TRIBUTYLTIN (TBT) IN ANTIFOULING PAINTS - AN ENVIRONMENTAL HAZARD

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ABSTRACT
Early in the 1970s organotins were introduced as effective components in marine antifouling paints. They soon showed to be extremely effective for their purpose and became common world-wide. However, serious environmental impact was found in the form of a high toxicity, a high potential for bioaccumulation, and specific long-term effects known as imposex (development of male characters in females of snails). Restrictions for the use of TBT were adopted in many countries but usually only valid for vessels less than 25 m in length. Still after some years of partial ban, the harm of TBT is clearly seen in most coastal areas as evidenced from studies along the Swedish west coast and in Iceland.

INTRODUCTION
Antifouling paints have been used on ships since the end of last century. The active components have been various metals such as lead, copper or arsenic. During the 1970s new formulations which contained organotin compounds were introduced and these showed to be very effective against growth of both algae, mussels and barnacles, *i.e.*, the most important fouling organisms.

Soon this kind of compounds also became common in impregnated nets for the aquaculture industry, as stabilizer additives in wall paints, textiles, biocides and in plastic. Thereby organotin compounds were introduced in many different areas of society. Tributyltin oxide (TBTO), the most commonly used formulation is hydrolytically stable but is slowly transformed in sunlight ($t_{1/2}$ > 89 days). The half-life of TBTO in soil at 25 °C is 70 days under aerobic conditions but >200 days under anaerobic conditions. TBTO is degradable in water. At 28 °C, half-lives recorded are 5 and 8 days and 9 days at 13 °C. In sediment the half-life at 28 °C is 6 days under aerobic conditions and 24 days under anaerobic conditions. Tin, like copper, is an element and cannot decompose. The solubility of TBTO in water is pH-dependent. At 20 °C water solubility is 0.7 mg l^{-1} at pH 5 and 7.0 mg l^{-1} at pH 7. TBTO binds strongly to soil and sediments. About 72 to 100 % of TBTO is adsorbed to humus in water. The bioconcentration factor (BCF) for fish varies between 1,000 and 2,600. BCF studies in bacteria and algae show values of up to 30,000. Bioaccumulation studies of TBTO from sediment to mussels show that accumulation is proportional to concentration in the sediment. TBTO is accordingly thought to be highly bioaccumulable.

The acute toxicity of TBTO has been studied in a large number of different organisms and is very high. The median effect concentration (EC_{50}) for algae is 1 μg l^{-1}, for copepods 0.7 μg l^{-1}, for shrimps 0.5 μg l^{-1} and for fish 30 μg l^{-1}. Chronic tests on oysters and mussels show toxic effects at concentrations down to 20 ng l^{-1}; the no effect concentration (NOEC) for fish has been shown to be 10 ng l^{-1} and sublethal effects in dogwhelks (snails) occur at 1-2 ng l^{-1}. TBTO has a moderately acute toxicity to birds (EC_{50} = 3,926-4,899 mg kg^{-1}).

However, the use of organotin compounds in antifouling paints were gradually found to give drastic environmental effects. This was first manifested at the beginning of the 1980s when, in addition to their extremely high toxicity, they also were found to cause abnormal shell development in oysters cultured along the French and Spanish coasts giving great economic loss. Another very specific effect was the development of male primary sexual characteristics in female gastropods (Bryan & Gibbs 1991). This phenomenon has been known as "imposex" and can now be found globally in marinas, harbours, and coastal areas with intense shipping.

Today there is, in most countries, a partial ban on organotin use on boats or ships. However, mostly the ban is valid only for vessels of less than 25 metres in length. Still no regulations exist for their use in land-based activities, for example the treatment of timber in Australia and New Zealand. Also dumping of organotin contaminated dredged material from harbours discharged into the marine environment, have recently shown to cause biological effects (Ten Hallers-Tjabbes & van Hattum 1995). In coastal waters and harbours with restricted water turnover there may be a high risk of accumulation of organotins to levels which are toxic to fauna and flora and it is evident that the use of these compounds has to be further restricted, a problem which is now focused on by authorities and is the subject to intensified ecotoxicological research.

The aim of this paper is to give some examples of biological effects and levels of organotins in coastal waters in Northern Europe. Some own field and laboratory experiments are presented.

MATERIALS AND METHODS

Swedish investigations

One year before the restricted ban on organotin in antifouling paints in Sweden 1989, a field experiment was performed in a frequently used harbour for pleasure boats on the west coast of Sweden. Due to lack of local mussels in the area, caged specimen of blue mussels (*Mytilus edulis* L.) were used. Sampling of mussels was performed monthly from different sites in a gradient from the marina and the samples were chemically analysed for TBT. The experiment continued for two years in order to follow up the situation before and after the ban.

Two years later, a general inventory of the state of pollution took place along the northern part of the Swedish west coast. At 12 different localities from the city of Göteborg to the Norwegian border mussels, macroalgae and fish were taken for chemical analyses of inorganic and organic pollutants including organotins in order to compare the pollution impact at different sites.

Icelandic investigations

The impact of organotins in an Arctic environment with low water temperatures, was studied in the southern part of Iceland. The degradation of TBT in these waters is considered to be very slow due to low water temperatures (0-10 °C). As test animals the gastropod whelks (*Buccinum undatum* L.) were used. These snails are very common in northern waters. They are caught commercially by fishermen and represent hereby a certain economical value. In Dutch studies this species has been found to be very sensitive to organotin contamination (Ten Hallers-Tjabbes *et al.* 1994). Earlier investigations using dogwhelks (*Nucella lapillus* L.) and blue mussels (*Mytilus edulis L.*) indicated that tributyltin pollution is widely distributed in Icelandic waters (Svavarsson & Skarphédindóttir 1995; Skarphedinsdottir *et al.* 1996).

The snails were caught in baited traps in a remote area of Iceland known to be fairly unpolluted. For the experiment we used females with a total length of 68 ± 18 mm and the frequency of imposex was measured in a subsample according to a method described by Ten Hallers-Tjabbes *et al.* (1994).

Contaminated sediment was sampled by grab in a harbour with dense traffic of ships. A reference sediment was also taken from an area supposed to be unpolluted. The collected sediment was filled in a layer of 5 cm in glass tanks (25 litre). Samples of sediment were also frozen for later chemical analysis. In order to find out whether imposex could be induced by leakage of bioavailable organotins from the sediment, the experiment was run in a continuous flow system for three months. In some tanks we increased the leakage further by dosage of suspended sediment from the harbour. In all, three different treatments: clean sediment, contaminated sediment with and without addition of suspended sediment were used at two temperatures, 2 and 8 °C. For each treatment four replicates were run with 14 specimens in each tank. A semipermeable membrane device (SPMD, Huckins *et al.* 1990) was placed in the water flow from the tanks to estimate the concentration in water during the exposure time. The SPMD consists of a semipermeable polyethylene tube filled with fat, where the organotins are accumulated. After three months the snails were checked for imposex characteristics and the tissues analysed for organotin compounds.

Imposex examination

The whelks were released from their shells and the weight of the soft tissue measured. The vagina and the gonads were dissected and weighed. Each individual was then examined for indication of imposex including the presence and the total length of penis in the females. The animals were then frozen for chemical analysis.

Chemical analyses

Thawed whelks were run in a mechanical homogenizer (Braun AG) in groups of five from each treatment. The material was then freeze-dried. The fat content and organotin compounds were analysed according to standardised procedures (Dirkx *et al.* 1994; Pereiro *et al.* 1996; Szpunar *et al.* 1996). Sediment samples and SPMD:s were also analysed.

RESULTS AND DISCUSSION

Swedish investigations

The results from the chemical analyses of the caged mussels from the marina showed very good agreement between the high activity of boats in the harbour during summer and high levels of TBT in mussels and in the water. Also the positive effects of the restricted ban 1989 are clearly seen in the material from 1990. However, still after two years it was possible to find concentrations in water which were high enough to cause imposex in dogwhelks (Tab. 1).

In the chemical monitoring programme 1992 the concentrations of tributyltin were found to be elevated especially in harbours and in the vicinity of dense shipping traffic routes. This indicates a continuous use and leakage from ships. The ratio between tributyltin and the degradation product dibutyltin was highest in connection with an oil refinery with a dense traffic of ships greater than 25 m length (Tab. 2). The high ratio indicates recent discharges, in this case a leakage of TBT from tankers, and stresses the need for a total ban of organotins (Tab. 3).

Table 1. Estimated levels of tributyltin in water (ng l^{-1}) along the Swedish west coast 1992, three years after the ban for pleasure boats < 25 m.

TBT	3.3-6	4.2-4.8	5.8-9.1	2.0-3.3

Table 2. The ratio of tributyltin/dibutyltin in water at different sites along the Swedish west coast, 1992.

	Göteborg seaport	Industrial area	Refinery	Remote control area
TBT/DBT	5.0	4.3	7.2	3.8

Table 3. Levels of tributyltin in water in a marina and in an open bay at the Swedish west coast before and after the ban. Lowest TBT concentration in water to give detectable effects (imposex) in marine gastropods is approximately 1 ng l^{-1}.

	Marina	Open bay
June 1987	130	37
August 1987	900	134
January 1988	100	7
June 1991		10
July 1991		5
January 1992		3

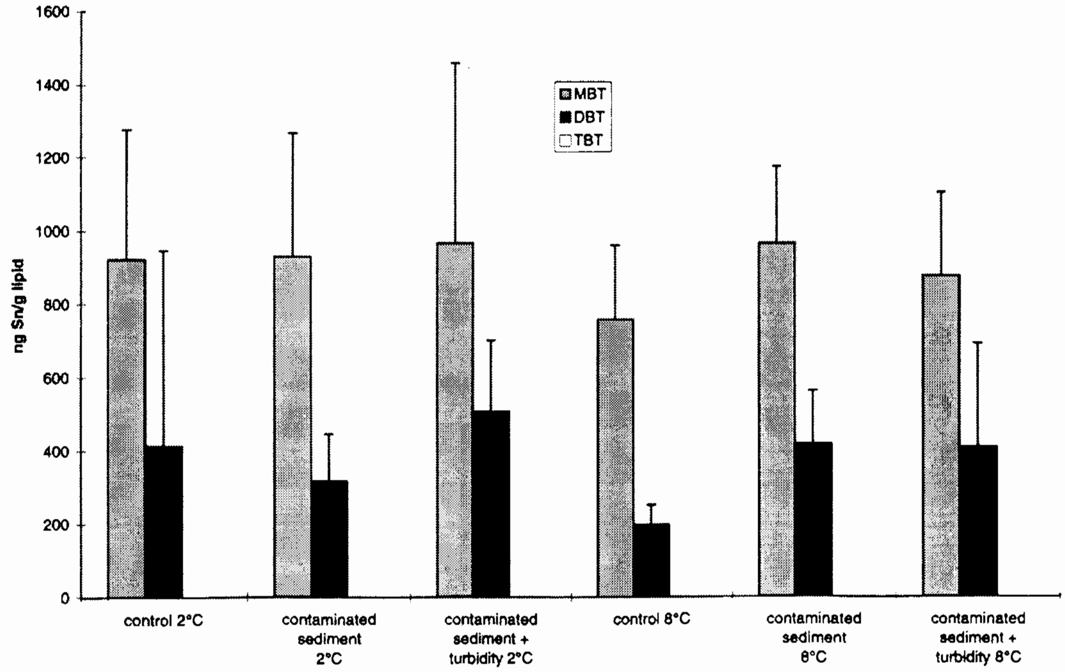

Figure 1. Concentrations of organotins in *Buccinum undatum* L. exposed during three months in different treatments with contaminated sediment. Vertical bars indicate 95 % confidence intervals.

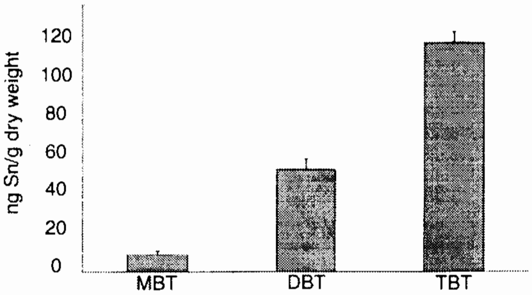

Figure 2. Concentrations of organotins in sediment from a contaminated harbour. Vertical bars indicate 95 % confidence intervals.

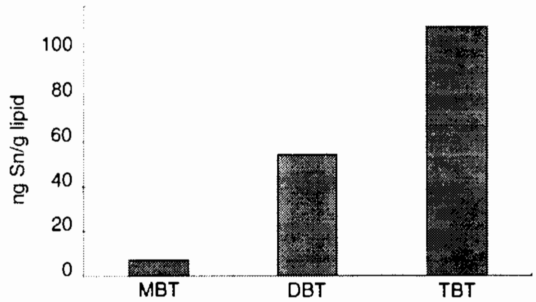

Figure 3. Concentrations of organotins expressed as nanogram g^{-1} lipid weight in a semipermeable membrane device (SPMD) exposed during three months in the outflow from experimental tanks with contaminated sediments.

Icelandic studies

The results showed very little uptake of organotin compounds in the snails and only minor differences between the control animals and those from the different treatments (Fig. 1). No tributyltin was found but only degradation products as dibutyl- and monobutyltin. The quite different composition of butyltins in sediment and water (Figs. 2, 3), where TBT predominated, indicates that whelks have a very good ability to metabolise TBT. Furthermore, no increase of imposex was found among the differently treated groups of snails after three months of exposure (Fig. 4). Statistical calculations using G-test for one-way classification (Fowler & Cohen 1992) showed that no sig-

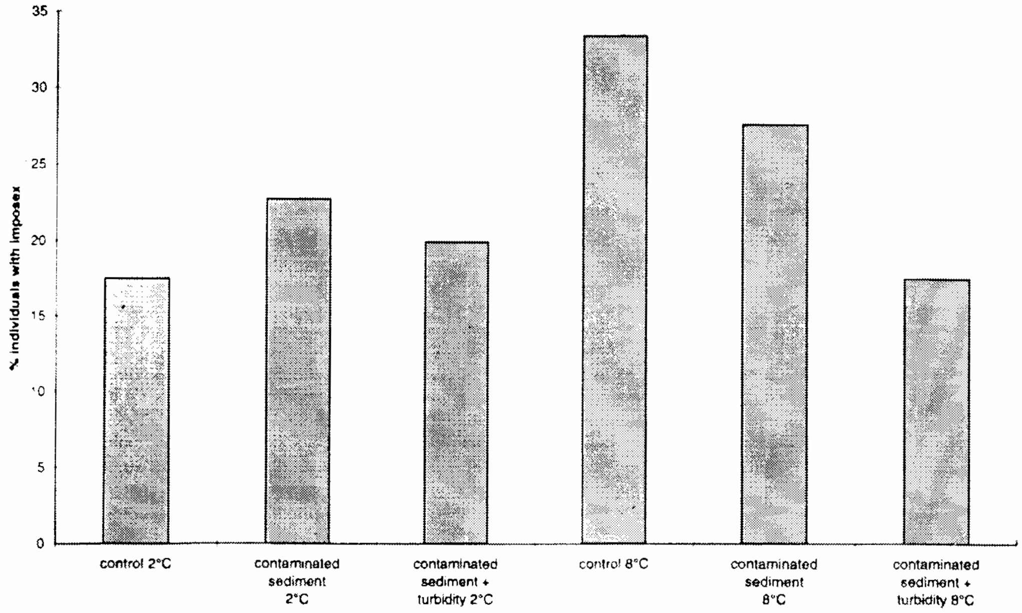

Figure 4. Percentages of *Buccinum undatum* L. with imposex after three months exposure in different treatments with contaminated sediment.

nificant differences between treatments exist. The reason for this may be that the time to develop imposex probably is very long in these northern waters with low water temperatures and low metabolic activity during winter. However, in the present investigation only adult specimens were used. It is probable that developmental stages of *Buccinum* are more sensitive to organotins which has been found in other species (Ruiz *et al.* 1995). The results may indicate that dredging operations in TBT-contaminated harbours in cold waters do not cause as serious effects as have been suggested, especially if performed during winter time when no reproduction occurs.

CONCLUSIONS

The restricted ban of organotins resulted in lower levels in harbours and coastal areas. Still, organotins are of environmental concern due to a general use on ships > 25 m. In waters with low temperatures the development of imposex in whelks may take a long time and the use of this parameter in this species as an early indicator of pollution by organotin antifouling paints may be less suitable.

The risk of dredging operations may be less if performed during winter time.

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