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R.J. Maguire and S.P. Batchelor

NWRI Contribution No. 02-311

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Management Perspective

The antifouling agent tributyltin (TBT) is the most toxic chemical that has ever been deliberately introduced to aquatic environments. It is a classic endocrine disrupting substance, exhibiting effects in marine snails at concentrations as low as 0.5 ng Sn/L, and sterilizing female snails at concentrations at about 3-5 ng Sn/L. Many countries have regulated TBT use in antifouling paints, with varying degrees of success with respect to environmental recovery. The International Maritime Organization has recently adopted a ban on TBT in antifouling paints that, if ratified by member States, will see TBT antifouling use banned in 2003, and the presence of TBT on ships banned by 2008. The recent Canadian regulation of TBT antifouling paints is consonant with the IMO initiative. This work illustrates qualitatively the persistence of TBT in a sediment core from Toronto Harbour. Results of this work will be useful to PMRA in its regulation of TBT. The results of this work also provide some support to the conclusion that TBT is a Track 1 substance under Canada's Toxic Substances Management Policy.

Sommaire à l'intention de la direction

L'agent antisalissure tributylétain (TBT) est la substance chimique la plus toxique des produits introduits volontairement dans les milieux aquatiques. C'est un perturbateur endocrinien classique, dont les effets se font sentir sur les limaces à des concentrations de seulement 0,5 ng Sn/L, et qui stérilise les limaces femelle à des concentrations d'environ 3 à 5 ng Sn/L. Beaucoup de pays ont limité l'utilisation du TBT dans les peinture antisalissure, avec divers degrés de succès pour ce qui est du rétablissement environnemental. Dernièrement, l'Organisation maritime internationale s'est prononcée en faveur d'une interdiction du TBT dans les peintures antisalissure qui, si elle est ratifiée par les états membres, prévoit l'interdiction de cette utilisation en 2003, et l'interdiction de la présence de TBT sur les bateaux en 2008. Au Canada, la réglementation récente des peintures antisalissure au TBT appuie l'initiative de l'OMI. Cette étude illustre qualitativement la persistance du TBT dans une carotte de sédiments du port de Toronto. Les résultats de cette étude seront utiles à l'ARLA, qui doit appliquer la réglementation prévue pour le TBT; de plus, ils appuient la conclusion que le TBT est une substance du niveau 1 aux termes de la Politique de gestion des substances toxiques du Canada.

Abstract

The concentration of the antifouling agent tributyltin (TBT) was determined in sections of a dated sediment core collected in 1995 from the Harbour Castle Hilton slip of Toronto harbour. The sediment core shows a peak in TBT concentration of 1769 ng Sn/g dry weight in 1977, which is consistent with its use pattern in Canada and elsewhere, peaking in the early 1980s before the banning of TBT from vessels < 25 m in length in Canada in 1989. The observation of significant concentrations of TBT in pre-1960 core sections (*i.e.*, before its use as an antifoulant) indicates that there has been some downward movement of TBT residues in the core, possibly as a result of diffusion, turbulent physical mixing of sediments in this area, or bioturbation. Consequently, the persistence of TBT in the sediment core could not be estimated with any confidence. Nevertheless, the results provide qualitative support to the notion of the long persistence of TBT in sediment. The TBT concentrations in the sediment core can affect growth in two sensitive benthic organisms, the mayfly *Hexagenia* and the amphipod *Hyalella azteca*. The results support a prediction that there may be a "legacy problem" in sediments in some locations in Canada for perhaps 20 to 30 years after a total ban on TBT in antifouling paints.

Résumé

On a dosé l'agent antisalissure tributylétain (TBT) dans des segments d'une carotte de sédiments datée, recueillie en 1995 dans la darse Harbour Castle Hilton du port de Toronto. La concentration de TBT de cette carotte présentait un maximum de 1 769 ng Sn/g en poids sec en 1977, ce qui correspond bien à son profil d'utilisation au Canada et ailleurs, qui a atteint un maximum au début des années 1980, avant l'interdiction du TBT pour les bateaux de moins de 25 m de longueur au Canada, en 1989. L'observation de concentrations significatives de TBT dans des segments de carottes d'avant 1960 (c.-à-d. avant son utilisation comme agent antisalissure) indique qu'il y a eu un déplacement des résidus de TBT vers le bas dans la carotte, peut-être dû à la diffusion ou au mélange physique turbulent des sédiments dans ce secteur, ou à la bioturbation. Par conséquent, il se peut que l'estimation de la persistance du TBT dans la carotte de sédiments ne soit pas fiable. Néanmoins, ces résultats appuient qualitativement la notion de persistance à long terme du TBT dans les sédiments. Les concentrations de TBT dans les carottes de sédiments peuvent nuire à la croissance de deux organismes benthiques sensibles, l'éphémère *Hexagenia* et l'amphipode *Hyalella azteca*. Ces résultats appuient la conclusion que les sédiments de certaines régions du Canada pourraient causer des problèmes de toxicité jusque 20 à 30 ans après une interdiction totale du TBT dans les peintures antisalissure.

Introduction

The tributyltin (TBT) species[1] is perhaps the most toxic chemical that has ever been deliberately introduced into the aquatic environment. Tributyltin compounds are primarily used as antifouling pesticides, wood and material preservatives, and slimicides (for reviews on TBT and other organotin compounds, see Fent, 1996; de Mora, 1996; Champ and Seligman, 1996; Abalos *et al.*, 1997; Lopez-Avila *et al.*, 1997; World Health Organization, 1999a,b; Maguire, 2000). It is the antifouling use of TBT that has caused the greatest environmental concern, because of its extremely high aquatic toxicity. TBT is a classic endocrine disrupting substance (*e.g.*, Matthiessen and Gibbs, 1998). The induction of "imposex" (the imposition of male sexual characteristics on females) in dogwhelks (*Nucella lapillus*, a marine gastropod) occurs at a TBT concentration of 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). As a consequence of the extremely high toxicity of TBT to aquatic organisms, many countries, including Canada, regulated TBT in the 1980s or early 1990s (see Maguire, 2000). In 2001, the International Maritime Organization (IMO) adopted an "International Convention on the Control of Harmful Anti-fouling Systems on Ships" (International Maritime Organization, 2001). It will enter into force 12 months after 25 States representing 25% of the world's merchant shipping tonnage have ratified it. The announcement called for a ban on the application of TBT-containing paint on ships by January 1, 2003, and a ban on its presence on ships by January 1, 2008. Many countries, including Canada (Pest Management Regulatory Agency, 2000), have been taking regulatory action against TBT-containing antifouling paints in harmony with the objectives and deadlines of the IMO convention.

The persistence of TBT in sediment is a matter of some concern. TBT appears to be at least moderately persistent, with measured half-lives of degradation of the order of months (with the exception of a half-life of 1-4 days for abiotic degradation in sterilized sediments high in silt and clay content reported by Stang *et al.*, 1992), and estimated half-lives for TBT in sediment cores up to 15 years (see Maguire, 2000). Maguire (2000) concluded that the weight of available evidence indicated that the half-life of TBT in sediments is greater than one year, and consequently that TBT met the persistence criterion for sediment (half-life $\geq$ 1 year) for a Track 1 substance under Canada's Toxic Substances Management Policy. To our knowledge the only direct Canadian data (as opposed to inferences from core data) on the persistence of TBT in sediments are from a laboratory study of Toronto Harbour sediments that

[1] The tributyltin (TBT) species and its degradation products, the dibutyltin (DBT) and monobutyltin (MBT) species exist in water as cations (*e.g.*, Bu_3Sn^+) or complexes with other solutes (*e.g.*, Maguire, 1987; Arnold *et al.*, 1997). For brevity, they are referred to here as tributyltin, dibutyltin and monobutyltin. All alkyl groups are *n*-alkyl.

indicated a half-life of five months in the dark (Maguire and Tkacz, 1985). This study was undertaken to estimate from sediment core data the persistence of TBT in sediments in Toronto Harbour *in situ*.

Experimental Section

Materials

Analytical grade organotin standards (purity >97%) were obtained from Aesar/Johnson Matthey (Ward Hill, MA) as their chlorides. Methanol (Caledon Laboratories, Georgetown, Ont.), hexane (Burdick and Jackson, Toronto, Ont.), and toluene (BDH Chemicals, Toronto, Ont.) were used to prepare the stock, the spiking and injection standards and for sediment extractions. Silica gel (Merck, 70-230 mesh) was heated at 200 °C overnight and deactivated by adding 5% (w/w) purified water (Barnstead). Sodium sulfate (BDH Chemicals) and glass µ-columns were heated at 500 °C overnight. All other reagents were used as received from suppliers: sodium chloride, glacial acetic acid (BDH Chemicals), tropolone, ethylmagnesium bromide (Aldrich) and glass wool (Supelco). All glassware was detergent washed and soaked in a 10% nitric acid bath overnight before use. Reagent blanks were run prior to sample analysis and no interferences were observed.

Sediment Core Collection

Four sediment cores were collected from the Harbour Castle Hilton slip in Toronto Harbour on October 25, 1995 (43° 38' 25.6"N; 79° 22' 25.6"W) with a benthos corer (7.5 cm inner diameter). The sediment was silty-clayey, with a colour transition from light brown at the top of the cores to light gray at the bottom. Samples were immediately extruded (using a concentric stainless steel ring of diameter 5.0 cm to avoid sampling the outer smeared portion of the core) and placed into prewashed polycarbonate jars and frozen. Cores 1, 2, and 3 were sampled in 1 cm sections for the first 10 cm, and then in 5 cm section to 30 cm. The fourth core was sampled in 1 cm slices for the entire length (88 cm) in order to do dating analysis in addition to the butyltin analysis.

Sediment Core Dating

The sections from the fourth core were weighed, freeze-dried, and then reweighed. These weights were used to calculate porosity and the uncompacted depth. The core was dated using a variation of the procedure of Eakins and Morrison (1978) that is standard procedure at the National Water Research Institute (Turner, 1990), and the results for the core analyzed for this study are given in Turner (1996). There was very close agreement in core sample dates between the two Constant Initial Concentration model approaches (uncompacted depth and cumulative dry weight) and the Constant Rate of Supply model

(cumulative dry weight) down to an approximate uncompacted depth of 106 cm, corresponding to the year 1954. Disagreement between model estimates below an uncompacted depth of 106 cm was thought to be due to variability in sedimentation rate.

Sediment Analysis for Butyltin Species

All samples were freeze-dried and ground with a mortar and pestle and stored at room temperature in their original jars in a dark environment until extracted. Any large particles such as zebra mussels or wood chips were removed from the sample prior to grinding. Wet and dry weights were recorded to determine moisture content.

Analyses of the butyltin species were done generally according to methods established previously (*e.g.*, Chau *et al.*, 1997), which are described briefly here. A 1 g subsample was placed in a 250 mL screw-top Erlenmeyer flask, spiked with 200 µL of a 5 ppm tripentyltin chloride (TPeTCl) solution in methanol and allowed to dry at room temperature. Sodium chloride (8 g), purified water (20 mL), glacial acetic acid (20 mL), and 15.0 mL of a 0.1% (w/v) tropolone in toluene solution were added and stirred magnetically for 1 hour. A 4.0 mL aliquot of the organic phase was then transferred to a test tube, and evaporated under a gentle stream of nitrogen at 35 °C until almost dry. (In some cases, it was necessary to centrifuge the sample in Teflon bottles at 4000 rpm for 15 minutes to separate the aqueous and organic phases before an aliquot was removed.) Hexane was then added with stirring to the test tube, followed by 300 µL of the derivatizing agent ethylmagnesium bromide (3 M in ethyl ether), which was allowed to react for at least 10 minutes. The excess Grignard reagent was removed by extracting the sample with 2 mL of 0.5 M sulfuric acid. The hexane layer was passed through a µ-column containing 4 cm of prerinsed silica gel and a layer of sodium sulfate. The eluant was evaporated at room temperature under nitrogen to a final volume of 1.0 mL.

Analyses of the tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT) derivatives, and that of the surrogate spike, tripentyltin (TPeT), were performed using a Hewlett-Packard 5890 Series II gas chromatograph equipped with a splitless injector, dual columns, and two detectors, a flame photometric detector (FPD) and a mass spectral detector (HP 5971A). The dimensions of both columns were 0.25 mm i.d x 30 m length x 0.25 µm film thickness (DB-5, Chromatographic Specialties, Brockville, Ont. and HP-5MS, Hewlett-Packard, Palo Alto, CA) The FPD was used for quantitative analysis by running an external standard containing known concentrations of the three butyltin species and tripentyltin. The fuel gas flow rates were 100 mL/min for both the hydrogen and air. The helium carrier gas and the nitrogen auxiliary gas flow rates were 0.75 and 30 mL/min, respectively, at 50 °C. The FPD was fitted with a filter that allowed 80% light transmittance over the wavelength range 610-2200 nm (Corion

Inc., Holliston, MA). The mass spectral detector was used in single ion monitoring (SIM) mode for qualitative confirmation of identity. The ions used were m/z 121, 149, and 179 for MBT and DBT, 121, 149, and 177 for TBT, and 121, 151, and 221 for TPeT. Concentrations of the butyltin species in sediment are reported in units of ng Sn/g dry weight. The limit of quantitation for TBT, DBT and TPeT (3 x noise) was approximately 5 ng Sn/g dry weight for a 1-g dry sediment sample, and 10 ng Sn/g dry weight for MBT. Concentrations of the three butyltin species were corrected for recovery of TPeT (average 104%±12% for all cores, range 70%-136% for the dated core 4, n = 88).

Results and Discussion

Figure 1 shows the concentrations of the three butyltin species in sediment core 4. The depth profiles in the other three sediment cores were generally similar to that of core 4, but because they were not dated, they will not be discussed further. Core 4 shows a peak in TBT concentration of 1760 ng Sn/g dry weight in 1977, which is consistent with its use pattern in Canada and elsewhere, peaking in the early 1980s before the banning of TBT from vessels < 25 m in length in Canada in 1989. However, the observation of significant concentrations of TBT in pre-1960 core sections (*i.e.*, before its use as an antifoulant) indicates that there has been some downward movement of TBT residues in the core, possibly as a result of diffusion, turbulent physical mixing of sediments in this area, or bioturbation. The Harbour Castle Hilton slip had apparently not been dredged for at least 25 years preceding core sampling. Significant concentrations of the two degradation products DBT and MBT were also found throughout the core, but TBT was clearly the predominant species.

The concentrations of TBT found in the sections of the sediment core were in the range 14-1760 ng Sn/g dry weight (mean 496 ng Sn/g dry weight, n = 71). That range is about 5-30 times higher than concentrations found in five sediment cores taken from British Columbia harbours in 1993 (Stewart and Thompson, 1997). TBT concentrations in sections of this sediment core were also generally much higher than those found in a 1994 survey of TBT in surficial sediment in freshwater in Canada (Chau *et al.*, 1997). In that study, TBT was found in 42 of 80 locations, with a range of 4-975 ng Sn/g dry weight, a mean concentration where detected of 100±173 ng Sn/g dry weight, and a median detected concentration of 33 ng Sn/g dry weight. There is considerable potential for toxicity to benthic organisms of the TBT in sediment at the Harbour Castle Hilton slip. Day *et al.* (1998) determined the toxicity of TBT in sediment in fresh water to four benthic invertebrates, the oligochaete worm *Tubifex tubifex*, the chironomid *Chironomus riparius*, the amphipod *Hyalella azteca* and the mayfly *Hexagenia*. The results of that work indicated that *Hexagenia* was the most sensitive benthic organism to TBT of the four organisms tested (by factors up to about 7), with an IC_{50} (growth) value for TBT of 600 ng Sn/g dry weight. That

value is only slightly higher than the mean TBT concentration of the sediment core of 496 ng Sn/g dry weight. The TBT concentration at several depths in the sediment core exceeds the IC_{50} (growth) value for TBT of 600 ng Sn/g dry weight in *Hexagenia*, as well as the IC_{50} (growth) value for TBT of 1400 ng Sn/g dry weight in *Hyalella azteca* (Day *et al.*, 1998).

Some researchers have estimated degradation half-lives of TBT from sediment core profiles in the range of about 1-15 years (see Table 1). Such estimates must be viewed with caution because they are based on several questionable assumptions such as constant sedimentation rate, constant flux of TBT to the sediments, ignoring post-depositional processes such as bioturbation, and degradation being the only removal process for TBT. For core 4 in this study, and assuming first-order kinetics, a plot of ln[TBT] vs. time in years from the time of the [TBT] maximum in 1977 to the bottom of the core indicated a good linear fit, with $r^2 = 0.87$ and a slope (k) of –0.0416. The first-order half-life of decay, ($T_{1/2} = -(\ln 2)/k$), is 16.7 years. Although such an estimated half-life is consistent with some earlier estimates, it is felt that this estimate is unreliable in view of the observation of TBT in core sections corresponding to dates before TBT was used as an antifoulant, and in view of the assumptions described above. However, the observation of significant concentrations of TBT in sediment from this location in Toronto Harbour dating back more than 20 years is qualitative evidence of the persistence of TBT in sediment, and supports a prediction (Maguire, 2000) that there may be a "legacy problem" in sediments in some locations in Canada for perhaps 20 to 30 years after a total ban on TBT antifouling paints.

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Table 1. Estimated TBT degradation half-lives from sediment core data			
Medium	**Half-live, years**	**Location**	**Reference**
Fresh water/estuarine sediment	0.9-5.2	Southeast England	Dowson *et al.* (1993)
Estuarine sediment	3.8	Georges River, NSW, Australia	Kilby and Batley (1993)
Marine sediment	1.85	Tamaki Estuary, Auckland, N.Z.	de Mora *et al.* (1989)
	> 8-15	Arcachon Bay, France	Astruc *et al.* (1990)
	6.9	Chinhae Bay, Korea	Hwang *et al.* (1999)
	8.7	A marina on Vancouver Island, B.C.	Stewart and Thompson (1997)
	2.1	Oleron Island, France (southwest Atlantic coast)	Sarradin *et al.* (1995)
	2.5	Near Auckland, N.Z.	de Mora *et al.* (1995)

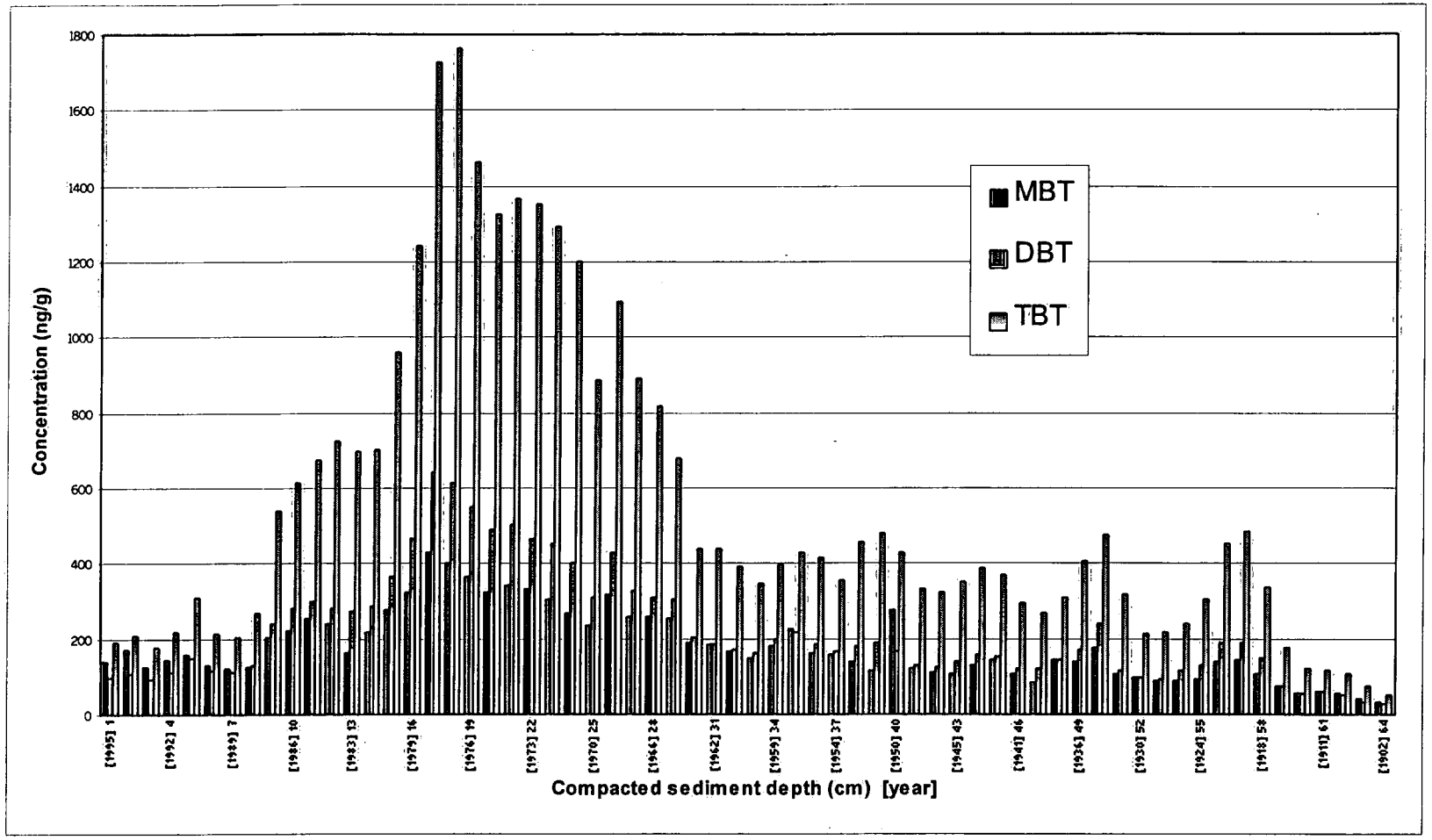

Figure 1. Concentrations (ng Sn/g dry weight) of TBT, DBT and MBT as a function of compacted (natural) depth and date in sediment core 4 from the Harbour Castle Hilton slip, Toronto Harbour, 1995.

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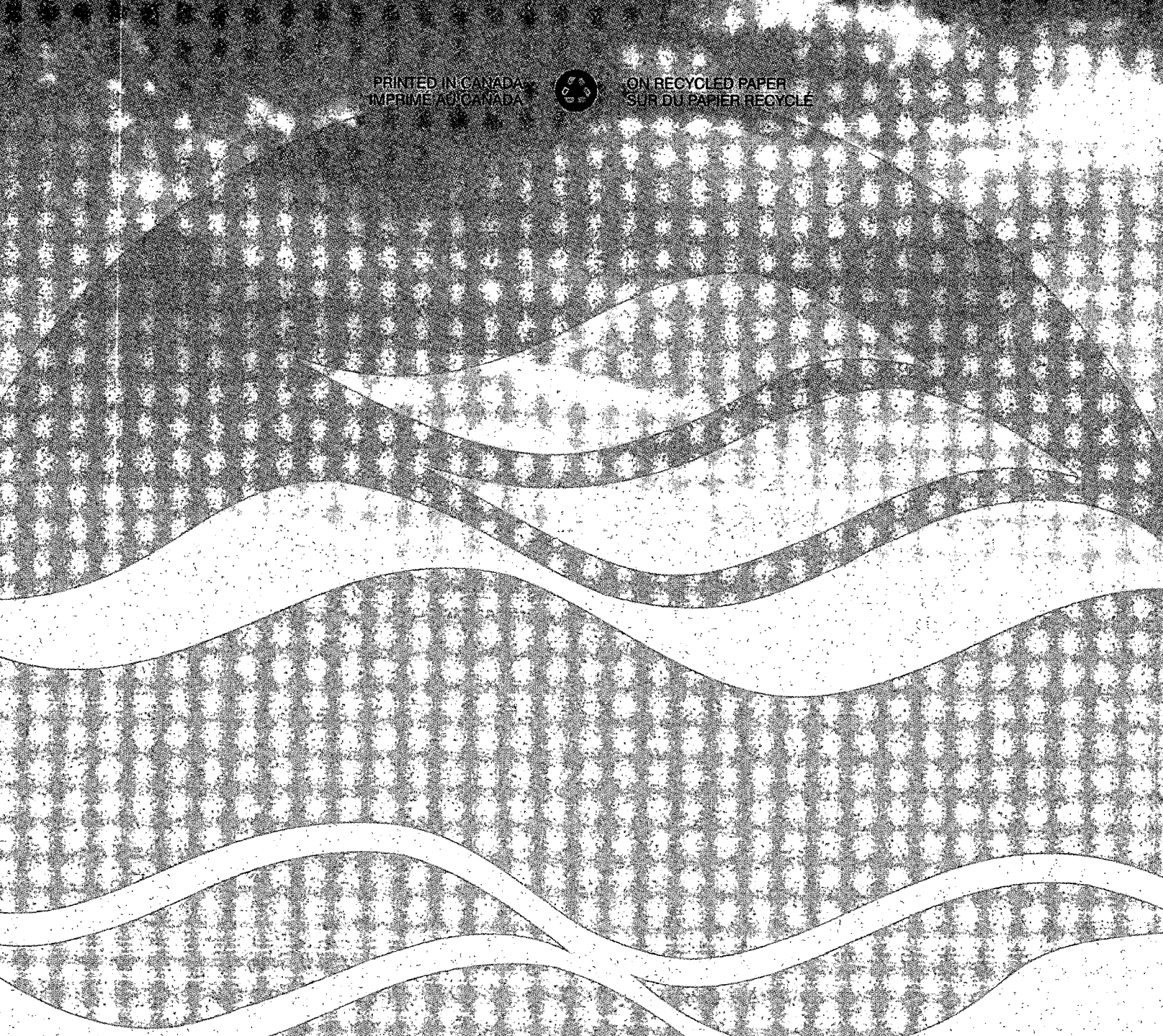

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