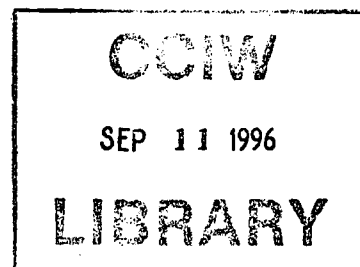
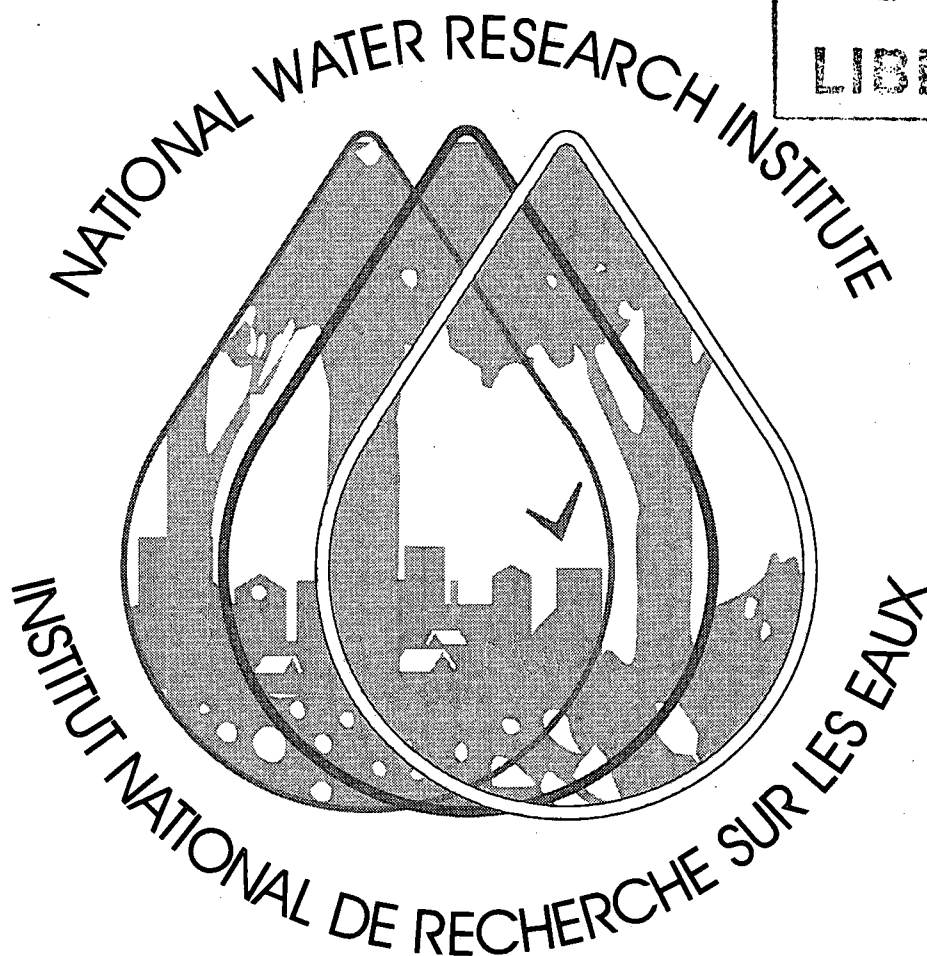


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**ORGANOTIN CONCENTRATIONS IN THE  
SURFACE MICROLAYER OF BRITISH  
COLUMBIA COASTAL WATERS IN 1994**

**J.A.J. Thompson, R.J. Maguire, Y.K. Chau,  
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COLUMBIA COASTAL WATERS IN 1994**

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## MANAGEMENT PERSPECTIVE

Tributyltin is perhaps the most toxic chemical that has ever been deliberately introduced into the aquatic environment. It is an endocrine disruptor with reproductive effects in some aquatic organisms at concentrations less than 1 ng Sn/L. It is also immunotoxic (thymus effects) to aquatic organisms and mammals and exerts effects on the thyroid gland in mammals. Through its use as an antifouling agent tributyltin has been responsible for population-level effects on whelks, dogwhelks, periwinkles, clams and oysters in Europe and elsewhere.

Because of the extremely high toxicity of tributyltin, many countries in the 1980s and 1990s regulated its antifouling uses. This article reports the results of a small survey of the marine surface microlayer in 15 locations in southwestern British Columbia for the occurrence of tributyltin and other organotin species. This study complements a study of neogastropod imposex frequency in those same locations, and a survey of organotin compounds in water and sediment across Canada, both of which were undertaken to determine the effectiveness of the 1989 Canadian regulation of antifouling uses of tributyltin.

## **SOMMAIRE À L'INTENTION DE LA DIRECTION**

Le tributylétain est peut-être le produit chimique le plus toxique à être délibérément introduit dans le milieu aquatique. Il s'agit d'un perturbateur endocrinien avec des effets sur la reproduction chez certains organismes aquatiques à des concentrations inférieures à 1 ng Sn/L. C'est aussi un immunotoxique (effets sur le thymus) pour les mammifères et les organismes aquatiques, et il agit sur la glande thyroïde des mammifères. En tant qu'agent antisalissure, le tributylétain a eu des effets sur les populations de buccins, de pourpres de l'Atlantique, de bigorneaux, de myes et d'huîtres, en Europe et ailleurs dans le monde.

À cause du caractère extrêmement toxique du tributylétain, de nombreux pays ont réglementé dans les années 1980 et 1990 son emploi comme agent antisalissure. Le présent article donne les résultats d'une petite étude de l'occurrence du tributylétain et d'autres organo-étains dans la microcouche superficielle marine, à 15 emplacements dans le sud-ouest de la Colombie-Britannique. Cette étude complète une autre étude sur la fréquence de l'imposexe chez les néogastropodes dans ces mêmes endroits, et une enquête sur les organo-étains dans l'eau et les sédiments à travers le Canada, toutes deux ayant été effectuées pour déterminer l'efficacité de la réglementation canadienne de 1989 sur les utilisations du tributylétain comme agent antisalissure.

## **ABSTRACT**

A study was conducted of the occurrence of organotin species in the surface microlayer of sea water at 15 locations in southwestern British Columbia in 1994. The only organotin species found were the extremely toxic antifouling pesticide tributyltin, as well as its degradation products dibutyltin and monobutyltin, and the dimethyltin and monomethyltin species, which may arise from natural methylation processes or the leaching of organotin-stabilized poly(vinyl chloride). Tributyltin was only found infrequently, but at concentrations that, if persistent, were above chronic and acute toxicity thresholds for sensitive organisms. The other species were found much more frequently, but their concentrations were far below chronic toxicity thresholds in sensitive organisms, based on the limited available toxicity data. This is the first report of the occurrence of dimethyltin and monomethyltin in the surface microlayer of natural waters.

## RÉSUMÉ

En 1994, on a procédé à une étude sur l'occurrence d'organo-étains dans la microcouche superficielle de l'eau de mer à 15 emplacements du sud-ouest de la Colombie-Britannique. Les seuls organo-étains détectés étaient le tributylétain, avec ses produits de dégradation, le dibutylétain et le monobutylétain, ainsi que le diméthylétain et le monométhylétain, qui peuvent se former par des processus naturels de méthylation ou par lessivage du poly(chlorure de vinyle) stabilisé par des organo-étains. Le tributylétain n'a été détecté que rarement, mais à des concentrations qui, si elles sont persistantes, se situent au-dessus des seuils de toxicité chronique et aiguë pour les organismes sensibles. Les autres espèces chimiques ont été détectées beaucoup plus souvent, mais leurs concentrations étaient très inférieures aux seuils de toxicité chronique chez les organismes sensibles, si on se fonde sur les rares données de toxicité disponibles. Il s'agit là du premier rapport sur l'occurrence de diméthylétain et de monométhylétain dans la microcouche superficielle d'eaux naturelles.

## INTRODUCTION

The surface microlayer of natural waters is often enriched in metals, lipophilic contaminants, nutrients, dissolved and particulate organic matter, and microorganisms (*e.g.*, MacIntyre, 1974; Liss, 1975; Münster *et al.*, 1996). Enrichment in metals and organic contaminants from terrestrial and atmospheric sources may be due to associations with surface-active material, adsorption to particulate material, and uptake by surface-dwelling organisms. Concentration enrichment was first associated with surface slicks. Calm areas, or slicks, are often found on the surface of natural waters. The slick is the result of localized damping of capillary waves by surface-active material, which may originate from the leaching of allochthonous matter, the decomposition of aquatic plants and animals, and the introduction of petroleum products. Surface films may contain alcohols, fatty acids, fatty acid esters, lipids, proteinaceous material, hydrocarbons and carbohydrates (Baier, 1972, 1981; Eisenreich *et al.*, 1978; Williams *et al.*, 1986). Contaminants may also be enriched at the air-water interface through the above mechanisms, but under conditions in which compaction forces are not great enough to produce an observable slick (*e.g.*, Piotrowicz *et al.*, 1972). Enrichment of contaminants at the air-water interface may have a negative impact on organisms which spend part or all of their lives at the interface. Typical inhabitants of the microlayer are bacteria, ciliates, and algae which serve as a food source for copepods and larger organisms. In addition, eggs and larvae of many fish and invertebrate species are temporary inhabitants of the surface microlayer.

Surface microlayer enrichment is also an important phenomenon in the cycling of contaminants between air and water. An enormous quantity of material can be transferred from water to the atmosphere as jet and film drops ejected from air bubbles bursting at the surface of water (MacIntyre, 1974; Liss, 1975; Blanchard and Syzdek, 1975; Piotrowicz *et al.*, 1979). In addition, there is evidence that volatilization of lipophilic pesticides from the surface microlayer of natural water after aerial spraying is the main route of dissipation (Maguire and Hale, 1980; Maguire *et al.*, 1988; Maguire, 1991).

The surface film is usually sampled as part of the surface microlayer, whose thickness is operationally defined by the type of collector used (Garrett, 1965; Harvey and Burzell, 1972; Hatcher and Parker, 1974; Larsson *et al.*, 1974; Baier, 1970; Carlson, 1982). Estimates for the thickness of up to 300  $\mu\text{m}$  are common. The enrichment factor (EF) is defined as the ratio of the concentration of a chemical in the surface microlayer to its concentration in subsurface water. Enrichment factors in surface microlayers and destabilized foams of up to  $5 \times 10^4$  have been observed for a wide variety of contaminants (Eisenreich *et al.*, 1978; Piotrowicz *et al.*, 1972; Larsson *et al.*, 1984; Seba and Corcoran, 1969; Duce *et al.*, 1972; Szekiolda *et al.*, 1972; Bidleman and Olney, 1974; Elzerman *et al.*, 1979; Elzerman and Armstrong, 1979; Lion and Leckie, 1982; Eisenreich, 1982; Rice *et al.*, 1982; Meyers and Kawka, 1982; Lion *et al.*, 1982; Barnes *et al.*, 1982; Hardy *et al.*, 1985a,b; Maguire *et al.*, 1982, 1983; Platford *et al.*, 1985; Maguire and Tkacz, 1987). Contaminants in surface microlayers are probably concentrated in films only a few molecular layers thick. Hence the actual enrichment factors for films may be up to  $3 \times 10^4$  times larger than those observed for the surface microlayers, resulting in extremely high contaminant concentrations at the air-water interface. In a few cases it has been shown that microlayer enrichments were so high that the amount of a particular chemical in the surface microlayer was either a significant fraction of, or greater than, that in the whole depth of subsurface water (Pellenbarg and Church, 1979; Maguire *et al.*, 1982; Platford *et al.*, 1985; Maguire and Tkacz, 1987). There is very little information in the literature on the temporal stability of high concentrations of toxic chemicals in surface microlayers. Pellenbarg and Church (1979) have shown that microlayer enrichments can be significant over long periods. They observed that the microlayer in a Delaware salt marsh carried an average of 10% of the copper, 19% of the zinc and 23% of the iron in terms of the total metal flux, including the dissolved and particulate components. In contrast, Maguire and Tkacz (1988) showed that over a one year period the surface microlayer of the Niagara River carried insignificant amounts of chlorinated hydrocarbons relative to subsurface water, despite occasional very high surface microlayer enrichment factors.

The purpose of this study was to determine concentrations of organotin species in the surface microlayer of water at selected coastal locations in southwestern British Columbia. This study



complemented a study of neogastropod imposex frequency in those same locations (Tester *et al.*, 1996), which was undertaken to determine the extent of recovery from imposex after the 1989 Canadian regulation of antifouling uses of the extremely toxic pesticide tributyltin (Agriculture Canada, 1989). In addition to tributyltin, the occurrence of 13 other organotin species was also determined. These species included degradation products of tributyltin, other organotin pesticides, organotin species used industrially as stabilizers of poly(vinyl chloride), and species that can be produced through natural methylation processes. These 13 additional species are monomethyltin, dimethyltin, trimethyltin, tripropyltin, monobutyltin, dibutyltin, monooctyltin, dioctyltin, monophenyltin, diphenyltin, triphenyltin, dicyclohexyltin, and tricyclohexyltin. All these compounds in aqueous media are present as cations or in complex forms, depending upon the nature and concentration of other solutes. For brevity, they are referred to in this report as though they exist only in cationic form.

## EXPERIMENTAL METHODS

### Materials

The carrier gas for the gas chromatograph - atomic emission spectrometry (GC-AED) system used in the organotin analyses (see Table 1) was high purity helium, 99.999%, and the reagent gases were oxygen (99.999%) and hydrogen (99.999%), all from Canox Ltd. (Mississauga, Ontario). Monobutyltin trichloride, dibutyltin dichloride, tributyltin chloride, tripropyltin chloride and dicyclohexyltin dichloride were obtained from Alfa Products (Ward Hill, MA, U.S.A.). Monooctyltin trichloride, dioctyltin dichloride, monomethyltin trichloride, dimethyltin dichloride, trimethyltin chloride, triphenyltin chloride, tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one) and ethylmagnesium bromide (2.0 M in tetrahydrofuran) were obtained from Aldrich Ltd. (Milwaukee, WI, U.S.A.). Diphenyltin dichloride and monophenyltin trichloride were obtained from Gelest, Inc. (Tullytown, PA, U.S.A.). All solvents, acids and common laboratory reagents were of analytical grade. Distilled water, further purified by passage through a Milli-Q system (Millipore, Bedford, MA, U.S.A.), was used throughout. Stock solutions of organotin compounds (1000 mg/mL as Sn) were

prepared in methanol or in toluene. The purity of organotin compounds was assessed, after oxidation, by inductively-coupled plasma emission spectrometry, and compared to a standard made from high purity tin metal (99.9%) dissolved in hydrochloric acid. All glassware was solvent-rinsed before use. The sodium sulfate was fired at 450 °C before use, and aluminum foil used to line the tops of the sediment jars was fired at 100 °C before use.

### Sampling

Surface microlayer samples were collected in July and August 1994 at 15 coastal locations around Vancouver Island, the Strait of Georgia, and around Vancouver. The locations are listed in Table 2, and shown in Tester *et al.* (1996). The samples were collected using a section of glass (45 cm x 70 cm x 5 mm) similar to the method reported by Harvey and Burzell (1972). Adhering water was removed using a rubber edge and collected by Teflon funnel into precleaned glass bottles. One L of surface microlayer could be collected with this sampler in 5-10 minutes, and the surface microlayer thickness was estimated to be 60 µm. The surface microlayer samples (1 L) were acidified to pH 1 with 2 mL of 70% Ultrex nitric acid, and kept at 4 °C, protected from light, before shipment to the laboratory in Burlington, Ontario, where they were kept in the dark at 4 °C before extraction. Subsurface water samples were not collected in this study.

### Analysis

Water samples (1 L volume) previously acidified to pH 1 were extracted in separatory funnels with 50 mL of hexane after the addition of 400 mL of a phosphate buffer solution (17.77 g  $K_2HPO_4$  and 9.41 g citric acid in 1 L of water) to bring the pH to 5 (measured with pH paper), 2 mL of sodium diethyldithiocarbamate (NaDDC) solution (2.5 g NaDDC in 10 mL of water) and 50 µL of triphenyltin chloride solution (1 mg Sn/mL) as internal standard. After separation of the hexane phase, the water was again shaken with 25 mL of hexane. The two hexane fractions were combined and dried by passage through anhydrous sodium sulfate, evaporated under reduced pressure in a rotary evaporator at 30 °C to 2-3 mL, transferred to a test tube, and finally evaporated to 1 mL by

a stream of nitrogen. Ethylmagnesium bromide solution (0.3 mL, 2.0 M) was added and the mixture was allowed to stand for about 10 min. The excess ethylmagnesium bromide was destroyed by shaking for 1 min. with 2 mL of 1 M H<sub>2</sub>SO<sub>4</sub>. The organic phase (final volume 2 mL) was transferred to an autosampler vial. Spike recovery experiments showed that the recoveries of all species spiked into water at 1 µg Sn/L each were in the range 87-107%.

Sample extracts after derivatization were analyzed for organotin species with a GC-AED system from Hewlett-Packard (HP - Avondale, PA, U.S.A.), consisting of a gas chromatograph (HP 5890, Series II) equipped with a split/splitless injection port, a microwave plasma atomic emission detector (HP 5921A), and an autosampler (HP 7673A). The system was factory-interfaced. The operation was computer-controlled using the HP 35920A ChemStation software. Operating parameters for the GC-AED system are listed in Table 1. Standard mixtures of the ethyl derivatives of all 15 organotin species (including the triphenyltin internal standard) in the expected concentration ranges were prepared and used to calibrate detector responses. Quantitation was by peak area response vs. external standards. All concentrations of organotin species in this article are expressed as Sn. Chromatographic "windows" were typically 0.04 min. at most at 15 min. retention time. The presence of an organotin species was taken to be tentatively confirmed if (i) it occurred within the appropriate chromatographic window, and (ii) the concentrations were above the limit of quantitation (LOQ) for the particular sample, *i.e.*, approximately three times the noise level. LOQ and LOD (limit of detection) values for each organotin species in water were 2.5 ng Sn/L and 0.5 ng Sn/L, respectively, for a 1 L sample. LOQ values for each species in water in this study are four-fold lower than LOQ values in our surveys in the 1980s, in which analyses were by packed column gas chromatography with either a flame photometric detector (FPD) (*e.g.*, Maguire, 1984) or an atomic absorption spectrophotometric detector (AAS) (*e.g.*, Maguire *et al.*, 1986).

Reagent blanks were analyzed according to the methods given above. No contamination was evident. Concentrations of organotin species reported in this article were not corrected for recovery.

## RESULTS AND DISCUSSION

The only organotin species found in the surface microlayer samples were tributyltin, dibutyltin, monobutyltin, dimethyltin and monomethyltin. Their concentrations are shown in Table 2. Tributyltin, dibutyltin and monobutyltin have been found in surface microlayers before in Canada and elsewhere (see Table 3). Their presence in these water samples is likely due to the antifouling use of tributyltin (Chau *et al.*, 1996). To our knowledge, this is the first report of dimethyltin and monomethyltin in surface microlayers. There are at least two reasons for the finding of methyltin compounds in aquatic environments, biological methylation of tin and methyltin species, and/or leaching from poly(vinyl chloride) pipe that has been stabilized by dimethyltin and monomethyltin compounds (Environment Canada and Health and Welfare Canada, 1993). In what follows, the concentrations of each organotin species in the surface microlayer samples are compared to concentrations determined in other studies, and then attempts are made to assess their toxicological significance on the assumption that such concentrations may reflect the usual situation. It should be noted that the thickness of the surface microlayer is operationally defined by the type of collector used, and that concentrations of analytes in surface microlayers sampled by different techniques may vary greatly. It is also acknowledged that due to limitations in the toxicity data base, the only available organotin toxicity data may not be the most appropriate - *i.e.*, there are few data on organotin toxicity to organisms that spend part or all of their lives at the air-water interface.

### Tributyltin

Tributyltin was only found in 2 of the 15 surface microlayer samples, at concentrations of 3.1 ng Sn/L and 2.6 ng Sn/L. These are in the same range found for subsurface sea water in samples collected in 1994 (not from the same locations) (Chau *et al.*, 1996). In that survey, tributyltin was found in 25 of 34 subsurface sea water samples, and the concentration range and mean concentration (where detected) were n.d.-27.2 ng Sn/L and 7.7 ng Sn/L, respectively. Tributyltin concentrations found in the surface microlayer in this survey were

far less than those found in surface microlayers in earlier studies conducted before, or just after, regulations of antifouling uses of tributyltin in Canada, the U.K. and the U.S.A. (see Table 3).

For tributyltin, the most sensitive marine organism in acute toxicity tests appears to be the macroalga *Phyllospora comosa* (Burridge *et al.*, 1995), for which the no-observed-effect-concentration (NOEC) and lowest-observed-effect-concentration (LOEC) values for mortality in a 96 hr. exposure period were  $< 0.37$  ng Sn/L (which is below the LOD of 0.5 ng Sn/L for a 1 L sample in this survey). These values are exceeded by the tributyltin concentration in the surface microlayer in both locations at which it was found. Consequently, acute effects due to tributyltin may be expected in those locations.

As far as chronic toxicity is concerned, the Canadian Water Quality Guideline for tributyltin for the protection of marine biota is 0.41 ng Sn/L (Moore *et al.*, 1992). It was derived by applying a safety factor of 10 to the lowest reported chronic effect (4.1 ng Sn/L for the inability of oyster (*Crassostrea gigas*) spat to compensate for hypoxia (Lawler and Aldrich, 1987); also, growth inhibition in the clam *Mercenaria mercenaria* (Laughlin *et al.*, 1988)). In addition, the induction of imposex (imposition of male sexual characteristics on females) in dogwhelks, *Nucella lapillus* (L.) occurs at about 0.5 ng Sn/L, and sterilization of females is initiated at about 3-5 ng Sn/L (Bryan *et al.*, 1988; Gibbs *et al.*, 1988). The guideline concentration of 0.41 ng Sn/L was also exceeded by the tributyltin concentrations in the two surface microlayer samples in question. Consequently, chronic toxic effects due to tributyltin may be expected in those locations.

### **Dibutyltin**

Dibutyltin was found in 8 of 15 surface microlayer samples, in the concentration range n.d.-20.1 ng Sn/L, and with a mean concentration (where detected) of 6.1 ng Sn/L. These are in the same general range found for subsurface sea water in samples collected in 1994 (not from the same locations) (Chau *et al.*, 1996). In that survey, dibutyltin was found in 8 of 34 subsurface sea water samples, and the concentration range and mean concentration (where detected) were n.d.-6.4 ng Sn/L

and 3.8 ng Sn/L, respectively. Dibutyltin concentrations found in the surface microlayer in this survey were generally far less than those found in surface microlayers in earlier studies conducted before, or just after, regulations of antifouling uses of tributyltin in Canada, the U.K. and the U.S.A. (see Table 3).

For dibutyltin, the most sensitive marine organism tested in acute toxicity tests appears to be the diatom, *Skeletonema costatum*. The 72-h  $EC_{50}$  for growth for this diatom was 10,000 ng Sn/L (Walsh *et al.*, 1985). The highest concentration of dibutyltin in surface microlayers in this study was 20.1 ng Sn/L, which was a factor of about 500 lower. Therefore, based on the available toxicity data, dibutyltin concentrations in these surface microlayer samples were far below the acute toxicity threshold in those locations in which it was found.

There are few data on the chronic toxicity of dibutyltin to marine organisms. The most sensitive organism identified was *Mytilus edulis* larvae, for which NOEC and LOEC values of 1.0 and 10.2  $\mu$ g Sn/L, respectively, were determined for shell growth and mortality over a 25-day period (Lapota *et al.*, 1993). Even with the application of a factor of 10 to the LOEC value (*e.g.*, Moore *et al.*, 1992), a dibutyltin concentration of 1  $\mu$ g Sn/L is a factor of about 50 higher than the highest dibutyltin concentration found in the surface microlayer in this survey. Therefore, based on the limited available toxicity data, dibutyltin concentrations in sea water were far below the chronic toxicity threshold in those locations in which it was found.

### Monobutyltin

Monobutyltin was found in 14 of the 15 surface microlayer samples, in the concentration range n.d.-55.5 ng Sn/L, and with a mean concentration (where detected) of 11.1 ng Sn/L. These findings are in striking contrast to the results of a survey of subsurface sea water in 1994 (not in the same locations), in which monobutyltin was not found in any of 34 samples (Chau *et al.*, 1996).

For monobutyltin, the only acute toxicity data found for marine organisms were for yeasts, and the most sensitive marine yeasts are *Aureobasidium pullulans*, *Candida albicans*, and *Sporobolomyces alborubescens*, with 48-h  $IC_{50}$  values for growth of 2,100,000 ng Sn/L (Cooney *et al.*, 1989). Such a value is about 38,000 times higher than the highest concentration of monobutyltin found in surface microlayers in this study.

No data were found for the chronic toxicity of monobutyltin in sea water to marine organisms, so the chronic toxicity of monobutyltin residues in surface microlayers can not be assessed.

### Dimethyltin

Dimethyltin was found in 12 of 15 surface microlayer samples, in the concentration range n.d.-233.0 ng Sn/L, and with a mean concentration (where detected) of 52.8 ng Sn/L. The frequency of occurrence, range and mean concentration are all much greater than those in a survey of subsurface sea water in 1994 (not in the same locations), in which dimethyltin was only found in 2 of 34 samples, with a mean concentration (where detected) of 4.7 ng Sn/L (Chau *et al.*, 1996).

As far as the acute toxicity of dimethyltin is concerned, Cooney *et al.* (1989) found a 48-hr.  $EC_{50}$  value for growth of the yeast *Aureobasidium pullulans* of 1,900,000 ng Sn/L, and Cooney (1995) found a minimum inhibitory concentration of 1,200,000 ng Sn/L for bacterial isolates. The lower of these two values is about 5,000 times higher than the highest dimethyltin concentration found in surface microlayer samples in this survey (233.0 ng Sn/L). Therefore, based on the limited available toxicity data, dimethyltin concentrations in surface microlayers were far below the acute toxicity threshold in those locations in which it was found. No data were found on the chronic toxicity of dimethyltin to marine organisms.

### Monomethyltin

Monomethyltin was found in 10 of 15 surface microlayer samples, in the concentration range n.d.-22.8 ng Sn/L, and with a mean concentration (where detected) of 11.0 ng Sn/L. These results are in striking contrast to those of a survey of subsurface sea water in 1994 (not in the same locations), in which monomethyltin was not found in any of 34 samples (Chau *et al.*, 1996).

The most sensitive organism identified was the diatom *Skeletonema costatum*, for which the 72-hr. EC<sub>50</sub> for growth was determined to be 40,000 ng Sn/L (Walsh *et al.*, 1985). This concentration is about 1750 times greater than the highest concentration of monomethyltin found in surface microlayers in this study. Therefore, based on the limited available toxicity data, monomethyltin concentrations in surface microlayers were far below the acute toxicity threshold in those locations in which it was found.

In summary, the only organotin species found in 15 marine surface microlayer samples collected in southwestern British Columbia in 1994 were tributyltin, dibutyltin, monobutyltin, dimethyltin and monomethyltin. Tributyltin was only found infrequently, but at concentrations that, if persistent, were above chronic and acute toxicity thresholds for sensitive organisms. The other species, dibutyltin, monobutyltin, dimethyltin and monomethyltin, were found much more frequently, but their concentrations were far below chronic toxicity thresholds in sensitive organisms, based on the limited available toxicity data.



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Table 1. Operating conditions for GC-AED.

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GC parameters

injection port	splitless
injection port temperature	250 °C
injection volume	1 $\mu$ L
column	SPB-1, 30 m x 0.53 mm i.d., film thickness 1.5 $\mu$ m
column head pressure	He, 100 kPa (14.5 p.s.i.)
temperature program	60 °C for 2 min., then 20 °C/min to 250 °C, with 3.5 min. final hold

AED parameters

transfer line	SPB-1 (see above - 0.5 m length)
transfer line temperature	270 °C
cavity temperature	270 °C
solvent vent time	1.2 min.
spectrometer purge gas	N <sub>2</sub> at 2 L/min.
makeup gas	He at 240 mL/min.
Sn wavelength	271 nm
H <sub>2</sub> pressure	414 kPa (60 p.s.i.)
O <sub>2</sub> pressure	138 kPa (20 p.s.i.)

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Table 2. Concentrations (ng Sn/L) of butyltin and methyltin species in the surface microlayer of sea water around Vancouver Island, British Columbia in 1994.\*

No.	Location	TBT	DBT	MBT	DMT	MMT
1	Lighthouse Park (Horseshoe Bay)	d		d	12.0	
2	Chesterman Beach (Tofino)	d		3.2	10.4	10.4
3	Wickanninish Beach (Tofino)	d	4.9	15.1	25.9	7.8
4	Pachena Beach (Bamfield)	d	4.4	9.0	29.6	14.2
5	Eagle Harbour Yacht Club (Horseshoe Bay)	d	3.2	4.1	6.0	3.0
6	Big Beach (Ucluelet)			3.0	20.7	6.3
7	Whytecliff Park (Horseshoe Bay)	d	3.2	4.0	9.1	
8	Clover Point (1)	2.6		11.4		
9	Clover Point (2)			2.9		
10	Wizard Islet (Bamfield)		3.5	5.5	14.5	6.4
11	10 Mile Point (Victoria)			3.8		
12	Dogfish Bay, Quadra Island	3.1	20.1	55.5	17.5	10.7
13	Bold Point, Quadra Island	d	5.1	21.3	40.4	12.7
14	Campbell River		4.1	11.3	214.6	22.2
15	Granite Bay, Quadra Island			5.8	233.0	15.8
Frequency of occurrence		2/15 (13%)	8/15 (53%)	14/15 (93%)	12/15 (80%)	10/15 (67%)
Range of values		n.d.-3.1	n.d.-20.1	n.d.-55.5	n.d.-233.0	n.d.-3.0-22.8
Mean where detected		2.9±0.3	6.1±5.7	11.1±13.9	52.8±80.6	11.0±5.6
Median detected value		2.6	4.1	5.5	17.5	10.4

\*TBT - tributyltin, DBT - dibutyltin, MBT - monobutyltin, DMT - dimethyltin, MMT - monomethyltin. Samples were collected in July and August of 1994. Blanks mean below limit of detection (LOD) (0.5 ng Sn/L); "d" means above LOD but below limit of quantitation (LOQ) (2.5 ng Sn/L); "n.d." means not detected. Locations are shown in Tester *et al.* (1996).



Table 3. Concentrations of butyltin species found in the surface microlayer in other studies\*

Water	Location	Concentration, ng Sn/L						Reference
		TBT	DBT	MBT	TBT+DBT	Sampler	Thickness, $\mu\text{m}$	
fresh water	Ontario lakes and rivers	n.d.-24,900	n.d.-1,328,000	n.d.		glass plate	75	Maguire <i>et al.</i> (1982)
fresh water	St. Clair River, Ontario	n.d.-33	n.d.-5	n.d.		rotating drum	60	Maguire <i>et al.</i> (1985)
fresh water	Ontario lakes and rivers	n.d.-473,000	n.d.-365,000	n.d.-66,800		glass plate	60	Maguire and Tkacz (1987)
sea water	U.K.				n.d.-3620	screen	280-300	Cleary and Stebbing (1987a)
sea water	U.K.				n.d.-1069	screen	280-300	Cleary and Stebbing (1987b)
estuarine water	Chesapeake Bay	21-2454	4-1032	n.d.-696		glass plate	60	Mathias <i>et al.</i> (1988)
sea water	British Columbia	n.d.-35	28-116	n.d.		glass plate	60	Cullen <i>et al.</i> (1990)
sea water	U.K.	n.d.- > 300			n.d.-800	screen	280-300	Cleary (1991)

\* TBT - tributyltin, DBT - dibutyltin, MBT - monobutyltin. In some studies, a non-specific method was used that only measured the concentration of TBT+DBT, not the concentrations of the individual species; "n.d." means not detected.

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