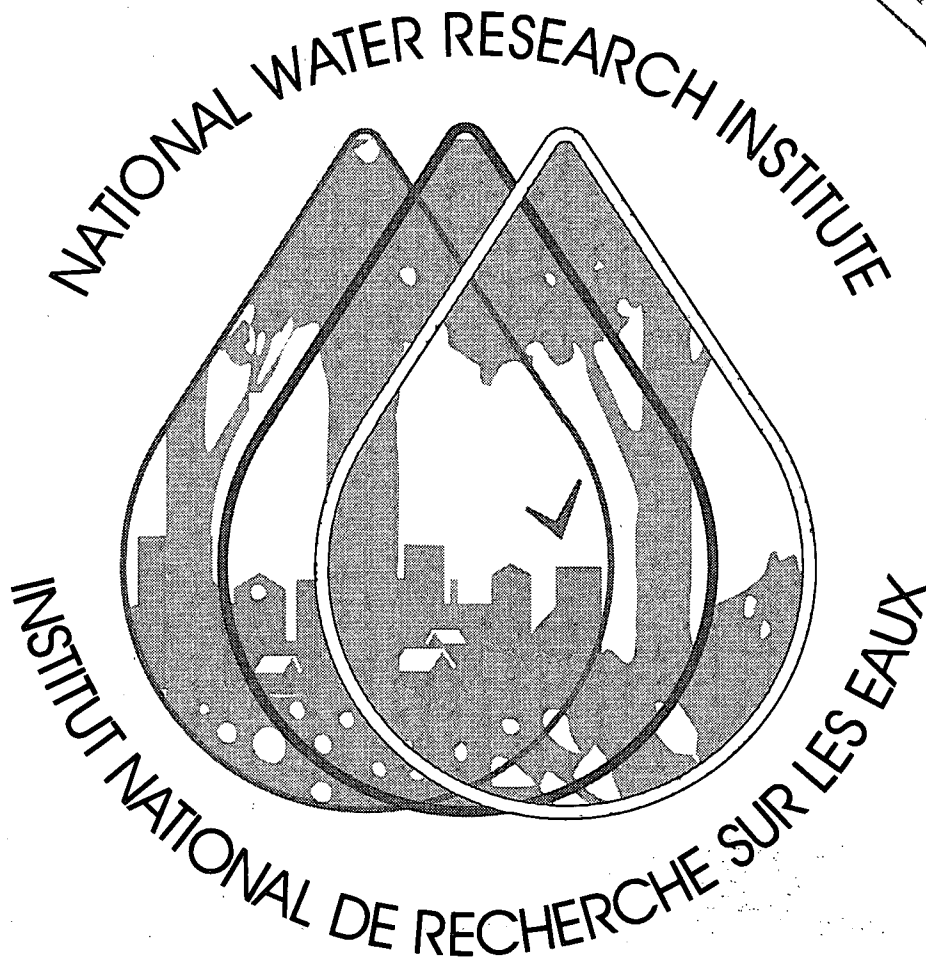
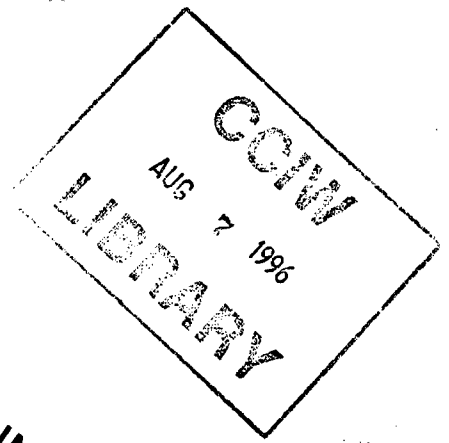


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**OCCURRENCE OF ORGANOTIN
COMPOUNDS IN THE CANADIAN
ENVIRONMENT FIVE YEARS AFTER THE
REGULATION OF ANTIFOULING USES OF
TRIBUTYL TIN IN 1989**

**Y.K. Chau, R.J. Maguire, M. Brown,
F. Yang and S.P. Batchelor**

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**OCCURRENCE OF ORGANOTIN COMPOUNDS IN THE CANADIAN
ENVIRONMENT FIVE YEARS AFTER THE REGULATION OF
ANTIFOULING USES OF TRIBUTYL TIN**

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MANAGEMENT PERSPECTIVE

Tributyltin (TBT) 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 TBT 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 TBT, many countries in the 1980s and 1990s regulated the antifouling uses of TBT. This article reports the results of a survey that was conducted of water and sediment from across Canada in 1993-1994 to assess the effectiveness of the 1989 regulation of antifouling uses of tributyltin (TBT) under the Pest Control Products Act. The main conclusion is that the 1989 regulation has only been partially effective. It has had some effect in the reduction of TBT concentrations in fresh water, but not in sea water. It has had less effect in the reduction of TBT concentrations in sediment, probably because of the longer persistence of TBT in sediment than in water. In some areas there may be potential for recycling TBT from contaminated sediments back into the water column. In addition, it appears that large harbours that handle ships legally painted with TBT-containing antifouling paints will continue to experience ecotoxicologically significant TBT contamination. Further work will be carried out to assess levels of TBT in aquatic organisms, and effects on fresh water organisms. The potential for designating TBT as a Track 1 substance under the Toxic Substance Management Policy will be assessed in the future.

The results of this survey for mono- and dimethyltin, butyltin and octyltin species in water also confirm the conclusion of the Canadian Environmental Protection Act assessment of non-pesticidal organotin compounds, which was based on data collected in the 1980s, that such species are not toxic as defined under the Act.

SOMMAIRE À L'INTENTION DE LA DIRECTION

Le tributylétain (TBE) est peut-être la substance chimique la plus toxique à avoir été introduite délibérément dans le milieu aquatique. C'est un agent perturbateur des fonctions endocriniennes qui a des effets sur la reproduction de certains organismes aquatiques à des concentrations inférieures à 1 ng Sn/L. Il est également immunotoxique (effets sur le thymus) pour des organismes et mammifères aquatiques et il agit sur la glande thyroïde des mammifères. Son utilisation comme agent antisalissure est responsable d'effets sur les populations de buccins, de pourpres de l'Atlantique, de bigorneaux, de bivalves fouisseurs et d'huîtres en Europe et ailleurs.

Comme le TBE est extrêmement toxique, de nombreux pays ont réglementé son utilisation comme agent antisalissure dans les années 1980 et 1990. Le présent article présente les résultats d'une étude qui a été effectuée sur les eaux et les sédiments au Canada en 1993-1994. Cette étude avait pour objectif d'évaluer l'efficacité de la réglementation de 1989 sur l'utilisation du TBE comme agent antisalissure aux termes de la Loi sur les produits antiparasitaires. La principale conclusion est que la réglementation de 1989 n'a été que partiellement efficace. Elle a eu certains effets sur la réduction des concentrations de TBE dans l'eau douce, mais non dans l'eau de mer. Elle a eu moins d'effets sur la réduction des concentrations de TBE dans les sédiments, probablement à cause de la plus grande persistance du TBE dans les sédiments que dans l'eau. À certains endroits, il pourrait être possible de recycler le TBE présent dans les sédiments contaminés et de remettre les sédiments dans la colonne d'eau. En outre, il semble que les grands ports où évoluent des bateaux légalement peints avec des peintures antisalissures renfermant du TBE continueront de connaître une contamination par le TBE ayant des effets écotoxicologiques significatifs. D'autres travaux seront effectués pour évaluer les concentrations de TBE chez les organismes aquatiques et leurs effets sur les organismes d'eau douce. On examinera plus tard s'il est possible de classer le TBE comme substance de voie 1 aux termes de la Politique de gestion des substances toxiques.

Les résultats de cette étude qui avaient trait au mono- et au diméthylétain, au butylétain et à l'octylétain dans l'eau confirment la conclusion obtenue à la suite de l'évaluation des composés organostanniques non pesticides aux termes de la Loi canadienne sur la protection de l'environnement, fondée sur des données recueillies dans les années 1980, soit que ces espèces ne sont pas toxiques au sens de la Loi.

ABSTRACT

A survey was conducted of water and sediment from across Canada in 1993-1994 to assess the effectiveness of the 1989 regulation of antifouling uses of tributyltin (TBT) under the Canadian Pest Control Products Act. The survey was also designed to assess concentrations of 13 other organotin species in water and sediment, and in sewage treatment plant influents, effluents and sludges. The main conclusion is that the 1989 regulation has only been partially effective. It has had some effect in the reduction of TBT concentrations in fresh water, but not in sea water. It has had less effect in the reduction of TBT concentrations in sediment, probably because of the longer persistence of TBT in sediment than in water. In many locations the TBT concentration was high enough to cause acute and chronic toxicity to aquatic and benthic organisms. In some areas there may be potential for recycling TBT from contaminated sediments back into the water column. In addition, it appears that large harbours that handle ships legally painted with TBT-containing antifouling paints will continue to experience ecotoxicologically significant TBT contamination. Other organotin species found appear to pose no acute or chronic hazards to fresh water or marine organisms, but nothing is known of their hazards to benthic organisms. The presence of monooctyltin and dioctyltin in sediments is reported for the first time, and tripropyltin is quantified in sediments for the first time.

Keywords: Butyltin Compounds; Organotin Compounds; Water; Sediment; Sewage; Sludge; Canada

RÉSUMÉ

On a effectué une étude sur les eaux et les sédiments au Canada en 1993-1994, qui avait pour objectif d'évaluer l'efficacité de la réglementation de 1989 sur l'utilisation du tributylétain (TBE) comme agent antisalissure aux termes de la Loi sur les produits antiparasitaires. L'étude avait également pour but de déterminer les concentrations de 13 autres espèces organostanniques dans l'eau et les sédiments, ainsi que dans les influents, les effluents et les boues des usines de traitement des eaux usées. La principale conclusion est que la réglementation de 1989 n'a été que partiellement efficace. Elle a eu certains effets sur la réduction des concentrations de TBE dans l'eau douce, mais non dans l'eau de mer. Elle a eu moins d'effets sur la réduction des concentrations de TBE dans les sédiments, probablement à cause de la plus grande persistance du TBE dans les sédiments que dans l'eau. À de nombreux endroits, les concentrations de TBE étaient suffisantes pour avoir des effets toxiques aigus et chroniques sur les organismes aquatiques et benthiques. À certains endroits, il pourrait être possible de recycler le TBE présent dans les sédiments contaminés et de remettre les sédiments dans la colonne d'eau. En outre, il semble que les grands ports où évoluent des bateaux légalement peints avec des peintures antisalissures renfermant du TBE continueront de connaître une contamination par le TBE ayant des effets écotoxicologiques significatifs. Les autres espèces organostanniques mesurées ne semblent pas présenter de dangers à court et à long terme pour les organismes dulçaquicoles ou marins, mais on n'a pas déterminé les dangers pour les organismes benthiques. La présence de mono-octylétain et de dioctylétain dans les sédiments est signalée pour la première fois, et c'était également la première fois qu'on mesurait la concentration de tripropylétain dans les sédiments.

Mots clés : butylétain; composés organostanniques; eau; sédiments; eaux usées; boues; Canada

INTRODUCTION

Tributyltin (TBT) is perhaps the most toxic chemical that has ever been deliberately introduced into the aquatic environment. Although it has been used as a molluscicide in the control of Schistosomiasis in Africa, and as a general lumber preservative, it is the antifouling use of TBT that has caused the greatest environmental concern (*e.g.*, Maguire, 1987; Fent, 1996; de Mora, 1996). Antifouling uses of TBT began in the 1960s and 1970s. France was the first country to restrict the use of TBT in antifouling paints. French authorities had observed a decrease in growth rates of oysters in some Atlantic coastal areas as early as 1975. Abnormal spatfall, decrease in survival rates and shell malformations had also been observed since about 1974. By the early 1980s effects on oysters in Arcachon Bay in France were linked to TBT, and in 1982 France banned the use of TBT-containing antifouling paints on vessels shorter than 25 m (Alzieu, 1991). Many other countries have adopted similar regulations, *e.g.*, the United Kingdom in 1987 (Dowson *et al.*, 1994), the U.S.A. in 1988 (Huggett *et al.*, 1992), Australia (Batley and Scammell, 1991) and Canada in 1989 (Agriculture Canada, 1989), the Netherlands (Ritsema, 1994), Switzerland (Becker-van Slooten and Tarradellas, 1995) and Japan (Yonezawa *et al.*, 1993) in 1990, Denmark in 1991 (Kure and Depledge, 1994), and Hong Kong in 1992 (Ko *et al.*, 1995).

Attempts have been made in several countries to assess the effectiveness of their TBT regulations. In general it appears that the regulations have resulted in reduced TBT contamination of water and some organisms, and recovery of populations of some organisms, particularly those close to marinas. In general, such reductions have not been observed in areas frequented by large vessels that continue to be painted legally with TBT-containing antifouling paints. Reductions of TBT concentrations in water have been observed in France (Alzieu, 1991), the United Kingdom (Douglas *et al.*, 1993; Waite *et al.*, 1991; Cleary, 1991; Dowson *et al.*, 1993, 1994), Ireland (Minchin *et al.*, 1995, 1996), and Switzerland (Fent and Hunn, 1995; Becker-van Slooten and Tarradellas, 1995). However, in some of those countries, at the time of sampling, concentrations of

cause for continuing concern (e.g., Cleary, 1991; Douglas *et al.*, 1994; Fent and Hunn, 1995). In some areas of The Netherlands (Ritsema, 1994) and the United Kingdom (Dowson *et al.*, 1992) there was little or no decrease in TBT concentrations in water at the time of sampling. In addition, many researchers have noted little or no reductions in TBT concentrations in sediments several years after TBT regulations were enacted (e.g., Waite *et al.*, 1991; Dowson *et al.*, 1993, 1994; Quevauviller *et al.*, 1994; Sarradin *et al.*, 1994; Becker-van Slooten and Tarradellas, 1995; Fent and Hunn, 1995), and this has been attributed to the appreciable persistence of TBT in sediments. TBT-contaminated sediments may continue to pose a hazard to benthic organisms and to organisms in the water column, either indirectly through eating benthic organisms, or directly, after sediment resuspension.

TBT concentrations in bivalves in some locations have declined after TBT regulations in the United Kingdom (Waite *et al.*, 1991), the U.S.A. (Uhler *et al.*, 1993) and Australia (Batley *et al.*, 1992), but in other locations TBT concentrations had not declined at the time of sampling, for example in the U.S.A. (Uhler *et al.*, 1993) and in Switzerland (Becker-van Slooten and Tarradellas, 1995). As far as population-level effects are concerned, there is a substantial body of literature indicating that TBT has had a drastic effect on some organisms. For example, declines in dogwhelk (*Nucella lapillus*) populations have been attributed by many researchers to TBT (see below), and Ruiz *et al.* (1995a,b) concluded that TBT has probably reduced the recruitment into some United Kingdom clam (*Scrobicularia plana*) populations by preventing the successful development of a significant proportion of their embryos. In Europe, there is general evidence of recovery of populations of (i) oyster (*Crassostrea gigas*) (Alzieu, 1991; Waite *et al.*, 1991; Dyrinda, 1992; Minchin *et al.*, 1996), (ii) dogwhelk (*N. lapillus*) (Douglas *et al.*, 1993; Evans *et al.*, 1991, 1994, 1996; Bailey and Davies, 1991), (iii) periwinkle (*Littorina littorea*) (Matthiessen *et al.*, 1995), and (iv) flame shell (*Lima hians*) (Minchin, 1995). However, oyster deformities were still common in Arcachon Bay in France five years after the 1982 French regulation (Sarradin *et al.*, 1994), and imposex in *N. lapillus* was still widespread in west Brittany waters in 1992-1994 (Huet *et al.*, 1996). In

addition, Ten Hallers-Tjabbes *et al.* (1994) have noted imposex in whelks (*Buccinum undatum*) collected in 1991-1992 from the open North Sea in areas of heavy shipping, indicating that such problems may not be restricted to marinas, harbours and nearby areas.

In Canada there are very few data on the environmental occurrence of TBT, or the recovery of affected organisms, after the 1989 regulation of its antifouling uses. Tester *et al.* (1996) have observed recovery from imposex in some whelk species collected in 1994 on the west coast of Vancouver Island and in some locations in the Strait of Georgia, but no clear evidence of recovery near Victoria and in Vancouver Harbour. This article reports the results of a 1994-1995 survey for TBT in Canadian water and sediment to determine the effectiveness of the 1989 regulation of antifouling uses of TBT. In addition to TBT, the occurrence of 13 other organotin species was also determined in environmental samples and in sewage treatment plant influents, effluents and sludges. These species include degradation products of TBT, other organotin pesticides, organotin species used industrially as stabilizers of poly(vinyl chloride) (PVC), and species that can be produced through natural methylation processes. These 13 additional species are monomethyltin (MMT), dimethyltin (DMT), trimethyltin (TMT), tripropyltin (TPrT), monobutyltin (MBT), dibutyltin (DBT), mono-octyltin (MOT), dioctyltin (DOT), monophenyltin (MPT), diphenyltin (DPT), triphenyltin (TPT), dicyclohexyltin (D-c-HT), and tricyclohexyltin (T-c-HT). 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 article as though they exist only in cationic form.

2. MATERIALS AND METHODS

1.2.1. Reagents

The carrier gas for the gas chromatograph - atomic emission spectrometry (GC-AED) system used in the organotin analyses 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.

2.2. Sample collection

The following kinds of samples were collected in 1993-1994: (i) surface water (plus industrial effluent and landfill leachates) and sediment from 131 locations across Canada (detailed site descriptions are given in Chau *et al.*, 1996a), and (ii) influent, effluent and sludge from 10 sewage treatment plants (STP) across Canada. Surface water samples (50 cm below the surface) were collected in 4-litre amber glass bottles with Teflon-lined caps, and acidified immediately to pH 1 with hydrochloric acid that had been solvent-washed to remove organic contaminants. The water samples were shipped to our laboratory where they were kept at 4 °C before extraction. Sediment samples were collected with an Ekman grab sampler. The top 2 cm of sediment was scraped off into amber glass jars and frozen, then freeze-fried, ground and sieved to pass an 850 μm screen before extraction. STP samples were collected by treatment plant personnel, and shipped to our

laboratory in coolers without sample treatment. These samples were stored at 4 °C in the dark until extraction.

2.3. Sample extraction

The determination of organotin species in environmental samples basically follows methods established in our laboratories in the early 1980s. Since then some changes have been made to improve the methods, or simply for convenience. Brief procedures are described here for each type of sample matrix.

2.3.1. Extraction of water samples

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 μ L 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_2SO_4 . 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 μ g Sn/L each were in the range 87-107%.

2.2.3.2. Extraction of sediment and sewage sludge samples

Sediment (2 g dry weight) samples were magnetically stirred for 1 hr. after the addition of 100 μ L of a solution of triphenyltin chloride (1 mg Sn/mL) as internal standard, 20 mL of concentrated acetic acid, 20 mL of water, 8 g NaCl and 15 mL of a 0.5% solution of tropolone in toluene. An aliquot (7.5 mL) of the extract was removed and evaporated almost to dryness using a stream of nitrogen. One mL of hexane was added, and the solution was again evaporated almost to dryness. The volume of the extract was adjusted to 1 mL with hexane, and the extract was allowed to react with 0.3 mL of ethylmagnesium bromide solution (2.0 M) for 10 min. The excess of ethylmagnesium bromide was destroyed as described above. The coloured substances derived from sediment, and the excess of tropolone, were removed by a silica gel clean-up with a Pasteur pipette mini-column (15 cm x 5 mm i.d., containing approximately 1 g of silica gel). The extract was applied to the column and eluted with 5 mL of hexane. The eluate was reduced in volume to 1 mL before analysis (Chau *et al.*, 1996b). The overall recoveries of the 14 organotin compounds spiked into sediment at 1 μ g/g dry weight were satisfactory (77-134%) except for the three methyltin species (11-57%) and TPtT (42%) (Chau *et al.*, 1994).

The procedures were slightly modified for sludge samples. After the addition of 100 μ L of a solution of triphenyltin chloride (1 mg Sn/mL) as internal standard and 20 mL of concentrated acetic acid to 100 mL of sludge sample, the mixture was left inside a fume cupboard overnight for digestion and evolution of gases. After the addition of 40 g of NaCl and 20 mL of a 0.5% solution of tropolone in toluene, the mixture was magnetically stirred for 1 hr. and then transferred to a Teflon bottle for centrifugation at 3000 r.p.m. for 15 min. An aliquot (10 mL) of the extract was transferred to a test tube and evaporated almost to dryness at room temperature with a stream of nitrogen. The volume was adjusted to 1 mL with hexane for ethylation with ethylmagnesium bromide as described in the preceding section. The clean-up procedure for sludge required slight modifications in that a larger column was used. The column (15 cm x 1.5 cm i.d.), containing about 6 g of silica gel was packed from bottom to top in the following order: glass wool, 1 cm layer of anhydrous sodium sulfate, silica gel bed, and 1 cm layer of

anhydrous sodium sulfate. All 14 organotin species sought could be quantitatively eluted with 40 mL of hexane. After reduction of the volume to 1-2 mL under reduced pressure in a rotary evaporator at 30 °C, the extract was transferred to a test tube and evaporated to 1 mL in a stream of nitrogen, and stored in an autosampler vial. The overall recoveries of these compounds spiked into sediment at 1 µg/g dry weight were satisfactory (74-102%) except for the three methyltin species (9-56%) and DPT (56%) (Chau *et al.*, 1994).

2.3.3. *Extraction of sewage samples*

Sewage samples (influent and effluent, 500 mL), previously acidified to pH 1 with HCl at the time of collection, were neutralized to *ca.* pH 5-6. After addition of the triphenyltin internal standard, the samples were processed in the same manner as for water. A silica gel cleanup similar to that used for sediment extracts was usually required for the influent samples, but not always necessary for the effluent samples, which were generally clear. Spike recovery experiments were not done for the influent and effluent samples.

2.4. *Analysis*

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 and LOD values for each organotin species in sediment were 2.5 ng Sn/g dry weight and 0.5 ng Sn/g dry weight, respectively, for a 2 g sample. LOQ values for each species in water and sediment in this survey 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).

In two sample extracts the tentative identification of some organotin species (TBT, DBT, MBT, MMT and TPT) was given more weight by co-chromatography with known standards on a HP GC with a different column stationary phase and a FPD with a filter that allowed 80% light transmittance over the wavelength range 610-2200 nm filter (Corion Inc., Holliston, MA, U.S.A.). In addition, because the concentrations of the TBT, DBT, MBT, MMT and TPT were sufficiently high, their identities were confirmed by GC with selected ion monitoring mass spectrometry (GC-SIM-MSD) using a HP 5971A MSD. Operating parameters for the GC-FPD and GC-SIM-MSD system are also listed in Table 1.

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.

3. RESULTS

3.1 Butyltin species

TBT found in aquatic environments is usually the result of leaching from antifouling paints, although it has been found as a result of slimicide use in a power plant (Bacci and Gaggi, 1989). The DBT and MBT found in aquatic environments usually result from the degradation of TBT. However, because DBT and MBT compounds are common PVC stabilizers (Environment Canada and Health and Welfare Canada, 1993), in some samples such as industrial and STP effluents they may arise from the leaching of PVC.

3.1.1 In water and sediment

Table 2 shows concentrations of TBT, DBT and MBT in water and sediment at 35 sea water locations and 90 fresh water locations, and their concentrations in 2 industrial effluents and 4 landfill leachates. Most of the data in Table 2 are for 1994. Only 10 locations were sampled in 1993, and the results were similar to those for the 1994 samples.

In fresh water samples collected in 1994, TBT was found in 12 of 89 locations (13%) at concentrations ranging up to 17.8 ng Sn/L. In 9 of those 12 locations the TBT concentration exceeded the interim Canadian water quality guideline of 3.3 ng Sn/L for the protection of fresh water life (Moore *et al.*, 1992) by factors of 1.2-5. As in earlier surveys of the occurrence of TBT in Canada, TBT in the 1994 survey was primarily found in harbours and marinas with intensive shipping and boating activity. The highest TBT concentration, 17.8 ng Sn/L, was found in the Wye Heritage Marina in Midland Bay, Ontario (location 45). It should be noted that TBT concentrations observed in fresh water in this study were similar to those found in Switzerland in 1993 (Fent and Hunn, 1995). DBT was found in 5 of 89 fresh water locations (6%) in 1994 at concentrations ranging up to 9.3 ng Sn/L. It was mainly found in harbours and marinas, and its presence was

likely due to the degradation of TBT. The highest DBT concentration, 9.3 ng Sn/L, was also found in the Wye Heritage Marina in Midland Bay, Ontario (location 45). MBT was found in 6 of 89 fresh water locations (7%) in 1994 at locations ranging up to 14.9 ng Sn/L. It too was mainly found in harbours and marinas, and its presence was likely due to the degradation of DBT, which was in turn produced from the degradation of TBT. The highest MBT concentration, 14.9 ng Sn/L, was found close to a dry dock in Montréal Harbour (location 119).

In sea water samples collected in 1994, TBT was found in 25 of 34 locations (74%) at concentrations ranging up to 27.2 ng Sn/L. In all 25 locations the TBT concentration exceeded the Canadian water quality guideline of 0.41 ng Sn/L for the protection of marine life (Moore *et al.*, 1992) by factors of 7-66. As in earlier surveys of the occurrence of TBT in Canada, TBT in the 1994 survey was primarily found in harbours and marinas with intensive shipping and boating activity. The highest TBT concentration, 27.2 ng Sn/L, was found at a ship yard site in Burrard Inlet, British Columbia (location 14). DBT was found in 8 of 34 sea water locations (24%) in 1994 at concentrations ranging up to 6.4 ng Sn/L. It was mainly found in marinas and large harbours, and its presence was likely due to the degradation of TBT. The highest DBT concentration, 6.4 ng Sn/L, was found close to a yacht club in Burrard Inlet, British Columbia (location 26). MBT was not found in any of the 34 sea water samples collected in 1994.

In sediment samples from fresh water collected in 1994, TBT was found in 42 of 80 locations (53%) at concentrations ranging up to 975 ng Sn/g dry weight. As with the results for water, TBT in sediment in the 1994 survey was primarily found in harbours and marinas with intensive shipping and boating activity. The highest TBT concentration, 975 ng Sn/g dry weight, was found in Kingston Harbour at the mouth of the Cataraqui River (location 102). DBT was found in 43 of 80 locations (54%) at concentrations ranging up to 391 ng Sn/g dry weight. It was mainly found in harbours and marinas, and its presence was likely due to the degradation of TBT. The highest DBT concentration, 391 ng Sn/g dry weight, was also found in Kingston Harbour at the mouth of the

Cataraqui River (location 102). MBT was found in 33 of 80 locations (41%) at locations ranging up to 327 ng Sn/g dry weight. It too was mainly found in harbours and marinas, and its presence was likely due to the degradation of DBT, which was in turn produced from the degradation of TBT. The highest MBT concentration, 327 ng Sn/g dry weight, was found in the Wye Heritage Marina in Midland Bay, Ontario (location 45), the location at which the highest TBT and DBT concentrations in fresh water were found (see above).

In marine sediment samples collected in 1994, TBT was found in 30 of 32 locations (94%) at concentrations ranging up to 2525 ng Sn/g dry weight. As with the results for water, TBT in sediment in the 1994 survey was primarily found in harbours and marinas with intensive shipping and boating activity. The highest TBT concentration, 2525 ng Sn/g dry weight, was found close to a ship yard in Burrard Inlet in British Columbia (location 19). DBT was found in 29 of 32 locations (91%) at concentrations ranging up to 537 ng Sn/g dry weight. It was mainly found in harbours and marinas, and its presence was likely due to the degradation of TBT. The highest DBT concentration, 537 ng Sn/g dry weight, was also found close to a ship yard in Burrard Inlet in British Columbia (location 19). MBT was found in 29 of 32 locations (91%) at locations ranging up to 189 ng Sn/g dry weight. It too was mainly found in harbours and marinas, and its presence was likely due to the degradation of DBT, which was in turn produced from the degradation of TBT. The highest MBT concentration, 189 ng Sn/g dry weight, was also found close to a ship yard in Burrard Inlet in British Columbia (location 19).

3.1.1.1 Ratios of TBT to total butyltin concentrations

The ratio of the TBT concentration to the total butyltin concentration of a water or sediment sample has been used as an approximate measure of the extent to which TBT has undergone degradation at any particular location (*e.g.*, Page *et al.*, 1996). A high TBT/total butyltin concentration ratio indicates little degradation of TBT and/or recent input of TBT to the ecosystem. The mean TBT/total butyltin concentration ratio for

samples collected in 1994 was 78% for fresh water, 92% for sea water, 51% for sediment in fresh water locations, and 59% for marine sediment (see Table 3). The averages for fresh water and marine sediment are similar to the overall average TBT percentage for Arcachon Bay sediments of 49% (Sarradin *et al.*, 1994), but are lower than overall average TBT percentages of 73% for Boston Harbor (Makkar *et al.*, 1989) and 77% for surface sediments from various European sites (Quevauviller and Donard, 1990), presumably reflecting more degradation on average than was observed in those two studies. It should be noted, however, that for the water and sediment samples in this study, the concentration of TBT varied over a wide range up to 100% of the total butyltin concentration. In some locations, the high percentage of TBT relative to total butyltins indicated recent TBT contamination. While this was expected in large marine harbours where there is continuing leaching of TBT from the hulls of large vessels, high TBT percentages in fresh water small craft marinas such as the Wye Heritage Marina in Midland Bay (location 45) (59% in water) may indicate fairly recent contamination by TBT leaching from small boats. However, an alternative explanation, namely the resuspension of TBT-containing sediments in that location, cannot be dismissed.

3.1.1.2 Trends

Comparisons of butyltin concentrations determined in water and sediment in 1994 with butyltin concentrations observed in the period 1982-1985 (Maguire *et al.*, 1986) should be viewed with caution since the samples in question were only single grab samples. In addition, not all locations sampled in 1982-1985 were sampled again in 1994. Table 4 compares the overall results from the two surveys a decade apart. All three butyltin species were found in fresh water much less frequently in 1994 than in 1982-1985, and their concentration ranges and means were much lower. By contrast, TBT and DBT (but not MBT) were found more frequently in sea water in 1994. In sediment in fresh water, TBT was found more frequently in 1994 than in 1982-1985, and the ranges and means were similar. The same was true for DBT. MBT was found more frequently in 1994 than a decade earlier, but its range and mean concentrations were less. In marine

sediment all three butyltin species were found more frequently in 1994 than a decade earlier, but their concentration ranges and mean concentrations were greatly reduced. Comparisons can also be made for those locations sampled in 1982-1985 and again in 1994. Table 5 shows butyltin concentrations for the 43 sea water and fresh water locations in common in the two studies. It is clear that butyltin concentrations in fresh water were much higher in 1982-1985 (mean where detected 623 ± 857 ng Sn/L) than in 1994 (mean where detected 5.4 ± 1.8 ng Sn/L). The highest TBT concentration found in 1994 was 8.5 ng Sn/L, while a decade earlier the highest TBT concentration was 2340 ng Sn/L. TBT was found in too few sea water samples in the two surveys to make a meaningful comparison. In sediments, the situation was more complicated. Table 6 shows butyltin concentrations for the 32 marine and fresh water sediment locations in common in the two studies. In (fresh water) sediment the mean TBT concentration (where detected) increased from 68.8 ± 68.1 ng Sn/g dry weight to 120.0 ± 230.9 ng Sn/g dry weight. The highest TBT concentration found in 1994 was 975.1 ng Sn/g dry weight, while a decade earlier the highest TBT concentration was 190 ng Sn/g dry weight. Comparisons were less meaningful for marine sediments because there were only four common locations, and one extremely high concentration in 1982-1985 (10,780 ng Sn/g dry weight) greatly affected the mean.

3.1.2 In industrial effluents

Two industrial effluents in Ontario and four leachates from an Ontario landfill were also analyzed for butyltin species (see Table 2). No butyltin species were found in effluent from a pulp and paper mill in Terrace Bay, Ontario (location 40) or in effluent from a specialty chemicals manufacturer on the St. Clair River, Ontario (location 53). Butyltin species were generally not found in the four leachate samples from the Gloucester Landfill in Ontario (locations 108-111), with the exception of monobutyltin, which was found in one sample at 4.7 ng Sn/L.

3.3.1.3 In sewage

Table 7 shows concentrations of the butyltin species in influent, effluent and sludge at 11 sewage treatment plants across Canada in 1993 and 1994. The three butyltin species were found in most influent samples both years, at concentrations up to 228, 85 and 23 ng Sn/L for TBT, DBT and MBT, respectively. It is difficult to comment definitively on the effectiveness of the sewage treatment processes because the influent and effluent samples were grab samples, and no provision was made for time of travel through the STP. However, if the influents and effluents represent a steady state, it can be stated that there was in general a significant, but not complete, reduction in concentrations of each butyltin species, and of the sum of the butyltin species. The highest concentrations of TBT in influents were 228 ng Sn/L in Winnipeg in 1993 and 175 ng Sn/L in Sarnia in 1994. The highest concentrations of TBT in effluents were 24 ng Sn/L in Burnaby in 1993 and 32 ng Sn/L in Winnipeg in 1994. Significant amounts of the butyltin species were accumulated in the sludge. The highest concentrations of TBT in sludge in 1993 and 1994 were found in Winnipeg (317 and 661 ng Sn/g dry weight, respectively).

A comparison of these data to data obtained in the early 1990s (Chau *et al.*, 1992a,b, 1994) shows that concentrations of the three butyltin species in STP influents have declined by factors of up to 1000 in just a few years. The reason for this decline is unknown. In addition, TBT and DBT were found much more frequently in STP influents in 1993 and 1994 than in samples collected in 1990-1991. It is concluded that the input of such compounds to STPs is highly variable, and further study is required in order to establish reliable baseline data.

The presence of the butyltin species in sewage treatment plant influents can arise from at least two sources. It is known that DBT and MBT compounds are used as stabilizers in PVC, and that they can be leached from PVC by water (Environment Canada and Health and Welfare Canada, 1993). In addition, it has recently been demonstrated that

TBT can be leached from PVC pipe by water (Forsyth, 1996). TBT is not used *per se* as a PVC stabilizer; consequently its presence in PVC leachates is likely due to being a contaminant of DBT and/or MBT stabilizer formulations. In addition, TBT (with its degradation products DBT and MBT) may be present in STP influents as a result of its use as a general lumber preservative and as a slimicide (e.g., in cooling towers).

3.2 Methyltin species

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 PVC pipe that has been stabilized by MMT and DMT compounds (Environment Canada and Health and Welfare Canada, 1993). Although TMT is not used as a PVC stabilizer, its environmental occurrence may be due to the methylation of DMT or the possibility that it was an impurity in MMT or DMT stabilizer formulations for PVC.

3.2.1 In water and sediment

Table 8 shows concentrations of TMT, DMT and MMT in water and sediment at those locations at which they were found (location numbers correspond to those in Table 2).

In fresh water samples collected in 1994, TMT was found in 4 of 89 locations (4%) at concentrations ranging up to 6.2 ng Sn/L (at Detroit River 1 - location 59). DMT was found in 10 of 89 fresh water locations (11%) in 1994 at concentrations ranging up to 47.4 ng Sn/L. The highest concentration was found in the Welland River (location 71) downstream from a PVC manufacturing plant, and may have been the result of the discharge of a dimethyltin-containing PVC stabilizer. This site also had the highest DMT concentration (17.4 ng Sn/L) of those few samples collected in 1993. MMT was not found in any of 89 samples.

In sea water samples collected in 1994, TMT and MMT were not found in any of 34 locations. DMT was found in 2 of 34 samples (6%), at concentrations of 4.4 and 5.0 ng Sn/L.

In sediment samples collected from fresh water locations in 1994, TMT was not found in any of 80 locations, and DMT was found at only 1 of 80 locations (1%), at 5.4 ng Sn/g dry weight. However, MMT was found in 24 of 80 locations (30%), at concentrations up to 294 ng Sn/g dry weight. In general the highest concentrations of MMT were in the sediment of large harbours, notable Hamilton and Montréal Harbours. The three highest concentrations were found in Hamilton Harbour (294, 138 and 54 ng Sn/g dry weight).

In marine sediment samples collected in 1994, TMT and DMT were not found in any of 32 locations. However, MMT was found in 21 of 32 samples (66%), at concentrations up to 42 ng Sn/g dry weight (in St. John's Harbour - location 130). As was the case with sediment from fresh water, the highest concentrations of MMT were found in large harbours.

3.2.1.1 Trends

Comparisons of methyltin concentrations determined in water and sediment in 1994 with methyltin concentrations observed in the period 1982-1985 should also be viewed with caution since the samples in question were only single grab samples. In addition, not all locations sampled in 1982-1985 were sampled again in 1994. Table 9 compares overall results from the two surveys a decade apart. TMT and DMT were found in fresh water in 1994 about as infrequently as in 1982-1985, but at lower concentrations. MMT was not found in any of 89 fresh water samples in 1994, although it was found in 15% of samples in 1982-1985. All three methyltin species were found infrequently or not at all in sea water in 1994, which was similar to findings in 1982-1985. In sediment in fresh water and in marine sediment, TMT and DMT were found only rarely in 1994, which was similar to findings in 1982-1985. By contrast, MMT was found in 30% of

sediment samples in fresh water in 1994, although it was found in only 2% of samples in 1982-1985. In marine sediment, MMT was found in 66% of all locations sampled in 1994, compared to 18% of all locations sampled in 1982-1985.

4.3.2.2 In industrial effluents

Two industrial effluents in Ontario and four leachates from an Ontario landfill were also analyzed for methyltin species (see Table 8). No methyltin species were found in effluent from a pulp and paper mill in Terrace Bay, Ontario (location 40) or in effluent from a specialty chemicals manufacturer on the St. Clair River, Ontario (location 53). TMT was found in all four leachate samples from the Gloucester Landfill in Ontario (locations 108-111), in the concentration range 4-22 ng Sn/L. DMT and MMT were only found in one of the leachate samples, at concentrations of 14.5 and 86.3 ng Sn/L, respectively. It is not known why TMT would be found in these leachates in the general absence of DMT and MMT.

3.2.3 In sewage

Table 10 shows concentrations of the methyltin species in influent, effluent and sludge at 11 sewage treatment plants across Canada in 1993 and 1994. The results were similar to those for STPs in Toronto and Hamilton in 1990-1991 (Chau *et al.*, 1994). DMT was present in most influents at concentrations up to 454 ng Sn/L (in Edmonton in 1993). Its presence may be due to leaching from dimethyltin-stabilized PVC piping. There was in general a significant, but not complete, reduction in concentrations of each methyltin species, and of the sum of the methyltin species. Methyltin species were found in sewage sludge at much lower concentrations than the butyltin species.

3.3 Octyltin species

MOT and DOT compounds are commonly used as stabilizers for PVC for food and beverage packaging (Environment Canada and Health and Welfare Canada, 1993). In this survey, MOT and DOT were not found in any natural water sample, but they were found, generally co-occurring, in several sediment samples from fresh water and sea water locations, as shown in Table 11.

In sediment samples collected in fresh water in 1994, DOT was found in 6 of 80 locations (8%). The concentrations were generally less than 5 ng Sn/g dry weight, with the exception of one value of 22 ng Sn/g dry weight, which was found for a location in Redhill Creek where it enters Hamilton Harbour (location 100). This location is immediately downstream of the effluent of a STP, and it is possible that the STP was the source of the DOT. MOT was found in 7 of 80 locations (9%), at concentrations up to 7 ng Sn/g dry weight. The highest concentration, 7.3 ng Sn/g dry weight, was also from Redhill Creek, Hamilton Harbour.

DOT was found in 1 of 32 marine sediments (St. John's Harbour), at 2.8 ng Sn/g dry weight. MOT was not found in any of 32 locations.

No octyltin species was found in the two industrial effluents in Ontario and four leachates from an Ontario landfill. However, DOT and MOT were found in STP influents, effluents and sludges, as shown in Table 12. The two species were found only infrequently in STP influent and effluent, but were found more frequently in sludge, at concentrations up to 22 and 50 ng Sn/g dry weight for DOT and MOT, respectively. Such concentrations were generally much lower than concentrations of butyltin species in sludge.

Although DOT and MOT have been found in beverages stored in octyltin-stabilized PVC (e.g., Forsyth *et al.*, 1992), to our knowledge this is the first report of these species in sediments and STP influents, effluents and sludges.

3.4 Phenyltin species

The phenyltin species were only found infrequently in sediment (generally co-occurring), and were not found in samples of water, industrial effluent, landfill leachates or STP influents, effluents or sludges. Table 13 shows concentrations of the three phenyltin species in sediment at the only locations at which they were found. These concentrations were similar to those that have been observed in sediments previously in other countries (e.g., Fent and Hunn, 1991, 1995; Fent *et al.* 1991; Tolosa *et al.*, 1992; Tsuda *et al.*, 1991; Shiraishi and Soma, 1992; Gomez-Ariza *et al.*, 1995; Ståb *et al.*, 1994; Lalère *et al.*, 1995). Although TPT compounds have been used in some countries as agricultural pesticides (Bock, 1981; Muller *et al.*, 1989), they have not been used in Canadian agriculture since the 1980s, and it is unlikely that their presence in harbours is due to anything other than antifouling uses. It should be noted that TPT has never been a registered antifoulant in Canada.

In sediment samples collected in fresh water in 1994, TPT was found in 3 of 80 locations (4%), at concentrations up to 19.6 ng Sn/g dry weight. DPT was found in only 1 of 80 samples (1%), at 4.3 ng Sn/g dry weight. MPT was found in 4 of 80 samples (5%), at concentrations up to 10 ng Sn/g dry weight. Where they were found, TPT and its degradation products were generally found in areas that could accommodate large vessels painted outside Canada. An exception was the finding of MPT in the small Wye Heritage Marina in Midland Bay (location 45). Its presence in this area may reflect an illegal use of TPT-containing antifouling paint, or, and perhaps less likely, the contamination of TBT-containing antifouling paint with TPT.

In marine sediment samples collected in 1994, TPT was found in 2 of 32 locations (6%), at 25 and 27 ng Sn/g dry weight. DPT was not found in any of the 32 locations sampled. MPT was only found in the same two locations at which TPT was found, at concentrations of 9 and 10 ng Sn/g dry weight. The two locations in question, Burrard Inlet (5) (location 15) and Halifax harbour (2) (location 127) are both areas that could accommodate large vessels legally painted with TPT outside Canada.

3.5 Dicyclohexyltin species

Dicyclohexyltin was found only rarely in sediment in Canada (see Table 14) and was not found in any samples of water, industrial effluent, landfill leachates or STP influents, effluents or sludges. The tricyclohexyltin and monocyclohexyltin species were not found at all.

In sediment samples from fresh water collected in 1994, D-c-HT was found in only 1 of 80 locations (1%), at 3.9 ng Sn/g dry weight (Montréal Harbour (3), location 116). In marine sediment samples collected in 1994, it was found in 1 of 32 samples (3%), at 13.5 ng Sn/g dry weight (St. John's Harbour (2), location 131). The reason for the occurrence of D-c-HT in these locations is unknown. It likely did not arise from agricultural applications (agricultural uses of T-c-HT in Canada ceased in the late 1980s). It is possible that it was a contaminant of some organotin-containing antifouling paint formulations. There were substantial concentrations of total butyltin species in the sediment at both locations (216 and 222 ng Sn/g dry weight for Montréal Harbour (3) and St. John's Harbour (2), respectively). It is also possible that the presence of D-c-HT in these two locations is due to sewage discharge.

3.6 Tripropyltin species

Tripropyltin was found only rarely in sediment in fresh water, but was found frequently in marine sediment (see Table 15). It was not found in any samples of water, industrial effluent, landfill leachates or STP influents, effluents or sludges. The

dipropyltin and monopropyltin species were not found at all. In sediment samples from fresh water collected in 1994, TPrT was found in only 1 of 80 locations (1%), at 4.8 ng Sn/g dry weight (Wye Heritage Marina, Midland Bay - location 45). In marine sediment samples collected in 1994, it was found in 13 of 32 samples (41%), at concentrations up to 24 ng Sn/g dry weight. All of these locations are sites of heavy boating or shipping traffic, with elevated total butyltin concentrations (> 74 ng Sn/g dry weight).

There is very little information in the literature on the use or environmental occurrence of TPrT. It has been investigated as an experimental molluscicide (e.g., Ritchie *et al.*, 1964; Danil'chenko and Stroganov, 1974), and it was apparently an agricultural fungicide in Japan (Hattori *et al.*, 1984). Jewett and Brinckman (1981) found TPrT in an aqueous leachate of a marine antifoulant developed by the U.S. Navy that contained TPrT methacrylate in addition to TBT. Lobinski *et al.* (1992) found, but did not quantify, TPrT and DPrT in a water sample and a sediment sample from an unidentified location. To our knowledge, the results presented here are the first quantitative data on the occurrence of TPrT in aquatic environments. It is possible that the TPrT found was a contaminant of some TBT-containing antifouling paint formulations, or was used itself as an antifoulant, although apart from the report by Jewett and Brinckman (1981), there appears to be no other information in the literature on the use of TPrT-containing antifoulants. It should be noted that the use of TPrT as a spiked internal standard in organotin occurrence studies would obscure the presence of TPrT that was in such samples, either as a result of deliberate pesticidal use, or resulting from contamination of other organotin formulations.

3.7 Other organotin species

In some of our studies conducted in the 1980s, methylated butyltin species were found, albeit rarely and at lower concentrations than the butyltin species (Maguire, 1984; Maguire *et al.*, 1996). Such species were not found in the present study, nor were there any other organotin peaks in the GC-AED Sn-channel chromatograms that could not be tentatively identified by retention time matching with available known standards.

4. DISCUSSION

The toxicity of organotin compounds has been studied extensively (e.g., Hall and Pinkney, 1985; Snoeij *et al.*, 1987; Cooney and Wuertz, 1989; Boyer, 1989; Maguire, 1991; Cooney 1995; Fent, 1996, and de Mora, 1996, and references therein). In this discussion concentrations of the butyltin and methyltin species in subsurface water and sediment were compared to toxicological endpoints and/or to Canadian water quality guidelines, where these were available. Comparisons were not made for MOT, DOT, TPT, DPT, MPT, D-c-HT and TPrT because these species were only found in sediments, and there were no acute or chronic benthic toxicity data available for these species. Comparisons were also not made between toxicological endpoints and concentrations of butyltin and methyltin species in STP effluents because such effluents are subject to large dilutions in receiving waters, and it was likely that such dilutions would reduce the concentrations of such species to below those found in natural waters in this survey.

4.1 Butyltin species

4.1.1 In freshwater

4.1.1.1 acute toxicity of TBT

For TBT, a coelenterate (*Hydra* sp.) was the most sensitive fresh water organism in acute toxicity tests. The 48-hr. EC_{50} (response to prodding) was 400 ng Sn/L (Brooke *et al.*, 1986). The highest concentration of TBT in fresh water in this survey was 17.8 ng Sn/L, which was a factor of 22 lower. Therefore, based on available toxicity data, TBT concentrations in fresh water were far below the acute toxicity threshold in those locations in which it was found.

No data were found on the acute toxicity of TBT in sediment to benthic fresh water organisms; consequently an assessment of the acute toxicity of TBT found in sediments in fresh water in this survey can not be done.

4.1.1.2 chronic toxicity of TBT

The interim Canadian water quality guideline for TBT of 3.3 ng Sn/L for the protection of fresh water life (Moore *et al.*, 1992) was derived by applying a safety factor of 10 to the lowest reported chronic effect, a 33-day lowest-observed-effect-level (LOEL) of 33 ng Sn/L for growth of post-hatch fathead minnows (*Pimephales promelas*) (Brooke *et al.*, 1986). (The 90-day LOEL of 13 ng Sn/L for TBT for histopathological changes in the guppy (*Poecilia reticulata*) (Wester and Canton, 1987) was not used to derive the interim guideline because this fish species is not native to Canada.) TBT was found in 12 of 89 fresh water locations in 1994 at concentrations ranging up to 17.8 ng Sn/L. In 9 of these 12 locations the TBT concentration exceeded the guideline value of 3.3 ng Sn/L for the protection of fresh water life by factors of 1.2-5; consequently, chronic toxicity due to TBT in these locations may be expected. Eight of the 12 locations were harbours that have large vessels that could legally be painted with TBT-containing antifouling paints in Canada or elsewhere. Therefore, the continued presence of TBT in those locations was not unexpected. However, four locations (45, 46, 87, 102) are only small craft harbours. The presence of TBT in water in these locations may be due to desorption of TBT from contaminated sediments, the illegal use of TBT-containing antifouling paints, or, and perhaps less likely, the possibility that the TBT leached from boats that were painted before 1989. It should be noted that although antifouling uses of TBT were regulated in 1989, it appears that the regulation did not recall existing TBT-containing antifouling paints to the distributor or manufacturer, nor stipulate that TBT-containing paints only be applied by licensed applicators (Maguire *et al.*, 1996). Consequently, it is not known for certain when existing stocks of TBT-containing paints were legally used up on small boats in Canada. The four locations in question, and selected other small marinas, will be monitored for TBT in the future.

No data were found on the chronic toxicity of TBT in sediment to benthic fresh water organisms; consequently an assessment of the chronic toxicity of TBT found in sediments in fresh water in this survey can not be done.

4.1.1.3 acute toxicity of DBT

For DBT, the alga *Scenedesmus obliquus* was the most sensitive fresh water organism in acute toxicity tests. The 96-hr. EC_{50} value (growth) was 6,500 ng Sn/L (Huang *et al.*, 1993). The highest concentration of DBT in fresh water in this survey was 9.3 ng Sn/L, which was a factor of 700 lower. Therefore, based on available toxicity data, DBT concentrations in fresh water were far below the acute toxicity threshold in those locations in which it was found.

No data were found on the acute toxicity of DBT in sediment to benthic fresh water organisms; consequently an assessment of the acute toxicity of DBT found in sediments in fresh water in this survey can not be done.

4.1.1.4 chronic toxicity of DBT

The most sensitive fresh water organism identified in chronic toxicity tests with DBT was rainbow trout (*Oncorhynchus mykiss*), with a LOEC (mortality) of 95,000 ng Sn/L (de Vries *et al.*, 1991). This value is about 1,000 times higher than the highest concentration of DBT found in fresh water in Canada. Therefore, based on available toxicity data, DBT concentrations in fresh water were far below the chronic toxicity threshold in those locations in which it was found.

No data were found on the chronic toxicity of DBT in sediment to benthic fresh water organisms; consequently an assessment of the chronic toxicity of DBT found in sediments in fresh water in this survey can not be done.

4.1.1.5 acute toxicity of MBT

For MBT, the bacterium *Pseudomonas putida* was the most sensitive fresh water organism identified in acute toxicity tests. Its 4-hr. EC_{10} (growth) was 53,000 ng Sn/L (Steinhauser *et al.*, 1985). The highest concentration of MBT in fresh water in this survey was 14.9 ng Sn/L, which was a factor of about 3,500 lower. Therefore, based on available toxicity data, MBT concentrations in fresh water were far below the acute toxicity threshold in those locations in which it was found.

No data were found on the acute toxicity of MBT in sediment to benthic fresh water organisms; consequently an assessment of the acute toxicity of MBT found in sediments in fresh water in this survey can not be done.

4.1.1.6 chronic toxicity of MBT

No data were identified on the chronic toxicity of monobutyltin to fresh water organisms. Even with the application of a factor of 20 to convert from the 4-hr. EC_{10} (growth) value of 53,000 ng Sn/L for the bacterium *Pseudomonas putida* to a chronic NOEL (*e.g.*, Environment Canada and Health and Welfare Canada, 1993), there was still a margin of safety of about 180 between the NOEL and the highest MBT concentration. Therefore, based on the very limited available toxicity data, MBT concentrations in fresh water were far below the chronic toxicity threshold in those locations in which it was found.

No data were found on the chronic toxicity of MBT in sediment to benthic fresh water organisms; consequently an assessment of the chronic toxicity of MBT found in sediments in fresh water in this survey can not be done.

4.1.2 In sea water

4.1.2.1 acute toxicity of TBT

For TBT, the most sensitive marine organism in acute toxicity tests appears to be the macroalga *Phyllospora comosa* (Burrige *et al.*, 1995), for which the NOEC and 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). This value was exceeded by the TBT concentration in all 25 sea water samples in which it was found. Consequently, acute toxic effects due to TBT may be expected in those locations.

No data were found on the acute toxicity of TBT in sediment to benthic marine organisms; consequently an assessment of the acute toxicity of TBT found in marine sediments in this survey can not be done.

4.1.2.2 chronic toxicity of TBT

The Canadian water quality guideline for TBT of 0.41 ng Sn/L for the protection of marine life (Moore *et al.*, 1992) 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, *N. 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). (Bryan *et al.* (1988) have shown that exposure of the dogwhelk *N. lapillus* to 200 ng Sn/L DBT did not promote the development of imposex. Moreover, injections of 0.5-1 μ g of DBT or MBT per animal were not effective in promoting imposex.) The guideline concentration of 0.41 ng Sn/L and the imposex induction concentration of 0.5 ng Sn/L were exceeded by the TBT

concentration in all 25 sea water samples in which it was found. Consequently, chronic toxic effects due to TBT may be expected in those locations.

Some data were found on the chronic toxicity of TBT in sediment to benthic marine organisms. Matthiessen and Thain (1989) found that populations of the polychaete *Scoloplos armiger* and the amphipod *Urothoe poseidonis* were reduced over 5 months at an initial TBT concentration in sediment of 41 ng Sn/g dry weight (a concentration exceeded at 19 of 42 locations in this survey). Langston and Burt (1991) and Ruiz *et al.* (1994) have also found evidence of chronic toxic effects in the clam *S. plana* at TBT concentrations in sediment of 300 ng Sn/g dry weight (a concentration exceeded at 6 of 42 locations in this survey). Ruiz *et al.* (1994) also noted that burying activity of the clam *S. plana*, with possible effects on its ability to avoid predators, was significantly reduced with respect to controls. Consequently, chronic toxicity due to TBT in heavily contaminated sediments in this survey may be expected.

4.1.2.3 acute toxicity of DBT

For DBT, the most sensitive marine organism tested 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 DBT in sea water in this survey was 6.4 ng Sn/L, which was a factor of about 1,560 lower. Therefore, based on the available toxicity data, DBT concentrations in sea water were far below the acute toxicity threshold in those locations in which it was found.

No data were found on the acute toxicity of DBT in sediment to benthic marine organisms; consequently an assessment of the acute toxicity of DBT in marine sediments in this survey can not be done.

5.4.1.2.4 chronic toxicity of DBT

There are few data on the chronic toxicity of DBT to marine organisms. The most sensitive organism identified was *Mytilus edulis* larvae, for which NOEC and LOEC values of 1.0 and 10.2 $\mu\text{g Sn/L}$, 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 DBT concentration of 1 $\mu\text{g Sn/L}$ is a factor of 156 higher than the highest DBT concentration found in sea water in this survey. Therefore, based on the limited available toxicity data, DBT concentrations in sea water were far below the chronic toxicity threshold in those locations in which it was found.

No data were found on the chronic toxicity of DBT in sediment to benthic marine organisms; consequently an assessment of the chronic toxicity of DBT in marine sediments in this survey could not be done.

4.1.2.5 acute toxicity of MBT

For MBT, the only 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). MBT was not found in any sea water sample in this survey.

No data were found on the acute toxicity of MBT in sediment to benthic marine organisms; consequently an assessment of the acute toxicity of MBT in marine sediments in this survey could not be done.

4.1.2.6 chronic toxicity of MBT

No data were found for the chronic toxicity of MBT in sea water to marine organisms.

No data were found on the chronic toxicity of MBT in sediment to benthic marine organisms; consequently an assessment of the chronic toxicity of MBT found in marine sediments in this survey could not be done.

4.2 *Methyltin species*

4.2.1 *In fresh water*

4.2.1.1 *TMT*

Wong *et al.* (1982) found a 4-hr. IC_{50} value of 570,000 ng Sn/L for primary productivity of a mixture of Lake Ontario algae. Huang *et al.* (1993) found a 96-hr. EC_{50} for growth of the alga *Scenedesmus obliquus* to be 232,000 ng Sn/L. Nagase *et al.* (1991) found a 48-hr. LC_{50} value of 3,400,000 ng Sn/L for the red killifish (*Oryzias latipes*). The lowest of these values is 37,400 times higher than the highest TMT concentration found in fresh water in this survey (6.2 ng Sn/L). Therefore, based on available toxicity data, TMT concentrations in fresh water were far below the acute toxicity threshold in those locations in which it was found. Stroganov *et al.* (1966) found that exposure to 10,700 ng Sn/L resulted in 67% reduction of number of *Daphnia magna* progeny over a period of 30 days. That concentration is 1730 times higher than the highest TMT concentration found in fresh water in this survey. Therefore, based on available toxicity data, TMT concentrations in fresh water were far below the chronic toxicity threshold in those locations in which it was found.

4.2.1.2 *DMT*

The most sensitive organism identified was *Daphnia magna*, for which the 48-hr. LC_{50} value was determined to be 30,000 ng Sn/L (Steinhauser *et al.*, 1985). This value was 632 times higher than the highest DMT concentration found in fresh water in this survey (47.4 ng Sn/L). Therefore, based on available toxicity data, DMT concentrations in fresh

water were far below the acute toxicity threshold in those locations in which it was found. No data were found on the chronic toxicity of DMT to fresh water organisms.

No data were found on the acute or chronic toxicity of DMT in sediment to benthic fresh water organisms; consequently an assessment of the acute or chronic toxicity of DMT found in the one sediment sample in this survey can not be done.

4.2.1.3 MMT

No data were found on the acute or chronic toxicity of MMT in sediment to benthic fresh water organisms; consequently an assessment of the acute or chronic toxicity of MMT found in the sediment samples in this survey can not be done.

6.4.2.2 In sea water

4.2.2.1 TMT

TMT was not found in any sea water or sediment sample.

4.2.2.2 DMT

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 240,00 times higher than the highest DMT concentration found in sea water in this survey (5.0 ng Sn/L). Therefore, based on the limited available toxicity data, DMT concentrations in sea water were far below the acute toxicity threshold in those locations in which it was found. No data were found on the chronic toxicity of DMT to marine organisms.

4.2.2.3 MMT

No data were found on the acute or chronic toxicity of MMT in sediment to benthic marine organisms; consequently an assessment of the acute or chronic toxicity of MMT found in the sediment samples in this survey can not be done.

5. CONCLUSIONS

The 1989 Canadian regulation of antifouling uses of TBT appears to have had a marked effect on TBT concentrations in fresh water in that it was found much less frequently in 1994 than in 1982-1985, and its concentration range and mean concentration were much lower in 1994 than a decade earlier. However, it was still found in some locations at concentrations that exceeded the interim Canadian water quality guideline for the protection of fresh water aquatic life, indicating a high potential for adverse effects in such locations. In addition, there may be fresh sources of TBT in some small marinas and harbours that require further investigation. The regulation appears to have had less effect on concentrations of TBT in sediment in fresh water, where TBT was found more frequently in 1994 than a decade earlier, and with a similar concentration range and mean concentration.

The situation in sea water was somewhat different. TBT was found frequently in 1994 compared to 1982-1985, and in every case its concentration exceeded acute and chronic toxicity endpoints, indicating a high potential for adverse effects in the particular locations. In marine sediment TBT was found more frequently in 1994 than a decade earlier, but its concentration range and mean concentration were greatly reduced. Nevertheless, in about half of all marine sediments in which TBT was found its concentration exceeded chronic toxicity thresholds, indicating a high potential for adverse effects in the particular locations.

The overall conclusion is that the 1989 regulation has been only partially effective. It has had some effect in the reduction of TBT concentrations in fresh water, but not in sea water. It has had less effect in the reduction of TBT concentrations in sediment, probably because of the longer persistence of TBT in sediment than in water. In some areas there may be potential for recycling TBT from contaminated sediments back into the water column. In addition, it appears that large harbours that handle ships legally painted with TBT-containing antifouling paints will continue to experience ecotoxicologically significant TBT contamination. As an extension of this work, work is in progress in this laboratory on the accumulation of TBT and other organotin species in bivalves and other organisms in and close to harbours and marinas.

Based on this survey, DBT and MBT, which are primarily degradation products of TBT, appear not to pose acute or chronic hazards to fresh water or marine organisms, but nothing is known of their hazards to benthic organisms. The same conclusion holds for the three methyltin species. In addition, no conclusions could be made about the toxicological significance of the finding of MOT, DOT, TPT, DPT, MPT, D-c-HT and TPrT in sediment because no acute or chronic benthic toxicity data were available with which to make comparisons. Benthic toxicity data for organotin species other than butyltin species are required before an assessment can be made of the toxicological significance of their concentrations in sediment. Another area for research is the toxicological significance of organotin residues in sewage sludge.

The results of this survey for mono- and dimethyltin, butyltin and octyltin species in water also confirm the conclusion of the Canadian Environmental Protection Act assessment of non-pesticidal organotin compounds (Environment Canada and Health and Welfare Canada, 1993), which was based on data collected in the 1980s, that such species were not considered toxic as defined under the Act.

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Table 1. Operating conditions for GC-AED, GC-FPD and GC-MSD.

GC-AED**GC parameters**

injection port	splitless
injection port temperature	250 °C
injection volume	1 µL
column	SPB-1, 30 m x 0.53 mm i.d., film thickness 1.5 µm
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 ₂ at 2 L/min.
makeup gas	He at 240 mL/min.
Sn wavelength	271 nm
H ₂ pressure	414 kPa (60 p.s.i.)
O ₂ pressure	138 kPa (20 p.s.i.)

GC-FPD

splitless injection	purge time 1.0 min.
injector temperature	250 °C
injection volume	1 µL
column	DB5, 30m x 0.25 mm i.d., film thickness 0.25 µm
carrier gas	He, constant flow mode, 10 p.s.i. at 50 °C
temperature program	50 °C for 1 min., then 20 °C/min to 280 °C, with 2.5 min. final hold
combustion gases	H ₂ and air, each at 100 mL/min.
detector temperature	200 °C

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Table 1 cont'd

GC-SIM-MSD

splitless injection	purge time 1.0 min., He carrier
injector temperature	250 °C
injection volume	1 µL
column	DB5, 30m x 0.25 mm i.d., film thickness 0.25 µm
carrier gas	He, constant flow mode, 10 p.s.i. at 50 °C
temperature program	50 °C for 1 min., then 20 °C/min to 280 °C, with 2.5 min. final hold
detector temperature	280 °C
electron impact mode	
ionization potential	70 eV
source temperature	190 °C
scan	50-300 amu, solvent delay 4.0 min.
species (ethyl derivatives)	ions monitored
MMT	135, 165, 193
DMT	135, 151, 179
TMT	135, 157, 165
MBT	121, 149, 179
TPrT	121, 151, 193
DBT	121, 149, 179
MPT	197, 255, 121
TBT	121, 149, 177
MOT	179, 149, 121
DPT	120, 197
D-c-HT	149, 179
DOT	151, 121, 179
TPT	120, 197
T-c-HT	151, 233

Table 2. Concentrations of butyltin species in water and sediment in selected Canadian locations in 1993 and 1994 (also includes two locations in New York State, U.S.A., two industrial effluents and four leachate samples from an Ontario landfill).*

No.	Location	Water (ng Sn/L)				Sediment (ng Sn/g) (dry weight)			
		TBT	DBT	MBT	TOTAL	TBT	DBT	MBT	TOTAL
Part 1 - 1993									
Ontario									
1	Hamilton Harbour					97.9±2.3	48.9±2.5	49.0±3.5	195.8
2	Toronto Harbour					9.7±0.5	13.6±0.8	9.0±1.5	32.3
3	St. Clair River					n.s.	n.s.	n.s.	n.s.
4	Welland River	d	d			3.0±0.9	6.5±2.3	2.7±0.6	12.2
Québec									
5	St. Lawrence River at Québec					179.0±9.9	102.4±2.5	80.9±3.1	362.3
New Brunswick									
6	Saint John Harbour	3.2±0.4			3.2	3212.0±228.1	313.7±7.1	140.9±23.1	3666.6
Prince Edward Island									
7	Charlottetown Harbour								
Nova Scotia									
8	Halifax Harbour					1347.7±163.8	345.8±49.4	161.5±48.7	1855.0
9	Sydney Harbour					8.8±2.3	15.7±1.7	3.9±0.4	28.4
Newfoundland									
10	St. John's Harbour					147.3±5.9	72.9±0.6	26.5±0.7	246.7

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Table 2 cont'd												
No.	Location	Water (ng Sn/L)				Sediment (ng Sn/g) (dry weight)						
		TBT	DBT	MBT	TOTAL	TBT	DBT	MBT	TOTAL			
43	St. Marys River (2) (s)											
44	St. Marys River (3) (s)					7.8±0.8	6.7±0.3					14.5
45	Midland Bay	17.8±2.4	9.3±1.8	3.3±0.0	30.4	390.6±0.7	270.7±0.4	327.0±0.7				988.3
46	Penetang Harbour	3.1±0.2	d	d	3.1	88.7±15.9	81.0±7.2	56.9±4.3				226.6
47	Collingwood Harbour (1)			d		412.8±14.3	129.5±0.6	50.8±0.3				593.1
48	Collingwood Harbour (2)	d				35.0±1.3	23.8±0.3	17.4±0.9				76.2
49	Collingwood Harbour (3)			d		8.0±0.2	7.5±0.3	6.1±0.5				21.6
50	Owen Sound Harbour (s)											
51	St. Clair River (1) (s)											
52	St. Clair River (2) (s)					d	d	d				
53	St. Clair River (3)					n.s.	n.s.	n.s.				n.s.
54	St. Clair River (4) (s)											
55	St. Clair River (5) (s)											
56	St. Clair River (6) (s)											
57	Lake St. Clair (s)			4.9±1.2	4.9							
58	Thames River											
59	Detroit River (1) (s)											
60	Detroit River (2)					d	d	d				
61	Detroit River (3)					d	d	d				
62	Detroit River (4)					d	d	d				
63	Detroit River (5)	d				d	4.8±0.6	5.5±0.3				10.3
64	Port Stanley			d		d	4.7±0.8	4.7±0.8				9.4
65	Port Dover (1)	d	d			12.3±1.6	6.8±0.8	d				19.1
66	Port Dover (2)	d				10.8±0.2	6.3±0.7	d				17.1
67	Nanticoke	d				4.6±0.7	5.3±0.4	d				9.9
68	Port Colborne					n.s.	n.s.	n.s.				n.s.
69	Welland Canal (1)					d	d	d				

70	Welland Canal (2)	d	d	d	d	n.s.	n.s.	n.s.	n.s.
cont'd next page									
Table 2 cont'd									
No.	Location	Water (ng Sn/L)				Sediment (ng Sn/g) (dry weight)			
		TBT	DBT	MBT	TOTAL	TBT	DBT	MBT	TOTAL
71	Welland River	d	d	d		11.3±1.1	18.1±2.2	11.5±1.2	40.9
72	Port Weller	12.4±0.1	4.6±0.1	d	17.0	254.5±7.7	101.9±4.1	37.4±3.0	393.8
73	Buffalo Harbor (1) (New York State, U.S.A.)					d	d	d	
74	Buffalo Harbor (2) (New York State, U.S.A.)			d		d	d	d	
75	Niagara River (1)			2.7±0.3	2.7	n.s.	n.s.	n.s.	n.s.
76	Niagara River (2)					n.s.	n.s.	n.s.	n.s.
77	Lake Erie (1)								
78	Lake Erie (2)								
79	Lake Erie (3)								
80	Lake Ontario (1)								
81	Lake Ontario (2)								
82	Port Dalhousie	d	d	d					
83	Belleville (s)			d		4.1±0.2	3.8±1.3	d	7.9
84	Port Hope (1)					3.6±0.4	4.9±0.3		8.5
85	Port Hope (2)						5.3±0.4	d	5.3
86	Whitby Harbour (1)	d				4.8±0.6	d		4.8
87	Whitby Harbour (2)	4.7±0.7	d		4.7	89.6±2.0	49.3±1.5	29.3±0.5	168.2
88	Port Credit					3.7±0.3	7.3±1.2	6.0±1.7	17.0
89	Humber River (s)						d	d	
90	Toronto Harbour (1)	d	d	d				d	
91	Toronto Harbour (2)		d			29.6±0.4	35.5±2.7	27.1±1.3	92.2
92	Toronto Harbour (3)	d		d		9.0±0.0	7.9±0.2	8.1±2.3	25.0
93	Toronto Harbour (4)	3.1±0.8	d	d	3.1	18.1±1.2	19.1±1.4	13.5±1.8	50.7
94	Toronto Harbour (5)	d	d			327.7±20.1	167.7±10.1	68.3±5.0	563.7
95	Toronto Harbour (6)	d		d		70.6±3.3	48.1±2.1	36.1±2.1	154.8
96	Toronto Harbour (7)	d	d	d		76.8±9.9	38.9±4.4	26.7±2.4	142.4
97	Hamilton Harbour (1)	2.6±0.1	4.4±1.1	2.9±0.8	9.9	28.9±0.2	22.0±1.2	11.7±0.2	62.6
98	Hamilton Harbour (2)	d		d		46.3±2.9	28.5±1.6	45.5±14.3	120.3

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Table 2 cont'd											
No.	Location	Water (ng Sn/L)				Sediment (ng Sn/g) (dry weight)					
		TBT	DBT	MBT	TOTAL	TBT	DBT	MBT	TOTAL		
99	Hamilton Harbour (3)	d	d	d		79.4±5.9	51.6±3.9	162.8±28.2		293.8	
100	Hamilton Harbour (4)	4.5±0.4		d	4.5	62.8±4.6	64.7±2.8	42.0±1.2		169.5	
101	Hamilton Harbour (5)	d	d	d		131.6±24.6	54.2±10.7	32.5±8.0		218.3	
102	Kingston Harbour (1)	4.0±0.3			4.0	975.1±104.1	390.8±26.5	127.1±28.5		1493.0	
103	Kingston Harbour (2)	d	5.0±1.9		5.0	30.2±1.9	18.6±0.6	11.0±0.9		59.8	
104	St. Lawrence River at Maitland										
105	St. Lawrence River at Cornwall (1)					19.2±1.8	9.4±0.8	6.8±0.4		35.4	
106	St. Lawrence River at Cornwall (2)					n.s.	n.s.	n.s.		n.s.	
107	St. Lawrence River at Cornwall (3)	n.s.	n.s.	n.s.	n.s.						
108	Gloucester Landfill (1)					n.s.	n.s.	n.s.		n.s.	
109	Gloucester Landfill (2)		d	4.7	4.7	n.s.	n.s.	n.s.		n.s.	
110	Gloucester Landfill (3)					n.s.	n.s.	n.s.		n.s.	
111	Gloucester Landfill (4)					n.s.	n.s.	n.s.		n.s.	
Québec											
112	Richelieu River at Sorel (1) (s)					4.6±0.5	4.0±0.8	d		8.6	
113	Richelieu River at Sorel (2) (s)										
114	Montréal Harbour (1)					198.2±39.9	73.8±21.0	60.4±14.7		332.4	
115	Montréal Harbour (2)	4.6±0.5		3.3±0.5	7.9	181.3±52.7	79.0±20.9	42.3±9.6		302.6	
116	Montréal Harbour (3)					108.0±6.2	56.7±2.8	51.3±4.0		216.0	
117	Montréal Harbour (4)	5.3±1.0		d	5.3	52.1±6.3	34.5±9.1	34.4±2.0		121.0	
118	Montréal Harbour (5)	d	d			n.s.	n.s.	n.s.		n.s.	
119	Montréal Harbour (6)	4.1±0.5	3.9±0.4	14.9±2.7	22.9	21.7±1.5	25.9±9.3	15.0±4.4		62.6	

Table 3. Distributions of butyltin species in water and sediment in selected Canadian locations in 1993 and 1994 (also includes two locations in New York State, U.S.A., two industrial effluents and four leachate samples from an Ontario landfill).*

No.	Location	Water (%)			Sediment (%)		
		TBT	DBT	MBT	TBT	DBT	MBT
Part 1 - 1993							
Ontario							
1	Hamilton Harbour						
2	Toronto Harbour				50	25	25
3	St. Clair River				30	42	28
4	Welland River				n.s.	n.s.	n.s.
					25	53	22
Québec							
5	St. Lawrence River at Québec				49	28	22
New Brunswick							
6	Saint John Harbour	100			88	9	4
Prince Edward Island							
7	Charlottetown Harbour						
Nova Scotia							
8	Halifax Harbour				73	19	9
9	Sydney Harbour				31	55	14
Newfoundland							
10	St. John's Harbour				60	30	11
cont'd next page							
Table 3 cont'd							

No.	Location	Water (%)			Sediment (%)		
		TBT	DBT	MBT	TBT	DBT	MBT
Part 2 - 1994							
British Columbia							
1	Nanaimo Harbour				n.s.	n.s.	n.s.
2	Esquimalt Harbour	100			n.s.	n.s.	n.s.
3	Victoria Harbour	100			n.s.	n.s.	n.s.
4	False Creek (1)	100			35	36	29
5	False Creek (2)	73	27		50	37	13
6	False Creek (3)	100			36	44	20
7	False Creek (4)	100			47	40	14
8	False Creek (5)	100			42	42	16
9	False Creek (6)	100			51	37	12
10	False Creek (7)				45	39	17
11	Burrard Inlet (1)	100			38	39	23
12	Burrard Inlet (2)	100			75	17	8
13	Burrard Inlet (3)	100			69	21	10
14	Burrard Inlet (4)	86	14		73	20	7
15	Burrard Inlet (5)	63	37		85	14	1
16	Burrard Inlet (6)	100			75	18	7
17	Burrard Inlet (7)	100			75	20	6
18	Burrard Inlet (8)	100			53	30	17
19	Burrard Inlet (9)	80	20		78	17	6
20	Burrard Inlet (10)	100			52	34	14
21	Burrard Inlet (11)	100			70	23	7
22	Burrard Inlet (12)				80	15	6
23	Burrard Inlet (13)	n.s.	n.s.	n.s.	35	44	21
24	Burrard Inlet (14)	76	24		42	45	13
25	Burrard Inlet (15)	75	25		36	42	22
26	Burrard Inlet (16)	69	31		31	39	30
cont'd next page							
Table 3 cont'd							
No.	Location	Water (%)			Sediment (%)		

		TBT	DBT	MBT	TBT	DBT	MBT
Alberta							
27	North Saskatchewan River (1) (s)						
28	North Saskatchewan River (2)				n.s.	n.s.	n.s.
29	North Saskatchewan River (3)						
30	Bow River (1)				67	33	
31	Bow River (2)				n.s.	n.s.	n.s.
Saskatchewan							
32	South Saskatchewan River (1)				n.s.	n.s.	n.s.
33	South Saskatchewan River (2) (s)						
Manitoba							
34	Red River (1)				35	31	34
35	Red River (2)						
Ontario							
36	Thunder Bay (1)				100		
37	Thunder Bay (2)						
38	Thunder Bay (3)						
39	Nipigon Bay						
40	Terrace Bay				n.s.	n.s.	n.s.
41	Marathon						
42	St. Marys River (1)				76	17	6
43	St. Marys River (2) (s)						
44	St. Marys River (3) (s)				54	46	
45	Midland Bay	59	31	10	40	27	33
46	Pencelung Harbour	100			39	36	25
47	Collingwood Harbour (1)				70	22	9
cont'd next page							
Table 3 cont'd							
No.	Location	TBT	Water (%)	MBT	TBT	Sediment (%)	MBT
			DBT			DBT	

[illegible]

No.	Location	1994				1982-1985			
		TBT	DBT	MBT	TOTAL	TBT	DBT	MBT	TOTAL
1	Nanaimo Harbour					d	d		
2	Esquimalt Harbour	4.1			4.1				
3	Victoria Harbour	3.8	d	d	3.8	d	d	d	
11	Burrard Inlet (1)	5.7			5.7				
27	North Saskatchewan River (1)	d							
28	North Saskatchewan River (2)								
30	Bow River (1)							10	10
31	Bow River (2)								
32	South Saskatchewan River (1)								
33	South Saskatchewan River (2)					d		d	
34	Red River (1)								
35	Red River (2)								
36	Thunder Bay (1)					80	10	d	90
39	Nipigon Bay								
40	Terrace Bay					490	d		490
42	St. Marys River (1)	d				1680	90		1770
44	St. Marys River (3)					110	d		110
49	Collingwood Harbour (3)								
50	Owen Sound Harbour								
53	St. Clair River (3)								
57	Lake St. Clair					70			70
58	Thames River								
61	Detroit River (3)								
64	Port Stanley					290	200	1890	2380
67	Nanticoke								
69	Weiland Canal (1)							d	
75	Niagara River (1)								
83	Belleville					10	1360		1370
85	Port Hope (2)					2340	40	280	2660
87	Whitby Harbour (2)	4.7	d		4.7	1720	740	420	2880
88	Port Credit					30	d		30
89	Humber River					d			
cont'd next page									
Table 5 cont'd									

Table 6. Comparison of butyltin concentrations in sediment (ng Sn/g dry weight) in 1994 (this work) with those from the same locations in 1982-1985.*

No.	Location	1994				1982-1985			
		TBT	DBT	MBT	TOTAL	TBT	DBT	MBT	TOTAL
11	Burrard Inlet (1)	11.0	11.2	6.5	28.7	d			
12	Burrard Inlet (2)	68.9	15.1	7.5	91.5	150	40		190
13	Burrard Inlet (3)	97.7	29.7	13.6	141.0	110	90	20	220
23	Burrard Inlet (13)	77.2	94.9	45.6	217.7	10780	8510	3360	22650
27	North Saskatchewan River (1)		d						
30	Bow River (1)	5.8	2.9		8.7				
33	South Saskatchewan River (2)								
34	Red River (1)	4.3	3.9	4.2	12.4				
35	Red River (2)								
36	Thunder Bay (1)	11.1	d		11.1				
39	Nipigon Bay								
42	St. Marys River (1)	195.0	44.7	16.6	256.3				
57	Lake St. Clair					40	10	d	50
58	Thames River								
61	Detroit River (3)	d	d	d					
64	Port Stanley	d	4.7	4.7	9.4	10	d		10
67	Naincoke	4.6	5.3	d	9.9				
83	Belleville	4.1	3.8	d	7.9				
85	Port Hope (2)		5.3	d	5.3				
87	Whitby Harbour (2)	89.6	49.3	29.3	168.2	160	220	400	780
88	Port Credit	3.7	7.3	6.0	17.0	10			10
89	Humber River		d	d		d			
95	Toronto Harbour (6)	70.6	48.1	36.1	154.8	40		70	110
96	Toronto Harbour (7)	76.8	38.9	26.7	142.4			110	110
102	Kingston Harbour (1)	975.1	390.8	127.1	1493.0		150	210	360
104	St. Lawrence River at Maitland								
112	Richelieu River at Sorel	4.6	4.0	d	8.6	d			
114	Montréal Harbour (1)	198.2	73.8	60.4	332.4	190	350	370	910
115	Montréal Harbour (2)	181.3	79.0	42.3	302.6		40	70	110
116	Montréal Harbour (3)	108.0	56.7	51.3	216.0	40	20	d	60
117	Montréal Harbour (4)	52.1	34.5	34.4	121.0	d		d	
120	Bassin Louise at Québec	55.4	37.1	d	92.5	60	d	d	60

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Table 6 cont'd		1994					1982-1985				
No.	Location	TBT	DBT	MBT	TOTAL	TBT	DBT	MBT	TOTAL		
Frequency of occurrence	Fresh water	17/28	18/28	12/28		8/28	6/28	6/28			
Range of values	Fresh water	3.7-975.1	2.9-390.8	4.2-127.1		10-190	10-350	70-400			
Mean where detected	Fresh water	120.0±230.9	49.5±89.0	36.6±33.8		68.8±68.1	131.7±135.3	205.0±148.8			
Frequency of occurrence	Sea water	4/4	4/4	4/4		3/4	3/4	2/4			
Range of values	Sea water	11.0-97.7	11.2-94.9	6.5-45.6		110-10780	40-8510	20-3360			
Mean where detected	Sea water	63.7±37.2	37.7±38.9	18.3±18.5		3680±6149	2880±4876	1690±1670			
*Sample numbers correspond with those of Table 2. The 1982-1985 results are from Maguire <i>et al.</i> (1986). The statistics presented refer only to those locations common to both studies, not to all locations in each study.											

Species in Influent, Effluent and Sludge from some Canadian Sewage Treatment Plants in 1993 and 1994.*

[illegible]

No.	Location	Water (ng Sn/L)			Sediment (ng Sn/g) (dry weight)		
		TMT	DMT	MMT	TMT	DMT	MMT
11	Burrard Inlet (1)						d
12	Burrard Inlet (2)						d
13	Burrard Inlet (3)						d
16	Burrard Inlet (6)						d
17	Burrard Inlet (7)						d
18	Burrard Inlet (8)						2.7±0.5
19	Burrard Inlet (9)						4.7±0.4
20	Burrard Inlet (10)						5.0±0.4
21	Burrard Inlet (11)	d					8.0±1.8
22	Burrard Inlet (12)						3.2±0.5
23	Burrard Inlet (13)	n.s.	n.s.	n.s.			7.4±1.4
24	Burrard Inlet (14)	d	4.4±0.5				16.6±3.3
25	Burrard Inlet (15)		d				12.8±2.5
26	Burrard Inlet (16)		5.0±0.1				4.0±0.2
Alberta							
29	North Saskatchewan River (3)		4.5±0.2				
31	Bow River (2)	d	d		n.s.	n.s.	n.s.
Ontario							
45	Midland Bay		4.1±0.9				
46	Penetang Harbour		3.5±0.5				
47	Collingwood Harbour (1)		d				
48	Collingwood Harbour (2)	d	d				
49	Collingwood Harbour (3)		d				
58	Thames River	d	d				
59	Detroit River (1) (s)	6.2±1.4	d				
60	Detroit River (2)	5.5±0.2	d				
61	Detroit River (3)	d	d				
62	Detroit River (4)	d					
cont'd next page							
Table 8 cont'd							
No.	Location	Water (ng Sn/L)			Sediment (ng Sn/g) (dry weight)		

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Table 8 cont'd

No.	Location	Water (ng Sn/L)			Sediment (ng Sn/g) (dry weight)		
		TMT	DMT	MMT	TMT	DMT	MMT
Québec							
	114	Montréal Harbour (1)					29.1±4.7
	115	Montréal Harbour (2)					37.1±5.0
116	Montréal Harbour (3)					12.8±1.9	
117	Montréal Harbour (4)		d			12.9±2.7	
118	Montréal Harbour (5)	d			n.s.	n.s.	
119	Montréal Harbour (6)		d			7.5±1.8	
120	Bassin Louise at Québec		d				
121	Québec Harbour						3.8±0.8
122	Québec Harbour - Quai de la Reine		d		n.s.	n.s.	n.s.
New Brunswick							
123	Saint John Harbour						d
Prince Edward Island							
124	Charlottetown Harbour (1)						d
125	Charlottetown Harbour (2)	d					
Nova Scotia							
126	Halifax Harbour (1)						8.1±1.7
127	Halifax Harbour (2)						22.9±4.6
128	Halifax Harbour (3)						13.7±2.8
Newfoundland							
129	St. John's Harbour (1)	d	d				37.4±5.3
130	St. John's Harbour (2)						42.1±10.5
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Table 8 cont'd							
No.	Location	Water (ng Sn/L)			Sediment (ng Sn/g) (dry weight)		

[illegible]

Table 11. Concentrations of octyltin species in sediment in selected Canadian locations in 1993 and 1994.*

No.	Location	Concentration (ng Sn/g) (dry weight)	
		DOT	MOT
Part 1 - 1993			
Ontario			
1	Hamilton Harbour	d	d
Québec			
5	St. Lawrence River at Québec	2.6±0.3	2.7±0.3
Nova Scotia			
9	Sydney Harbour	3.5±1.5	
Newfoundland			
10	St. John's Harbour	d	d
Part 2 - 1994			
British Columbia			
9	False Creek (6)		d
Ontario			
88	Port Credit	d	d
93	Toronto Harbour (4)	d	d
94	Toronto Harbour (5)	3.0±0.0	2.5±0.1
95	Toronto Harbour (6)		d
96	Toronto Harbour (7)	2.7±0.5	2.7±0.6
99	Hamilton Harbour (3)	d	3.1±0.5
100	Hamilton Harbour (4)	21.6±1.7	7.3±0.8
101	Hamilton Harbour (5)	3.0±0.7	4.5±0.7
Québec			
114	Montréal Harbour (1)	4.8±0.9	3.0±0.3
115	Montréal Harbour (2)	3.8±0.6	3.6±1.0
116	Montréal Harbour (3)		d
117	Montréal Harbour (4)	d	d
Newfoundland			
131	St. John's Harbour (2)	2.8±1.0	d

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Table 11 cont'd			
No.	Location	Concentration (ng Sn/g) (dry weight)	
		DOT	MOT
Summary of 1994 data			
Limit of quantitation		2.5	2.5
Limit of detection		0.5	0.5
Frequency of occurrence	Fresh water	6/80 (8%)	7/80 (9%)
Range of values	Fresh water	2.7-21.6	2.5-7.3
Mean where detected	Fresh water	6.5±7.4	3.8±1.7
Median detected value	Fresh water	3.0	3.1
Frequency of occurrence	Sea water	1/32 (3%)	0/32 (0%)
Range of values	Sea water		
Mean where detected	Sea water	2.8	
Median detected value	Sea water		

*DOT - dioctyltin, MOT - monoctyltin. Sample numbers correspond with those of Table 2. Missing location numbers indicate that the octyltin species were not found in those locations. The octyltin species were not found in any water sample. Samples from British Columbia, Nova Scotia and Newfoundland were from sea water, and samples from Ontario and Québec were from fresh water. d - detected, but below limit of quantitation; blanks mean below limit of detection. Sediment samples were divided into three subsamples and analyzed separately. Statistics given above do not include data for the industrial effluent or landfill leachate samples.

[illegible]

Table 13. Concentrations of phenyltin species in sediment in selected Canadian locations in 1993 and 1994.*

No.	Location	Concentration (ng Sn/g) (dry weight)		
		TPT	DPT	MPT
Part 1 - 1993	None detected			
Part 2 - 1994				
British Columbia				
15	Burrard Inlet (5)	25.1±14.1	d	10.2±2.2
16	Burrard Inlet (6)		d	d
17	Burrard Inlet (7)	d	d	d
18	Burrard Inlet (8)			d
21	Burrard Inlet (11)	d	d	d
22	Burrard Inlet (12)			d
Ontario				
42	St. Marys River (1)	14.3±2.9		8.9±0.9
45	Midland Bay			5.7±0.4
72	Port Weller	3.2±0.6	4.3±1.0	5.5±0.6
87	Whitby Harbour (2)	d		d
102	Kingston Harbour (1)	19.6±2.7	d	10.4±2.2
Nova Scotia				
127	Halifax Harbour (2)	27.4±7.2		8.7±2.3
Newfoundland				
131	St. John's Harbour (2)	d		
Summary of 1994 data				
Limit of quantitation		2.5	2.5	2.5
Limit of detection		0.5	0.5	0.5
Frequency of occurrence	Fresh water	3/80 (4%)	1/80 (1%)	4/80 (5%)
Range of values	Fresh water	3.2-19.6		5.5-10.4
Mean where detected	Fresh water	12.4±8.4	4.3	7.6±2.4
Median detected value	Fresh water	14.3		5.7
Frequency of occurrence	Sea water	2/32 (6%)	0/32 (0%)	2/32 (6%)
Range of values	Sea water	25.1-27.4		8.7-10.2
Mean where detected	Sea water	26.3±1.2		9.5±0.8
Median detected value	Sea water			

*TPT - triphenyltin, DPT - diphenyltin, MPT - monophenyltin. Sample numbers correspond with those of Table 2. Missing location numbers indicate that the phenyltin species were not found in those locations. Phenyltin species were not found in any water sample. Samples from British Columbia, Nova Scotia and Newfoundland were from sea water, and samples from Ontario were from fresh water. d - detected, but below limit of quantitation; blanks mean below limit of detection. Sediment samples were divided into three subsamples and analyzed separately. Statistics given above do not include data for the industrial effluent or landfill leachate samples.

Table 14. Concentrations of dicyclohexyltin in sediment in selected Canadian locations in 1993 and 1994.*

No.	Location	Concentration (ng Sn/g) (dry weight)
Part 1 - 1993		
Québec		
5	St. Lawrence River at Québec	3.3±0.1
Nova Scotia		
8	Halifax Harbour	7.1±1.9
Newfoundland		
10	St. John's Harbour	3.5±1.2
Part 2 - 1994		
Québec		
116	Montréal Harbour (3)	3.9±0.8
Newfoundland		
131	St. John's Harbour (2)	13.5±0.9
Summary of 1994 data		
Limit of quantitation		2.5
Limit of detection		0.5
Frequency of occurrence	Fresh water sediment	1/80 (1%)
Range of values	Fresh water sediment	
Mean where detected	Fresh water sediment	3.9
Median detected value	Fresh water sediment	
Frequency of occurrence	Sea water sediment	1/32 (3%)
Range of values	Sea water sediment	
Mean where detected	Sea water sediment	13.5
Median detected value	Sea water sediment	

*Sample numbers correspond with those of Table 2. Missing location numbers indicate that the dicyclohexyltin species was not found in those locations. Dicyclohexyltin was not found in any water sample. Samples from Nova Scotia and Newfoundland were from sea water, and samples from Québec were from fresh water. Sediment samples were divided into three subsamples and analyzed separately. Statistics given above do not include data for the industrial effluent or landfill leachate samples.

Table 15. Concentrations of tripropyltin in sediment in selected Canadian locations in 1993 and 1994.*

No.	Location	Concentration (ng Sn/g) (dry weight)
Part 1 - 1993	None detected	
Part 2 - 1994		
British Columbia		
7	False Creek (4)	3.3±0.7
8	False Creek (5)	d
9	False Creek (6)	3.9±0.7
10	False Creek (7)	3.8±1.3
14	Burrard Inlet (4)	d
15	Burrard Inlet (5)	3.2±1.0
17	Burrard Inlet (7)	3.7±0.5
18	Burrard Inlet (8)	d
19	Burrard Inlet (9)	23.7±1.7
20	Burrard Inlet (10)	5.3±1.8
21	Burrard Inlet (11)	8.8±3.3
22	Burrard Inlet (12)	d
23	Burrard Inlet (13)	6.5±2.1
24	Burrard Inlet (14)	21.1±2.7
25	Burrard Inlet (15)	5.0±0.7
26	Burrard Inlet (16)	d
Ontario		
45	Midland Bay	4.8±0.9
Nova Scotia		
127	Halifax Harbour (2)	18.1±2.8
Newfoundland		
131	St. John's Harbour (2)	2.8±0.7
Summary of 1994 data		
Limit of quantitation		2.5
Limit of detection		0.5
Frequency of occurrence	Fresh water	1/80 (1%)
Range of values	Fresh water	
Mean where detected	Fresh water	4.8
Median detected value	Fresh water	
Frequency of occurrence	Sea water	13/32 (41%)
Range of values	Sea water	2.8-23.7
Mean where detected	Sea water	8.4±7.4
Median detected value	Sea water	5.0

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Table 15 cont'd		
*Sample numbers correspond with those of Table 2. Missing location numbers indicate that tripropyltin was not found in those locations. Tripropyltin was not found in any water sample. Samples from British Columbia, Nova Scotia and Newfoundland were from sea water, and the sample from Ontario was from fresh water. d - detected, but below limit of quantitation. Sediment samples were divided into three subsamples and analyzed separately. Statistics given above do not include data for the industrial effluent or landfill leachate samples.		

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