The case against tributyltin

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The use of paints containing tributyltin (TBT) *to keep boat hulls clean is threatening marine* life in some coastal regions, especially where boating for pleasure is popular. Research so far has shown that very low concentrations of the chemical have lethal or mutagenic effects on some marine invertebrates and stop the growth of phytoplankton. Legislation is being drawn up by many countries to control the use of these paints, but the author fears that it may be too little and too late for some populations of organisms.

Threats to marine organisms are many and varied. One such threat is posed by a little-known substance widely used as an ingredient in paints to prevent the growth of 'fouling' organisms, for example, seaweeds, barnacles, tube worms, mussels and hydroids. In 1952 2000 species (including 615 plants) had been identified as foulers, and the list is now probably more than twice as long (Fischer *et al.*, 1984). The increased loading produced by marine growth on static structures (for example, oil platforms) and the increase in fuel consumption of vessels where fouling increases drag are acutely damaging to commercial and military interests. In the past, inorganic metal compounds (particularly of copper) were the main toxins employed in anti-fouling paints but, more recently, organic tin compounds have been used with considerable success. The most widely used is tributyltin (TBT), usually as tributyltin oxide (TBTO), but, as reviewed here, this has recently been shown to be a significant pollutant.

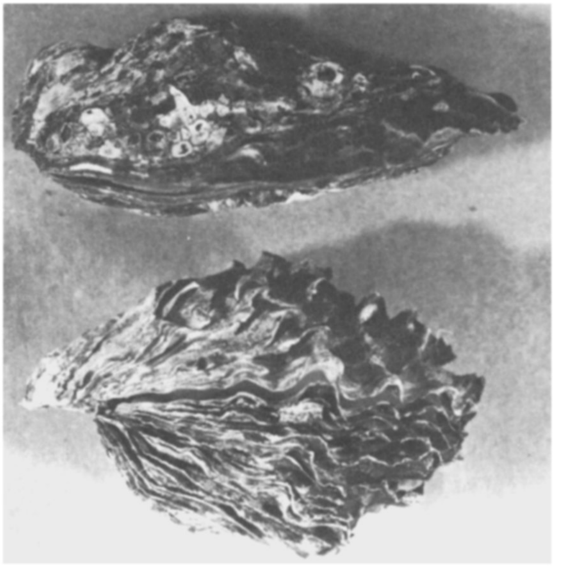
Anti-fouling paints work by the controlled release of poisons. In modern co-polymer coatings the surface wears away to release the toxic chemical. Pleasure-boat owners usually replace old paint every year. Boats are sanded down, and sandings of old paint are washed into the sea. Pollution effects are, therefore, likely to be most marked in areas of high boating activity, for example, marinas and harbours. So, despite recent steps to protect the marine environment, such as the declaration of marine reserves, populations of plants and animals in or near popular boating areas may be at considerable risk.

In 1975 world consumption of organotin compounds was estimated to be 25,000 tonnes (Evans and Smith, 1975), and this has since grown rapidly. It was originally believed that one of the great advantages of TBT, when compared to other anti-fouling toxins, was that it rapidly degraded in the sea into non-toxic inorganic salts (Evans and Smith, 1975; Smith and Smith, 1975). Even in a recent review, Blunden and Chapman (1982) concluded that TBT breakdown in most cases produced inorganic tin, and consequently organotins were unlikely to be a serious long-term pollution hazard. However, from samples taken and examined in the same year (Waldock and Miller, 1983), a UK government laboratory had already found that this was not the case. They measured TBT levels in marinas, harbours and elsewhere, and found high concentrations where many pleasure craft were present. Concentrations varied seasonally and with the number of craft, but approached levels already known to be toxic to larval animals. Maximum concentrations were recorded when the majority of boats first entered the water in early summer. Cleary and Stebbing (1985) reported maximum concentrations in the UK of 0.88 μg per litre in Plymouth harbour, and noted that in Canada concentrations of 2.91 μg per litre had been recorded at Lake St Clair marina. Slightly lower concentrations were reported from 13 other sites in England, Canada and France. The minimum concentration at which TBTO was detectable at that time by most workers (Cleary and Stebbing, 1985) was 0.1 μg per litre, but the compound is known to be harmful to some organisms at and below this level.

The effects of TBT at concentrations recorded in some coastal waters range from lethal to mutagenic, and some organisms may also accumulate the toxin in their body tissues. One widely reported effect, which has been worrying shellfishermen in the UK and France for some time, is shell deformities in oysters, which significantly reduce their commercial value. Waldock and Thain (1983) showed that the Pacific oyster *Crassostrea gigas* grew poorly and showed pronounced shell thickening in TBT concentrations as low as 0.15 μg per litre. Alzieu and Portman (1984) had noted similar effects in the shells of *C. gigas* growing in France. An increase in the weight of shell and a reduction in amount of meat were observed. This greatly reduced the acceptability of the shellfish to buyers.

Planktonic organisms are also very susceptible to TBTO. When minute swimming crustaceans, the copepods *Acartia tonsa*, were exposed to low concentrations of TBTO, acutely toxic effects were evident, even at 0.4 μg per litre (U'Ren, 1983), and the planktonic larvae of the common mussel *Mytilus edulis* were killed by 0.1 μg per litre (Beaumont and Budd, 1984). However, perhaps the greatest cause for immediate concern is the effect on plant plankton, as expressed by the British Secretary of State for the Environment (Pain, 1985): 'Less than one teaspoonful in 20 million gallons is sufficient to stop the growth of the phytoplankton'.

The effects of TBT on other invertebrate animals has been investigated with similar results. TBTO had been proposed for use as a freshwater molluscicide against the intermediate hosts of the schistosomiasis parasites that cause bilharzia, but Chliamovitch and Kuhn (1977) found that it also affects fish behaviour at a concentration of 12 μg



The Pacific oyster *Crassostrea gigas* showing, top, normal shell growth and, below, abnormal shell thickening *(R. Lucibell and M. Simmonds)*.

per litre. TBT is also toxic to mammals, despite earlier publicity that indicated reasonable safety to handlers. In a review, Jensen (1977) showed that TBT had approximately the same toxicity to mammals as DDT and some other established pesticides. Walsh *et al.* (1982) showed that 0.007 μg per litre TBT in drinking water produced behavioural changes in rats after 21 weeks. No direct effects on man have been shown and might be difficult to identify. However, it is noted that intake may be increased, not only from handling the paint, but also from eating shellfish. Oysters, for example, can concentrate TBT in their body tissues to levels up to 10,000 times over that of their environment (Waldock and Thain, 1983).

Only one mutagenic effect of TBT is documented (Smith, 1981; Bryan *et al.*, 1986) and that is 'imposex', a condition in which female gastropod molluscs take on male features; the oviduct becomes penis-like and breeding is likely to be prevented. Bryan *et al.* (1986) have shown that, around the south-west peninsula of England, imposex affects every population of the common dogwhelk *Nucella lapillus* sampled. They have shown imposex to be clearly related to the concentration of organic tin (from boat anti-fouling paints) in the animals' bodies, and also that it is

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induced by a concentration as low as 0.02 μg per litre of tin (leeched from paint) in seawater. They believe that a concentration of 0.001 μg per litre could induce this unfortunate effect, and this concentration is even lower than that which had been worrying scientists in relation to other marine organisms. Bryan *et al.* (1986) recorded deformities in male as well as female dogwhelks, including a variety of malformed reproductive organs. The snails' tentacles, which bear the eyes and which are close to the sexual apparatus, may also be affected. Individuals with one or three eyes were not unusual. Three marine snails are now known to show this sort of deformation, and it can be postulated that any other marine organisms may be affected, but in ways less easy to detect (the structures on dogwhelks can be seen with a handlens). Reports from other parts of the country are likely to show the same picture with respect to dogwhelks, and it is noted that this species has already disappeared from some sites.

In France, largely because of protests from the shellfishing industry, regulations concerning the use of TBT-based paints became law in October 1982. The use of anti-fouling paint containing TBT on vessels of up to 20 metres, or 50 tonnes or less, became illegal. Subsequently, fewer shell malformations were recorded in oysters, and within two years the spatfall (settlement of young oysters) increased from near zero to 'excellent' levels (Alzieu and Portman, 1984). In the UK legislation is following more slowly. On 13 January 1986 the *sale* of modern co-polymer paints containing more than 7.5 per cent organotin, or more than 2.5 per cent organotin added to boost the performance of other toxins was restricted for use only on vessels of 12 metres or more (this excludes almost all pleasure craft). Aluminium-hulled vessels, however, are not included in the restrictions and, where alternative paints will increase corrosion, TBT paints may still be used. It is noted that, while the sale of these paints is legislated against, the *use* is not. The British Government has encouraged further research on the problem, and invited the paint industry to co-operate in a screening procedure for new anti-fouling preparations. Advice concerning safer procedures for scraping and repainting vessels with TBT coatings has recently been produced in the form of 175,000 pamphlets published by the Royal Yachting Association in 'close consultation' with the Paintmakers' Association, the Shellfish Association, the Ship and Boatbuilders' National Federation and the Department of the Environment. In the USA, North Carolina recently regulated the use of TBT. From January 1985 'safe' water quality standards for triorganotins of 0.002 μg per litre in saltwater, and 0.008 μg per litre in freshwater, were established. Other states seem likely to follow suit (Anon., 1985).

The delay in legislation in some countries is probably because there is no effective replacement for TBT in anti-fouling coatings (although recently some 'non-toxic' anti-fouling paints have been advertised) and a ban on its use could present serious economic problems. The Paintmakers' Association (in an earlier leaflet campaign) has claimed that the case against TBTO is not proven. They argue that legislation would lead to a return to 15-year-old technology. Certainly the economic considerations are considerable: ships, submarine hulls, sonar domes,

A selection of fouling animals: the common mussel *Mytilus edulis*, barnacles *Semibalanus balanoides*, and in the background the hydroid *Nemertisia* (*R. Lucibell and M. Simmonds*).

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offshore platforms, oceanographic instruments, navigational buoys and the water-cooling pipes of coastal power stations are all subjected to fouling. As an illustration, in 1979 the US Navy spent approximately $200 million on maintenance related to marine deterioration, in addition to $180 million that was spent on extra fuel needed to overcome the additional drag caused by fouling (Bacioccio, 1984). The Navy annually prepares and paints some 10 million square feet of ships' hulls, and it can cost over $200,000 to dry-dock one major aircraft carrier. Clearly, the better the anti-fouling toxin, the less often this is necessary. In commercial shipping, operations vessels are dry-docked every 1–3 years with a considerable associated loss of trade.

The evidence presented here regarding TBT is drawn only from those references that illustrate the major points (and from which most other information available on this topic may be traced), and shows TBT to be a serious threat to many coastal marine organisms and that a more acceptable replacement is urgently needed. Copper (as copper oxide) is still the most widely used toxic agent in hull coatings and is, therefore, perhaps the obvious answer. It too is a poison introduced to the environment, although it has been found to be only one-tenth as toxic to copepods as TBT (U'Ren, 1983). However, it is perhaps of some concern to the paint industry and to boat-owners that some organisms have developed a tolerance to copper paints, which, for example on European tankers, achieve temporary protection against fouling animals but are unable to control the growth of attached seaweeds (see Fischer *et al.*, 1984). Development of a new anti-fouling preparation could take between five and ten years. In the meantime, it is clearly essential to monitor TBT levels, especially where there is much boating activity, and legislation should be quickly introduced to keep concentrations in the sea below those levels that affect marine organisms.

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