

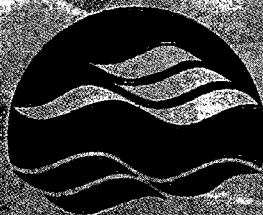
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**PROFILES OF BUTYLTIN COMPOUNDS IN
SEDIMENT CORE AND WATER COLUMN IN THE
MIDDLE OF LAKE ONTARIO**

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NWRI Contribution No. 00-024

Profiles of butyltin compounds in sediment core and water column in the middle of Lake Ontario

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Management Perspective

The antifouling use of tributyltin (TBT) has caused great environmental concern because of its extremely high toxicity. Since the late 1980s, the use of TBT as an antifouling agent has been regulated in many countries. In Canada, regulations were introduced in 1989 under the Pest Control Products Act. TBT-containing paints were not allowed on vessels <25 m in length, with the exception of those with aluminium hulls. In this study, vertical distributions of organotin compounds have been measured in one sediment core and in the water column at two sites in the middle of Lake Ontario. In addition, butyltin compounds were also determined in the three surface sediment samples and paint chips from some small boats. The results of the study indicated that in 1998 TBT was still found in antifouling paints used in small boats, and it was being released into the lake. Compared to harbours and marinas in Lake Ontario, the water and sediment from the middle of Lake Ontario was less contaminated by butyltin compounds.

Sommaire à l'intention de la direction

L'utilisation de l'agent antisalissure tributylétain (TBT) a causé de graves inquiétudes pour la protection de l'environnement à cause de son extrême toxicité. Depuis la fin des années 1980, l'utilisation du TBT comme agent antisalissure est réglementée dans de nombreux pays. Au Canada, on a adopté des règlements en 1989 dans le cadre de la *Loi sur les produits antiparasitaires*. On a interdit l'utilisation des peintures au TBT sur les coques des bateaux de moins de 25 m de longueur, à l'exception de ceux qui ont des coques en aluminium. Dans cette étude, on a mesuré les distributions verticales des composés d'organoétain dans une carotte de sédiments et dans la colonne d'eau à deux sites du milieu du lac Ontario. De plus, on a dosé les composés de butylétain dans trois échantillons de sédiments de surface et dans des éclats de la peinture de certains petits bateaux. Selon les résultats de cette étude, on trouvait encore du TBT en 1998 dans les peintures antisalissure utilisées pour les petits bateaux et il y avait des rejets dans l'eau du lac. Cependant, par rapport aux marinas et aux ports du lac Ontario, l'eau et les sédiments du milieu du lac Ontario étaient moins contaminés par les composés de butylétain.

Abstract

Vertical distributions of organotin compounds have been measured in one sediment core and in the water column at two sites in the middle of Lake Ontario. In addition, butyltin compounds were also determined in three surface sediment samples and in paint chips from some small boats. For the sediment core, only trace amounts of MBT and DBT were found in the top 1-8 cm. Butyltin compounds were detected at a depth of 0.5 m in one water sample, and were not found in the deeper water samples. MBT and DBT were also found in the surface sediments at three sites. Butyltin compounds were quantitatively determined in paint chips from non-aluminium and aluminium hulled boats which were of less than 10 m in length, and the total concentrations in the paint chips ranged from 9 to 402 $\mu\text{g/g}$. The results indicated that TBT was still being used in antifouling paints used in small boats in 1998, and it was being released into the lake. Compared to harbours and marinas in Lake Ontario, the water and sediment from the centre area of Lake Ontario were less contaminated by butyltin compounds.

Key Words

butyltin compounds, Lake Ontario, sediment core, water column, paint chips

Résumé

On a mesuré les distributions verticales des composés d'organoétain dans une carotte de sédiments et dans la colonne d'eau à deux sites du milieu du lac Ontario. De plus, on a aussi dosé les composés de butylétain dans trois échantillons de sédiments de surface et dans des éclats de peinture de certains petits bateaux. Dans le cas des carottes de sédiments, on n'a mis en évidence que des traces de MBT et de DBT dans la couche supérieure de 1 à 8 cm. On a détecté des composés de butylétain dans un échantillon d'eau prélevé à 0,5 m, mais non dans ceux prélevés à une plus grande profondeur. On a également décelé la présence de MBT et de DBT dans les sédiments de surface à trois sites. On a dosé les composés de butylétain dans les éclats de peinture de coques, en aluminium ou non, de bateaux de moins de 10 m de longueur, et les concentrations totales dans les éclats de peinture étaient comprises entre 9 et 402 $\mu\text{g/g}$. Selon les résultats de cette étude, on trouvait encore du TBT en 1998 dans les peintures antisalissure utilisées pour les petits bateaux et il y avait des rejets dans l'eau du lac. Cependant, par rapport aux marinas et aux ports du lac Ontario, l'eau et les sédiments du milieu du lac Ontario étaient moins contaminés par les composés de butylétain.

Mots clés

composés de butylétain, lac Ontario, carottes de sédiments, colonne d'eau, éclats de peinture

INTRODUCTION

The antifouling use of tributyltin (TBT) began in the late 1960s and has caused great environmental concern because of its extremely high toxicity. Release of TBT compounds from antifouling paints into seawater has resulted in deleterious effects on a variety of non-target organisms. The high toxicity of TBT to some shellfish became evident in the mid 1970s¹⁻³. For example, declines in Pacific Oyster (*Crassostrea gigas*) and dogwhelk (*Nucella lapillus*) populations have been attributed to TBT by many researchers.⁴⁻⁸ Since the late 1980s, the use of TBT as an antifouling agent has been regulated in many countries.⁹ In Canada, regulations were introduced in 1989 under the Pest Control Products Act¹⁰⁻¹³. TBT-containing paints were not allowed on vessels < 25 m in length, with the exception of those with aluminum hulls. For vessels > 25 m in length, the release rate of TBT could not exceed 4 micrograms per square centimetre per day.

Two surveys for TBT had been conducted on water and sediment from across Canada in 1982-85 and 1993-94 in order to assess the presence of TBT and the effectiveness of the 1989 regulation of antifouling uses of TBT.^{9,14} The main conclusion from the latter study was that the 1989 regulation had been only partially effective. It had achieved little effect in the reduction of TBT concentration in sediment, probably due to the long persistence of TBT in sediment, and the continual input of TBT from antifouling paints. In many locations the TBT concentrations were high enough to cause acute and chronic toxicity to aquatic and benthic organisms. In 1998, a study of the occurrence and seasonal variation of TBT in five marinas in Lake Ontario was conducted.¹⁵ It was noticed that TBT in the

marina waters primarily originated from antifouling paint on pleasure boats, even though the use of TBT as an antifouling agent was regulated in 1989.

To complement studies of the occurrence of butyltin compounds in marinas and harbours around Lake Ontario, this study reports analyses of sediment and water samples from the middle of the lake. Vertical distributions of organotin compounds have been measured in one sediment core and in the water column at two sites. Three surface sediment samples from the lake, as well as some paint chips from small boats, were also analysed for butyltin compounds.

EXPERIMENTAL SECTION

Apparatus

Analyses were performed with a gas chromatograph - atomic emission detector (GC-AED) system consisting of a Hewlett-Packard model 5890 series II GC equipped with a split/splitless injection port, a Hewlett-Packard model 5921A microwave plasma AED, and a model 7673A autosampler.

Reagents

The carrier gas for the GC-AED system was helium, and the reagent gases were oxygen and hydrogen. All gases were high-purity (99.999%), supplied by Canox Ltd

(Mississauga, Ontario, Canada). Monobutyltin (MBT) trichloride, dibutyltin (DBT) dichloride, tributyltin (TBT) chloride and triphenyltin (TPeT) chloride (used as internal standard) were obtained from Alfa Products (Ward Hill, MA, USA). Ethylmagnesium bromide (1.0 M in tetrahydrofuran) was obtained from Aldrich Ltd. (Milwaukee, WI, USA). All solvents, acids and reagents were of analytical grade. Distilled water, further purified by passage through a Milli-Q system (Millipore, Mississauga, Ontario, Canada), was used throughout. Stock solutions of organotin compounds ($1000 \mu\text{g mL}^{-1}$ as Sn) were prepared in methanol or in toluene. Standard solutions ($0.1 \mu\text{g mL}^{-1}$ as Sn) were made monthly from stock solutions.

Sample collection and extraction

Sample collection. The samples consisted of one sediment core, two water column and three surface sediment samples. A map of the sampling sites is shown in Fig.1. The sediment cores of up to 20 cm depth were collected at stations 1034, 1032 and 1007. At stations 403 and 64, water samples were collected from depths of 0.5 m and then every 30 m to the bottom (depth: 174m at 403 and 194m at 64). The sediment and water samples were collected in June of 1998, and October of 1998, respectively.

The surface sediment samples were collected as follows. The surface sediments were resuspended into water by stirring the water above the sediment cores in tubes, then the water was quickly removed into another beaker. After the sediment deposited at the bottom of the beaker, the water was carefully decanted, and the surface sediments were

freeze dried. The sediment core at station 1034 was sectioned into 1 cm layers and freeze dried.

Paint chips from peeling boats were taken with the owners' permission from 11 non-aluminum and aluminum boats which were being moved out of the water before winter.

Analytical Procedure. With slight modification, the methods of Chau et al.⁹ were used for the determination of butyltin compounds in water, sediment and paint chips. The analytical procedure is as follows. Water samples (2 L) were extracted by spiking with 100 μ L of 100 ppb (as Sn) triphenyltin chloride as internal standard. After the addition of 600 mL of a phosphate buffer solution (17.77 g K_2HPO_4 and 9.41 g citric acid in 1 L water), and 6 mL of sodium diethyldithiocarbamate (NaDDC) solution (2.5 g NaDDC in 10 mL water), the water samples were extracted twice with hexane. After concentration, 1 mL of the hexane extract was ethylated and analyzed using the GC-AED system.

For sediment and paint chip samples, after the addition of acetic acid and water, they were extracted by 0.3% tropolone in toluene with stirring for 1 hour. An aliquot of the extract was removed and evaporated to dryness. The residue was redissolved in 1 mL hexane and ethylated with ethylmagnesium bromide. After clean-up by silica gel micro-column, the extract was analysed by GC-AED.

The limits of detection and quantitation for each butyltin species were 0.3 ng Sn/L and 1.3 ng Sn/L for the water samples, and 0.5 ng Sn/g dry weight and 2.5 ng Sn/g dry weight for the sediment and paint chip samples.

RESULTS AND DISCUSSION

Vertical distribution of butyltin compounds in sediment core, water column and surface sediment samples in the middle of Lake Ontario

The concentrations of butyltin compounds in one sediment core and in water column samples from two sites are shown in Table 1 and Table 2. Trace amounts of MBT and DBT were found in the top 8 cm of the sediment core, with most concentrations lower than the limit of quantitation. The sedimentation rate is low in the middle of Lake Ontario,¹⁶ and the distribution of butyltin compounds in the top 8 cm section of the sediment core could reflect the butyltin contamination in the lake sediment generally. That only MBT and DBT were detectable indicated the complete degradation of TBT in those sediment samples. Butyltin compounds could only be determined at a depth of 0.5 m in one water column and was not found in the deeper water samples. These results indicated a lower butyltin contamination in water and sediment in the middle of Lake Ontario. The interim Canadian water quality guideline for TBT is 3.3 ng Sn/L for the protection of freshwater life.¹¹

The concentrations of butyltin compounds in the three surface sediment samples are shown in Table 3. Only MBT could be quantitatively determined in two samples.

Compared to the concentration of MBT in the sediment core, much higher MBT level found in the surface sediment suggested a recent source of butyltin compounds.

Adsorption and partitioning to particulate material, with subsequent sedimentation, is the primary transport route for butyltin compounds from water to sediment.¹⁷ The finding of

butyltin compounds in the surface sediment suggested that most TBT degraded during its transport from water to sediment in the middle of Lake Ontario. This conclusion was also supported by the low sedimentation rates in these areas. This observation is quite different from the occurrence of butyltin compounds in surface sediment in marinas in where the water depth is less than 3 m, and appreciable amounts of TBT were found.¹⁶ The concentrations of MBT found in different locations were apparently related to boating activity. The highest concentration of MBT was found in station 1007 which is close to Toronto and Hamilton and there is more traffic in this area.

Concentrations of butyltin compounds in paint chips from boats

Butyltin compounds were found in some paint chips collected from aluminum and non-aluminum boats (Table 4), with the total concentration of butyltin compounds ranging from 9 to 402 $\mu\text{g Sn/g}$. The average ratio of $[\text{TBT}]/[\text{Total BT}]$ is 0.45 for non-aluminum boats and 0.60 for aluminum boats. The high concentrations of DBT and MBT were presumably due to aging of the antifouling paint. Larger ratio of $[\text{TBT}]/[\text{Total BT}]$ likely indicates newer paints on the aluminum boats. The results indicated that butyltin compounds were still found in some antifouling paints on small boats in 1998, and still being released into the lake.

In conclusion, butyltin contamination in the middle of Lake Ontario is much lower than in harbors and marinas around the lake, especially for TBT in sediment. Although the use

of TBT has been regulated since 1989, TBT was still found in peeling paint chips from some small non-aluminum boats. TBT-containing antifouling paints are also believed to be applied to some large ships currently visiting Lake Ontario. Therefore fresh input of TBT into the lake still occurs. Because of the effects of dilution and degradation in such a big lake, a lower concentration of butyltin compounds in water and sediment in the middle of the lake was expected. That TBT was not found in sediment at the middle of the lake was believed to be due to the low sedimentation rate, which resulted in degradation of TBT during its transportation from the water surface to the sediment in these areas.

The 1989 Canadian regulation did not recall TBT-containing antifouling paint stocks to the distributor/manufacturer levels, nor stipulate that TBT-containing paints only be applied by licensed applicators¹³. Therefore it is likely that TBT containing paint continues to be used on some small non-aluminum boats in violation of the spirit of the regulation, if not the letter.

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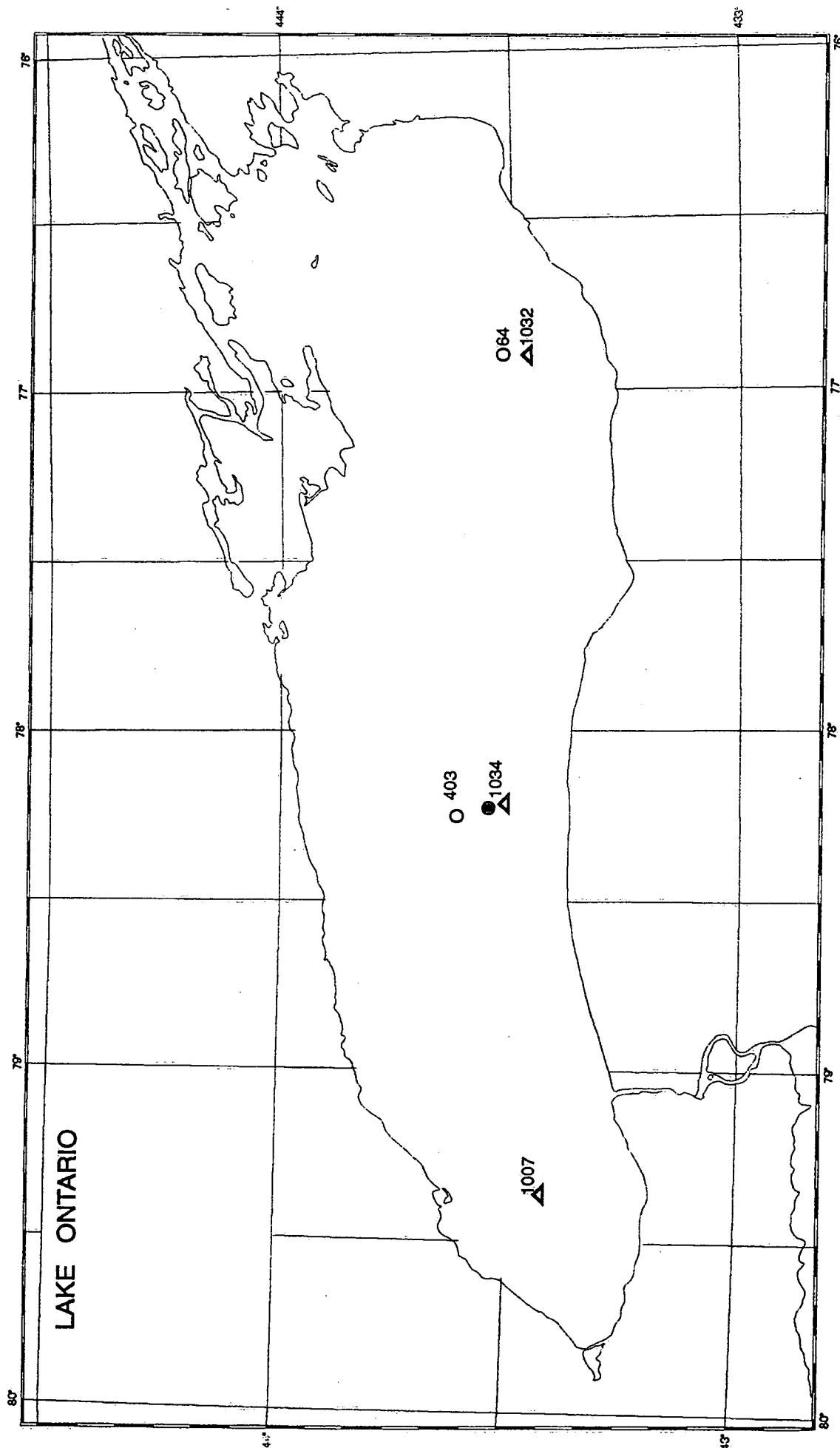


Fig.1. Sampling sites in Lake Ontario (● - sediment core, ○ - water column, Δ - surface sediment).

Table 1. Concentration of butyltin compounds in sediment core at station 1034 in Lake Ontario (ng as Sn/g dry weight)

Depth(cm)	MBT	DBT	TBT
0-1	2.5	d	-
1-2	2.5	d	-
2-3	d	d	-
3-4	d	d	-
4-5	d	-	-
5-6	d	d	-
6-7	d	-	-
7-8	d	-	-
8-9	-	-	-
10-20 *	-	-	-

* determined in every cm from 10-20 cm; d - detected (2.5-0.5 ng as Sn/g dry weight); - not detected (<0.5ng as Sn/g dry weight).

Table 2. Concentration of butyltin compounds in water column samples at station 403 and 64 in Lake Ontario (ng as Sn/L)

Station	Depth(m)	MBT	DBT	TBT
403	0.5	d	d	1.4
	20-174*	-	-	-
64	0.5	-	-	-
	35-194*	-	-	-

* determined in every 30 m; d- detected (1.3-0.3 ng as Sn/L); - not detected (<0.3 ng as Sn/L).

Table 3. Concentrations of butyltin compounds in surface sediment samples in middle of Lake Ontario (ng Sn/g dry weight).

Station	MBT	DBT	TBT
1032	d	-	-
1034	18.9	d	-
1007	28.0	d	-

d - detected (2.5-0.5 ng as Sn/g dry weight); - not detected (<0.5ng as Sn/g dry weight).

Table 4. Concentration of butyltin compounds in paint chips from small boats boats ($\mu\text{g Sn/g}$).

Boat type	Sample	MBT	DBT	TBT	[TBT]/Total BT*
non-aluminum	Paint Chip1	-	-	-	
	Paint Chip2	-	-	-	
	Paint Chip3	-	-	-	
	Paint Chip4	4	18	11	0.33
	Paint Chip5	25	51	40	0.35
	Paint Chip6	24	58	64	0.44
	Paint Chip7	1	2	6	0.67
aluminum	Paint Chip8	14	43	97	0.63
	Paint Chip9	17	30	35	0.43
	Paint Chip10	12	98	292	0.73
	Paint Chip11	32	96	202	0.61

*Total BT = [TBT]+[DBT]+[MBT]; - not detected.

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