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THE STATUS OF THE ORGANOTIN ISSUE IN CANADA

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EXECUTIVE SUMMARY

The Status of the Organotin Issue in Canada

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An account is given of how the organotin issue developed in Canada, how it was addressed under the Environmental Contaminants Act, how it is presently being managed under the Pest Control Products Act, and NWRI's contribution in demonstrating the occurrence and persistence of the very toxic tributyltin species.

Management Perspective

Agriculture Canada is now requiring that tributyltin-containing antifouling paints be registered under the Pest Control Products Act. Such a requirement will allow interested departments such as DOE an opportunity to register objections to registration. It appears that the likely resolution of the tributyltin problem will be a ban on TBT-containing paints on boats less than 25 m in length.

RÉSUMÉ ADMINISTRATIF

État de la question de l'organo-étain au Canada

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Il s'agit d'un compte rendu sur les points suivants : comment le problème de l'organo-étain s'est développé au Canada, comment on s'y est attaqué en vertu de la Loi sur les contaminants de l'environnement, comment on le gère actuellement en vertu de la Loi sur les produits antiparasitaires et enfin comment l'INRE contribue à montrer l'apparition et la persistance des formes très toxiques d'étain tributyle.

Perspective-gestion

Agriculture Canada exige maintenant que les peintures antisalissure à l'étain tributyle soient enregistrées en vertu de la Loi sur les produits antiparasitaires. Les ministères touchés, comme le MDE, pourront ainsi recueillir les objections portées contre l'enregistrement de tels produits. L'interdiction de l'utilisation des peintures à l'étain tributyle sur les bateaux de moins de 25 m semble la solution la plus probable au problème de l'étain tributyle.

The Status of the Organotin Issue in Canada

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The intent of this paper is to present the regulatory status of organotins (OTs) in Canada as of September, 1987. To put this into perspective there is a need: first, to identify the mandate under which government resources have been spent to obtain information as a basis for the assessment and regulated use of organotins in Canada; second, to identify current data gaps as to sources and quantities of OTs to the environment; third, to relate the major accomplishments of research projects carried out under the environmental assessment mandate; and fourth, to relate current issues associated with use of organotins in Canada and the need for regulations.

The Environmental Contaminants Act came into force April 1, 1976, under the purview of the Department of Fisheries and Environment and the Department of National Health and Welfare. It was implemented in part, through development of a List of Priority Chemical Substances. This List has been amended periodically as needed as new information has been acquired. The List, as the name implied, provided priority ranking to those substances which had been identified and designated as toxic or hazardous and for which investigative or regulatory action was required (1).

The current Priority List as set out in the Canada Gazette (2) has three categories described as follows:

Category I: Those substances for which regulations or specific control strategies are being developed under the Environmental Contaminants Act;

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Category II: Those substances which are being investigated to determine the nature and the extent of the danger to human health or the environment and the appropriate means to alleviate the danger;

Category III: Those substances which may pose a significant danger to health or the environment and about which further detailed study or information (for example toxicology, amounts used or concentrations in the environment) is necessary.

For example, chemicals representative of those in Categories I, II, and III are polychlorinated biphenyls, chlorobenzenes, and organotins, respectively.

Organotins have been in the Priority Chemicals List, Category III, since its inception, when it was announced in the Canada Gazette (3) that: "The number and quantities of these substances currently in use are large and increasing. The number of particular uses, many of which suggest losses to the environment, is also increasing." Organotins were suggested for inclusion in the List of Priority Chemicals because they constituted a relatively novel group of compounds (viz. organometallics) and some were known to be highly toxic to microorganisms. Although some basic information was known about these intriguing organo-metallic compounds, there was little information available which would permit an assessment of their danger to health or the environment in Canada.

This lack of information was confirmed by Environment Canada through a detailed review of organotins by M.F. Millson and P.A. Jones in 1979. Abbreviated versions of the review were made available as an in-house information note (4) and in a synopsis report (5). Distribution of these information summaries was to researchers and other interested parties to identify the information gaps which needed to be filled before further assessment of the organotins could be undertaken. The information needs were characterized in the synopsis report (5) as follows:

1. Identification of the chemical species of OTs in the environment and determination of their concentration.
2. Determination of the fate of OTs in the environment, especially their rates of degradation, the nature of their transformation products, and their sorption properties.
3. Determination of the bioaccumulation and chronic toxicity of OTs.
4. Identification of trends in the quantities and types of organotins imported, produced, and used in Canada.

The most heavily consumed OTs in Canada and their major uses are those in Table 1 (5).

Table 1 ORGANOTINS USED IN CANADA (Jones et al., 1982)

	Compounds	Use
(1)	dibutyltin bis (isooctylmercaptoacetate)	stabilizer for PVC used in siding, eavestrough, and soffits
(2)	dibutyltin dilaurylmercaptide	polyurethane foam catalyst; feed additive
(3)	*stannous 2-ethylhexoate (m)	polyurethane foam catalyst
(4)	dibutyltin oxide	precursor for dibutyltin dilaurate
(5)	dibutyltin dilaurate (m)	chicken feed additive; catalyst for urethanes; esterification catalyst
(6)	tributyltin oxide (TBTO)	slimicide in cooling water towers; antifouling additive for marine paint; wood preservative
(7)	tributyltin fluoride (TBTF)	antifouling additive for marine paint
(8)	dioctyltin maleate	stabilizer for rigid PVC pipe for potable water supplies
(9)	dibutyltin diacetate	catalyst for flexible foams
(10)	dioctyltin bis (isooctylmercaptoacetate)	stabilizer for plastics used in food packaging

*not a true organotin as defined in Jones et al., 1982

(m) manufactured in Canada

The estimated total annual Canadian market for OTs in the early 1980's was in excess of one million kilograms. At that time estimates were made of end uses for OTs as follows: PVC stabilizers, 80-82%; catalysts, 16-17%; and bioactive or biocidal uses, 2-3% (5). More recent information on OT consumption to establish trends is not available, but based on estimates derived from Statistics Canada import data, the total consumption of OTs remains at approximately the same level (6).

The OTs used in bioactive products include three main compounds:

fenbutatin oxide
cyhexatin
tributyltin oxide (TBTO)

These three compounds are currently registered as pesticide active ingredients under the Pest Control Products Act (PCP Act) which is administered by Agriculture Canada (7). Fenbutatin oxide is used in very limited quantities as a miticide in fruit and vegetable production, as is cyhexatin. However, the U.S. registrants for cyhexatin are in the process of voluntarily withdrawing the cyhexatin registrations worldwide, and in that context cyhexatin is now being withdrawn from the Canadian market as of August, 1987 (8, 9).

Tributyltin oxide (TBTO) is the active ingredient in 46 different products used as wood preservatives, slimicides, and material preservatives that are registered under the PCP Act by 16 registrants (10). Unregistered and unaccounted for is the TBT in the multitude of paints and coatings used as anti-foulants and marine growth inhibitors on commercial ship and pleasure craft hulls and steel and wood structures exposed to marine and freshwater environments. With respect to these currently unregistered products Agriculture Canada has informed the paint and coatings industry, through the release of a Trade Memorandum, T-1-254, dated Feb. 12, 1987, of a requirement to register both active ingredients in, and end-use products for, antifouling paints and waxes in accordance with Section 4 of the Pest Control Product Act (11). As noted in the T-memorandum these registration requirements will serve a minimum of two purposes with respect to information needs for assessment of these products. First, for those antifouling paints and waxes containing TBT, release rate data will be required and will be submitted when application is made for registration, and second for all the active ingredients in this class of pest control products, additional data on environmental effects will be submitted for assessment. Applications for the registration of antifouling paints and waxes were to be submitted to Agriculture Canada prior to October 1, 1987.

In the short term there is an immediate need to curb unwitting releases of TBT into the environment, such as has occurred recently when products which contained the very toxic TBT as the active ingredient were used to treat salmon pen nets and lobster traps to extend their useful life.

In British Columbia, as in other areas, fin fish farming is a growth industry with 1985 sales of salmon close to $1.5 million and projected sales of $100 million by 1989 (12). Use of anti-foulants on salmon farm nets, which is an unregistered use under the PCP Act, led to mortality and shell thickening in oysters in adjacent shell fish prodution areas (13). This problem was not confined to the west coast of Canada but also occurred in the Maritime provinces as well (14). Use of TBT treated nets had not only affected oyster production but has also led to contamination of salmon (15). The status and resolution of this problem was that in February 1987 Agriculture Canada successfully impounded the TBT containing products used for net treatment (16). As well, the B.C. Salmon Farming Association circulated an information bulletin to member companies advising against use of TBT-treated sea pen nets (17). In addition to these steps, on Feb. 24, 1987 representatives of several aquaculture companies, net pen manufacturers, and the federal and provincial governments involved with the fin fish industry met to discuss development of voluntary quality control standards for aquaculture equipment and products which will include chemicals and antibiotics used by the industry (18).

Use of TBT containing products to treat wooden lobster traps, currently an unregistered use under the PCP Act, has been a continuing concern in the Maritime provinces. There has been no resolution of this problem.

Organotins as produced and used in Canada can enter the environment at time of production, during processing, from product use, and through disposal. Losses via these routes are largely unknown.

In Canada, losses, if any, to the environment at time of OT production would be limited to one site, since there is only one known manufacturing facility. This one converts dibutyltin oxide to dibutyltin dilaurate. Losses during production are probably minimal and the wastes are treated chemically before disposal (5).

Another source to the environment is during processing when OTs may be released into air, water or solid industrial wastes from plants that produce polyurethane or PVC resins stabilized with OTs. Unknown quantities of OTs enter the environment via this route (5).

Also unknown are the quantities of OTs released to the environment through their use as biocidal coatings and preservatives, since there is little knowledge as to the quantities used for these purposes and their rate of leaching from treated material (5). Statistics Canada had estimated that the total imports in 1986 of TBTO for all purposes exceeded twelve metric tonnes (6).

Another source of OTs to enter the environment is through their direct application into the environment for crop protection purposes, as the active ingredient in miticides. As noted previously, this source is very limited since use is now restricted to only one minor use product, fenbutatin oxide.

Quantities of TBTO released to the environment as a result of its registered uses in wood preservatives, slimicides, and material preservatives are also unknown (5). Furthermore, information on quantities of TBTO consumed for these purposes is not publicly available.

Since the majority of OTs are used as stabilizers and catalysts in industrial and consumer products, then it follows that the bulk of the losses of OTs to the environment should occur when the products are ultimately disposed of in landfills or through incineration (5). However the quantities of solid wastes in Canada containing OTs is unknown as is the leaching rate of OTs from the plastic matrices in landfills under Canadian conditions. Although it is unclear whether the loss of OTs into the environment via this route is of significance it is assumed that it will be minimal since the calculated value for life-time leaching of OTs from plastic matrices is in the order of thousands of years (19).

Excluding the organotin bioactive products only a bare minimum of information is available on OT uses, consumption, sources to the environment, and fate following disposal. This lack of specific information prohibits a full and meaningful assessment of the impact on the environment of the majority of OTs consumed in Canada. It is anticipated that the next initiatives undertaken by government will address the information gaps identified above to further an assessment of OTs to determine if there is a need for regulation of the non-biocidal uses of OTs under current or proposed legislation.

In a more positive vein knowledge of the occurrence and concentration of OTs in the Canadian environment has been greatly expanded during the past several years. This was made possible by the development of suitable analytical systems followed by or in conjunction with surveys for organotins in water, sediment, and biota.

Although research on suitable analytical systems for OTs was carried out at various centres in Canada, the main effort was centered at the National Water Research Institute (NWRI) at Burlington, Ontario.

Maguire and Huneault (20) refined an earlier method for analysis of OT compounds which involved 1) extraction of tributyltin, dibutyltin, monobutyltin, and Sn^{4+} from water; 2) derivatization with a pentyl Grignard reagent to form the various butyl-pentyl- tin species, and 3) analysis by gc-fpd.

Following development of suitable methods to detect and quantify organotins in environmental samples and with the knowledge that tri-n-butyltin produced maximal biological activity (21), then research was directed towards studies of the butyltins. The first concrete result of this effort was the identification of tributyl tin at levels that were biologically significant in samples of Canadian water from four widely spaced locations in the Great Lakes basin (22).

These initial findings were supplemented when butyltin and methyltin species were reported in water samples from lakes, rivers, and harbors from the western edge of Lake Superior to the St. Lawrence River (23).

As the next logical step, a method was developed for analysis of butyltin species and inorganic tin in sediments (24). As a result of analyses of Ontario lake, river, and harbor sediments for these compounds, Maguire (24) reported that although inorganic tin occurred frequently in sediments at most collection stations where OTs had been reported in water, butyltin species were found mainly in the harbor sediments. Although tri-n-butylmethyltin and di-n-butyldimethyltin were identified in four harbor sediments, and although this was considered as evidence that some butyltin species could be methylated in aquatic environments (24), it was later discounted as a significant pathway for transformation of butyltin species because in a national survey for OTs their presence in sediment samples occurred so infrequently (25).

A comprehensive report on the extent of contamination of waters on the Canadian side of the Great Lakes basin by methyltin and butyltin compounds was compiled, primarily from previously reported results of analyses of water and sediment, as referenced above (26). Also provided were analytical results for methyltin species in selected whole fish samples from two small harbors in Lake Ontario. The majority of the tin in these samples was present as monomethyltin at less than 1 ppm, wet weight.

During this stage of the OT investigations, Thompson et al. (27) reviewed, in depth, the available literature on analyses, occurrence and fate of OTs in the environment and concluded that further information on those OTs likely to occur in Canada, including methyl-, butyl-, phenyl-, and cyclohexyltin, would be required before environmental and human health risk assessments could be made.

On-going with the OT field studies were laboratory studies on some physical and chemical characteristics of the tributyltin (TBT) cation, as derived from TBTO, which provided an estimate of its aquatic persistence and its routes of degradation and dissipation (23). The bottom line was that in the absence of other faster degradation processes, the sunlight photolysis of the TBT moiety, although slow ($t_{1/2}$ >89 days), was the significant chemical route of TBT degradation in natural waters at depths no greater than 0.5-1m. At greater depths, biotransformation was credited as the limiting factor in persistence of TBT in fresh water ecosystems; where the estimated half-life at 20°C was in the order of 6 weeks to a few months (23, 28, 29, 30).

Other routes investigated for dissipation of TBT included bioaccumulation and biotransformation. At algal cell concentrations far in excess of natural populations the green alga, Ankistrodesmus falcatus, exposed to sublethal concentrations of the TBT cation converted 50% of the TBT to dibutyltin as the major product over a 4 week period at 20°C. During that period there was an estimated apparent algal bioconcentration factor of 3×10^4 (31). Additionally, Maguire and Tkacz (28) demonstrated that oligochaetes could take up and degrade sediment-associated TBT, thus making it potentially available to bottom feeding fish.

In summary, evidence to date indicates that the limiting factor in persistence of TBT in freshwater ecosystems is biological degradation and the half-life of degradation under Canadian conditions would be of the order of several weeks or longer.

With adequate protocols developed to determine the presence and concentration of OTs in fresh water ecosystems, with emphasis on the Great Lakes basin, then a national survey was undertaken for butyltin and methyltin species and inorganic tin in fresh water and marine waters (25). When completed, all ten provinces were represented by the water and sediment samples from 265 locations. In 10% of the water samples TBT was found at concentrations which could cause growth retardation to rainbow trout yolk sac fry, one of the more sensitive stages and species, when chronically exposed. High concentrations of TBT were found in some sediment samples, primarily from harbors with heavy shipping traffic and low flushing rate, e.g., Vancouver harbor. However, in general the bioavailability of the sediment-associated TBT is unknown. In comparison to the general presence of TBT and its transformation products in water and sediment, methyltin species were found much less frequently and were confined to major shipping channels and harbors (25).

The initial survey for OTs in Ontario waters identified high concentrations of OTs in samples of unfiltered surface microlayer water (23). More recently high concentrations of TBT were found in 24 surface microlayer samples in a survey of 74 locations in Ontario, Quebec and New York State (32). In 6 of these 24 locations the concentrations of TBT in the surface micro layer exceeded the 24-hr LC-50 value for adult rainbow trout, and at one location in Ontario it was 42 times that value. At a few locations the concentration of butyltins in the surface microlayer was so much greater than that in the subsurface water that the microlayer contained a significant amount of the dibutyltin relative to the total in the whole water column.

The work carried out on TBT and its transformation products over the past few years at the National Water Research Institute has now been placed in perspective to the work on OTs carried out elsewhere, through a recent review by Maguire (33) of methods of analysis, toxicity, environmental occurrence, persistence and fate. In addition, it was proposed that information gaps still extant on OTs could be closed by instituting research responding to the following: 1) development/refinement of analytical methods for TBT and its transformation products in water, sediment, fish and shellfish tissue; 2) further development of low cost resin sampling techniques for TBT and its transformation products in water; 3) determination of the bioavailability of TBT in sediments; 4) determination of the temporal variability of TBT in subsurface water and the surface microlayer at any particular location; and 5) determination of the persistence of TBT in a variety of different ecosystems in order to develop predictions in other locations. Information obtained through addressing these information gaps should, over a period of time, provide a broader and sounder data base for assessment of the bioavailability, persistence and fate of OTs already present in or being released into the environment.

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