ANTI-FOULING PAINTS AND THE MARINE ENVIRONMENT: THE OVERSEAS EXPERIENCE

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Preamble

Anti-fouling paints are designed to inhibit the growth of algae and animals such as barnacles on the hulls of ships, resulting in reduced drag and fuel consumption.

The first generation anti-fouling paints depended to a large extent on the biocidal properties of copper. Copper occurs naturally and is only mildly toxic but more significantly perhaps, the bioavailability of ionic copper is rapidly reduced on release into seawater by binding/complexing with low levels of dissolved organic matter.

Over the past 15 years or so anti-fouling paint formulations have increasingly relied upon the incorporation of organotin compounds as the active agent(s), although cuprous oxide is still used sometimes in combination with organotin.

Chemically organotins are defined as R_4Sn, R_3SnX, R_2SnS_2 and $RSnX_3$ where R is alkyl group or aryl group and X is a halide, oxide, hydoxide or other functional group.[3] Organotins are used as stabilizers in polyvinyl chloride, as catalysts in the manufacture of foam and rubber, as antioxidants, fire proofing and water-repellent agents, and as biocides (fungicides, bactericides, miticides, molluskicides etc). The total world production of organotins was estimated at 30,000 tons per year, in 1982.[2]

The organotins have become very popular with manufacturers and users of anti-fouling paints because of:-

(1) Their very powerful biocidal action.

Organotins can be extremely toxic, the tri-organotins being more toxic than the di-organotins which are in turn more toxic than the mono-organotins. They are apparently more effective than copper based paints in preventing weed and slime growth immediately below the water line.

(2) Their chemical structure which enables them to be built into polymers to form the long lasting 'self-polishing' (or 'ablating') copolymer paints (see below).

(3) The fact that they are essentially colourless and can therefore be tinted to a wide range of hull colours.

Tributyl Tin (TBT) is the most commonly used organotin in anti-fouling paints. The first TBT containing anti-fouling paints became commercially available in the mid 1960's but were not used in significant quantities until the early 1970's. In 1985 the USA produced about 400 tonnes of TBT pesticide about one third of which was used in anti-fouling paints (note: there is no evidence that TBT is naturally produced in any measurable quantity).[2]

TBT paints are formulated in two ways:-

(1) Conventional or "free association" Paints

TBT is added directly as either the oxide (TBTO) or fluoride. Upon exposure to water TBT is released by diffusion out of the paint. Such paints have early high release rates and relatively short periods of effectiveness. The release pattern is inefficient in that much more biocide than is necessary to prevent fouling is released at the beginning of the boating season.

(2) Copolymer or "self-polishing" Paints

These are formed by chemical incorporation of TBT into a polymer such as methacrylate. Upon exposure of such paints to water TBT is released through hydrolysis. The release of TBT is effected by water movement over the painted surface, which is gradually polished away. Such paints are characterized by slow, almost constant, release rates which have both technological and economic advantages - they last longer.[2] Because of their more efficient pattern of release, co-polymer paints are thought to present less risk to non-target organisms than the so called "free association" paints but there is some doubt about this (ref Stebbing 1985).[10]

Environmental Effects

The scientific community became aware of the TBT invasion of the environment in the late 1970's, largely as a result of work undertaken to determine the cause of reduced growth rate, spatfall failures and shell malformations affecting commercial oyster farming operations along the coast of France and England, particularly in the vicinity of marinas. Laboratory experiments indicated that TBT was the culprit, although Stebbins (1985) has suggested that the evidence is not conclusive.[10]

To date, TBT has been linked with:-

(a) Malformations of Pacific oyster Crassostrea gigas shells at several sites on the Atlantic Coast of France and England, with degree of malformations being positively correlated with intensity of boating activity in adjacent waters;[2]

(b) Reduced flesh growth (up to 25-fold reduction) in oysters and elevated tissue levels at the same sites;[2]

(c) Decline or loss of natural spatfalls in some areas implying that gametogenesis and/or survival of planktonic oyster larvae have also been affected;[10]

(d) Widespread incidence of 'imposex' characteristics in dogwhelk Nucella lapillus populations around the south-west coast of England. Imposex is the superimposition of male characteristics notably a penis and vas deferens on the female. In the laboratory imposex characteristics can be readily induced by exposure to TBT compound leached from anti-fouling paints;[5]

(e) A decline in the diversity of marine life in many California marinas over the past 10 years.[2]

Over the past two or three years there has been an increasing amount of concern expressed by marine scientists in both Europe and North America as to the environmental fate and toxicity of TBT to non-target organisms; there is now a considerable world literature on the topic. This concern has been fueled by laboratory findings indicating a variety of sublethal effects at various trophic levels (see below). The concern is that the oyster/whelk type of phenomena referred to above may be just the 'tip of the iceberg' in terms of total impact on the marine environment.

Toxicity of TBT

TBT is now widely aknowledged as one of the most toxic substances known to man, being demonstrably toxic at tens of parts per trillion in the laboratory.[3]

Hall and Pinkney (1985) present an interpretative literature evaluation of the acute and sublethal effects of organotin compounds on aquatic biota. They note that organotin compounds are generally more toxic to various aquatic biota than other contaminants such as polycyclic aromatic hydrocarbons, chlorinated insecticides and polychlorinated biphenyls.[3]

In a recent article entitled "TBT - An Environmental Dilemma" E D Goldberg, a professor of chemistry at Scripps Institute of Oceanography, La Jolla, California, described TBT compounds as "probably the most toxic compounds ever deliberately introduced by societies into natural water".[2]

A report commissioned by the World Wildlife Fund and recently published by the Marine Conservation Society indicated that not only are algae, molluscs, crustacea and fish being poisoned but the whole food chain is affected, threatening the birdlife that feeds on the estuaries and in the coastal waters. In commenting on the report a WWF-UK ecologist Dr Chris Tydeman noted that the conclusions are extremely worrying given that TBT strikes right at the base of the food chain and is shown to be having detrimental effect down to the limits of chemical detection.[11]

Stebbing 1985 has discussed some of the difficulties involved in the interpretation of laboratory - derived toxicity data, the difficulty of establishing causal relationships in particular.[10] An obvious problem with TBT is that because toxicological and analytical thresholds are of the same order, there is a real possibility that chemically undetectable levels are biologically significant. Another problem relates to the relative significance of levels of TBT in water as opposed to (accumulated) body tissue levels and hence the importance of experiment duration. Goldberg (1986) suggests that, for a number of (specified) reasons, most laboratory studies have underestimated the levels of which TBT is toxic. He notes that TBT is slow acting and that short term laboratory experiments may lead to an underestimate of its biological activity.

Goldberg states that for some zooplanktan species acute organotin toxicity occurs at levels as low as 400 ppt. He cites a 96-hour LC_{50} of 5,000 ppt for some estuarine and marine fish.[2]

LC_{50} levels tend to decrease with the duration of the experiment, so although the 48h LC_{50} for Mytilus edulis larvae is 2,300 ppt TBTO, a lower 15 day LC_{50} value of 100 ppt has been found by others.

Clearly the level at which death occurs (acute toxicity) is of limited value as a measure of effect. Laboratory experiments have demonstrated that a variety of sub-lethal effects are possible at lower levels including effects on reproduction, gametogenesis and growth. Field observations in the USA have shown that indigenous organisms are often absent in marinas when the TBT concentration reaches much above 100 ppt.[2]

Some of the more significant findings of Pinkney and Hall's literature survey were:-

(1) Inhibition of algal respiration and photosynthesis at TBTC1 water concentrations at 1.9 ppm (cf recent work by Beaumont and Newman 1986, suggesting that primary production in three species of microalgae may be significantly affected by TBT levels as low as 0.1 ppb.)

(2) Zooplankton rapidly accumulate TBTO from the water column, thus initiating accumulation in the food chain.

(3) Larval stages of macroinvertebrates are generally sensitive to levels of toxicity about two orders of magnitude lower than their adults.

(4) Estuarine shellfish (molluscs) seem to be particularly susceptible due to the ability of shellfish to bioconcentrate organotin from both water and suspended materials. (Note: organotin compounds, like many metals, absorb onto particles in the water column. The mobile particulate fraction tends to be retained in estuaries and to be readily available to benthic filter feeders. This probably explains the particular vulnerability of oysters).

(5) Sole larvae (bottom feeders) were found to be 18X more sensitive to TBTO than adults.

(6) Sublethal effects have been recorded for a number of trophic groups, including:- growth reductions, impairment of egg production, histological changes, imposex and avoidance behaviour.

There are, as yet, no reported human health impacts resulting from the dispersion of TBT about the environment.[2] However, a recent report from Alaska suggests that TBT could enter the human food chain via salmon flesh. Researchers have found that chinook salmon can absorb the compounds from anti-fouling paint on the pens, where the fish are reared.[7]

Environmental Levels

The levels of TBT attained in the water at any given site are reported to be affected by a number of variables including:- the number of vessels, the input rate (type of paint, water movement), the flushing rate/retention time within the system, degradation rate, temperature and turbidity. Obviously marina sites or harbours with restricted circulation are particularly susceptible to accumulation.

MAFF laboratories in the UK have found TBT levels in estuaries on the east coast of England as high as 2,200 ppt. Levels of 80-430 ppt TBT were found in the Crouch Estuary and oysters transplanted from open ocean areas rapidly development malformed shells at these levels.[2]

Goldberg (1986) records TBT values of up to 150 ppt in the Detroit and St Clair rivers in Canada, 2910 ppt in a marina in Lake St Claire, 100 ppt in well flushed marinas in San Francisco Bay (with flourishing mussel populations) and 500 ppt in a less flushed marina in SFB (with an absence of fauna).[2]

In coastal waters in the US, adjacent to marinas, TBT concentrations can be in the order of about 10 to 20 ppt.

It seems then that TBT levels in overseas harbours and marinas can and to exceed the levels known to be lethal to oyster larvae and certain species of zooplankton. A variety of sublethal effects could be expected, at different trophic levels.

What Levels are Environmentally Acceptable?

In the US it has been found on the basis of preliminary observations, that certain native organisms (e.g., mussels and tunicates) that were quite abundant a decade ago, may have now disappeared from the docks and piers of marinas where TBT levels are greater than 100 ppt.[2] At present there are no effluent guidelines or water quality criteria for TBT in the USA.

In the UK, British scientists have proposed 20 ppt as an acceptable level of TBT in natural waters. This is based on the disruption of growth of Ostrea edulis at 250 ppt and of C gigas at 160 ppt (an average of 200 ppt), with a safety factor of 10.

Mode of Action

It appears that TBT can gain entry to the body of marine organisms either by direct absorption from the water column or via ingestion of particles to which it is attached. The later applies to filter feeders such as zooplankton and bivalve molluscs. There appears to be little information on accumulation in fish flesh.

TBT seems to exert its toxic influence via the nervous or hormonal system but at high concentrations it can act as a surfactant distorting sensitive epithelial tissues.[4]

Goldberg (1986) has drawn a parallel between DDT and TBT referring to the later as "... a potential DDT of the waterways". In identifying similarities and dissimilarities, he suggests that there may be lessons to be learnt from the DDT experience.[2]

Similarities between TBT and DDT:-

(1) Both are highly toxic at very low levels;

(2) Neither occur naturally and both persist in the environment (albeit for a shorter time period in the case of TBT - see below);

(3) Both affect non-target species;

(5) Both are concentrated in fats;

(6) Neither affect human health, as far as can presently be determined.

Dissimilarities between TBT and DDT:-

Some of the highly undesirable effects of DDT do not appear to be associated with TBT.

(1) TBT has a much shorter residence time (measurement in weeks or months), in contrast with the persistence of DDT (measured in years);

(2) The degradation products of TBT are far less toxic than is TBT itself (see below), whereas DDT produces a host of toxic decay products;

(3) Whilst DDT is subject to long range translocation (hundreds or thousands of miles), the ionic nature of TBT compounds keeps them generally within the water domain and within miles of their entry into natural waters.

Degradation

TBT in seawater is known to degrade over a period of weeks, to the (far less toxic) dibutyl and monobutyl tins. The final decay product can be inorganic tin which at the levels involved, is not toxic at all. These decay products frequently occur at high levels in the bottom sediments of marinas.

Scientific, Administrative and Political Response

There is increasing scientific concern about the effect of TBT in the aquatic environment - both marine and freshwater.

In 1982, the French Government banned the use of TBT anti-fouling paints on vessels less than 25 m in length.[2] The rationale for this move presumably related to the fact that smaller (pleasure) boats are moored for long periods in marinas/estuaries, whereas the larger ocean going vessels spend much of their time at sea. Although the ban has been incomplete there has apparently been a significant and sustained decline in shell abnormalities in pacific oysters in the worst affected areas and larval settlement has increased (Alzieu and Portmann 1984, cited in Stebbing 1985).

In January 1986 the British Government introduced the Control of Pollution (Anti-fouling Paints) Regulations banning the production of TBT copolymer paints with more than 7.5 percent TBT and of other paints with copper or other accompanying anti-fouling agents with more than 2.5 percent TBT (the latter restriction effectively prohibits the use of "free association" paints).[6] More recently, the Environment Minister has asked the Paint Manufacturers Association (PMA) to restrict immediately the sale of TBT paints in the Norfolk Broads area and Government has threatened to ban the use of tin-based anti-foulants altogether.[7] The British Government's latest move has been to classify anti-fouling paints as pesticides rather than paints[8], presumably to achieve a greater degree of legislative and administrative control.

In the UK, the Royal Yachting Association, in consultation with the PMA and other concerned groups, has produced guidelines for the anti-fouling user.[9]

In the USA, the US Environmental Protection Agency (USEPA) registers organotins as anti-foulants but they have not been registered for use on stationary structures that would have a continuous source discharge. The USEPA has proposals to regulate the use of TBT paints by 1988.

Recently one of the USA's foremost workers on TBT, E D Goldberg of Scripps Institute has called for a <u>total ban</u> on the use of TBT in paints for <u>commercial</u> and <u>pleasure</u> craft, stating:-

> "The loss of native organisms in marinas provides a warning that the vitality of communities of organisms in adjacent waters can be threatened. Estuarine food webs, which are the base for much of our commerical fisheries, must be protected. The strong parallel between the impact of TBT an non-target organisms and that of DDT in the 1960's is patent. DDT was banned by the US and many other countries after the unacceptable ecological disasters became too evident. Clearly the time to act against TBT is now"[2]

In Japan, TBT's have received a lot of media attention because of the high content of seafood in the diet and the desire to avoid another "Minimata" - type disaster. The Japanese government is apparently considering bringing in legislation to control the use of TBT.

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