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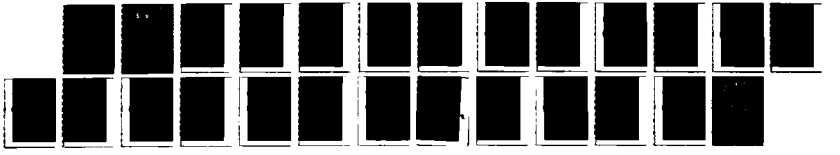

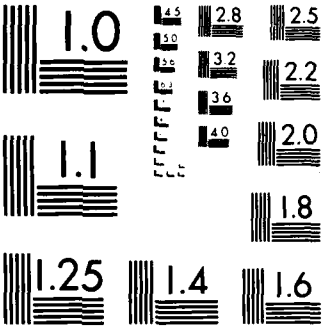

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Tributyltin compounds were shown to be slow-acting toxins causing acute toxicity or two amphipod species at concentrations as low as 10 g/L^{-1}. Orchestia traskiana was exposed to bis (tributyltin) oxide (TBTO) or tributyltin flouride (TBTF) as single compounds. Both Compounds were acutely toxic in 10 days at concentrations of 10 g/L^{-1} and above. Gammarus oceanicus were exposed to tributyltin leachates from panel painted with two different antifouling paint formulations. Following 48 hr immersion, aqueous tributyltin concentrations increased with increasing painted surface area, but one type of paint leached tributyltins about ten times faster than the other. Amphipod mortality in short-term tests was directly correlated with increases in painted surface area and leaching rates. Gammarus oceanicus was more sensitive than Orchestia traskiana based on measured trinutyltins concentrations, with final leachate concentrations of 4.8 g/L^{-1} causing total mortality in 5 days. The results of these experiments show that tributyltins compounds are very toxic to some non-target organisms.

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ACUTE TOXICITY OF TRIBUTYLTINS AND TRIBUTYLTIN LEACHATES FROM MARINE ANTIBIOFOULING PAINTS.

by

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ABSTRACT.

Tributyltin compounds were shown to be slow-acting toxins causing acute toxicity to two amphipod species at concentrations as low as 10 $\mu g/L^{-1}$. Orchestia traskiana was exposed to bis (tributyltin) oxide (TBTO) or tributyltin fluoride (TBTF) as single compounds. Both compounds were acutely toxic in 10 days at concentrations of 10 $\mu g/L^{-1}$ and above.

Gammarus oceanicus were exposed to tributyltin leachates from panels painted with two different antifouling paint formulations. Following 48 hr immersion, aqueous tributyltin concentrations increased with increasing painted surface area, but one type of paint leached tributyltin about 10 times faster than the other. Amphipod mortality in short-term tests was directly correlated with increases in painted surface area and leaching rates.

Gammarus oceanicus was more sensitive than Orchestia traskiana based on measured tributyltin concentrations, with final leachate concentrations of 4.8 $\mu g L^{-1}$ causing total mortality in 5 days. The results of these experiments show that tributyltin compounds are very toxic to some non-target organisms. Thus the intelligent choice of antibiofouling paint formulations depends upon an acceptable compromise between leach rates, which are effective at the painted surface but minimize effects on non-target organisms.

Résumé.

On démontre que les composés de tributylétain sont des toxiques à action lente qui provoquent une toxicité aigüe chez deux espèces d'amphipodes à des concentrations aussi faibles que 10 µg/l. Orchestia traskiana a été exposée à la fois à l'oxyde de tributylétain ou au fluorure de tributylétain en tant que composés simples. Les deux composés étaient extrêmement toxiques en l'espace de 10 jours à des concentrations de 10 µg/l et à des concentrations supérieures.

Gammarus oceanicus a été exposé à des lixiviats de tributylétain provenant d'éprouvettes peintes avec deux formulations différentes de peinture antisalissure. Après 48 heures d'immersion, les concentrations de tributylétain aqueux ont augmenté avec un niveau de surface peinte accru. Toutefois, un type de peinture a lixivié le tributylétain 10 fois plus vite que l'autre. La mortalité des amphipodes, lors des essais à court terme, était directement liée aux accroissements de surface peinte et aux taux de lixiviation.

Gammarus oceanicus était plus sensible que Orchestia traskiana si l'on se base sur les concentrations de tributylétain mesurées en avant des concentrations de lixiviat finales de 4,8 µg/l qui provoquent la mortalité complète en 5 jours. Les résultats de ces expériences montrent que les composés de tributylétain sont très toxiques pour certains organismes les moins voyants. Ainsi donc, le choix intelligent de formulations de peintures antisalissures dépend d'un compromis acceptable entre les taux de lixiviation qui sont efficaces au niveau de la surface peinte mais minimisent les effets sur les organismes les moins voyants.

INTRODUCTION.

Considerable effort has been expended in attempts to prevent biofouling on ships. Prevention is important not only to protect the ship itself from damage, but also to insure efficient and dependable operation. The most widely used paint formulations are based on copper, which leaches out as an ion, the active antibiofouling material. Copper has several drawbacks, including but not limited to short paint life, and the fate of copper as an environmental pollutant. The most widely promoted and used substitutes contain triorganotin compounds as the active agent (Evans, 1973; Dyckman, et al., 1973). However, before general use, their action on non-target organisms vis-a-vis their effectiveness in different paint formulations, has to be evaluated (Dyckerman, et al., 1973).

In this paper, we describe the action of two tributyltin compounds, bis(tributyltin) oxide (TBTO) and tributyltin fluoride (TBTF), and the toxicity of tributyltin containing leachates from two commercially available paint formulations. Typical persistence of single compounds and concentrations of butyltin leachates were determined for the different bioassay regimes. The [illegible] of the different antibiofouling [illegible] was observed. Antifoulants were [illegible] of their solubilities, effects and because of their ecological [illegible]. Formulations between the [illegible] single compounds and resultant levels of tributyltins [illegible] are also important aspects of this work.

MATERIALS AND METHODS.

Experiments were conducted in the U.S., using Orchestia traskiana, and in Sweden, with Gammarus oceanicus. In the experiments performed with O. traskiana, we were interested in assessing the effect of TBTO and TBTF added to the bioassay as single compounds. Experiments conducted in Sweden were performed with plexiglass panels painted with either of two commercially-available paint formulations. Specifics for each of the experimental protocols follows.

Adult amphipods, O. traskiana, were collected intertidally in a San Francisco Bay marsh and in the laboratory were maintained in 30 o/oo S water at 18°C. These were similar to ambient salinity and midday temperatures at the time of collection. The experimentals were acclimated for 3 days before toxicant exposure began.

Bioassay : Five amphipods were put into a 10 cm fingerbowl containing 150 ml of 30 o/oo S seawater. TBTO and TBTF solutions were prepared in acetone and added to the seawater with thorough mixing. Three replicates of each of the following toxicant concentrations were examined : acetone control (67 µl/150 ml seawater), 0.5, 1, 3, 6, 10 or 15 µg/L^{-1}. Daily, the exposure groups were censused, transfered to freshly prepared test media and fed pieces of the green algae Ulva and Artemia nauplii.

Gammarus oceanicus were collected in Tvärren Bay, 80 km S of Stockholm. In the laboratory, adult males were separated from Fucus and put into aquaria for 2-3 days prior to their use in the bioassays. The amphipods were fed Tetramin (R) commercial fish food during this pretest period, but no food was given while exposed to paint leachates.

This species was exposed to tributyltin cation from paint leachates. For the bioassay, 10 amphipods were put into each of 2 all-glass aquaria. The [illegible] was controlled by varying the area of plexiglass panels painted with [illegible] paints. Water in the tank was carefully [illegible] with new Baltic Sea water (salinity = 7 o/oo S) [illegible] were counted daily, and dead ones removed. Tests [illegible] Painted surface areas of [illegible] were painted with Interna [illegible] (R), [illegible] Both paints contain

only TBTF as the active agent.

Chemical Analysis.

Time dependent loss of single compouds : Flasks containing 500 ml of seawater with 50 $\mu g/L^{-1}$ TBTO were either plugged with cotton, without aeration, or were not plugged and were aerated lightly. The control consisted of seawater to which only acetone was added. The flasks were sampled at 0 and 24 hrs, and chemical analysis performed within 48 hrs.

Determination of tributyltin in paint leachates were performed on samples collected in Sweden and analyzed in the U.S. Five hundred mls were withdrawn directly from the aquaria during the bioassays, into 500 ml cleaned brown-glass bottles. Subsequently, they were shipped to the U.S. and analyzed within 2 months of collection. We have no information on the probable loss of tributyltin during the period between collection and analysis. However, given the amount measured, it appears that any loss which occurred was not large.

Chemical Analysis : The following procedure was used to determine tributyltin concentrations in the Orchestia traskiana experiment. TBTO concentrations, as the tributyltin hydride, were determined by gas chromatography using a Varian 2400 gas chromatograph with a 15 % OV-101 on a 100/120 Chromasorb G/HP column at 150°C. To a 200 ml seawater sample containing TBTO, 80 mg of sodium borohydride was added. The solution was allowed to stand for 20-30 min after which 10 µl of an internal standard solution containing dicyclohexyl (0.86 mg/ml) in acetone was added. The tribultyltin hydride and dicyclohexyl were extracted with 20 ml hexane. The hexane was dried ($MgSO_4$) and evaporated to ca 10 µl, being careful not to take the sample to dryness. The analyses reported in this paper deal with the behavior of TBTO. On the basis of a few additional samples of the same concentration of TBTF collected and analyzed in the same fashion, it appears that it displays identical behavior with respect to time-dependent loss from seawater used in this bioassay.

The analysis of tributyltin-containing paint leachates was similar to the above protocol, with the following modifications : only 40 mg of sodium borohydride was added, followed by stirring for 30 sec. These changes were necessitated by the presence of an unidentified interfering compound or compounds which appeared in the stored water samples. No interference was observed in reference samples analyzed with these modifications.

RESULTS.

Persistence of TBTO in seawater : In seawater, tributyltin concentrations remain stable for at least one day. The mean of three samples taken just after TBTO addition was 43.66 ± 1.27 $\mu g/L^{-1}$ (mean ± standard deviation). The concentration of TBTO in unaerated and aerated flasks 24 hrs later was not significantly different, 45.72 ± 6.02 and 45.05 ± 1.46 $\mu g/L^{-1}$, respectively. The acetone control had undetectable TBTO background levels (less than 0.2 $\mu g/L^{-1}$; Table 1). The differences between nominal and measured concentrations may be accounted for by slight inaccuracies in sampling methodology and probably by adsorption into container walls. The lack of additional loss caused by aeration indicates that volatilization was an insignificant loss route. The assumption that actual exposure levels were within 10 % of nominal ones is supported by the constancy of concentration with time.

Concentration of butyltins in paint leachates : For both paints, the amount of tributyltins measured in the water after 24 or 48 hrs increased with an increase in painted surface area. The data shown in Table 2 indicate that the different paint formulations leach significantly different quantities of butyltin within the period tested. Although the final tributyltin concentration ratio of the two paints showed no consistent value as the area of the painted surface increased, at least 3 times as much tributyltin leached from Interracing (R) than from Micron 25 (R). Leach rates from larger plates may have been inhibited as tributyltin concentrations approached the solubility limit assumed to be below 5 mg/L^{-1}.

Toxicity of TBTO or TBTF to Orchestia traskiana : Both TBTO and TBTF showed similar toxicity, with acute toxicity occurring at concentrations of 10 $\mu g/L^{-1}$ and above. In this experiment, 80 % of the control amphipods survived 9 day exposure to acetone (Fig. 1a). Amphipods exposed to 0.5 $\mu g/L^{-1}$ TBTO showed a slightly higher survival (87 %). Those in TBTO concentrations between 1 and 6 $\mu g/L^{-1}$ exhibited a decline in viability, which was not consistently dose-dependent when compared to controls. Even in 6 $\mu g/L^{-1}$, survival was 93 % at the end of 9 days. The two highest concentrations, 10 and 15 $\mu g/L^{-1}$, were significantly toxic. This became apparent only after the fifth day in 10 $\mu g/L^{-1}$, and after the fourth day in 15 $\mu g/L^{-1}$. Final survival values were 20 % and 7 % in 10 and 15 $\mu g/L^{-1}$ TBTO, respectively. Concomitant with the toxicity in these latter two groups was a loss of orientation and feeding behavior. Usually, limb or swimming movements were ataxic and very poorly coordinated.

Similar to the results of the TBTO bioassay, the date for amphipods exposed to TBTF cluster into two groups (Fig. 1). The first, comprised of exposure concentrations below 6 $\mu g/L^{-1}$, is above 50 % survival and does not display a dose-dependent pattern. Survival values of the 10 and 15 $\mu g/L^{-1}$ exposures were, respectively, 13 % (at the end of 9 days) and 0 % (at the end fo 8 days). These values indicate that there is no significant difference of toxicity between TBTF and TBTO to these non-target organisms. The behavioral derangements caused by TBTF exposure were similar to those described for TBTO.

Toxicity of paint leachates to Gammarus oceanicus : The toxicity of the two paint formulations shows a close correlation to the amount of tributyltin leached. No amphipods survived 5 days exposure to leachates from Interracing paint. Panels with a painted surface area of 1720 and 480 cm^2 caused 100 % mortality within 24 hrs. In tanks containing a painted surface of 48 and 5 cm^2, 100 % mortality occured in 2 and 5 days, respectively. Reference to Table 2 will show that estimated tributyltin concentrations ranged from 0.98 to .0048 mg/L^{-1} under the test conditions.

The concentration of leachate from the Micron 25(R) painted surfaces was shown to be much less than for the Interracing(R) paint, from 0.153 down to below 0.0014 mg/L. The mortality of the amphipods exposed to the leachate was also lower. During the first 24 hrs exposure, all the amphipods died in the tanks with a painted surface area of 1720 cm^2 but it required 48 hrs for complete mortality to occur in the tanks with 480 cm^2 painted surface. In the tanks containing 48 cm^2 of painted surface, 15 % of exposed amphipods survived 6 days, while those exposed to 5 cm^2 had a mean survival value of 65 %, which was just slightly lower than that for the controls, 75 %.

DISCUSSION.

The data presented in this paper show that tributyltin compounds either as single compounds or as leachates from antibiofouling paints are toxic to aquatic organisms. Concentrations of single tributyltin compounds as low as 10 $\mu g/L^{-1}$ caused differential mortality of Orchestia traskiana. Gammarus oceanicus appeared to be a bit more sensitive, with differential mortality occurring in tributyltin concentrations between 1 and 5 $\mu g/L^{-1}$. The increased sensitivity of G. oceanicus is more obvious when one remembers that final and time-averaged trialkyltin concentrations were different, with the latter being much lower, since the alkyltins were slowly appearing in the water phase during the 2 days between water changes.

Concentrations reported here are lower than ones widely reported to be toxic. In a review Zuckerman et al. (1978) reported that 50 $\mu g/L^{-1}$ was a common estimate of the LC_{50} of tributyltin compounds for aquatic organisms. However, other lower values have been reported. Ritchie et al. (1974) reported that TBTO levels as low as 1-10 ng/L significantly reduced maturation rates and egg production in snails, Biomphalaria glabrata, which had been exposed from hatching to these low levels. Lindén et al. (1979) reported a LC_{50} (96 hrs) of 3 $\mu g/L^{-1}$ for the copepod Nitocra spinipes exposed to TBTO. Survival and growth of larval lobsters, Homarus americanus, were significantly reduced in 1 $\mu g/L^{-1}$ TBTO. Exposure continued for ca. 21 days, the duration of larval development (Laughlin and French, 1980). Thus, it appears that the sensitivity of these two amphipod species resembles that recently measured for several other aquatic invertebrate species. It is probable that the actual sensitivity of most marine species to chronic exposure is considerably lower than the 50 $\mu g/L^{-1}$ generalization cited above.

The reason for the previous underestimation of toxicity occurs because these materials are slow-acting. The toxicity of TBTO and TBTF became apparent only after the first 5 days of exposure during the tests with Orchestia traskiana. The slow action of these compounds has been appreciated by industrial hygienists (Barnes and Stoner, 1959) but the knowledge was not carried over to environmental toxicology experimentation. Short-term toxicity tests seriously underestimate the toxicity and yield values which are much higher than maximum acceptable toxicant concentrations (Mahim, 1977).

The chemical form of a material in seawater in seawater can exert a profound effect on its biological behavior (Burton, 1979). The aqueous chemistry of trialkyltin compounds is influenced by pH and the concentration of other ions present (Tobias et al., 1978; Jewett, et al., 1979). In seawater which has a pH of ca. 8.0, and chloride and carbonate ions predominate under aerobic conditions, several reactions products are formed when TBTO is added. In addition to the hydroxide, also present in varying proportions are the aquo complex, the carbonate and the chloride (Guard et al., 1982). These findings suggest that with the probable exception of sulfide (which binds very strongly to trialkyltin compounds) a roughly similar proportion of tributyltin compounds forms in seawater, regardless of the anion present or molecules originally added. Thus this may explain why the anion in general exerts only a minor effect on the toxicity of the trialkyltin cation. The pH strongly affects the equilibrium mixture, at least for TBTO because the affinity for OH^- is about 10^6 greater than that for Cl^-, the most abundant anion in seawater. Thus, it should be expected that in areas such as estuaries or river mouths, where pH and ionic strengths may be less than in the open sea, distinctly different equilibrium proportions of tributyltin compounds would be formed. The possible effects on organisms due to shifts in the chemical equilibrium cannot be predicted with certainty, but may be significant.

Differential tributyltin leaching rates, a function of paint type, markedly affects the toxicity to non-target organisms. There is a direct correlation between the toxicity of the formulation and the quantity of tributyltin present in the seawater. Furthermore, there is fairly close agreement between the toxicity caused by a given quantity of single tributyltins dissolved in seawater, and that observed when a similar (measured) amount of tributyltin leaches from paints. Thus, at least with respect to biological activity, paints leach toxic tributyltin cation regardless of the anion at a rate influenced primarily by the paint type. Therefore any attempts to mitigate the biological effects would most profitably be directed toward reducing the amount of tributyltin leached commensurate with acceptable paint performance.

Since the studies presented here show that tributyltins are toxic at fairly low levels, and are stable in seawater for periods of at least days, additional studies of the environmental effects are warranted. Measurements of environmental concentrations, with particular attention to the amount present as the sulfide would be most useful. At present, our laboratory is conducting experiments to determine differences in biological

activity of the tributyltin sulfide and TBTO to determine if environmental chemical modifications will mitigate effects.

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Table 1. TBTO concentrations in seawater as measured by quantitative GLC. Nominal concentration was 50 $\mu g/L^{-1}$. Values are mean $\pm$1standard deviation.

Source.	n	Measured concentration ($\mu g/L^{-1}$)
Acetone Control	1	0.2
30 o/oo Seawater		
0 hr	3	43.86 $\pm$ 1.27
24 hrs		
unaerated	4	45.72 $\pm$ 6.02
aerated	3	45.85 $\pm$ 1.46.

Table [illegible] Concentrations of tributyltin leachates measured in terms of stirring amplitude and plexiglass panels painted with two different paints. The data are expressed as tributyltin oxide equivalents. The time point is the length of time a panel was submerged.

Paint Type	n	time	tributyltin ug/l
[illegible]			
[illegible]	1	24	.184
[illegible]	1	24	.027
[illegible]	1	48	.[illegible]
[illegible]	2	48	.[illegible]
[illegible]	1	48	.[illegible]14
[illegible]			
[illegible]	1	24	0.[illegible]
[illegible]	1	24	0.42
[illegible]	1	48	.[illegible]
[illegible]	1	48	.[illegible]
[illegible]			.[illegible]

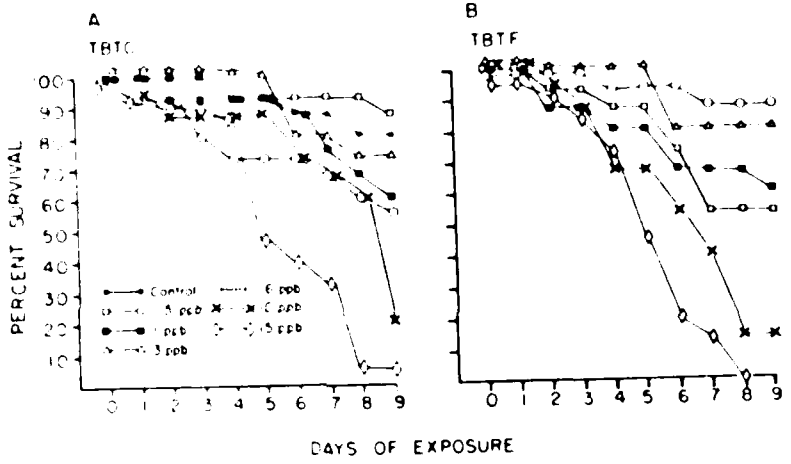
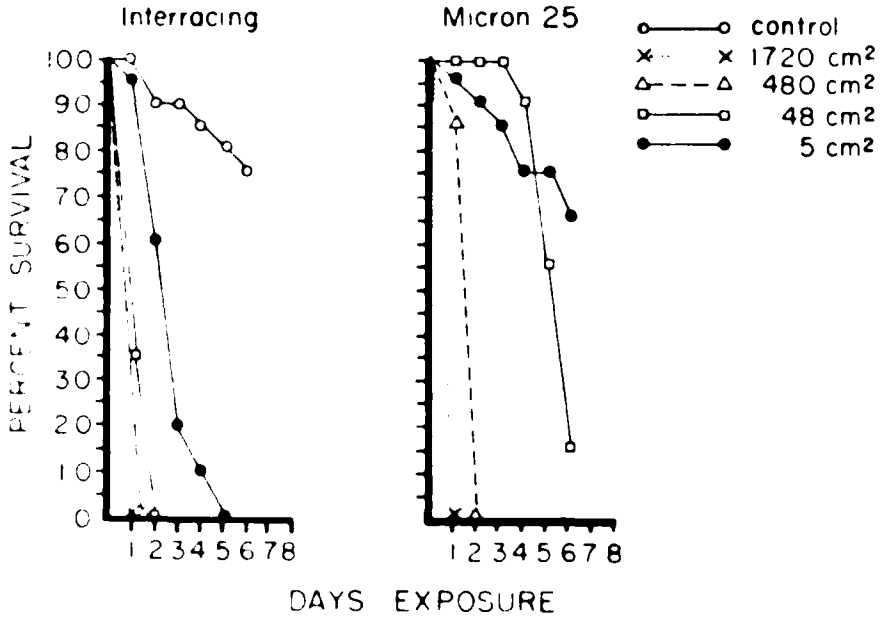


Fig. 1. Survival of adult Rotatoria trapeziana exposed to bis (tributyltin) oxide (A) or tributyltin fluoride (B).



[illegible] exposed to tributyltin [illegible] [illegible] concentrations of tributyltin [illegible] different areas are given in Table [illegible].

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