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The tributyltin debate: ocean transportation versus seafood harvesting

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1.1   Introduction

Tributyltin is not a compound in its own right, but only a constituent part of molecules in this class of organotin substances. It comprises three *n*-butyl chains attached to a single tin atom via covalent Sn–C bonds. As the tin exists in the form Sn(IV), the moiety displays an univalent positive charge. Commercial products are typically available in the form of *bis*(tributyltin) oxide (known as TBTO), acetate (TBT–OAc), halides (TBTF, TBTCl) and as the co-polymer with methylmethacrylate (TBTM). Industrial applications of TBT compounds followed the recognition of its biocidal properties, first noted in the early 1950s (Bennett, 1983). Although present applications include molluscicides, stone preservation, and disinfectants, the most important usage remains in wood preservatives and anti-fouling paints (Blunden & Evans, 1990). The production and use of TBT compounds in these two contexts are reviewed here in Chapter 2. Several other organotin compounds are routinely utilised in agricultural biocides, catalysts and as heat and light stabilisers for PVC. Reviews of environmental behaviour of such substances can be found elsewhere (Blunden, Hobbs & Smith, 1984; Maguire, 1991).

Because TBT can act as a broad spectrum biocide, it is useful in the preservation of wood, which is subject to decomposition via bacteria, fungi and insects. Unprotected soft woods degrade relatively quickly giving useful lifetimes of only one to two years. TBT treatment can extend this time to decades. TBT formulations have also proved useful for the preservation of marine timbers (Hill & Killmeyer, 1988). Although there are isolated exceptions, such as the deliberate discharge of 500–800 l of solvent containing approximately 40% TBT (de Mora & Phillips, 1992), wood treatment processes are relatively unimportant as a means of entry into the environment.

For the aquatic environment, tin-based anti-fouling paint represents the most important source of TBT. For a given location, the highest concentrations of TBT are generally found close to drydock and shipyard facilities where TBT-based paints are stripped from ships and yachts (de Mora, Stewart & Phillips, 1995; Stewart & de Mora, 1992; Waldock & Thain, 1988). However, anti-foulant paints work by the slow release into the water of a toxin that forms a thin veneer around the hull, thereby repelling nuisance organisms. Thus, TBT continually leaches from vessels utilising this anti-fouling agent.

As depicted in Figure 1.1, there are three main types of TBT paints (Champ & Pugh, 1987): contact leaching (conventional or insoluble matrix), ablative (soluble matrix), and self-polishing co-polymer (SPC). In conventional paints, relatively elevated amounts of TBT are incorporated into an insoluble matrix. The initial rate of TBT release tends to be high, but diffusion controlled release through microchannels from deeper within the matrix causes an exponential decrease of TBT loss with time. Leaching is further attenuated as the pores become clogged with carbonate, limiting the effective lifetime to less than two years and generally leaving a significant amount of TBT-based paint that is ineffective and must be removed prior to repainting. Ablative paints hold the TBT in a sparingly soluble matrix and TBT is again lost via diffusion. Periodic sloughing of the TBT-depleted matrix gives rise to erratic efficacy but extended lifetime, typically up to two years, with respect to anti-fouling performance.
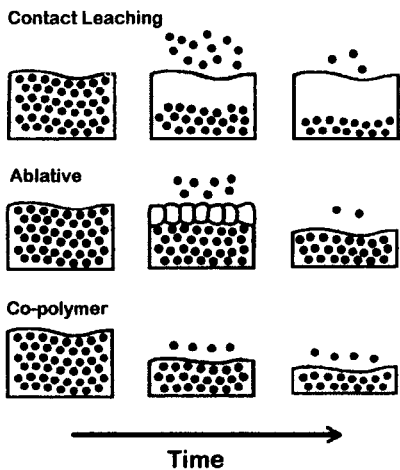

Figure 1.1   A schematic diagram of the three types of TBT-based anti-fouling paints highlighting the ageing characteristics and the mode of action.

Both of these types of paint are known as 'free association' paints as they incorporate relatively high concentrations of TBT compounds in dispersion and leaching is controlled via diffusion. In contrast, modern anti-fouling paints utilise TBT co-polymerised with methylmethacrylate (TBTM). A relatively slow and constant release rate of TBT throughout the lifetime of the paint is achieved by the gradual alkaline hydrolysis of the surface. The term self-polishing is applied as the hydrolysis continually erodes the surface exposing fresh TBTM. SPC paints contain lower concentrations of TBT than found in free association paints and the effective lifetime of the anti-foulant can be extended to five years.

First gaining EPA registration in 1978, the use of TBT-based SPC paints has increased dramatically. In 1991, 80% of ships greater than 4000 DWT utilised this anti-foulant. For pleasure craft, an added attraction of colourless TBT was that pigments could be incorporated into the paint giving rise to various colours not previously possible with copper-based coatings. The economic benefits of such paints, particularly for large oceangoing vessels should not be understated. Financial savings through enhanced fuel efficiency, reduced maintenance requirements and extended drydocking intervals amount to nearly \$US3 billion annually for the world marine fleet (Anon., 1992).

Thus, there are several advantages to TBT substances that have consequently seen widespread use as the active ingredient in anti-fouling paints. This serves as the prime mode of entry into the aquatic environment. However, TBT compounds have marked biocidal properties towards many organisms. Global attention was focussed on TBT when it was suggested that non-target organisms, particularly marine snails (Smith, 1981) and oysters (Alzieu *et al.*, 1981), were extremely sensitive and adversely affected by this anti-fouling agent. The conflicting interests of ocean transportation and sea harvesting has brought the utilisation of TBT-based products under close scrutiny.

1.2   Environmental chemistry

The speciation of organotin in the natural environment is complicated owing to the large number of possible species. Considering simply the butylated forms, $(C_4H_9)_X Sn$, all species for $X = 1$ to 4 have been found in the environment (Kuballa *et al.*, 1995). Methylation leads to the formation of mixed $Bu_m SnMe_n^{(4-m-n)+}$ species (Maguire, 1984; Rapsomanikis & Harrison, 1988), but such species are apparently of little environmental significance. Although (hydroxybutyl)tin compounds are formed via

biodegradation reactions (Lee, 1985; Lee, Valkirs & Seligman, 1989), their presence in the environment has yet to be ascertained. Free TBT ions do not exist in solution to any significant extent, but rather TBT exists in solution as the *bis*(tributyltin) oxide, the chloride or the carbonate, depending upon the dissolved CO_2 concentration, pH and salinity of the waters (Laughlin, Guard & Coleman, 1986). The solubility, estimated to fall in the range of $1–10\,mg\,l^{-1}$ as TBTO in sea water, is not likely to be exceeded (Blunden *et al.*, 1984).

The fate of tributyltin species in the water column is determined by a range of biogeochemical processes. The principal abiotic removal mechanisms are volatilisation, photolysis and adsorption onto suspended particles, in this case followed by sedimentation. Biotic pathways include biosorption, uptake and biodegradation. Degradative processes have been the subject of several reviews (Blunden & Chapman, 1982; Cooney, 1988; Maguire, 1987; Stewart & de Mora, 1990).

Volatilisation is not likely to be an important loss mechanism. The vapour pressure of TBTO is quite low, with estimates ranging from 6.4×10^{-7} to $1.2 \times 10^{-4}\,mm\,Hg$ at $20\,°C$ (Blunden *et al.*, 1984). Several laboratory-based experiments have failed to observe losses from fresh waters by this means over several months (Maguire, Carey & Hale, 1983; Maguire & Tkacz, 1985). Results from a marine mesocosm experiment suggested that volatilisation of TBT may have been a significant sink, but the influence of photolysis of TBT in the microlayer could not be ruled out (Adelman, Hinga & Pilson, 1990). As documented in Chapter 5, TBT does seem to accumulate at the sea–air interface. This behaviour is greatly facilitated in incubation experiments by the presence of phytoplankton cultures (St-Louis, 1995). This study also demonstrated that bubble formation could enhance the transfer of TBT to the atmosphere.

Photolysis can certainly be an important removal process for butyltin compounds (Blunden & Chapman, 1982). Typical Sn–C bond cleavage energies are about $210\,kJ\,mol^{-1}$; c.f. the energy of blue light of 400 nm is approximately $300\,kJ\,einstein^{-1}$. All experiments of the degradation of TBT in water–sediment systems have demonstrated faster rates in the light than in the dark (Maguire *et al.*, 1983; Maguire & Tkacz, 1985; Seligman, Valkirs & Lee, 1986; Watanabe, Sakai & Takatsuki, 1992). However, the photolytic mechanism may be biologically mediated as the degradative products under light conditions include (hydroxybutyl)tins in addition to DBT, observed as the sole yield in the dark (Lee *et al.*, 1989). The Devonport Drydock facility operated by the New Zealand Royal Navy has made use of TBT photochemistry. The TBT-contaminated

sludge accumulated during the removal of paint from ships cannot be released directly in Waitemata Harbour near Auckland. Instead, H_2O_2 is added, and the material is recirculated in a tank exposed to sunlight until TBT levels have declined to acceptable levels.

Several studies have demonstrated the importance of adsorption of tributyltin onto suspended material. Adsorption is due both to the hydrophobic character of the moiety and, to a lesser extent, its univalent charge. The bulky nature of the species would also provide a contribution from the entropy effect of displacing several water molecules. Laboratory-based adsorption experiments have shown that 72–100% of the TBT burden is adsorbed (Randall & Weber, 1986). TBT adsorption onto inorganic materials (bentonite, humic acid, ferric hydroxide and 'natural' suspended solids) followed a Langmuir adsorption isotherm (Leguille *et al.*, 1993). Perhaps surprisingly a second order rate law was obeyed. The activation energy was low, about $42\,kJ\,mol^{-1}$, and consistent with weak physical adsorption. A Freundlich adsorption model has also been used to explain the behaviour of TBT (Dowson, Bubb & Lester, 1993b). The adsorption of TBT is enhanced with a decrease in pH or with a decrease in salinity (Dowson *et al.*, 1993b; Randall & Weber, 1986). TBT adsorption was found to be reversible, which has implications for the mobility and partitioning in boundary zones, such as estuarine and interstitial waters (Unger, MacIntyre & Huggett, 1988).

The role of adsorption is important in the aquatic environment and serves to remove TBT from the water column relatively quickly. Such rapid kinetics can also have useful applications. About 81–92% of the TBT present in untreated waster water was associated with suspended solids (Fent & Muller, 1991). During treatment, adsorption onto sludge was found to be the most important elimination process for butylated tin compounds. Compared to the water column, degradation rates in the sediments are much slower, with half-lives on the order of years (de Mora, King & Miller, 1989; de Mora *et al.*, 1995; Dowson, Bubb & Lester, 1993a; Kilby & Batley, 1992). Sediments thus act as a relatively long term repository for TBT, and help maintain its persistence in the environment. The accumulation of TBT onto suspended material cannot be construed solely as a sink process because the TBT remains bioavailable, particularly for benthic organisms (Maguire & Tkacz, 1985) and filter feeders (Langston & Burt, 1991). Because the adsorption is relatively weak (Leguille *et al.*, 1993) and reversible (Dowson *et al.*, 1993b; Maguire & Tkacz, 1985), the sediments can act as a source of TBT should they be remobilised by storms or dredging. Some environmental evidence exists

for localised contamination via desorption following dredging activities (Dowson, Bubb & Lester, 1992). Dredge spoil dump sites can certainly contribute TBT to an otherwise unaffected area (de Mora *et al.*, 1995).

Living and detrital cells can also act as a substrate for TBT adsorption. Microbial biofilms have been shown to accumulate TBT, without subsequent degradation (Blair *et al.*, 1988). This behaviour is not surprising given that the water–octanol partition coefficient for TBT is about 5000 (Laughlin *et al.*, 1986). However, a free ion activity model has been utilised to describe the uptake of TBT by the marine microflagellate *Pavlova lutheri* (St-Louis, 1995). Surface adsorption was essentially an ionic process, well described by a Freundlich isotherm. Accumulation was the result of subsequent lipophilic intracellular absorption. Exposure of starfish *Leptasterias polaris* to dissolved TBT promoted accumulation on the external tissues and subsequent translocation to internal organs was retarded (Rouleau, Pelletier & Tjälve, 1995). Passive uptake also seems to be important for fresh water fish (Wong *et al.*, 1994). Pike exhibited TBT concentrations that varied seasonally, with highest values in the spring. Concentrations were independent of fish size, thereby suggesting that a food chain accumulation mechanism was unlikely.

The biodegradation of TBT is well documented and it can proceed under a wide range of conditions. Because of the importance of TBT as a biocide, early studies focussed on its degradation in soils. Loss was accelerated in unsterilised soils relative to sterilised ones (Barug & Vonk, 1980) and biodegradation during bacterial monoculture incubation was soon demonstrated (Barug, 1981). Fungal cultures were also shown to be capable of degrading TBT, a finding of importance due to the use of TBT as a wood preservative (Orsler & Holland, 1982). The fresh water green alga *Ankistrodesmus falcatus* was able to accumulate and debutylate TBT to produce DBT predominantly, but with some MBT and inorganic Sn (Maguire, Wong & Rhamey, 1984). With respect to the marine environment, diatoms and dinoflagellates were observed to debutylate TBT under dark conditions (Lee *et al.*, 1989). Alternatively, DBT and (hydroxybutyl)tins were produced in the light. The marine diatom *Skeletonema costatum* was found to be effective for debutylation even at 4 °C (Reader & Pelletier, 1992). In eelgrass *Zostera marina*, TBT was decomposed via a consecutive debutylation pathway with first order kinetics (François, Short & Weber, 1989). Crabs, oysters and fish have demonstrated the ability to metabolise tributyltin, administered in both *in vitro* and *in vivo* experiments as *bis*(tributyltin) oxide (TBTO), forming a range of hydroxylated products (Lee, 1985). Such products had previously been shown to result from the

reaction of TBT derivatives with the cytochrome P-450 monooxygenase enzyme system (Fish, Kimmel & Casida, 1976).

Considering sediments, the mechanism of microbial degradation under both aerobic and anaerobic conditions was observed to occur via debutylation (Shizhong, Chau & Liu, 1989). From the interpretation of profiles of butylated tin compounds in marine sediments, it has been suggested that the degradation is via methylation or debutylation, the specific pathway being dependent upon the dominant microbial activities in the sediment (Yonezawa *et al.*, 1994). The role of non-biological processes that might occur within sediments remains under dispute. The addition of cyanide was able to suppress degradation in water–sediment studies (Maguire & Tkacz, 1985). However, as noted above, biodegradation was not totally suppressed in sterilised soils (Barug & Vonk, 1980). Moreover, a rapid abiotic degradation has also been observed under experimental conditions (Stang, Lee & Seligman, 1992).

For a given environment, it is very difficult to estimate the relative importance of the various loss processes. However, their role can be inferred from the pattern of butyltin species preserved in the sediments. Considering in particular the sediments of Arcachon Bay (Sarradin *et al.*, 1991), sediments within the harbour exhibited high levels of TBT and the relative importance of MBT increased with distance from the TBT source. This behaviour was explained by differential rates of debutylation in waters versus sediments. Thus, much of the TBT initially released from small boats accumulated quickly via adsorption onto and deposition of particulate material near the source. As degradation rates within the sediments are slow, TBT was essentially preserved. In contrast, the TBT that was advected from the harbour into the adjacent bay, as either particulate or dissolved forms, underwent accelerated photolytic and microbial degradation while in the water column. As a result, comparatively more DBT and MBT was deposited in the bay than in the harbour.

1.3 Biological effects

The biological response of organisms to TBT varies enormously. TBT provokes a wide range of harmful effects (sublethal to mortal) to numerous organisms (bacteria to fish) at greatly differing scales (RNA damage to local extinctions). In this book, Chapters 4 and 6 survey such deleterious effects towards fresh water and marine organisms. Chapter 7 is devoted to the description of TBT-induced responses in marine snails. Hence, the intent here is to highlight briefly only two aspects of TBT

pollution, namely the plight of oyster shellfisheries and the loss of some species of snails from coastal ecosystems, in order to unfold the case study of TBT as a contaminant of global concern.

In terms of public and political impact, the seminal TBT publication was that of Alzieu *et al.* (1981) ascribing shell deformation of Pacific oysters *Crassostrea gigas* to tributyltin derived from the anti-foulant in marine paints. As shown in Figure 1.2, the shells of contaminated oysters are severely thickened or 'balled' and contain multiple cavities or chambers, the number being a function of the TBT burden of the individual (King, Miller & de Mora, 1989). Despite some initial scepticism, the role of TBT in oyster shell deformation became well established following several experiments and field observations in both France and the United Kingdom (Alzieu *et al.*, 1986; Chagot *et al.*, 1990; Paul & Davies, 1986; Waldock & Thain, 1983). Shell calcification has also been observed for *Crassostrea gigas* in Australia (Batley *et al.*, 1989) and New Zealand (King *et al.*, 1989). Considering shell deformities in other oyster species, thickening was observed in the native rock oyster of New Zealand *Saccostrea glomerata* (Smith & Curtin, 1986) and shell curl has been
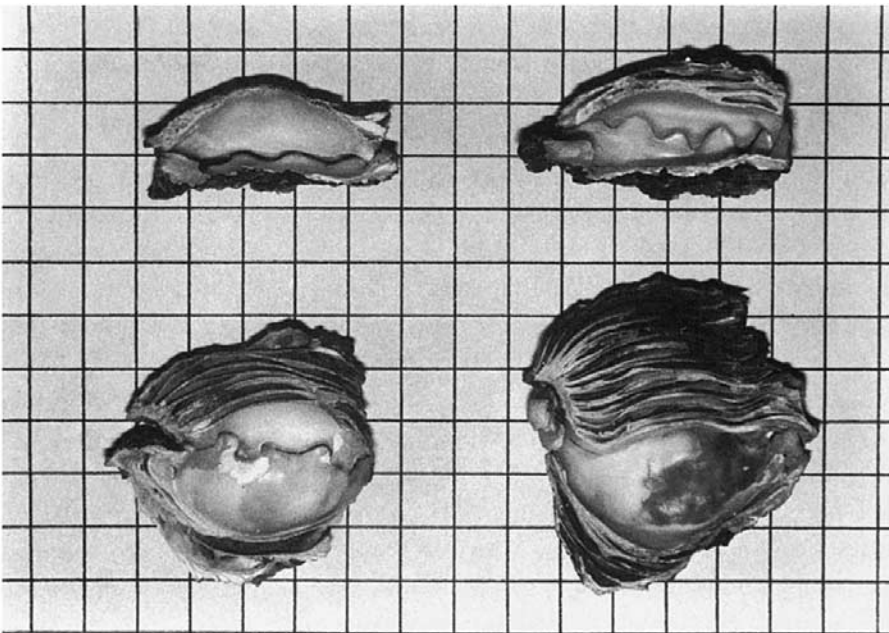

Figure 1.2   Examples of TBT-induced shell thickening in Pacific oysters *Crassostrea gigas* from New Zealand (de Mora *et al.*, 1989).

reported for the Sydney rock oysters *Saccostrea commercialis* (Batley *et al.*, 1989). As an obvious consequence of shell thickening, the volume of the body cavity is relatively small, resulting in unacceptable body weights for commercial exploitation. This feature led to a decline in the shellfisheries of oysters at sites in France and, in turn, prompted the first political action in the form of legislation controlling the use of TBT on small boats. As with the effect on oyster shells, this response was also global in character.

Imposex, a term coined by Smith (1971), in marine gastropods refers to the masculinization of females manifested by the formation of a penis and vas deferens. This mutation was subsequently shown to result from TBT (Smith, 1981). Marine snails are so sensitive to TBT that a no observed effect limit (NOEL) has yet to be confirmed. Certainly, the level is less than typical detection limits for present analytical techniques. Furthermore, it is of some concern that imposex has been observed in whelks *Buccinum undatum* from the open North Sea (Ten Hallers-Tjabbes, Kemp & Boon, 1994). In the extreme case, it is possible that the females are transformed into functioning males (Stewart *et al.*, 1992). At a community level, the reproductive failure prevents local recruitment to the site (Bryan *et al.*, 1986; Gibbs & Bryan 1986). This can cause populations to comprise ageing males and masculinised females. For neogastropods that lack a motile larval stage, this ultimately leads to local extinctions of populations as found for *Nucella lapillus* along parts of the English coastline (Gibbs, Bryan & Pascoe, 1991). Imposex has been observed in 45 species of neogastropods from locations throughout the world (Ellis & Pattisina, 1990), thereby providing a compelling example of the global nature of TBT as a pollutant.

Given that TBT has been extensively used because of its biocidal properties, it is of interest to note that increasingly there are studies characterising TBT-resistant bacteria. Such microorganisms have been isolated from sea water (Suzuki, Fukagawa & Takama, 1992) and from sediments underlying both fish and estuarine waters (Wuertz *et al.*, 1991a). As described previously, several marine phytoplankton demonstrate the ability to degrade TBT to DBT and (hydroxybutyl)tin species without apparent harm to themselves (Lee *et al.*, 1989; Reader & Pelletier, 1992). Similarly, higher organisms can metabolise TBT (Lee, 1985). One can speculate that such biological processes will play an important role in the long term decontamination of TBT polluted environments.

The toxic effects of TBT to humans have not been well documented. Occupational exposure in various incidents has led to dermatitis, and the irritation of eyes and the respiratory tract (Blunden & Evans, 1990).

However, worker protection during spray paint applications can be ensured by using suitable disposable clothing and respirators. Non-occupational exposure to TBT is slight, and possible pathways are via skin absorption or food intake. A wide range of household commodities was analysed in order to evaluate exposure via skin contact, and TBT was undetected in all 95 items (Yamada *et al.*, 1993). Considering foodstuffs, a recent survey of wines in Canada found TBT to be below detection (i.e. $<0.1\,\mu g\,l^{-1}$) in most wines, but a maximum concentration of $18.7\,\mu g\,l^{-1}$ was recorded (Forsyth, Weber & Dalglish, 1992). Higher concentrations were observed for DBT, which was believed to have been leached from PVC. TBT content in commercially available salmon ranged from 0.081 to $0.20\,\mu g\,g^{-1}$ (Short & Thrower, 1986). Sea urchins (*Tripneustes gratilla*, local name *Cowaki*) and marine bivalves (*Anadara scapha*, local name *Kaikoso*), purchased at the Suva markets in Fiji, have also been analysed for TBT content (Stewart & de Mora, 1992). The respective concentrations were <15 and $90\,ng\,TBT–Sn\,g^{-1}$ (dry weight). Hence, such levels in seafood pose no threat to public health given that an acceptable daily intake (ADI) for TBT has been suggested to be $6\,\mu g\,kg^{-1}\,d^{-1}$ (O'Grady & Lawrence, 1988).

1.4   Legislative response

The dilemma of tributyltin was succinctly enunciated by Goldberg (1986) who noted that two superlatives apply. Firstly, TBT is an extremely effective anti-fouling agent that saves the US navy, among others, an estimated $US150 million annually. Secondly, TBT is a potent toxin only of anthropogenic origin that threatens seafood resources in coastal environments. The political response to the observation of TBT-induced damage to oysters in France was swift, but cautious. Swift because controls in France were established in 1982, based on the circumstantial evidence of Alzieu *et al.* (1981). Cautious because initially only a temporary ban was imposed on the use of anti-fouling paints containing more than 3% organotin on non-aluminium boats less than 25 m in length in ports along the French Atlantic coast. This was subsequently extended to become a permanent ban for all organotin-based paints at all coastal sites in France.

The database on which the first restrictions were imposed was perhaps limited (Huggett *et al.*, 1992; Stebbing 1985). Nevertheless, the United Kingdom also introduced regulations in 1985, setting a water quality target of $20\,ng\,TBT–Sn\,l^{-1}$ and prohibiting the sale of paint containing