Chapter 5
Behaviour of Organotins in the Coastal Environment

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5.1 Introduction

The use of TBT and TPT as constituents of antifouling compounds, over more than three decades, has left many coastal environments with a longstanding legacy of contamination. Inputs to water should no longer be an acute threat. However, despite recent actions by IMO to ban the use of these compounds, recovery will not be instantaneous and contamination could even increase at some locations where the legislation is ineffective, or where coatings are replaced, or sediments re-mobilised. Partitioning to solids is reversible and hence sediments may act as a persistent sink and secondary source of adsorbed organotins, as well as those residues entrained as paint flakes from boatyards and docks. Estimates of TBT half-times in sediments range from a few months to decades (in anoxic sediments), indicating that this 'reservoir' of organotins is likely to remain biologically relevant, and will require management, for a considerable period. For some ports and harbours, appropriate dredging and disposal of TBT-enriched sediments represents an extremely costly option to maintain viability, and it will be important to ensure that further harm to the environment does not ensue from remobilization of these residues. Based on example in the UK, we review here some of the factors which influence long-term partitioning behaviour and persistence of organotions (predominantly TBT) – and the likely timescales for recovery.

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5.2 Persistence of Organotins in Water and Sediments

Persistence of any chemical in the environment is a function of biological, chemical and physical degradation, together with physical removal mechanisms. Photolysis and chemical degradation of tri-substituted organotins (mainly TBT) has been demonstrated in the laboratory though, in nature, particularly in turbid estuaries where attenuation of UV light occurs within the upper few centimeters, microbially-mediated debutylation to DBT and, to a lesser extent MBT is the predominant mechanism by which these compounds are broken down (Seligman et al. 1996a). Only in the photic zone of clearer freshwater systems is abiotic photolysis likely to be of significance (half time ~3 months).

In seawater and estuarine water, half-times for TBT, derived from short-term laboratory experiments, are rather variable, but generally observe zero-order kinetics, with values ranging from 4 to 19 days (reviewed by Seligman et al. 1996a). However, longer term mesocosm studies suggest rather longer degradation (months), together with first-order kinetics and rate constants in the range 0.1–0.2 day^{-1}. There are some indications that the rate of degradation, expressed as the proportion of metabolites in the sample, is a function of residence time of the water body, and is also a function of microbial populations in the water column and temperature (low in winter). Relationships have been found between degradation and the presence of photosynthetic organisms such as diatoms and dinoflagellates. It is also possible that degradation rates may be enhanced by prior exposure of the microbial population to TBT or even other xenobiotics, though adaptation to TBT has not been widely demonstrated.

The fate of TBT is more complex once incorporated into sediment. Seligman and co-authors (1996a) have described rather rapid, sediment-enhanced degradation of spiked TBT in aerated conditions (half times 2–15 days); however TBT bound tightly to sediment or paint particles appears to be considerably more persistent. It has been suggested that TBT in paint particles may be considerably less bioavailable than that adsorbed to sediment particles and if so, may represent a much more persistent legacy. The proportion of paint particles in sediment could conceivably explain some of the variation in estimates of half lives seen in nature (see section 5.4), though as in water, there are numerous characteristics which influence behaviour.

Measured half times for TBT in experiments with unspiked sediments are invariably longer than in water and typically are of the order of several months (sometimes longer), with both bacteria and fungi contributing significantly to measured degradation rates through dealkylation to both DBT and, particularly, hydrophilic MBT (Seligman et al. 1996a). Several authors have indicated that sediment anoxia is a principal factor determining half times; in extreme cases estimates of half lives in benthic muds are in excess of 10 years, as suggested by Maguire (2000). Sediments where biological degradation was suppressed by KCN showed no degradation after ~1 year (Maguire and Tkacz 1985).

Our own laboratory experiments conducted in flow-through aquaria (complete water exchange daily), containing undisturbed sediments labeled with ^{14}C-TBT (0.3 mg kg^{-1}, as Sn), indicate very low rates of degradation. Half-times increased with depth in the sediment and ranged from 2.6 years at the surface (0–5 cm) to

3.5 years (at 5–10 cm), and to 8.5 years at the more anoxic bottom of the cores (10–15 cm). Degradation decreased with depth and the proportion remaining as TBT, after 4 years was 72%, 85% and 89% in upper middle and lower parts of the core, respectively. Loss rates via this mechanism were estimated to vary from 0.013% to 0.028% day^{-1}. Diffusive losses were also relatively small in these undisturbed cores (0.0015% day^{-1}), representing a leach rate of 1.37 μg m^{-2} day^{-1}. Clearly, in undisturbed sites in estuaries marinas and docks, sediments could retain loadings for perhaps a decade or more (see section 5.4). Not surprisingly, however, release rates increased as a function of flow rate over these cores.

Interestingly, the estimated TBT release rates from sediment cores are comparable to *in situ* measurements made at the sediment-water interface (Stang and Seligman 1987), and are of the same order as many estimates of leach-rates from anti-fouling paints. Seligman et al. (1996b) have shown the latter may vary considerably between coatings (0.1–2.8 μg cm^{-1} day^{-1}) but it would appear that sediments operate as a slow-release mechanism for TBT which is analogous to many paint matrices.

Experiments with sediments in mesocosms have confirmed that once incorporated into sediment, degradation is dramatically slowed to a rate of ~1×10^{-4} day^{-1}, most notably during a declining temperature regime (to 5°C) designed to simulate winter conditions (Seligman et al. 1996a). These authors have suggested a short-lived chemical (possibly catalytic) component to degradation of OTs at the sediment-water interface (with MBT as a predominant product) followed by a much longer period of microbial degradation lasting several months or more. Sediments thus act as a store for any TBT that is not degraded and may act as a slow release mechanism, depending on conditions.

Potentially, the biological activity of infaunal macro-organisms (bioturbation) could enhance the process of mobilization of organotins in sediments. In laboratory leaching studies with ^{14}C-TBT labeled sediment (0.3 mg kg^{-1}, as Sn), in flow through aquaria (complete water exchange daily), the presence of both worms *Nereis diversicolor* (at a density of 550 m^{-2}) and burrowing clams *Scrobicularia plana* (at a density of 165 m^{-2}) were shown to enhance release of TBT to overlying water compared to sediments devoid of macrofauna. This was particularly evident in the initial few days after fauna were added, as they established burrow systems. Average daily net losses due to bioturbation (over 69 and 128 day periods) were 0.0012% and 0.0008% day^{-1} for worms and clams, respectively. This is roughly equivalent in magnitude to losses by diffusion/desorption and represents a relatively small fraction of the sediment budget (<5%). Comparable behaviour has also been observed following colonisation of contaminated sediment by the mud-snail *Hinia reticulata* (Pope 1998), though losses were higher (>0.1% day^{-1}) due to the larger number of animals (300 m^{-2}) and their greater mobility. Figure 5.1 shows the influence of addition and removal of these snails on the release of TBT from sediment (10.2 μg g^{-1}) to overlying water. It is possible that major bioturbator species, such as burrowing shrimps belonging to the family Callianassidae, could have even larger effects on release and redistribution of TBT from, and within, sediment (through burial and re-working). The scale of these biological processes in different types of bioturbating organism, and their influence on the fate of organotins, are interesting topics for further study.

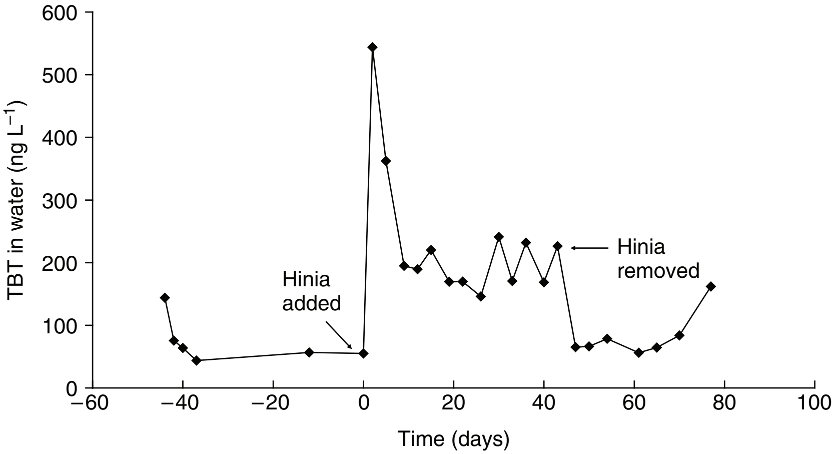


Fig. 5.1 Influence of bioturbation on the release of TBT to overlying water following the introduction (day 0) and removal (day 43) of the mud-snail *Hinia reticulata* to a flow-through sediment-water system equilibrated with ^{14}C TBT

Thus, whilst the rapid degradation of TBT observed in incubated water samples has led some authors to label TBT as relatively non-persistent, the fate in coastal ecosystems can be modified by a wide range of specific properties. The most meaningful evaluations of behaviour are therefore based on site-specific field observations (see section 5.4). Flushing rates, microbial populations and temperature are important variables. For example, the degradation of TBT is minimal below ~5°C and will consequently be very slow in cold climates and vulnerable polar areas. However, the influence of particulates, coupled with hydro- and sediment dynamics, is probably the most critical factor affecting the fate of TBT residues in coastal habitats. Many sediments will represent a substantial legacy of TBT use and may provide continuing inputs to the water column. Crucially, such sediments may also represent disturbed biological habitats and furthermore, delay the TBT degradation and loss processes significantly.

5.3 Determinants of Sediment-Water Partitioning

Given that the behaviour of organotins differs significantly in sediment and water, and that degradation rates are at least an order of magnitude longer in sediments, the long-term fate of these compounds will depend heavily on their relative partitioning between aqueous and particulate phases. Factors that promote adsorption of organotins to particulates will tend to increase their long-term retention, and in sheltered coastal and estuarine habitats, sediments will act as a reservoir and secondary source of contamination long after new inputs have ceased as a result of paint bans. Several models have been developed to describe the adsorption process, however, at low concentrations of solute, all sorption isotherm models predict linear sorption, leading to widespread acceptance of the linear (constant partitioning) model (Eq. 5.1) under these conditions:

$$q = K_p C \tag{5.1}$$

Where, at equilibrium, q is the mass of solute sorbed per unit mass of the solid phase, C is the concentration in solution and K_p is a constant termed the *partition coefficient*.

Most sorption isotherm models assume a condition of dynamic equilibrium and reversibility, suggesting that sorbed compounds will readily become desorbed when concentrations in the surrounding water drop below equilibrium levels. Experimental studies indicate this is the case for TBT in freshly spiked systems, at low concentrations (Langston and Pope 1995), though in organic rich benthic muds it is possible that a proportion of the compound may be bound in an irreversible state which in some cases may also be related to the "age" of the solute/sorbent combination. At higher concentrations, TBT sorption exhibits a Freundlich-type (non-linear) isotherm whereby the value of the partition coefficient varies with TBT concentration (K_p decreases as TBT increases). This is a feature of ionisable organic solutes and reflects decreasing solute-sediment affinities as more adsorption sites become filled.

A number of characteristics (of solute and sorbent) influence the sorption process. Firstly there is the hydrophilic-hydrophobic balance of the solute, usually measured as the degree to which the solute partitions between n-octanol and water – the octanol-water partition coefficient (K_{ow}). TBT is sequestered readily by suspended particulates (usually equilibrium occurs within a few hours), due to its low solubility and its hydrophobicity (log K_{ow} ~3.8). Therefore it has a relatively strong tendency to become incorporated into estuarine sediments where it may remain long after new inputs have ceased.

Secondly, because of the affinity of TBT for hydrophobic organic phases, the fractional organic carbon content (f_{oc}) of the solid phase can be important in determining concentration, such that an organic carbon normalised partition coefficient (K_{oc}) may be a useful way of comparing sediment contamination (Eq. 5.2), explaining some but not all of the variation.

$$K_{oc} = \frac{K_p}{f_{oc}} \tag{5.2}$$

However, organic content alone seldom explains partitioning behaviour totally. Several studies have observed inverse relationships between K_p and both particle concentration, and particle size; the latter can be partly explained by the total surface area available for sorption, although often this may be attributable to higher carbon content of smaller particles. It is also important to note that partitioning data derived from experiments can be influenced artificially by drying, oxidation or freezing of the sediment, unrealistic concentrations, inadequate phase separation and inadequate recovery. Together these factors explain some of the variability for reported K_p values for TBT (Table 5.1). Using radiolabelled ^{14}C-TBT, we have attempted to avoid these pitfalls and have determined equilibrium K_p values of 248–24,677 l kg^{-1} in batch experiments with 16 natural sediments from the south coast of England (Langston and Pope 1995; Pope 1998). Highest K_p values were associated with organic-rich silty sediments. Published *apparent* sorption coefficients, based on *in situ* field measurements of sediment and overlying water, exhibit a wide variety values (over three orders of magnitude), though often in the range 10^3–10^4 l kg^{-1}, at the high end of the scale found in laboratory-based equilibrium experiments. Harris et al. (1996) and others have suggested that, in the field, some of the higher values may signify the presence of antifoulant paint chippings, near boat maintenance facilities, though this has yet to be verified. It may be that higher K_p values occur *in situ* because the system is not at equilibrium: long-term desorption experiments support the hypothesis that sub-equilibrium levels of TBT are desorbed from benthic sediments which are not well-mixed (Pope 1998).

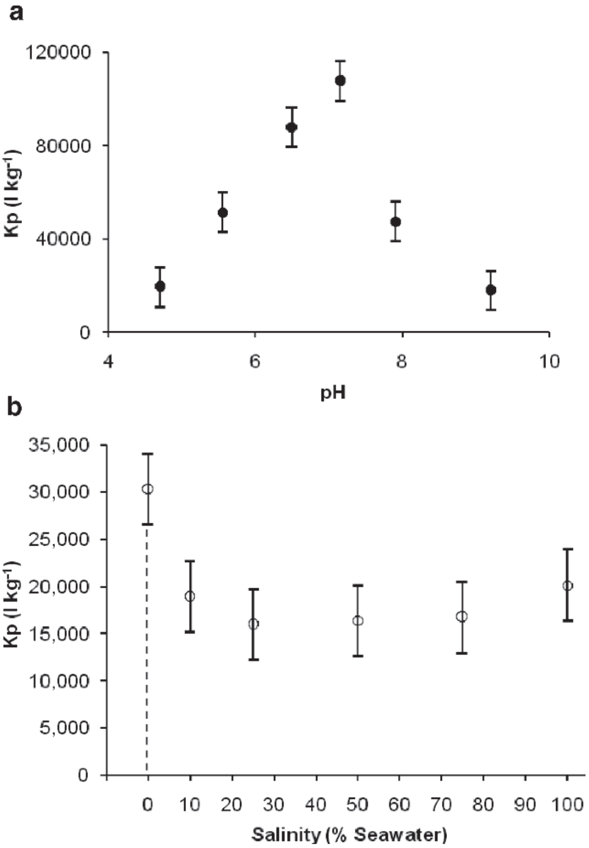
The nature of the aqueous phase may influence sorption in several ways. pH is one of the master variables for surface coordination reactions, reflecting solution hydrolysis, protonation of adsorbing ions and surface charge properties of the adsorbent. The effect of pH on TBT partitioning revealed highest values for K_p (~107,589 l kg^{-1}) at neutral pH (~7) (Fig. 5.2). The K_p decreased sharply with both increasing or decreasing pH (~19,243 and 17,667 l kg^{-1} at pH 4.65 and 9.19 respectively), reflecting increased solubility of TBT under these conditions. In estuarine environments, pH is usually buffered via the seawater carbonate system to near-neutral conditions (pH ~8) but it is feasible that under low salinity conditions in the upper reaches of estuaries, or under high freshwater flow, pH could become a relevant factor in TBT partitioning (Langston and Pope 1995).

Next to pH, competitive adsorption is probably the second most important way in which dissolved solutes affect adsorption of cations – notably bulk inorganic constituents (e.g. Ca, Mg) that mutually adsorb onto the same sites on the solid phase. The extent of competition depends upon relative concentrations of these solutes and affinities for the same sites. Ionic strength (or salinity) therefore influences sorption, affecting activities in solution and surface charge on particles. Increasing salinity also increases the aggregation of suspended particulates, which may in turn influence the kinetics of sorption – by necessitating solute diffusion into aggregate pore waters. Concomitantly the total surface area, and therefore the rapidly reversible component of sorption, decrease. Given this complexity it is not surprising that studies on the effects of salinity on TBT partitioning often showed conflicting results (Randall and Weber 1986; Unger et al. 1987, 1988; Harris et al. 1996); interpretation is confounded in some of these studies by use of unrealistic TBT levels, artificial substrates, processed sediments or non-natural waters. In attempting to avoid some of these inconsistencies, investigations with two natural sediments and estuarine water (Langston and Pope 1995; Pope 1998) showed highest K_p values in fresh water (60,613 and 30,333 l kg^{-1}) reducing to 15,000 and 17,200 l kg^{-1}, respectively, at salinities between 25% and 100% seawater. Concentrations in water were at a maximum between 25% and 75% seawater, perhaps reflecting the effect

Table 5.1 Reported sediment-water partition coefficients for TBT

Partition coefficient (l kg^{-1})	Suspended sediment load (mg l^{-1})	Salinity (g l^{-1})	pH	Notes	Reference
3,278–3,918	5.8–6.7	Sea water			Valkirs et al. (1986)
929	14	Sea water			
340	50	Sea water			
3,000	10	Sea water			M & T Chemicals (unpublished). Referred to in Valkirs et al. (1986)
1,500–1,900,000	10–1,000	Artificial sea water	6.2–8.2	Fulvic acid-coated hydrous iron oxide used as the solid phase	Randall and Weber (1986)
2,180	5,000	Sea water		Natural harbour sediment, unfiltered water	Maguire and Tkacz (1985)
111–8,200	No data	0–35 (Artificial seawater)		Only aqueous phase analysed	Unger et al. (1988)
6,250–55,439	No data	Sea water		*In situ* measurements in Pearl Harbor mesocosms	Stang and Seligman (1987)
4,608–39,352	1.6–8.6	Sea water			Valkirs et al. (1987)
200–1,400	60–100	0–32 (filtered seawater)		Sediments were freeze dried, ground, and sieved (100 mesh)	Harris and Cleary (1987)
17–4,500	1,000	Seawater		Experimentally determined values	Kram et al. (1989)
32–292,000				Calculated from field analyses of sediments and overlying water	
248–24,677	<1,300	Seawater		Extensive studies on TBT partitioning using radiolabelled ^{14}C-TBT	Langston and Pope (1995); Pope (1998)
30,333–60,613		River water		Natural sediments and water, effects of pH, salinity, sediment load and type	
19,243		Seawater	4.65		
107,589		Seawater	7.0		
17,667		Seawater	9.19		

Fig. 5.2 Effect of pH (a) and salinity (b) on TBT partitioning (Adapted from Langston and Pope 1995)



of chloride ion concentration on TBT speciation in solution: above 75% seawater there was a 'salting-out' effect due to lower solubility, consistent with most organic (hydrophobic) contaminants. The increasing removal to particulates at salinities below 25% seawater may reflect the growing influence of the ionic components of the TBT molecule and shifts in speciation, coupled with modifications to charges on the sediment surface, in water of low ionic strength.

5.4 Natural Resuspension, Dredging and Disposal of Contaminated Spoils – The Continuing Legacy of TBT

The partition coefficient does not appear to change markedly (<2-fold) over a wide range (30-fold) of suspended solids concentrations (Langston and Pope 1995), though obviously, as TBT partitions in favour of sediment, the amount of sediment in suspension will influence the transport budget of TBT, particularly in turbid estuaries and coastal systems. The fate and persistence of TBT in the water column and sediments is therefore dependent on a combination of hydrodynamic and biogeochemical factors (Ruiz et al. 1996). Localised circulation patterns and tidal flows usually determine the residence time for TBT and hence the ultimate loadings. Where water movements are strong, distributions of TBT may be fairly homogeneous, however in less dynamic environments, heterogenous distributions in sediments are more likely. Sediment sources will be of more significance where contamination levels, and K_p, are high. Seasonal trends can also markedly influence residence times for TBT, and hence the influence of sediment release on concentrations in water. A discussion of the dynamics of release and how sediment loadings might be simulated under estuarine conditions is provided by Harris et al. (1996). Although reasonable estimates of partition coefficients and degradation rates are now available to incorporate into such simulations, estimates of the total mass of exchangeable sediment and its exchange rate with the water column are often more difficult to parameterise. If mixing times are very rapid, relative to equilibration times for TBT partitioning, laboratory- derived K_p values may be less representative of natural partitioning.

Behaviour of TBT and the role of sediments as a secondary source will clearly be site specific. As TBT inputs to water decline there will be a tendency, over time, for K_p values to increase according to a logarithmic relationship favouring retention in sediments (Langston and Pope 1995). Thus, as sources of 'new' TBT are eliminated indications are that releases from relatively undisturbed sediments at most locations are likely to be slower, in relation to the original inputs. Nevertheless, any process that results in increased sediment/water mixing (tidal resuspension, dredging, bioturbation) would invariably be expected to remobilise and release some of the sediment-bound TBT. The potential for desorption of TBT, as sediments age, does not appear to vary greatly over relatively long periods (Pope 1998).

An example of natural tidal resuspension affecting transport and distribution of TBT is shown in the axial profile (summer) for the macro-tidal Tamar Estuary, UK, in Fig. 5.3, which encompasses sites from freshwater to the sea. Prior to TBT legislation TBT was dominated by inputs from the dockyards and marinas towards the mouth of the Estuary (concentrations were sometimes in excess of 100 ng l^{-1} here). These inputs have now all but ceased as a result of control measures and TBT concentrations are much lower whilst the estuarine profile is governed by natural physical and chemical processes. A dominant aspect is the sharp change occurring upstream (0–10 km from the tidal weir) near the freshwater-seawater interface. This region coincides with the region of maximum turbidity (note high suspended solids loads) caused by tidal-resuspension of particles at the salt wedge. Since there is no evident freshwater input for TBT, origins are presumed to be the legacy of sources near the mouth, described above. The type of profile exhibited in the Tamar is generated internally by interactions within the estuary, with the TBT maximum at the head resulting from upstream transport of tidally re-suspendable sediment, coupled with remobilization and desorption at low salinities (consistent with partitioning results, described above). This occurs primarily in the calmer low-flow summer period: in periods of high-flow (usually winter) distributions are more homogeneous as material

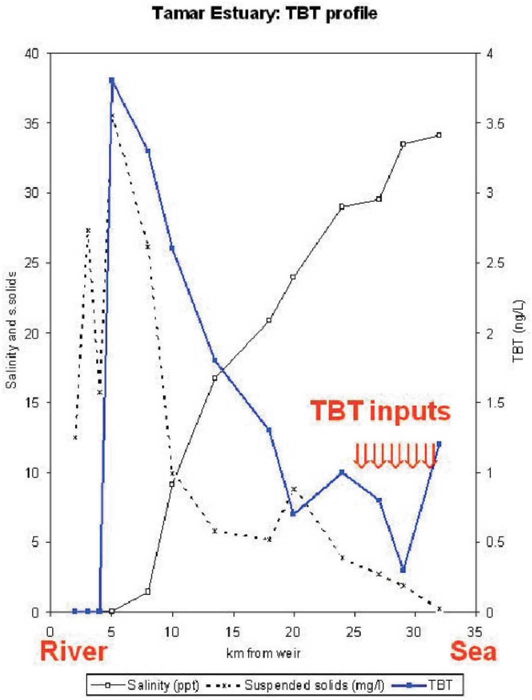


Fig. 5.3 Profiles showing TBT concentrations, salinity and suspended solids in the water column of the Tamar Estuary, UK

is transported back down estuary, completing the process of internal cycling. In the absence of significant net export from the system this pattern of cycling could mean that estuaries retain TBT burdens for a number of years.

Maintenance of the seasonal TBT 'inputs' at the turbidity maximum, typified in Fig. 5.3, can thus be envisaged as a continuous balance between recruitment from and deposition in estuarine sediment. This advective process is a more effective means of transferring TBT from sediment to the water column than diffusion alone and will be subjected not only to climatic variation but also to oscillations in spring/neap tidal energy inputs. Such pronounced reactivity may not be evident in less dynamic systems. Nevertheless, this example highlights the fact that estuarine particulates can become the dominating force determining distributions in the water column, following the removal of primary sources.

For port authorities, regulators and conservation agencies, concern arises where the re-mobilization of TBT from sediments is artificially enhanced following dredging or general disturbance (Brack 2002) and difficulties in managing this problem have frequently been highlighted (e.g. Svavarsson et al. 2001; Santos et al. 2004). For example, dredging of parts of Southampton Water during the last decade, to improve access to ports and marinas, has coincided with a halt in the decline of TBT levels in water at some sites. The time course of TBT reduction in waters can be substantially altered by prolonged activity, as indicated for the Hamble, Southampton, in Fig. 5.4; continuing use of TBT on shipping using the commercial

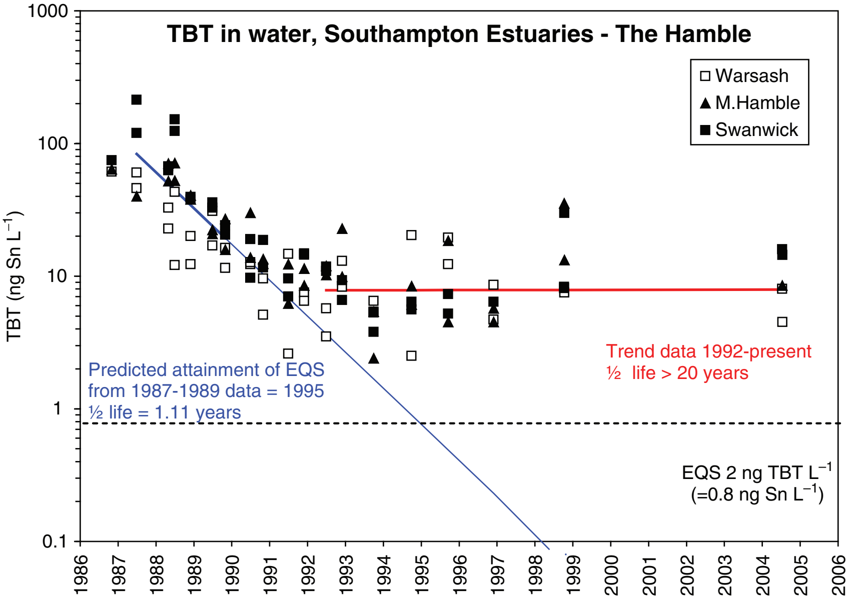


Fig. 5.4 TBT in water (ng l^{-1} as Sn), Hamble Estuary. Initial recovery, following legislation in 1987 has been halted, probably due to a combination of sediment re-release (including dredging) and some continuing use of TBT coatings

port, nearby, may have also contributed to the inputs from sediment disturbance. As a result, the system has been at steady-state in recent years – at concentrations substantially above the Environmental Quality Standard (EQS) of 0.002 µg l^{-1}.

Maritime ports are constantly under pressure to intensify the volume of containerised transport vessels to meet competition and, in Europe, there are plans to meet this demand by developing some ports as regional hubs (Marcadon 1999). Expansion could lead to enhanced remobilization of sediment-bound TBT and possibly even further recharge of sediments in some locations, depending on conditions. In addition, as channels may have to be extended and maintained to greater depths, to allow access to larger vessels (Side and Jowitt 2002), the impact of resuspension events and dredge spoil disposal may increase at sites which are currently unaffected by TBT (Svavarsson et al. 2001). This is particularly contentious where there is potential for resuspended material containing TBT to be transported extensively into adjacent statutory conservation areas. Recently for example, expansion of the Port of Southampton, UK, has been refused because of such concerns over designated sites. Given such important economic and conservation issues, there are strong arguments to establish better cause-effect relationships between dredged spoil disposal activities and the impacts of TBT on protected species and habitats. Without such evidence there is a risk of poor decisions being made: at one extreme this could result in failure to protect vulnerable species, at the other, over-precautionary actions could lead to unnecessary increases in disposal costs and possibly even port closure.

Clearly however, given the reversible nature of TBT adsorption in sediment, it is important to ensure that levels do not exceed thresholds for the most sensitive species as a result of remobilization events. Even where re-release is negligible, there may still be a significant threat from particulates enriched with TBT, since for infaunal species such as the clam *Scrobicularia plana* and mud snails *Hinia reticulata*, sediments are an important vector for bioaccumulation (Langston and Burt 1991; Pope 1998; *see* Chapter 16). Bioavailability and toxicity of sediment-bound TBT, like partitioning, will vary according to sediment characteristics of which organic carbon content is a primary determinant. Organic carbon appears particularly important in modifying desorption and bioavailability in species such as *Hinia* which derive body burdens through contact with sediment rather than ingestion, perhaps through its regulation of pore water concentrations. Thus, desorption tends to be highest where sediments are low in organics (low K_p and K_{oc}), and, correspondingly, aqueous routes of uptake – and toxicity – become more prominent (Meador et al. 1997; Pope 1998). There are undoubtedly other, more subtle, sediment influences, such as particle size, humic and colloidal content, which have yet to be explained.

5.5 Monitoring Temporal Trends in Coastal Systems

After initial legislation prohibiting the use of organotin antifouling on most leisure craft (1987 in the UK), TBT and TPT continued to be used on larger vessels, on the assumption that levels in offshore seas would be diluted sufficiently to prevent deleterious effects. Around the UK, on open coastlines, reduced contamination has been demonstrated by declining imposex severity and the recovery of dogwhelk *Nucella lapillus* populations (Fig. 5.5; Hawkins et al. 2002). Even so, this recovery process has been relatively slow (10+ years) and there are still populations of neogastropods which are heavily impacted close to ports, both in the UK and elsewhere (Galante-Oliveira et al. 2006; Gibbs 2009). Similarly, in Arcachon Bay, France, despite rapid reductions in seawater concentrations of between five- and ten-fold in the 3 years after legislation (1982), and accompanying improvements in *Crassosstrea gigas,* sediment contamination was still considered responsible for effects in oysters some 20 years after TBT legislation (Alzieu 2000). Furthermore, the assumption that removing TBT from the leisure market would be sufficient protection for the marine environment was not upheld by the evidence from a number of post-ban studies, notably those which demonstrated the continuing presence of imposex in snails close to offshore shipping routes and anchorages (Hallers-Tjabbes et al. 2003; Rato et al. 2006).

In a number of inshore and estuarine areas where small boats are predominant, such as the Crouch Estuary (Waldock et al. 1999) and Poole Harbour, UK (Langston et al. 1987, 1994) sediment-dwelling macrofauna have responded successfully to legislation and the earlier decline of populations of many species has been halted, as levels of bioavailable TBT are reduced. In other areas, however, reductions of TBT levels, and recovery of biota has been slower, perhaps because of the combination

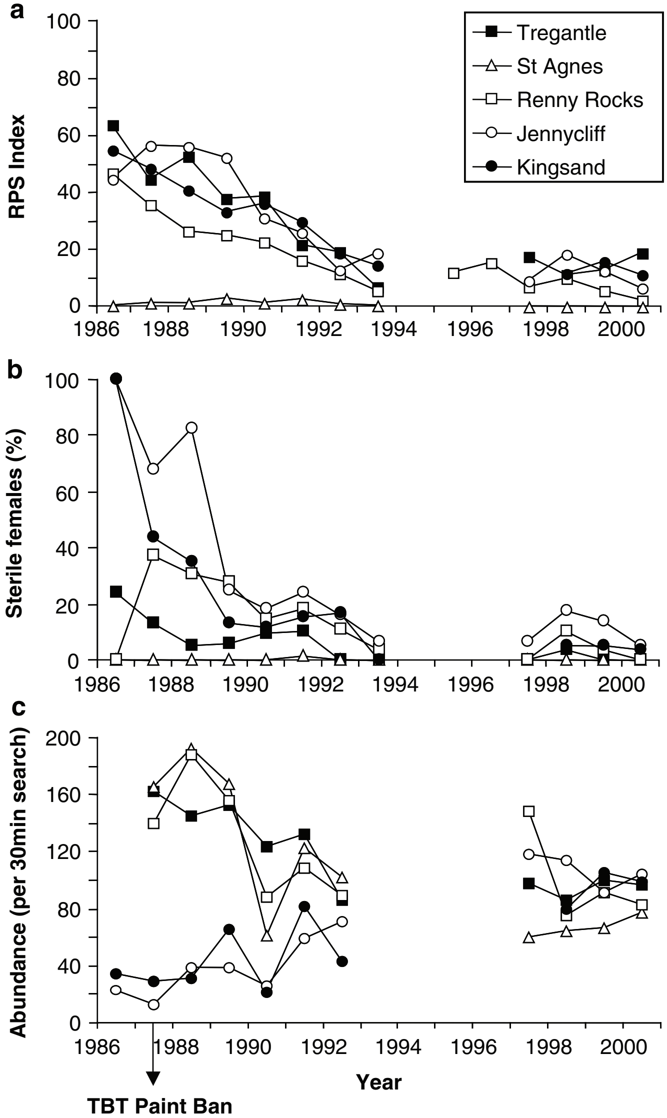


Fig. 5.5 Recovery of dogwhelks (*Nucella lapillus*) from TBT pollution following UK ban in 1987 on boats <25 m (Reproduced from Hawkins et al. 2002, with acknowledgements to Elsevier)

of protracted release of organotin bound up in sediments, and continuing inputs from the commercial fleet (Langston et al. 1990, 1994; Langston and Burt 1991; St.-Jean et al. 1999). This is evident for example, in parts of Southampton Water and its estuaries – a major port and sailing centre in the UK.

Table 5.2 compares half times for TBT in different environmental compartments at different sites in Poole Harbour and Southampton (for data up to 2004).

Table 5.2 Poole Harbour and Southampton Estuaries: Summary of TBT environmental half-times (months) in water, sediment, clams *Scrobicularia plana* (post-1987)

POOLE HARBOUR

Site	Harbour area	Boat traffic (mainly leisure)	Water	Half-times sediment	(months) *Scrobicularia*
Jerry's Point	South	Low	29	122	–
Brands Bay	South	Negligible	52	117	55
Wytch Farm	South	Negligible	39	85	57
Parkstone	North	Moderate	45	62	47
Power Station	North	Moderate	36	101	–
Sterte (Holes Bay)	North	Moderate-high	41	95	47
Lytchett Bay	North	Low-moderate	39	(NS)	68
Marina	North	High	18	–	–

SOUTHAMPTON ESTUARIES

Site	Estuary	Boat traffic	Water	Half-times sediment	(months) *Scrobicularia*
Totton	Test	Upstream of commercial port	NS	NS	NS
Cracknore	Test	Commercial and Naval	NS	NS	NS
Swanwick	Hamble	Leisure-high	23	55	44
Mid Hamble	Hamble	Leisure-high	31	55	44
Warsash	Hamble	Leisure-high	49	51	55
Upper Itchen	Itchen	Leisure low	30	89	91
St.Denys	Itchen	Leisure – moderate	36	NS	106
Northam	Itchen	Leisure – high	51	111	207
Woolston	Itchen	Leisure and commercial	96	NS	204

NS – Slope of regression not significantly different from zero.

Half-times are predictably influenced by the density and type of shipping/boating activity and also by nature of the site/sample type.

Poole Harbour, with its narrow entrance and limited tidal range and currents, was originally selected for study as a possible worst-case situation with regard to contamination from tin-based anti-fouling paints. This large natural lagoon is utilised by several thousand leisure vessels (and a relatively small number of commercial ships) and was therefore considered an ideal location to examine contamination in relation to boating patterns. Because of the predominance of small-vessels (prohibited from using TBT paints in 1987), it was also considered ideal for judging the effectiveness of legislation on reducing pollution; hence monitoring of water, sediment, and a variety of bioindicator species (clams *Scrobicularia plana*, *Mya arenaria*; worms, *Nereis diversicolor*; seaweed *Fucus vesiculosus* and snails *Littorina littorea*) has taken place at intervals over the last two decades (Langston et al. 1987, 1994). Elevated TBT residues were encountered in various parts of the Harbour during the 1980s, often in excess of 100 ng l^{-1} and sometimes in excess of 1 µg l^{-1}, notably near marinas and high-density moorings situated along the northern shoreline. In contrast, the southern shoreline is relatively undeveloped and contamination levels were correspondingly lower (several nanograms per liter) though still often exceeding the EQS (Langston et al. 1987). The success of TBT regulations, in reducing inputs to the water column, can be assessed from the summary of environmental half-lives in Table 5.2 and was most effective at marina sites. Following TBT legislation in 1987, environmental 'half lives' for TBT in Poole waters ranged between 18 and 52 months – presumably extended in comparison with laboratory estimates by continuing residual inputs from boats and sediment desorption (Table 5.2). The rate of decline in TBT concentrations in water may be slowing down at some sites and, occasionally, reversed. It is possible that small amounts of 'new' TBT are still being introduced illegally into the system, or that maintenance dredging is causing transient pulses of TBT in water.

The relatively high affinity of TBT for the particulate phase partly explains why high concentrations tend to be retained close to the major TBT sources (marinas) in the sheltered environment of Poole Harbour. Some entrainment of paint particles is also likely. The distribution of TBT in sediments closely resembles that described for water, with severest contamination being restricted to areas associated with high boating activity. Mean concentrations of TBT in surface sediments in the years immediately following the ban ranged from 0.014 μg g^{-1}(as Sn) at southern sites, to 0.52 μg g^{-1} at Parkstone in the north. Sediments in boatyards and marinas can be more than an order of magnitude higher. The environmental half-lives for TBT concentrations in sediment are longer than the equivalent values for TBT in overlying water, mostly ranging from 5 to 10 years, though at one site, Lytchett Bay, no significant change could be detected (Table 5.2). Despite reductions, TBT contamination throughout the Harbour has remained closely related to the densities of moorings and routes of major boat traffic.

TBT levels in bioindicators such as clams *S. plana* display comparable spatial and temporal trends to those described above. As with sediments, concentrations of TBT in *S. plana* varied by more than an order of magnitude between "clean" sites in the south (0.08 μg g^{-1}) and the more contaminated sites in the north (1.35 μg g^{-1}). Half-times for TBT in *S. plana*, post 1987, were of the order of 5–6 years.

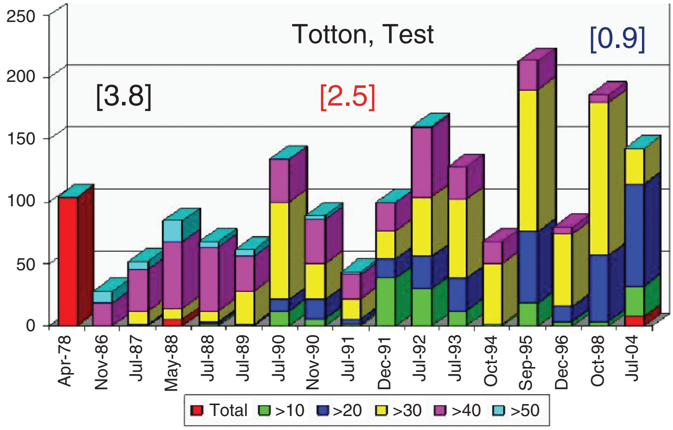
Populations of *S. plana,* were in decline at heavily contaminated sites in Poole during the 1980s and exhibited an inverse correlation between TBT levels and the occurrence and abundance of adult clams (Langston et al. 1990). Concentrations of sediment TBT in the range 0.1–0.3 μg g^{-1} (equivalent to levels in the more contaminated Poole sediments) would almost certainly result in poor survival of juveniles and contribute to a decline in clams numbers (Langston and Burt 1991): after more than a decade this trend has now been reversed as TBT levels fall. More rapid recovery has been observed in epifaunal pacific oysters *Crassostrea gigas* in the outer harbour, where previous attempts at culturing proved abortive, as TBT-induced shell-thickening resulted in abnormal and unmarketable oysters (Dyrynda 1992). In 1989, 2 years after the TBT ban, there was evidence of reversion to more normal growth both in the remnants of this stock, and in freshly laid oysters. However, animals laid in Holes Bay (an area of higher boat traffic, poor flushing and high sediment TBT) continued to show abnormal shell-thickening after legislation, consistent with delayed return of TBT concentrations to no-effects levels. The classic TBT indicator *Nucella lapillus* is not a native of Poole Harbour (unsuitable substrates and other physical and chemical constraints). Close to the entrance to Poole Harbour, in Poole Bay, the species appears to have been eliminated by TBT in the late 1980s.

Comparable monitoring of water, surface sediment and benthic biota has been undertaken over more than two decades in the three major estuaries which feed into Southampton Water, namely the Test (commercial and naval shipping), Itchen (mainly small boats, with the influence of commercial shipping at the mouth) and Hamble (large concentration of yachts) (Langston et al. 1994). In the Test Estuary, there were large differences in TBT concentrations in water depending on proximity to shipping (~1 ng/l upstream to ~100 ng/l, as Sn, near docks and boatyards). Despite spatial variation in concentration, temporal trends for TBT levels at individual sites consistently indicate that the 1987 legislation (banning TBT use on small vessels) has had little impact: at hotspots, concentrations may still exceed EQS by two orders of magnitude. The dominant factor here is the presence of commercial and naval shipping, and boatyards. Trends in sediment and biota from the Test are similar to that in water (half-lives cannot be determined, as regression slopes are not significantly different from zero, Table 5.2). In contrast, legislation was effective initially, in reducing TBT levels in water, sediment and biota in the Hamble Estuary, presumably because small boats predominate at this site. However, initial projections that the EQS would be attained by 1995 were not fulfilled due to a slow down in the reduction in levels (see Fig. 5.4). Delays to further improvements in water quality could be related to sedimentary sinks of the compound, to dredging, and to the presence, nearby (Test/Southampton Water), of commercial vessels (discussed above). For similar reasons this pattern is also observed for the Lower Itchen Estuary (Woolston), where attainment of EQS was initially predicted for 1998. Concentrations here also appear to be close to steady state and still exceed the EQS. In contrast, there have been rather more consistent improvements in water quality at sites in the upper Itchen Estuary (remote from TBT sources and considerably influenced by uncontaminated freshwater).

The summary of half lives for TBT in sediments and clams at each of the Southampton sites (Table 5.2) shows a similar spatial pattern to that in water, though often demonstrating greater persistence. Environmental half-times vary from 4 years upwards. Shortest times were in the small boat dominated Hamble, but in parts of the Itchen and particularly the Test, losses can scarcely be detected; half lives under such conditions are likely to be of the order of decades. TBT concentrations in sediments close to dockyards, marinas, and hull cleaning facilities often lie in the range 0.1–1 μg TBT g^{-1}, whilst chronic contamination of a few nanograms TBT per gram may be detected in deposits at considerable distance upstream from TBT sources (e.g. Upper Itchen and Totton in the Upper Test). As in Poole Harbour, populations of deposit-feeding clams *Scrobicularia plana,* have been in decline at several of the more TBT-contaminated sites around Southampton Water.

Thus, long-term trends in sediment TBT retention are reflected in slow recovery of benthic clams at some sites, notably at Cracknore in the Test Estuary, which is close to a ship repair facility and opposite the Port of Southampton. Here clams were eliminated for much of the 1980s (they were relatively abundant in 1978 prior to popular usage of TBT). Despite a successful settlement of larvae in the 1990s a sustainable population has not developed due to the persistence of high levels in sediment and overlying waters (Fig. 5.6). This contrasts with the site at Totton, upstream of sources, where the clam has remained viable, apparently because of low TBT levels (Fig. 5.6).

Progress towards recovery at sites in Poole Harbour and Southampton Water, as in other estuarine and coastal areas, is clearly variable and dependent on a range of site specific factors. The long lived nature of sediment-bound TBT and the nature and severity of (historical) inputs are amongst the most important of these. The presence of paint particles, hydrology and geochemistry of sediments, salinity and



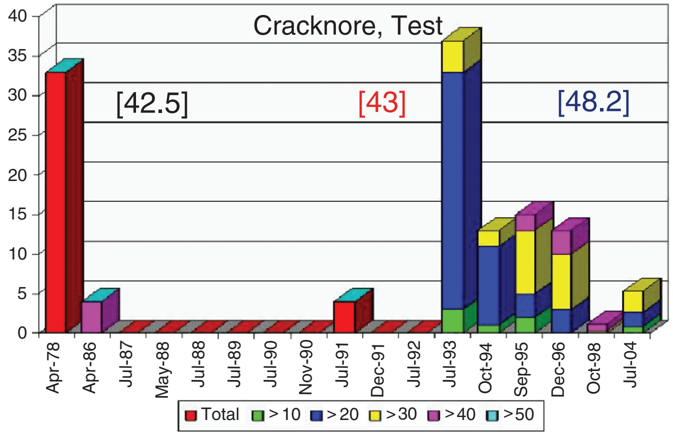


Fig. 5.6 *Scrobicularia plana*: trends in numbers of different size clams (cm) collected at two sites in the Test Estuary, Southampton. Totton is upstream of the Port and is characterized by low TBT. Cracknore is characterized by consistently high TBT contamination. Numbers in parenthesis are mean seawater TBT values (as Sn) for periods 1986–1988, 1990–1992, 2004

temperature regime, and the indigenous micro- and macro-biotic communities will contribute towards site-specific variations in the pattern of recovery. The possibility of illegal usage might also be a confounding feature at some sites in the immediate future, before the IMO recommendations begin to take hold.

5.6 Conclusions

Understanding the partitioning and persistence of organotins in sediments and water is paramount in terms of predicting fate, effects and recovery in coastal and estuarine systems. In the UK there have been widespread improvements in open coastal areas, following the introduction of legislation on small vessels in 1987, however response in estuarine locations in the UK such as Poole and Southampton has been variable, depending on conditions of the site and the relative influence of large ships. Uncontained discharges from boatyards have, until recently, posed a substantial threat to the local aquatic environment. Consequently, TBT levels remain biologically significant in some areas as a result of usage on commercial vessels and sedimentary sinks/sources. Even in some small-boat dominated areas in the UK, persistence in sediments is evident more than a decade after legislation and this secondary source may delay recovery for the foreseeable future. The longevity of effects will be affected by a combination of physicochemical parameters which determine partitioning behaviour, the hydrodynamic energy of the environment and bioturbator activity. Furthermore, longevity of impact will vary between taxonomic groups, with benthic molluscs amongst those slowest to return to normal. In light of the anticipated removal of TBT inputs from much of the global fleet in 2008, surveys of organotin concentrations and accompanying biological records should continue for benchmarking purposes and to broaden our understanding of long-term environmental trends and to assess the rates of recovery. There are still many lessons to be learned, particularly with regard to timescales, susceptibility, reversibility of damage, and longevity in sediments. The TBT ‘model’ represents a unique opportunity to chart the entire lifespan of a major pollutant, from its first introduction in the environment to its (anticipated) harmless conclusion. This may be invaluable for predicting and managing emerging chemical threats associated with alternative biocides.

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