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Distribution of tributyltin (TBT) in the Mandovi estuary

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10.1 BIOFOULING AND ITS EFFECTS

It is a common experience that when water is left in a bucket or in any other container for a long period of time, the area of the bucket in contact with water becomes slimy. This slimy layer is known as biofilm. Different steps are involved in the development of a biofilm. The first step is adsorption of dissolved organic matter onto a surface, thereby conditioning it. The conditioned surface is then colonized by micro-organisms, including bacteria, microalgae, fungi, protozoa, etc. Development of a biofilm on a surface may induce the settlement and metamorphosis of larvae of invertebrates such as barnacles, mussels, oysters, and algal spores. This results in the development of macrofouling visible to the naked eye. Biofilm and macrofouling together are defined as biofouling. The best example of biofouling is the growth you see on the hull of a ship. Biofouling on the hull or any other industrially useful material can cause considerable damage. It can increase frictional drag on the ship, thereby increasing fuel consumption, induce metal corrosion, impair heat-transfer efficiency of heat conductors, block flow in pipelines, reduce the life span of offshore platforms, etc. Such effects can cause huge economic losses to several industries, including naval and commercial shipping, nuclear and thermal plants, offshore oil production platforms, and many other installations in coastal areas. Several billion dollars are spent worldwide to control the problem of biofouling.

10.2 CONTROL OF BIOFOULING

To reduce economic losses due to biofouling, ship hulls and other surfaces are coated with antifouling paints containing toxic chemicals. The most commonly used antifouling compound is tributyltin (TBT) (Hoch 2001). Use of TBT-based antifouling paints helps the shipping industry save about US\$ 6 billion per year, which, in turn, results in fuel saving of about 7 million tonnes per year. TBT compounds are also used as stabilizers in the PVC industry, plastic additives, industrial catalysts, insecticides, fungicides, bactericides, and wood preservatives. Various sources responsible for the release of TBT compounds in a marine environment are shown in figure 10.1. There is no doubt that use of TBT results in several economic benefits. In addition, TBT usage in the shipping industry also offers some indirect

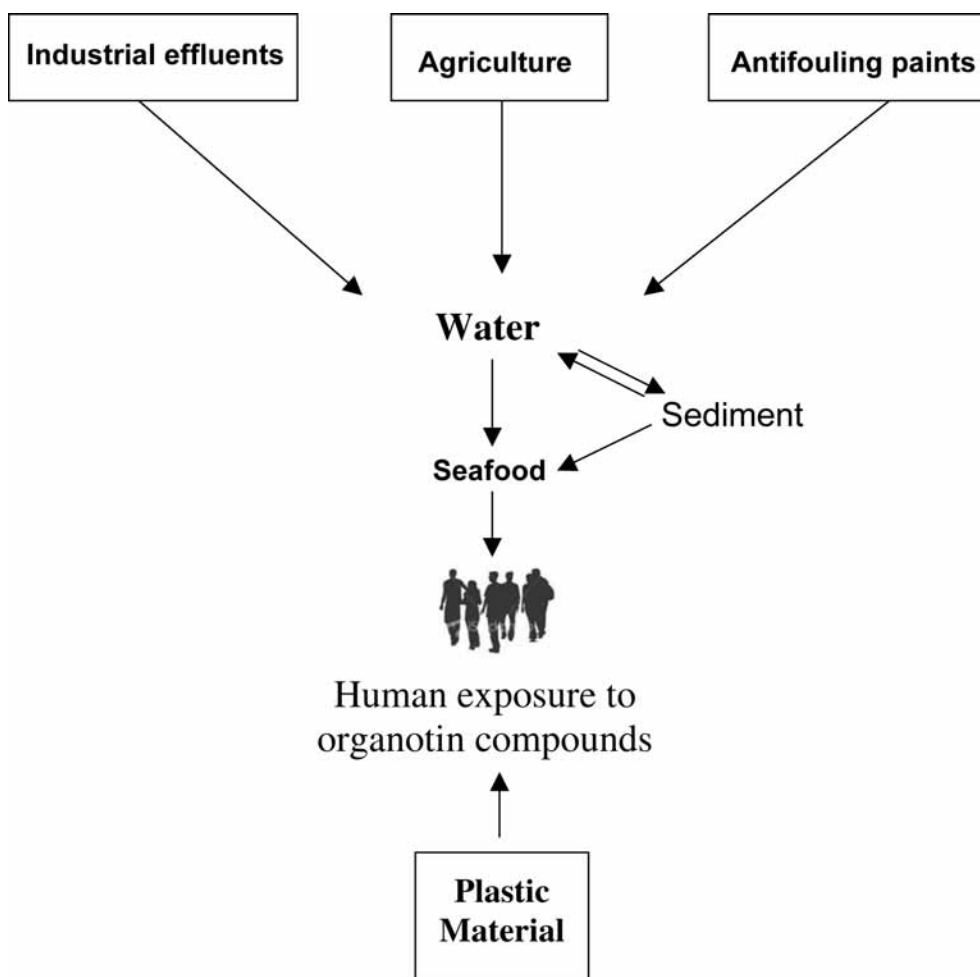


Figure 10.1 Sources of organotin compounds for human exposure (modified from Hoch 2001).

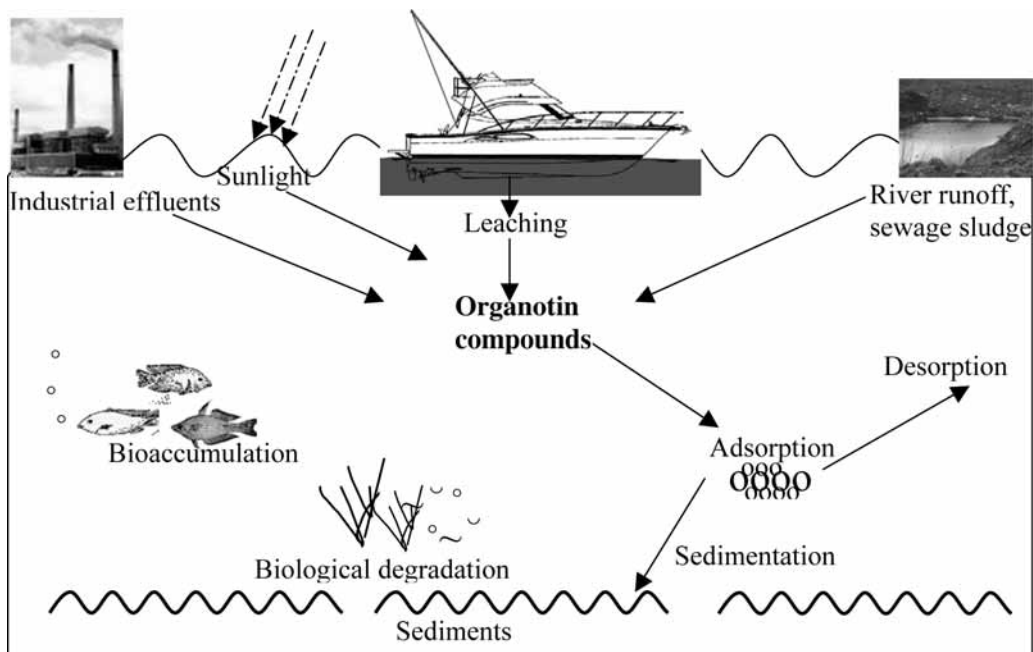


Figure 10.2 Distribution and fate of TBT compounds in aquatic environment (modified from Hoch 2001).

environmental benefits such as reduced production of greenhouse gases and suppression of bioinvasion of biofouling organisms. Nevertheless, when released into the marine environment, TBT undergoes several chemical and biological processes (figure 10.2). The most important concern in the use of TBT is that it is highly toxic to non-target organisms when released into marine waters.

10.3 ENVIRONMENTAL EFFECTS OF TBT

Use of organotin such as TBT has increased several fold during the last two decades. TBT compounds used in industrial applications, especially as a constituent of anti-fouling paints, have resulted in a high abundance of organotins such as TBT and other butyltin and phenyltin compounds in the water, sediment, and tissues of organisms from several aquatic and marine environments; most affected are harbour and near-shore areas (Hwang *et al.* 1999; Hoch 2001). It is well documented that TBT at the level of a few ng l^{-1} (nanograms per litre) is detrimental to non-target organisms. Some of these effects include high larval mortality, shell deformation, reduced reproduction in many invertebrates, imposex (change of sex, i.e., a female developing male sex organ) gastropods, including dogwhelks, retardation of growth in mussels, and inhibition of photosynthesis and growth in microalgae. Owing to

these concerns, many countries, particularly in the European Union, USA, and Japan have enforced strict laws to regulate use of TBT.

In the early 1980s, the first catastrophic environmental impact of TBT was noticed in Arcachon Bay, France, where the oyster fishery nearly collapsed. Abnormal thickening of the shells was observed in juvenile Pacific oysters from the bay. These abnormalities were attributed to the release of TBT from antifouling paint. Alzieu (2000) observed a connection between TBT levels and oyster-shell anomalies.

At about the same time, a decline in the population of dogwhelk *Nucilla lapillus* in southeast England was attributed to TBT contamination. Field and laboratory studies confirmed that TBT was highly toxic to non-target organisms. It was realized that TBT was one of the most toxic compounds ever introduced by man into the marine environment.

10.4 LEGISLATIVE RESTRICTIONS

Owing to these concerns, many countries, particularly the European Union, USA, and Japan, have established strict laws to regulate use of TBT.

On seeing the near-complete destruction of shell fishery in the Arcachon Bay, the French Government formulated laws to regulate the use of TBT-containing paints in January 1982 for vessels shorter than 25 m in length. Subsequently, similar action was taken by the governments of the United Kingdom in 1985, USA in 1988, and Canada in 1989. When it was realized that there was a strong connection between levels of TBT in the oyster tissues and deformities in oysters, use of TBT in antifouling paint was banned in Australia in 1989. In Japan, use of TBT in antifouling paints and aquaculture nets was banned or restricted. In view of the toxic effects, use of TBT was completely banned in Austria, Sweden, and Switzerland.

Such legislative action to restrict or ban use of TBT has resulted in benefits to marine farms. These measures were instrumental in decreasing levels of TBT in water, sediment, and organisms (Hoch 2000). In Great Britain, water quality improved enough to permit resumption of oyster farming (Alzieu 2006). Decrease in TBT in water led to a decrease in TBT levels in oysters. There was also a decrease in imposex in the gastropod population in Great Britain. These efforts were instrumental in decreasing levels of TBT in aquaculture farms. In the countries that did not impose any restrictions or regulations, concentrations of TBT remained relatively high, particularly in harbours with high levels of shipping activity.

India is one of the fastest developing countries in Asia. In India, TBT compounds are used in antifouling paints to control the growth of fouling organisms on commercial and naval ships as well as on other industrial structures that use seawater. There is no legal ban on the usage of TBT compounds in India. There is also little information available on the distribution of TBT compounds in water, sediments, and animals

collected from the coast of India. The Mandovi estuary is one of the very few marine areas of the country where some information on TBT levels is available. Hence, this chapter summarises what is known of TBT in the estuary.

10.5 STUDY AREA AND SAMPLE COLLECTION

The Mandovi estuary is used for transport of iron and manganese ore from the hinterland to Mormugao harbour. Along the Mandovi estuary, there are several small jetties and wharfs. Jetties are used for berthing fishing vessels and barges. Small workshops that are involved in repair, maintenance, and construction of small ships and barges are located on the banks of the river. The estuary has mangroves along its banks. They support several flora and fauna that are either resident or migratory, and act as nursery grounds and nutrient sources for a variety of economically and ecologically important organisms, including fishes, prawns, and many other invertebrates.

As a part of our study on TBT, seawater samples were collected using 5 l (litre) Niskin samplers at a depth of about 1 m from 10 locations in the Mandovi estuary (figure 10.3). The samples were filtered onto GF/F filters to remove suspended particulate matter. Sediment samples from the same locations (figure 10.3) were collected using van Veen grab, and stored at -20°C until used for analysis. Sediments were lyophilized, powdered, and stored at -20°C until analysis. Glassware used was cleaned with chromic acid and washed with distilled water, followed by UV-Milli-Q purified water, and dried in an oven. Before use, the glassware was rinsed with dichloromethane and kept covered with aluminium foil until use.

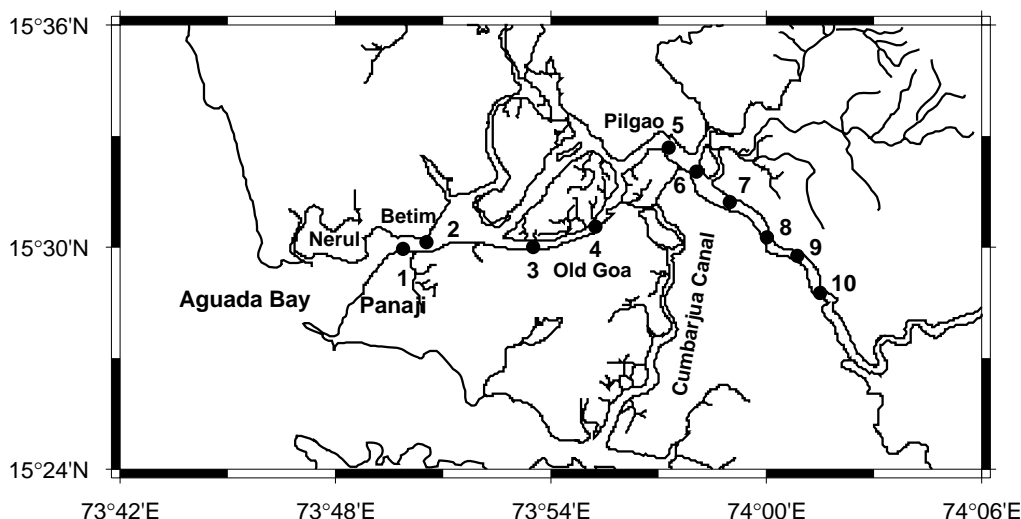


Figure 10.3 Map showing sampling sites along the Mandovi estuary.

10.6 EXTRACTION OF TBT COMPOUNDS

A known volume of un-filtered seawater was transferred to a teflon separating funnel. To the funnel, dichloromethane, 6% NaBH₄, and tripropyltin chloride (TPrT), the last as internal standard, were added. The contents of the funnel were mixed and then extracted for 10 minutes. After separating the organic layer the sample was subjected to extraction once again. Both the organic extracts were combined, dried using anhydrous sodium sulphate, and filtered through Whatman No 1 filter paper. The volume of the organic extract was reduced to 100 µl using nitrogen gas. The standard was prepared following the same procedure.

In order to extract TBT compounds from sediments or SPM, a known amount of sediment sample, or a GF/F filter containing SPM, was transferred to a test tube. To the test tube 0.1% of NaOH in methanol and a known amount of TPrT as an internal standard were added. 0.1% of NaOH in methanol served as a blank. The standard was prepared following the same procedure but without sample. The sample, standard and the blanks were vortexed for one hour to extract TBT. Then hexane and NaBH₄ were added to all the tubes and the reaction mixture was vortexed for 15 minutes and the hexane layer containing derivatized compounds was collected. The extraction step was repeated thrice and all the extracts were pooled together. The hexane extract was dried over anhydrous sodium sulphate and concentrated to 100 µl using nitrogen gas, and analysed by gas chromatography.

10.7 ANALYSIS OF TBT COMPOUNDS BY GAS CHROMATOGRAPHY

Separation and quantification of butyltin compounds were performed by a capillary gas chromatograph (Agilent HP6890 Series model). The gas chromatograph was equipped with a flame photometric detector (FPD), a tin-specific (610) filter, and a HP 5 capillary column (5 metres). One microlitre sample or standard mixture or blank was injected using a programmable on column injector when the initial temperature was 60°C. After 2 minutes, the oven temperature was programmed to 230°C at the rate of 20°C per minute and held at this temperature for 8 minutes. Nitrogen was used as a carrier gas (one ml min⁻¹). The injector was operated in track oven mode, while the FPD detector was maintained at 250°C with hydrogen and air flowing at 80 and 105 ml min⁻¹, respectively. Quantification of each peak in a sample was done by using the data handling system installed in the instrument.

10.8 BUTYLTINS IN WATERS AND SUSPENDED PARTICULATE MATTER OF THE MANDOVI ESTUARY

TBT was present in seawater samples collected from most of the stations that were sampled in the Mandovi estuary (figures 10.4a, b), but the concentration of TBT

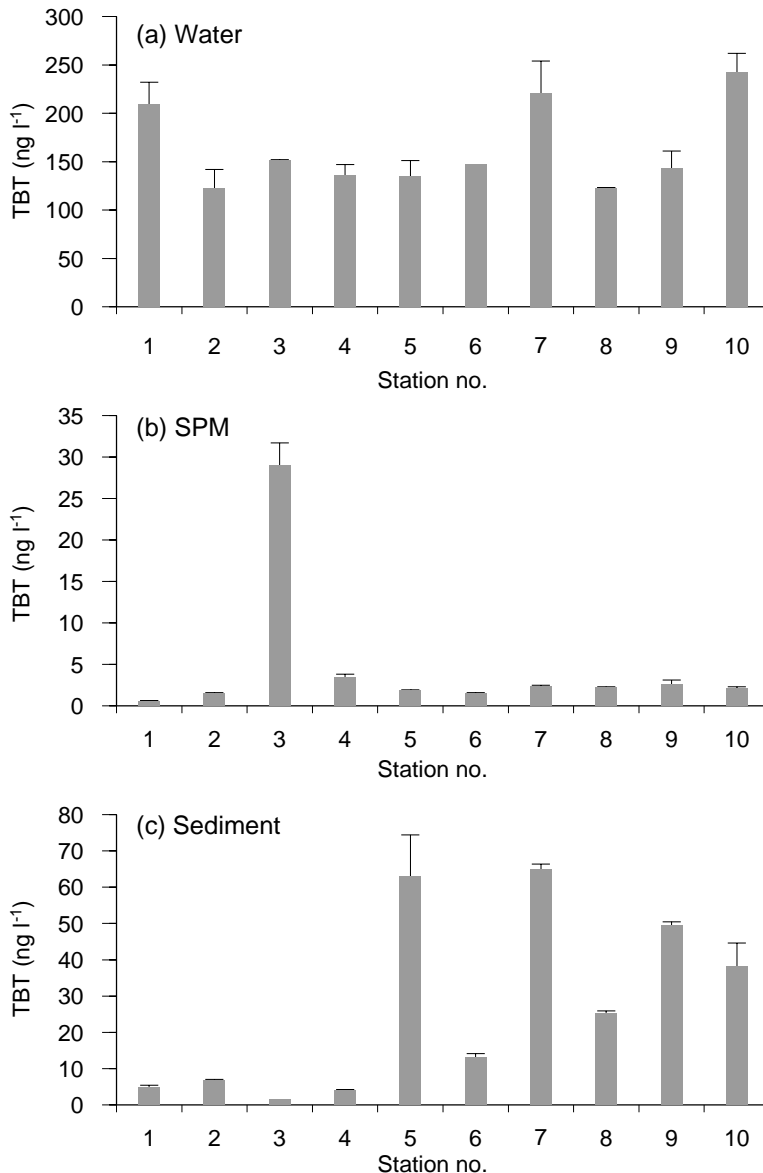


Figure 10.4 Distribution of TBT in (a) water, (b) suspended particulate matter, and (c) sediments, at various stations in the Mandovi estuary. The connection between station numbers and station locations is as follows. 1: Panaji Harbour; 2: Fishing Jetty at Betim; 3: Chorao Ferry; 4: Old Goa; 5: Piligao; 6: Sarmanas; 7: Amona; 8: Mayana-1; 9: Mayana-2; 10: Pali. The thin vertical bars indicate the standard deviation.

varied from station to station. For both water and SPM samples, no particular trend was recorded for the distribution of TBT in the Mandovi estuary.

The concentration of TBT varied from 4.9 ng g⁻¹ to 49 ng g⁻¹ dry wt of sediment of the Mandovi estuary. Concentration of TBT was relatively higher at stations 8, 9,

and 10 (figure 10.3). These higher concentrations of TBT in the sediments collected from stations such as 8, 9, and 10 in the Mandovi estuary probably indicate the effect of berthing of barges and small fishing boats at these locations.

10.9 IMPLICATIONS OF THE DISTRIBUTION OF TBT COMPOUNDS

Most of the locations sampled in the Mandovi estuary are influenced by activities such as dry docking, repair and maintenance of small ships and barges, and construction and painting of barges. Therefore, depending on the intensity of these activities at the sampled locations, the concentration of TBT varied. The observed TBT levels in water and sediments of the Mandovi estuary are comparable to those reported from other coastal areas of the world subject to shipping activity. The concentration of TBT in the waters of the Mandovi is similar to that recorded for the waters of other estuaries and coastal waters of the world before the TBT ban. A high concentration of TBT was observed at a few stations – for example, the sediment at stations 5–10 had high TBT concentration. The major source for such localized contamination of TBT is expected to be the release of TBT by barges and small boats used for fishing and recreational activities such as motor boating. Stations 5–10 are located in the vicinity of jetties and small ship repair workshops that construct, repair, overhaul, sandblast, and paint small commercial vessels. Such activities lead to release of TBT compounds through waste waters and effluents into the estuary. Moreover, the observed spatial distribution pattern of TBT may implicate the influence of bacterial degradation, tides, and currents at the sampling sites of the study.

TBT compounds have both lipophilic and ionic properties. Owing to their lipophilic nature, TBT compounds dissolve in lipids, whereas in ionic interactions, TBT compounds bind to macromolecules. Therefore, good relationships between TBT and total lipids and/or organic carbon helps in identifying the role of these factors in controlling the abundance of TBT compounds in marine waters. In the Mandovi estuary, we did not observe any relationship between TBT compounds and organic carbon or total lipids. This implies that organic carbon and lipids may produce variable effects on the distribution of TBT compounds, probably due to the influence of some local factors such as quality of organic matter and the waves, and currents in the study area.

Whatever may be the factors involved in controlling the distribution of TBT compounds in marine waters, the water and sediment samples of the Mandovi estuary appear to contain substantial amounts of TBT compounds. TBT is considered to be toxic to many marine organisms at levels of about 100 ng l^{-1} . Even at levels less than 10 ng l^{-1} , TBT can cause endocrine disruption, resulting in imposex, especially in gastropods (Hwang *et al.* 1999; Hoch 2001). The observed levels of TBT compounds in the Mandovi are higher than those known to induce imposex, and, in fact, imposex has been recorded in gastropods collected from Mormugao harbour. Bhosle

(2006) reported that oysters, mussels, clams, and fish collected from the nearby Mormugao harbour were contaminated with TBT, and that TBT can suppress normal functioning of the immune system of mammals. In view of this, consumption of TBT-contaminated fish and shellfish is a matter of concern. There is therefore need for legislation to regulate use of TBT compounds in the estuaries and coastal waters of India.

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