S.M., 1991. Reductions in TBT concentrations in UK estuaries following legislation in 1986 and 1987. *Marine Environmental Research*, **32**, 89–111.

Waldock, R., Rees, H.L., Matthiessen, P. & Pendle, M.A., 1999. Surveys of the benthic infauna of the Crouch Estuary (UK) in relation to TBT contamination. *Journal of the Marine Biological Association of the United Kingdom*, **79**, 225–232.

Submitted 17 December 2001. Accepted 30 September 2002.