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CHEMICALS IN THE ENVIRONMENT

VII. ORGANOTIN COMPOUNDS

Regional Program Report No. 95-06

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CHEMICALS IN THE ENVIRONMENT REPORT SERIES

This report is one in a series entitled "Chemicals in the Environment - Pacific and Yukon Region" prepared by Environment Canada, Environmental Protection Branch (EPB) - Pacific and Yukon Region. The objective of these reports is to provide the technical guidance necessary for: a.) the interpretation of environmental quality data on specific chemicals, and b.) the assessment of potential impacts resulting from the release of these chemicals into the environment.

The series focuses on both naturally occurring and synthetic compounds whose release to the environment is of concern due to their persistence, toxicity and/or bioaccumulative abilities.

These reports discuss highlights of existing environmental quality data for British Columbia and the Yukon. They provide information on environmental dynamics, potential impacts on the environment, and pertinent legislation and guidelines controlling both releases to the receiving environment and environmental quality.

This report is adapted from Garrett, C.L. and J.A. Shrimpton, "Organotin Compounds in the British Columbia Environment," Environmental Protection Branch, Pacific and Yukon Region, in preparation.

ABSTRACT

This report provides a summary of information on organotin compounds in the British Columbia environment obtained as a result of studies conducted by Environment Canada - Pacific and Yukon Region between 1984 and 1995. These studies were conducted to determine the presence of organotin compounds near known or suspected sources of release to the coastal environment of British Columbia. Although the studies focused primarily on butyltin compounds, limited information on cyclohexyltin and phenyltin compounds was also obtained.

The objective of this report was to document existing information on organotin compounds in British Columbia with respect to levels in the environment; past and present uses; current legislation and guidelines controlling the use and release of these compounds; and, where possible, the efficacy of these measures in reducing releases and improving environmental quality.

A general overview of toxicity and environmental levels of these compounds in other areas of Canada and the world has been provided to allow the reader to put the data for British Columbia into perspective.

RESUME

Ce rapport fournit un sommaire d'informations sur les composés organiques de l'étain dans l'environnement de la Colombie-Britannique et est le résultat d'études conduites par Environnement Canada - Pacific et la Région du Yukon entre 1984 et 1995. Ces études ont été conduites pour déterminer la présence de composé organiques de l'étain dans l'entourage des sources connues ou suspectées de diffusion à l'environnement côtier de la Colombie-Britannique. Bien que les études se soient concentrées sur les composés de butylétain, des informations limitées sur les composés de cyclohexylétain et phenylétain furent aussi obtenues.

L'objectif de ce rapport était de documenter les informations existantes sur les niveaux de diffusion dans l'environnement des composés organiques de l'étain en Colombie-Britannique; leurs utilisations passées et présentes; la législation courante et les directives contrôlant l'utilisation et la diffusion de ces composés; et, quand c'est possible, l'efficacité de ces mesures en réduisant les diffusions et en améliorant la qualité de l'environnement.

Une vue d'ensemble générale des niveaux de toxicité et d'environnement de ces composés dans d'autres régions du Canada et dans le monde a été fournie au lecteur afin de mettre en relief ces informations pour la Colombie-Britannique.

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EXECUTIVE SUMMARY

Organotin compounds are synthetic organometallic substances whose toxic properties have contributed to their diverse and widespread use. These compounds have been used mainly as heat stabilizers in polyvinyl chloride, industrial cooling water slimicides, agricultural biocides, wood preservatives, antifouling agents, and industrial catalysts in chemical reactions. Organotin compounds are not manufactured in Canada but are imported for use.

In British Columbia current use pattern information is not available, however, surveys conducted by Environment Canada, Pacific and Yukon Region in the 1980's documented the use of more than 100,000 kg/yr of butyltin heat stabilizers by industrial plants producing PVC products, as well as the use of more than 9,000 kg/yr by the resins, paints, and coatings industries. No information on releases to the environment from these sources was obtained.

Organotin-based pesticides have also been used in British Columbia. Plictran ®, a tricyclohexyltin compound, was registered between 1971 and 1989 and was the most widely used of these products. During this period approximately 4,000 kg/yr were used in British Columbia to treat hop, strawberry, peach, pear, and apple crops. Only Vendex ®, which is used as a miticide on ornamentals, is still registered for use in Canada.

Tributyltin (TBT)-based antifoulant paints have also been used worldwide to treat the hulls of boats and ships. Triphenyltin (TPT) has also been used for this purpose in some countries, but not in Canada. The volume of TBT used in marine antifoulant paints applied to boats and ships in British Columbia has not been quantified, but it was undoubtedly the largest source of butyltin compounds to the aquatic environment. Marinas and shipyards have been identified as major sources of butyltin compounds to the aquatic environment in British Columbia and elsewhere. In addition, approximately one third of the salmon farms operating in British Columbia used nets treated with a TBT-based antifoulant until the late 1980's. A survey conducted by Environment Canada revealed that, between 1982 and 1987, more than 13,000 litres of TBT-based antifoulants were used by the aquaculture industry in British Columbia. The use of TBT antifoulants in Canada has been greatly reduced since 1989 when regulations severely restricting their use were introduced.

Degradation rates of organotin compounds in the environment are variable and are influenced by environmental conditions. The half-life of TBT ranges from several days to a few weeks in water and from a few months to (possibly) years in bottom sediments. Under certain conditions organotin compounds can be remobilized from the bottom sediments into the water column, thus providing a continuing source of contamination to aquatic biota.

Information on the behaviour of organotin compounds in the terrestrial environment is limited. However, studies indicate that organotin compounds do not migrate significantly in soils and can be degraded by microorganisms and photolysis.

Although organotin compounds are less environmentally persistent than PCB and DDT, the high toxicity of these compounds (especially TBT) to aquatic life makes their release to the environment of great concern. Organotin compounds, particularly TBT, affect energy production, survival, growth, metabolism, and reproduction in aquatic organisms at ng/L to $\mu\text{g/L}$ concentrations. Molluscs are particularly sensitive to TBT. Exposure of bivalve species to low concentrations of TBT (less than $1\mu\text{g/L}$) can cause mortality in larval stages, abnormal development of the shell and gonad, and reduced larval settlement and growth.

In British Columbia, evidence of TBT toxicity has been observed in marine invertebrates from coastal areas. Growth and shell abnormalities characteristic of TBT toxicity were first observed in 1985 in commercial oysters growing adjacent to a salmon farm using TBT-based net treatments. In addition, a condition known as imposex (the development of male sex organs in females) was reported to be widespread throughout the Straits of Georgia and Juan de Fuca. All six species of gastropods examined were affected. Studies on the incidence of imposex in gastropods from coastal areas of British Columbia are continuing. This condition has been observed in many other countries and was attributed to TBT contamination.

Between 1984 and 1995, surveys were conducted in coastal areas of British Columbia to determine the presence of butyltin compounds and other organotin compounds. Surveys focused on areas of known or suspected sources of contamination including shipyards, harbours, commercial docks, marinas, recreational boating areas, and salmon farms. Many of the surveys were conducted prior to the introduction of regulations on the use of TBT-based antifoulants in Canada in 1989. Butyltin compounds were detected at elevated concentrations in surface waters, bottom sediments, and/or aquatic organisms collected at many sites. In some of these areas, TBT concentrations in surface waters continue to exceed the Canadian water quality guideline for the protection of marine life (1 ng TBT/L or 0.4 ng Sn/L).

In the 1980's, Environment Canada surveys detected TBT concentrations in the hundreds to thousands of ng Sn/L range in surface waters from Vancouver area marinas in False Creek and Coal Harbour. Several thousand ng Sn/g of TBT (wet weight) were detected in mussels from these marinas, while mussels collected from marinas on Vancouver Island contained several hundred ng Sn/g TBT. Butyltin compounds at concentrations of several thousand ng Sn/g (dry weight) were detected in sediments from several south coastal marinas.

Elevated concentrations of butyltin compounds were also detected in harbour areas of British Columbia. In Vancouver Harbour, TBT concentrations of up to 26 ng Sn/L in surface water and several thousand ng Sn/g (up to 42,000 ng Sn/g) in sediment were detected at various shipyards and commercial docks in 1988 and 1991. Mussels collected at these facilities contained several hundred ng Sn/g of TBT. Elevated concentrations of butyltin compounds

were also detected in other harbour areas. In the early 1990's, water and sediment collected near the Department of National Defense (DND) Base in Esquimalt Harbour on Vancouver Island contained 130 ng Sn/L and up to 26,000 ng Sn/g TBT, respectively. Mussels collected at this facility contained several hundred ng Sn/g TBT. Butyltin compounds at concentrations of several hundred ng Sn/g were prevalent in sediment collected throughout Victoria Harbour in 1990, with levels exceeding 1000 ng Sn/g at some sites. Concentrations of 100 to 1000 ng Sn/g TBT were detected in the hepatopancreas of Dungeness crab from Vancouver, Victoria and Esquimalt harbours, the Fraser estuary and False Creek. Crab muscle contained much lower concentrations. Concentrations of butyltin compounds were also elevated in clams, shrimp, and fish (especially in the liver tissue) from harbour areas.

In 1988, butyltin compounds were detected in water, sediment, and aquatic biota from some British Columbia salmon farms using TBT-based antifoulants. Water samples from TBT-treated net pens contained up to 63 ng Sn/L, while sediments contained up to 70 ng Sn/g. In farmed salmon, total butyltin concentrations of up to 3,320 ng Sn/g in the liver and 247 ng Sn/g in the muscle tissue were detected. In comparison, the liver and muscle tissue of wild salmon contained much lower levels (up to 16 ng Sn/g in liver and up to 5.8 ng Sn/g in muscle). At present, there are no Canadian guidelines for acceptable levels of butyltin compounds in fish or shellfish intended for human consumption. Butyltin compounds were also detected in rockfish and shellfish collected in the vicinity of salmon farms. Shortly after this survey was completed, salmon farms in British Columbia stopped using TBT-based antifoulants.

Elevated concentrations of butyltin compounds were also detected in shellfish from some recreational boating areas during peak summer boating season in 1988.

Evidence that butyltin compounds were present in unacceptable concentrations in the Canadian environment resulted in the introduction of regulations in 1989, under the *Pest Control Products Act*, which restrict the use of TBT-based antifoulants in Canada. The current regulations prohibit the use of these products on most recreational boats (vessels under 25 metres except those with aluminum hulls) and at aquaculture facilities. However, the use of low release products on many commercial vessels is still permitted.

In 1995, Environment Canada conducted additional surveys at select sites to determine whether concentrations of butyltin compounds have declined since regulations were introduced. The results of these surveys suggest that the current regulations may be effective at reducing environmental contamination originating from recreational boats, but may not be as effective at reducing contamination from commercial vessels in harbours and shipyards. TBT concentrations in mussels, and possibly surface waters, from recreational marinas in the False Creek and Coal Harbour areas have declined since the 1980's, while concentrations in the water and mussels at Vancouver Harbour shipyards and commercial docks have not.

TBT concentrations in surface waters from the Royal Vancouver Yacht Club (RVYC) Marina and the Bayshore Inn Marina in Coal Harbour were much lower in 1995 (8.3 to 23 ng Sn/L and 7.3 to 8.6 ng Sn/L, respectively) than in the late 1980's (17 to 820 ng Sn/L and 19 to 2600 ng Sn/L, respectively). However, sampling stations, season, and tidal conditions were not consistent from year to year. All of these factors have been shown to affect TBT levels in surface waters, therefore, additional water monitoring is required to confirm that TBT concentrations are decreasing in Coal Harbour. Elevated TBT levels were also detected in surface waters collected at the False Creek market marina in 1991 (33 to 35 ng Sn/L) and off the government Wharf/Fisherman's Terminal in 1988 (180 ng Sn/L). It is not known whether TBT concentrations have decreased at these sites in recent years, however, surface water samples collected off the nearby False Creek Yacht Club in 1995 contained much lower concentrations of TBT (2.4 to 3.2 ng Sn/L). TBT concentrations in all surface water samples collected from False Creek and Coal Harbour in 1995 were still in excess of the 1 ng/L (0.4 ng Sn/L) Canadian water quality guideline suggested for the protection of marine and estuarine species.

Concentrations of butyltin compounds in mussels from recreational boat marinas in False Creek, Coal Harbour and Crescent Beach have also declined since the late 1980's. Mussels collected from the market marina in False Creek in the late 1980's contained total butyltin concentrations of up to 9,400 ng Sn/g (1700 ng Sn/g TBT). Mussels collected from this site in subsequent surveys contained 550 to 990 ng Sn/g of total butyltin compounds (300 to 630 ng Sn/g TBT) in 1991 and 564 ng Sn/g of total butyltin compounds (200 ng Sn/g TBT) in 1995. Mussels collected from the RVYC and Bayshore Inn marinas in Coal Harbour in the late 1980's contained 1,500 to 4,370 ng Sn/g of total butyltin compounds (410 to 1,100 ng Sn/g TBT). By 1991, levels had declined to 550 to 826 ng Sn/g of total butyltins (220 to 420 ng Sn/g TBT). In 1995, mussels contained even lower levels of butyltin compounds, ranging from 104 to 235 ng Sn/g of total butyltins (64 to 120 ng Sn/g TBT). The greatest decrease over time was observed at the Crescent Beach Marina where concentrations in mussels decreased from 750 to 3,700 ng Sn/g total butyltin compounds (290 to 1,100 ng Sn/g TBT) in the late 1980's to 115 ng Sn/g total butyltin compounds (43 ng Sn/g TBT) in 1995.

Concentrations of butyltin compounds in mussels collected off the government wharf/Fisherman's Terminal in False Creek, which is utilized mainly by commercial fishing vessels, have also decreased since the 1980's but to a lesser extent than have concentrations in the recreational boat marinas. Total butyltin concentrations were in the 1,100 to 4,000 ng Sn/g range in the late 1980's compared to 820 to 830 ng Sn/g in 1995. The continued presence of elevated concentrations of butyltin compounds at this location is probably due to the fact that TBT-based antifoulants can still be legally used on many commercial fishing boats (those greater than 25 metres in length and/or those with aluminum hulls).

Although the data on surface waters from Vancouver Harbour were insufficient to document trends over time, concentrations of butyltin compounds in the 1990's remained elevated. At two sites concentrations were higher in samples collected in 1995 than in samples collected in 1988 or 1991. Most of the Vancouver Harbour water samples collected during Environment Canada surveys in 1988, 1991, and 1995 contained TBT concentrations in excess of the Canadian guideline of 1 ng/L (0.4 ng Sn/L) for marine waters.

Mussels collected off several commercial docks and shipyards in Vancouver Harbour in the late 1980's contained several hundred ng Sn/g of butyltin compounds. However, in contrast to the declining levels observed in mussels from some marinas, concentrations of butyltin compounds in mussels from shipyards and commercial docks remained elevated in the 1990's. Lower concentrations were observed in the 1995 samples at only one site.

The available data indicate that concentrations of butyltin compounds in sediments from False Creek and Coal Harbour marinas and from shipyards and commercial docks in Vancouver Harbour have not decreased since the introduction of regulations in 1989. However, trends in sediment concentrations can be difficult to establish. Also, TBT is more persistent in sediments than in surface waters and aquatic organisms, therefore, reduced inputs to the environment are more rapidly reflected in water and mussels than in the sediments.

Recent information on concentrations of butyltin compounds at salmon farms and boating areas is lacking. It is likely that butyltin concentrations have declined at these sites since the 1980's, as regulations have prohibited the use of TBT-based antifoulants at aquaculture facilities and on most recreational boats as of 1989, but confirmation is required.

Other organotin compounds are less frequently detected in the aquatic environment of British Columbia than are butyltin compounds. The past use of cyclohexyltin-based pesticides and the presence of foreign vessels coated with triphenyltin-based antifouling paints has not resulted in the widespread contamination of the coastal British Columbia environment. Triphenyltin was detected in some sediment samples collected in Vancouver, Victoria, and Esquimalt harbours but at much lower levels than was tributyltin. Tricyclohexyltin concentrations were below the level of detection in virtually all sediment samples collected in Vancouver, Victoria, and Esquimalt harbours and in the lower Fraser River system. With very few exceptions, phenyltin and cyclohexyltin compounds were not detected in various species of aquatic organisms from British Columbia.

Information on the presence of organotin compounds in fish-eating birds and aquatic mammals in British Columbia is lacking. However, birds and mammals feeding on fish and shellfish from marina and harbour areas may accumulate elevated levels of TBT.

In the past year Environment Canada, in cooperation with other agencies, has developed documents outlining best management practices for ship and boat building and repair facilities and for marinas and small boatyards in British Columbia. Industry compliance with the recommendations in these documents is voluntary but will be monitored. In addition, Environment Canada has prepared and distributed an information pamphlet recommending guidelines for the use of antifouling paints on pleasure craft.

Continued efforts are required to ensure that concentrations of butyltin compounds in the aquatic environment of British Columbia return to acceptable levels. The efficacy of existing regulations at reducing inputs of butyltin compounds to the environment must be seriously evaluated since the data obtained to date indicate that the regulations may be effective at reducing TBT inputs from recreational boats but not from commercial vessels. In addition, it is necessary to confirm that the existing regulations have been effective in reducing levels of contamination at coastal salmon farms and in popular recreational boating areas.

Documentation of the incidence of imposex in gastropods from coastal areas of British Columbia should continue on a regular basis. This is a sensitive and inexpensive method of monitoring changes in environmental levels of TBT over the long term.

No information is available on the presence of organotin compounds in the terrestrial environment of British Columbia. Possible sources include the past use of organotin based pesticides; emissions and wastes from the paints, plastics and resins industries; disposal and incineration of products containing organotin compounds; and the use of organotin-based wood preservatives.

1. USES AND SOURCES OF RELEASE

1.1 Uses

Organotin compounds are synthetic organometallic substances whose toxic properties have contributed to their diverse and widespread use. These compounds have been used mainly as heat stabilizers in polyvinyl chloride (dimethyl-, dibutyl- and dioctyltin); industrial cooling water slimicides and agricultural biocides (tributyl-, triphenyl-, and tricyclohexyltin); wood preservatives (tributyltin); antifouling agents (tributyltin and triphenyltin); and industrial catalysts in chemical reactions (dibutyltin). Organotin compounds used in Canada are imported (1,2,3,4).

Dibutyltin compounds, used for the stabilization of polyvinyl chloride products, are the most widely used organotin compounds in Canada. Leaching of mono- and dibutyltin from PVC plastics may be the primary non-pesticide related source of these compounds to the aquatic environment. Methyltin and octyltin compounds are also used for the stabilization of plastics (4).

Although information on current use patterns of organotin compounds in British Columbia is not available, an Environment Canada survey conducted in 1984 and 1985 revealed that industrial plants producing PVC products in British Columbia used 115,000 kg/yr of butyltin heat stabilizers. In addition, the resin industry reported an annual use of approximately 400 kg/yr (5), while the paint and coatings industry reported a use of at least 8,800 kg/yr (6).

Tributyltin is the organotin compound which has been released to the aquatic environment in the largest quantity. It has been used extensively as an antifouling agent in marine paints, on salmon net pens, and on lobster pots. An Environment Canada survey of the aquaculture industry and net and chemical supply companies indicated that, between 1982 and 1987, a minimum of 13,319 litres of the TBT-based product 'Flexgard®' was supplied to the aquaculture industry in British Columbia. The survey also revealed that approximately 34% of salmon farms operating in British Columbia at the time of the survey had, at one time, used nets treated with TBT antifoulants (7).

The volume of TBT contained in marine paints that have been applied to boats and ships in British Columbia has not been quantified. However, this was undoubtedly the largest source of butyltin compounds to the aquatic environment. High concentrations of tributyltin have been detected in the aquatic environment as a result of the use of TBT-based paints. As a result, severe restrictions on the use of this compound have been introduced in Canada and many other countries. Canadian restrictions are discussed under Regulations, Controls and Guidelines (Section 5).

Although little information on current Canadian use patterns for TBT-based paints was available, it is expected that the use of TBT paints in Canada has decreased significantly since the regulations were brought into effect in 1989. However, it is possible that illegal uses of TBT-based antifouling paints occur. Agriculture Canada responds to complaints of illegal TBT use, but is not currently monitoring the compliance of recreational boaters with the regulations.

In some countries, such as Japan and Switzerland, triphenyltin (TPT) has been used as a component of marine paints in combination with tributyltin (8,9). Although triphenyltin has not been registered for this use in Canada, the entry of foreign vessels into major Canadian ports may have resulted in the release of phenyltin compounds to Canadian waters.

Three organotin-based pesticides were registered for crop protection under the *Canadian Pest Control Products Act*. These included: fentin hydroxide (Du-Ter®) for use as a fungicide on potatoes; fenbutatin oxide or di(tri-(2-methyl-2-phenylpropyl)tin) oxide (Vendex®) for use as a miticide on ornamentals; and cyhexatin or tricyclohexyltin hydroxide (Plictran®) for use as a miticide on fruit crops and ornamentals. Du-Ter® was registered in Canada between 1972 and 1980. Vendex® was first registered in 1977 and is still registered. Plictran® was the most widely used of these products and was registered for use in Canada between 1971 and 1989. The estimated annual usage of this compound in Canada during this time was 20,000 kg, with approximately 20% used in British Columbia. It was estimated that 10% of the peach, pear, and apple orchards and 95% of the strawberry crops in British Columbia were treated with this pesticide. All of the 329 hectares used for hop production at that time were also treated (10,11).

Organotin compounds are also registered in Canada for other uses, including industrial slimicides in cooling water, material germistats, and wood preservatives. No information on such usage in British Columbia was available.

1.2 Sources of Release

Shipyards and marinas have been identified as major sources of butyltin compounds to the aquatic environment in British Columbia and elsewhere. Loadings from shipyards can be high but are usually intermittent, while inputs from marinas were continuous but variable, depending on seasonal boating activity. Wastewater collection and treatment systems at shipyards can be effective in reducing TBT releases to the environment but these practices are not currently in widespread use. Environment Canada, Pacific and Yukon Region, has developed a documents outlining best management practices (BMPs) for ship and boat building and repair facilities and for marinas and small boatyards in British Columbia (12,13). These documents were prepared in cooperation with British Columbia Ministry of Environment, Lands and Parks, Greater Vancouver Regional District, Department of Fisheries and Oceans,

and the Burrard Inlet Environmental Action Program. The recommendations from these documents will be applicable to government and private facilities that service commercial and recreational vessels of any size. Industry compliance with the recommendations in the document will be voluntary but will be monitored. In addition, Environment Canada distributed an information pamphlet recommending guidelines for the use of antifoulant paints on pleasure craft (14). Regulations on the use of TBT-based antifouling paints were introduced in Canada and many other countries in the late 1980's. As a result, inputs to the aquatic environment have been significantly reduced and it is hoped that the implementation of recommended practices in the BMP documents for shipyards and marinas will further decrease inputs.

Organotin compounds have been detected in sewage treatment plant wastewater and sludge. In Switzerland, plant influents contained butyltin compounds in the hundreds of ng/L. Approximately 90% was associated with particulate matter and was removed to the sludge during primary treatment. The sludge, which contained concentrations of butyltin compounds in the low mg/kg dry weight range, was considered to be a potential source of environmental contamination through disposal at sea or use as soil fertilizers (15,16,17).

Butyltin compounds have been detected in wastes from Canadian sewage treatment plants. Monobutyltin (MBT) was present consistently at $\mu\text{g/L}$ concentrations in the influent and effluent from all plants. Tributyltin (TBT) and dibutyltin (DBT) were detected in very few samples; none from the Vancouver area plant included in the study. MBT, DBT, and TBT were detected at concentrations in the hundreds of $\mu\text{g/g}$ (dry weight) range in sludge from some Canadian plants. However, sludge from the Vancouver plant did not contain detectable levels of butyltin compounds (18).

Methyltin compounds can be produced naturally in the environment by methylation or can originate from their use as stabilizers in PVC plastics. Studies in other countries have identified methyltin compounds in the wastewater of sewage treatment plants and in the discharges of plants manufacturing tin compounds (15). Methyltin compounds have also been detected in rainwater in the United States (19).

The disposal of waste products containing butyl- and methyltin compounds in landfills or municipal incinerators may result in the release of these compounds into the environment. No information on these potential sources to the British Columbia environment was available and information for other regions was very limited. Butyltin compounds were not detected in leachates collected from five landfills in southern Ontario in 1990 (18). However, TBT, DBT, and MBT at concentrations in the ng/g range, were detected in landfill leachate in Switzerland. These compounds were mainly associated with particulate matter of greater than $1.2 \mu\text{m}$. Phenyltin compounds, dioctyltin, and cyclohexyltin were not detected (20).

In the United Kingdom, fish and macroinvertebrate kills have been documented following accidental spills of wood preservatives containing mixtures of TBT and dieldrin or pentachlorophenol (21). In addition, the use of TBT-based slimicides in industrial cooling water can be a source of TBT release to the environment. In Italy a power plant using TBT-based slimicides released 7 kg/day of TBT (22). No information on TBT releases to the British Columbia environment from wood preservatives or industrial slimicides was available.

2. ENVIRONMENTAL DYNAMICS

2.1 Aquatic Systems

Organotin compounds entering aquatic systems can be dissolved in the water column or adsorbed to suspended sediments, algae, and microorganisms. Adsorption studies indicate that monomethyltin (MMT), monobutyltin (MBT), and tributyltin (TBT) compounds are strongly adsorbed on the solid phase. Dimethyltin (DMT), trimethyltin (TMT), and dibutyltin (DBT) compounds are adsorbed to a lesser extent (9,23 to 27). Some studies indicate that a relatively small proportion of TBT is bound to suspended particles, with the majority remaining in solution or binding to particles smaller than 0.2 μm in diameter. The proportion of TBT and other organotin compounds attached to, and transported with, particles is variable and depends on a combination of factors. These include pH, turbidity, grain size, organic content, and salinity (24,28 to 32).

Environmental variables may affect the adsorption of each compound differently. For example, declining salinity increases the adsorption of MBT and decreases the adsorption of DBT (15,23) and TBT (23,28,32) on to particulate matter. Levels of particulate matter (hydrous iron oxide) in the water column also affect the adsorption of butyltin compounds differently (23,24). Butyltin compounds usually exhibit decreased adsorption with increased pH (23) and dissolved oxygen content in the water (33).

The chemical speciation of TBT compounds in the aquatic environment is pH dependent. Under controlled experimental conditions, the TBT species detected in seawater include TBT hydroxide, TBT chloride, and a TBT carbonate species. Predominant species were strongly determined by the pH of the system (34). In the presence of sulfide, TBT sulfide forms rapidly in marine waters. Anoxic sediments may act as a sink for organotin compounds, due to their high sulfide content (35).

The mobility of organotin compounds associated with sediments is dependent on environmental conditions. Under abiotic conditions, virtually no desorption of TBT oxide from Toronto harbour sediments was observed over a 10 month period. However, in the presence of oligochaetes, degradation occurred and the formation of both butylated and methylated products was noted (36). Changes in environmental conditions may act to increase or decrease desorption of TBT from sediments (23 to 26,28,29,37).

The extent to which organotin compounds accumulate in the environment is determined by the rate of input, transformation, and removal. In the aquatic environment TBT can be degraded or removed by microorganisms, aquatic biota, photolysis and, to a much lesser extent, volatilization and hydrolysis. Elevated TBT concentrations in the environment are expected to decline within a period of weeks to months as the level of input decreases (34,38 to 43).

TBT is degraded by progressive debutylation to the less toxic and less hydrophobic degradation products, DBT and MBT, and finally to inorganic tin. The relative proportion of TBT compared to its degradation products in the environment is often used as an indicator of local degradation rates and also current inputs of TBT into the area. A strong predominance of TBT suggests a continuing input of TBT. Lab studies indicate that the half-lives for the biological degradation of TBT in water are in the range of several days to a few weeks, while the half-lives in sediments are usually in the range of months. However, some environmental studies involving the examination of sediment cores indicate that TBT may be more persistent in the environment than laboratory degradation studies suggest. Profiles of butyltin compounds in sediment cores suggest that, under certain conditions, TBT may persist in sediments for several years (44,45). Degradation rates for TBT vary depending on environmental conditions (2,36,43,46). Some studies indicate that degradation proceeds quite rapidly under aerobic conditions (half-lives in the order of one to two weeks), but more slowly under anaerobic conditions (half-lives of up to one year or more) (47,48). Other studies indicate that degradation occurs more rapidly under anaerobic conditions than under aerobic conditions (46,49). Biodegradation proceeds faster in water from marinas and harbour sites than from clean areas. This suggests that the microbial populations in contaminated areas may have acquired an enhanced ability to degrade TBT. This could occur as a result of species adaptations or through shifts in microbial populations which favour a higher proportion of microbes capable of degrading TBT (43,50). In contrast, microbes from some environments do not appear to have the ability to degrade TBT (51).

Temperature also affects the rate of TBT degradation in the aquatic environment. Longer TBT half-lives have been documented in the winter than in the summer, probably due to decreased microbial activity at colder temperatures (41,52,53). High levels of TBT in sediments may also inhibit degradation (39).

Some studies show that algae are potentially important in organotin degradation. The rate of degradation is dependent on the species and population density of algae, and also the water temperature and presence of light. Accelerated rates of biodegradation were observed as a result of incubating water samples under incandescent lamps, suggesting the involvement of photosynthetic microorganisms. There is evidence that photosynthetic microorganisms may be involved in the formation of tetrabutyltin (TTBT) (41,52,55).

Photolytic degradation of TBT is variable depending on the intensity and wavelengths of ultraviolet light and the presence of organics which may enhance photolysis (56,57). Half-lives of from one to one hundred days have been reported. Photolytic degradation would mainly affect TBT in the surface microlayer and the intertidal zone (47). Photolytic degradation of methyltin compounds has also been observed (58).

Based on the available data, volatilization and hydrolysis appear to have negligible effects on the removal of TBT from the aquatic environment (27,36,47).

The methylation of inorganic tin compounds may alter both toxicity and mobility in the environment. Methyltin compounds have been detected in fresh and marine waters and sediments and originate from both anthropogenic and natural sources. The presence of high levels of inorganic tin in the anoxic sediments of industrial areas can result in the production of methyltin compounds by both biological and chemical processes. As with mercury compounds, demethylation of methylated tin compounds can occur in the natural environment (15,24,27,49,59 to 63).

Little is known about the environmental fate of organotin compounds other than butyl- and methyltin compounds. Triphenyltin (TPT) degrades to diphenyltin (DPT) and monophenyltin (MPT) in the aquatic environment (64). Fent and Hunn (9) detected a higher proportion of TPT degradation products than TBT degradation products in sediment cores, suggesting that TPT may degrade faster than TBT. Photolytic degradation in water and on surfaces has been demonstrated, however, triphenyltin hydroxide is much more stable in the dark (9,65).

Similarly, the pesticide tricyclohexyltin (Plictran®) can undergo sunlight photolysis in the water and on surfaces, yielding di- and monocyclohexyltin and inorganic tin (66,67,68).

2.2 Terrestrial Systems

Information on the environmental fate and behaviour of organotin compounds in the terrestrial environment is limited and focuses mainly on the degradation of agriculturally applied organotin pesticides in soil.

Soil retention tests show that organotin compounds deposited in landfills will not migrate significantly. Tests with various soil types resulted in no more than 0.2% of the triorganotin compounds leaching out. Clay-based soils were particularly effective in immobilizing organotin compounds (69).

Adsorption studies demonstrate that the triphenyltin fungicide, Fentin®, is not mobile in sandy soils with varying organic contents. Very small amounts of phenyltin were detected in leachate. The fungicide was retained in the top ten centimetres of the soil (70).

Similarly, cyclohexyltin compounds are strongly adsorbed onto soil particles with more than 90% being retained in the top one centimetre of soil. Cyclohexyltin compounds enter soils mainly as a result of direct spray, runoff from sprayed vegetation, and rainwater runoff (71).

Photodegradation of cyclohexyltin hydroxide to dioctylhexyltin oxide, cyclohexylstannoic acid, and ultimately to inorganic tin, has been observed (68). Persistence of cyclohexyltin compounds in soil can occur under field conditions. Low soil temperatures in the winter can inhibit degradation. Elevated levels of cyclohexyltin and related compounds could occur in areas of repeated applications (71).

Degradation of triphenyltin compounds in soil has also been observed. At a concentration of 80 mg/kg in soil, triphenyltin was reduced to non-detectable levels in three to ten days. The rate of photodegradation increases at lower wavelengths of light. Degradation products of triphenyltin are di- and monophenyltin and inorganic tin (72 to 74). Other studies showed that microbial activity is also an important factor in the breakdown of triphenyltin in soils (75).

3. ENVIRONMENTAL LEVELS¹

3.1 Aquatic Systems

3.1.1 Water and Sediments²

General

TBT and its degradation products, DBT and MBT, are commonly detected in natural waters and sediments. Tetrabutyltin (TTBT), which is detected occasionally, probably occurs mainly as a result of its presence in some commercial TBT formulations. However, some studies indicate that microbial activity may lead to the formation of TTBT in the environment as a result of butyl group transfer (52).

TBT concentrations in aquatic systems are influenced by many factors including tidal effects, seasonal conditions (temperature, water exchange, salinity, suspended solids, boating activity), vertical stratification of the water column, and proximity to sources (76 to 79).

TBT levels in waters from well flushed or open coastal areas usually do not exceed 10 ng/L (77,80,81). The highest levels of TBT have been found in water and sediments collected from harbours, marinas, and areas of heavy boating activity, particularly in regions of poor water exchange. Water TBT concentrations in excess of 1,000 ng/L have been detected in some areas and, in many countries, levels in harbours and marinas commonly exceed 100 ng/L (82 to 84). Several thousand ng/L of TBT have been detected in the surface microlayer (76,77,80,85 to 91).

Concentrations of butyltin compounds in water are not constant. In marinas, pronounced differences have been observed between water samples collected over time and also in water samples collected simultaneously from different sites. Peak concentrations have often been observed at the start of the boating season (81,83,92).

High levels of TBT in the water column are normally reflected by high levels in the bottom sediments. Sediments typically contain TBT at levels approximately three orders of magnitude greater than the levels in the water. Concentrations of several hundred ng/g TBT

1. Data in this section are presented on a Sn basis. To convert data to a cation basis values should be multiplied by the factors listed in Appendix 1.
2. Organotin data for sediments are presented on a dry weight basis.

have been detected in the sediments from marinas and harbours. The highest loadings to harbours are from commercial shipyards and repair facilities. Concentrations of several thousand ng/g total butyltin compounds have been detected in sediments. Paint chips from hull scraping probably contribute to these high levels. The distribution of butyltin compounds in the bottom sediments is heterogeneous and concentrations often vary substantially within the same marina (83,93 to 98).

In recent years, the concentrations of TBT in surface waters and, to a lesser extent, sediments have been decreasing in many areas. This is probably a result of the introduction of regulations and restrictions on the use of TBT-based antifoulants (31, 99 to 101).

Methyltin compounds have also been detected in many freshwater and marine systems. Concentrations of up to 508 ng Sn/L of trimethyltin were detected in water samples from the Great Bay estuary in New Hampshire, United States (102). Trimethyltin (TMT) was absent from the sediments in this area, however, concentrations of monomethyltin (MMT) and dimethyltin (DMT) were comparable to those of butyltin compounds (103). In a cross Canada study, methyltin compounds were detected in only 3% of water samples and 10% of sediments samples collected. TMT and MMT levels in waters were below 1 μ g Sn/L and DMT was not detected. Concentrations of up to 17,000, 170, and 750 ng Sn/g of MMT, DMT and TMT, respectively, were detected in the sediments (104). In contrast, although TMT was rarely detected, MMT and DMT were detected in the majority of water samples collected in an Ontario survey. This is probably a result of the greater proportion of samples collected from industrialized areas in the Ontario survey (91).

Phenyltin compounds have been used with TBT in antifouling paints and also as agricultural pesticides in some countries. TPT and its degradation products, DPT and MPT, have been detected in the aquatic environment of Japan, Switzerland, Spain, and in Mediterranean coastal waters. As with TBT, the highest concentrations were associated with areas of heavy boating activity. In some cases, concentrations exceeded or were comparable with concentrations of butyltin compounds (8,9,65,105).

The agricultural pesticide, tricyclohexyltin, was not detected in water, sediments, or biota collected from Lake Lucerne in Switzerland (9). However, Muller *et al* (106) detected cyclohexyltin in Lake Zurich sediments.

British Columbia

Much of the data on butyltin compounds in the aquatic environment of British Columbia were generated in the late 1980's. During this period, the potential hazards of TBT release into the environment were recognized but regulations restricting the use of TBT-based antifouling paints had not yet been introduced. Regulations brought into effect in 1989 severely restricted the use of TBT-based antifoulants in Canada.

For this reason, current environmental levels of butyltin compounds in British Columbia (particularly near marinas, recreational boating areas, and salmon farms) may be lower than the levels presented in this report.

A.) Water

Limited information on concentrations of butyltin compounds in British Columbia surface waters was obtained. Most of the samples collected were grab samples (0.5 metres below the surface) and were not collected at the same stage in the tidal cycle or at the same time of the year. For this reason, subtle differences in butyltin concentrations between sites do not necessarily reflect actual differences in the levels of contamination between sites, but instead may reflect the differences in the environmental conditions at the time of sampling. In addition, most of the water samples were collected in glass containers (not silanized). Some researchers have suggested that adsorption of organotin compounds onto container walls may occur on non-silanized containers (107 to 109). However, no significant differences were noted between water samples collected in silanized and non-silanized containers in 1995 by Environment Canada (7). The high levels detected at some sites show that, on at least some occasions, the levels of TBT in surface waters have greatly exceeded suggested water quality guidelines for the protection of aquatic life (refer to Section 5.1). Data on surface water concentrations in British Columbia are limited and continued monitoring is required to ensure that concentrations of butyltin compounds are decreasing to acceptable concentrations.

In most samples TBT was the predominant butyltin compound detected in water samples, however, DBT and MBT were also frequently detected. The highest concentrations were detected in water samples from marinas where elevated levels of butyltin compounds were also detected in the sediments. In the late 1980's Environment Canada surveys detected total butyltin concentrations of up to 2,120 ng Sn/L (820 ng Sn/L TBT) and 5,400 ng Sn/L (2,600 ng Sn/L TBT) in water samples from the Royal Vancouver Yacht Club (RVYC) and the Bayshore Inn marinas in Coal Harbour, respectively. Samples collected from Coal Harbour since this time have contained significantly lower levels of butyltin compounds. Water samples collected at the RVYC and Bayshore Inn marinas in 1995 contained much lower levels of total butyltin compounds, ranging from 13.4 to 40.2 ng Sn/L (8.3 to 23 ng/L TBT) and from 12.9 to 14.9 ng Sn/L (7.3 to 8.6 ng Sn/L), respectively (7). However sampling stations, season, and tidal conditions were not consistent from year to year. All of these factors have been shown to affect TBT concentrations in surface waters (76 to 79,82,83,101).

Elevated TBT levels were also detected in False Creek surface waters collected at the market marina in 1991 (33 to 35 ng Sn/L) and off the Government Wharf/Fisherman's Terminal in 1988 (180 ng Sn/L). It is not known whether TBT concentrations have decreased at these sites in recent years, however, surface water samples collected off the nearby False Creek Yacht Club in 1995 contained much lower concentrations of TBT (2.4 to 3.2 ng Sn/L). TBT concentrations in all surface water samples collected from False Creek and Coal Harbour in 1995 were still in excess of the 1 ng/L (0.4 ng Sn/L) Canadian water quality guideline suggested for the protection of marine and estuarine species.

Butyltin compounds have also been detected in surface waters collected from other areas of Vancouver Harbour. Environment Canada surveys conducted in 1988 and 1991 detected total butyltin concentrations of up to 26 ng Sn/L at nearshore sites off various shipyards, commercial docks, and bulk loading facilities (7). Additional monitoring was conducted off some facilities in 1995. Water samples collected off Vanterm and Vancouver Shipyards in 1995 contained higher levels of butyltin compounds than did samples collected in 1988 or 1991 (7). However, the data are insufficient to document trends over time. Most of the Vancouver Harbour water samples from Environment Canada surveys conducted in 1988, 1991, and 1995 contained TBT concentrations in excess of the Canadian guideline of 1 ng/L (0.4 ng Sn/L) for marine waters (7).

In 1989, Cullen *et al* (110) detected butyltin compounds in surface water samples (up to 86 ng Sn/L) and in the surface microlayer (up to 105 ng Sn/L) at various locations within Vancouver Harbour. Cullen *et al* (110) also detected DBT and TBT at ng/L concentrations in surface water and microlayer samples in Saanich Inlet, Jervis Inlet, and Desolation Sound in 1989.

Maguire *et al* (104) reported that water samples collected from several locations on the Fraser River in 1984 did not contain detectable concentrations of butyltin compounds with the exception of one sample from John Manly Shipyard which contained 20 ng Sn/L.

In 1984 (104) and 1991 (7) trace concentrations of butyltin compounds were tentatively detected in surface waters from Victoria Harbour, while up to 170 ng Sn/L of total butyltin (130 ng Sn/L TBT) were detected in surface waters off the Department of National Defense (DND) base at Constance Cove in Esquimalt Harbour. Butyltin compounds were not detected in surface water collected from Comox Harbour in 1987 (7).

Surface water samples collected from TBT-treated net pens at British Columbia salmon farms in 1988 contained TBT concentrations of up to 63 ng Sn/L (7). The use of TBT at coastal salmon farms was terminated shortly after the survey. Although more recent data have not been obtained, it is likely that concentrations of butyltin compounds at salmon farms have decreased since the 1980's.

TBT was not detected in surface water collected at the reference sites at Crescent Beach in 1987 and 1991 or at French Beach in 1995 (7).

Very little information is available on concentrations of other organotin compounds in British Columbia waters. In 1984, Maguire *et al* (104) detected ng/L concentrations of methyltin compounds in a few water samples collected from Vancouver and Victoria Harbours.

Cyclohexyltin compounds were not detected in water samples collected from Vancouver Harbour in 1989 and 1991. Similarly, tricyclohexyltin was not detected in surface waters collected from other south coast locations sampled (7,111). However, Cullen *et al* (110) detected dicyclohexyltin at concentrations ranging from 4 to 7 ng Sn/L in water collected from Saanich Inlet and Desolation Sound in 1989.

Triphenyltin was not detected in water samples collected from Vancouver and Victoria harbours in 1991 (7), or from Esquimalt Harbour in 1986 (111) and 1991 (7).

B.) Sediments

Elevated concentrations of butyltin compounds have been detected in sediments collected from several British Columbia coastal marinas. The highest concentrations were detected in sediments from marinas in poorly flushed areas such as Coal Harbour, False Creek, the mouth of the Nicomekl River (Crescent Beach) and Tsehum Harbour (Vancouver Island). Concentrations of several thousands of ng Sn/g total butyltin compounds were first detected in sediments collected from marinas and/or government wharves at these locations by Environment Canada in the late 1980's. Subsequent surveys conducted in 1991, 1994, and 1995 confirmed that concentrations of butyltin compounds in marina sediments in False Creek and Coal Harbour remained elevated after the introduction of regulations on the use of TBT-based antifouling paints in 1989 (7). Concentrations of butyltin compounds in sediments from False Creek and Coal Harbour marinas are comparable to those detected in sediments from marinas in the Puget Sound area in Washington State (96).

Total butyltin concentrations in the hundreds of ng Sn/g range were detected in sediments collected in both 1991 and 1994 at several other locations within False Creek. Concentrations appeared to be stable between 1991 and 1994 and no changes in concentrations were observed over this period (7).

Very high concentrations of butyltin compounds were present in sediments collected off some shipyards and commercial docks in Vancouver Harbour. The highest total butyltin levels were detected in sediments collected off Metchosin Shipyard in 1984 (up to 23,000 ng Sn/g) and 1988 (up to 82,000 ng Sn/g); Seaboard Terminals in 1988 (up to 13,000 ng Sn/g); Versatile Pacific (was Burrard Yards) in 1984 (up to 7,350 ng Sn/g) and 1994 (8,814

ng Sn/g); Vancouver Shipyards in 1988 (5,320 ng Sn/g) and 1995 (up to 4,946 ng Sn/g); Vanterm in 1995 (up to 5,172 ng Sn/g); Allied Shipyards in 1988 (up to 45,000 ng Sn/g) and 1994 (44,000 ng Sn/g); and B.C. Marine Shipbuilders in 1984 (up to 16,000 ng Sn/g) (7,104). It is likely that the presence of paint chips in the sediments off ship repair facilities contributes significantly to the concentrations of butyltin compounds detected. Paint chips have been suggested as a source of butyltin contamination in bottom sediments from other coastal areas including New Zealand and the Mediterranean (96,112,113).

Several of the shipyards included in Environment Canada surveys, such as Menchion's Shipyard, Versatile Pacific, and B.C. Marine Shipbuilders, are now closed. Although recent data are very limited, total butyltin levels in sediments (357 ng Sn/g) collected off the Menchion's shipyard site in 1994 (several years after it closed) were much lower than the concentrations detected in the 1980's (3,460 to 82,000 ng Sn/g). This may be due to the extensive foreshore development and dredging which took place at this facility in the early 1990's.

It is difficult to establish trends over time in the concentrations of butyltin compounds in bottom sediments. Sediments are heterogeneous and the concentrations of butyltin compounds in bottom sediments can differ greatly at sites located only a few metres apart. Attempts to obtain samples from the same station are often confounded by boat movement, changing shorelines, and the absence of clear fixed markers on shore. Repeat sampling of sites can be especially difficult in harbours as access to sampling stations is often obstructed by the presence of large ships. As a result, some variation in the location of the stations may occur from year to year and may contribute to the variability in concentrations of butyltin compounds. In addition, past dredging activity is an important factor to consider when assessing concentrations of contaminants in sediments over time. A complete dredging history for many sites within Vancouver Harbour was not available.

However, at virtually all of the several sites within Vancouver Harbour for which multi-year information was obtained, concentrations of butyltin compounds in sediment samples collected in the 1990's were either similar to or higher than levels detected in the 1980's. This fact suggests that concentrations of butyltin compounds in sediments from many areas of Vancouver Harbour have not decreased since the 1980's. For example, sediments collected off the Versatile Pacific shipyard in 1994 contained 8,814 ng Sn/g of total butyltin compounds (compared to 2,120 to 7,350 ng Sn/g in the 1980's), despite the fact that this facility had been closed for several years.

In contrast to the very high concentrations of butyltin compounds detected in sediments off shipyards in Vancouver Harbour, levels in the sediments collected off shipyards on the Fraser River in 1984 were low or non-detectable, probably due to the rapid flushing that occurs in most areas of the river (7, 104).

Butyltin compounds at concentrations of several hundred ng Sn/g were prevalent throughout Victoria Harbour in 1990 with levels exceeding 1,000 ng Sn/g at some sites. The highest concentrations were detected at the Selkirk Waters trawl site (2,710 ng Sn/g), Upper Harbour midchannel trawl site (1,667 ng Sn/g), off the Boat Building Facility (2,350 ng Sn/g), and in the Inner Harbour off Trotac Marine/Capital City Boatyard (up to 8,000 ng Sn/g) (7). In nearby Esquimalt Harbour, concentrations were low in 1990 except near the Department of National Defense (DND) facility at Constance Cove where concentrations of up to 30,000 ng Sn/g were detected (7). In a 1986 study by Kaye *et al* (111), sediments collected from Constance Cove contained up to 9,020 ng Sn/g total butyltin and 7,000 ng Sn/g TBT. The highest concentrations were detected off the graving dock.

Sediments from recreational boating areas contained low concentrations (less than 20 ng Sn/g) of butyltin compounds. Sediment samples were collected in Prideaux Haven and Pendrell Sound at the beginning of the boating season (June) and again during peak boating season (August) to determine whether the summer boating activity was resulting in seasonally elevated concentrations. Although concentrations of butyltin compounds in sediments collected during peak season in Prideaux Haven were higher than those detected in June, the levels were still low and the observed variation could have resulted from the natural heterogeneity of the sediments. In contrast, the sediments collected during peak season in Pendrell Sound contained slightly lower levels of butyltin compounds than did the sediments collected in June (7).

Sediment samples collected off a salmon farm using TBT-based net treatments in Nanoose Bay in 1987 contained a mean TBT concentration of 259 ng Sn/g (114). Lower levels of butyltin compounds (less than 2 to 70 ng Sn/g) were detected in sediments collected in 1988 near net pens at several other salmon farms that had used TBT-based net treatments (7). No information on butyltin concentrations at aquaculture sites has been obtained since the use of TBT-based antifoulants on net pens was terminated in the late 1980's.

Butyltin compounds have been detected in the wastes from some sewage treatment plants in Canada. Sediments collected from the vicinity of a sewage treatment plant in the Fraser River estuary contained low but detectable concentrations (less than 5 ng Sn/g) of total butyltin compounds (7).

Information on butyltin concentrations in sediments from other areas of British Columbia is very limited. Stewart and Thompson (115) reported that low concentrations of butyltin compounds (less than 5 ng Sn/g) were detected in a core collected at a water depth of 377 metres from Ballenas Basin in the Strait of Georgia. These authors also reported traces of TBT in an intertidal river sediment. In 1992, British Columbia Ministry of Environment, Lands and Parks analyzed sediments from four sites on the Fraser River. Butyltin compounds were detected at three of the four sites at concentrations of up to 44 ng Sn/g (116).

Butyltin compounds were present at concentrations below or near the level of detection in sediments collected from reference sites at Warn Bay, St. Vincent Bay, French Beach, and Crescent Beach (7).

Butyltin compounds in sediments collected throughout coastal British Columbia were predominantly in the TBT form. DBT also comprised a significant portion of the butyltin detected in most samples, while contributions from MBT were generally much lower. In general, contributions from the degradation products, DBT and MBT, were greater in samples from marinas and from Victoria Harbour than in sediments collected from Vancouver Harbour and other coastal areas sampled (7). The observed variations in butyltin profiles can be attributed to site specific differences in TBT inputs, adherence to sediment particulates, and degradation rates.

Information on the presence of other organotin compounds in sediments from coastal areas of British Columbia is limited. Based on very few samples, Maguire *et al* (104) detected methyltin compounds in sediments from Vancouver Harbour but not in sediments from Victoria Harbour.

Tricyclohexyltin was below the level of detection in virtually all sediment samples collected in Vancouver, Victoria, and Esquimalt harbours in 1988, 1990, and 1991. Trace concentrations were tentatively detected in a few samples (7).

Triphenyltin was detected in some sediment samples collected in Vancouver, Victoria, and Esquimalt harbours in 1990 and 1991. The highest concentration (210 ng Sn/g) was detected off the DND facility at Constance Cove in Esquimalt Harbour. At all other locations, triphenyltin concentrations did not exceed 40 ng Sn/g (7).

Stewart and Thompson (115) reported that cyclohexyltin and phenyltin compounds were not detected in sediments collected from Point Grey and from three sites in the lower Fraser River system.

3.1.2 Aquatic Organisms

3.1.2.1 Uptake and Elimination

Organotin compounds in water are readily accumulated by aquatic organisms via the gills. There are significant differences in the abilities of aquatic species to accumulate organotin compounds, however, bioconcentration factors of several thousand have been reported for many species (117 to 119). Particularly high bioconcentration factors have been reported for filter-feeding bivalves (76).

The biomagnification potential of organotin compounds has not been well studied. Organotin compounds are degraded in the environment and can be metabolized and depurated by many species including bacteria, algae, fish, and mammals. In contrast, compounds known to be biomagnified (such as PCBs, methylmercury, and DDT) are environmentally persistent and are not readily metabolized or depurated. Until recently, the available information suggested that organotin compounds would not be biomagnified. Although uptake from food was identified as an important source of organotin compounds in some species, biomagnification through the food chain had not been observed. Some researchers noted that species at the higher levels of the food chain did not appear to contain higher concentrations of TBT than the lower species (120 to 122). However, in 1995 researchers in Japan (123) detected high concentrations of butyltin compounds in a variety of tissues from finless porpoise. The authors noted that this mammal appears to accumulate TBT more efficiently than fish species and suggested that the high concentrations detected indicate that butyltin compounds can be transferred through the food chain.

Organotin accumulation in individual organs and tissues is at least partially dependent on the lipid content of the organs. In bivalves TBT accumulation is highest in the gills followed by the viscera, kidney, mantle, and adductor muscle (119,124). In crustaceans the hepatopancreas is the main internal organ of accumulation (125,126), while in fish the liver, gallbladder/bile and kidney usually accumulate the highest concentrations. Significant quantities of TBT and metabolites have also been detected in the brain and reproductive tissues. The muscle tissue of aquatic species usually contains much lower levels (127 to 131).

The source of TBT exposure may influence the tissue distribution. For example, when the TBT accumulated is in association with particulate material or phytoplankton, as opposed to dissolved in water, the highest concentrations are observed in the viscera of bivalves and the hepatopancreas of crustaceans, rather than the gills (119,126).

Accumulation from water is the best studied route of uptake but accumulation from food appears to be important in some species, including bivalves and crabs (119,126). Studies with bivalves indicate that uptake of TBT associated with phytoplankton occurs more quickly than does TBT uptake from water (119). Especially high concentrations of organotin compounds have been observed in deposit feeding bivalves indicating that sediment may be an important source (83). It has been demonstrated that particulates are the main source of organotin compounds taken up by *Scrobicularia plana*. Similarly, a positive correlation between TBT concentrations in bottom sediments and some aquatic species has been identified (132).

Differences in the uptake and elimination of organotin compounds between marine and freshwater fish have been observed. These differences were attributed to the different chemical forms of organotin compounds found in fresh and seawater and to the physiological differences in the fish (133).

One factor which limits the bioaccumulation of organotin compounds is the ability of the organism to metabolize these compounds. There is evidence that fish and crustaceans utilize the cytochrome P-450 dependent mixed-function oxygenase (MFO) system to metabolize organotin compounds and other chemical contaminants. This system is responsible for the degradation of TBT to DBT, MBT, and other polar metabolites. Lower rates of metabolism in some species, especially bivalves, have been attributed to the low cytochrome P-450 content and MFO activity (134,135).

Uptake and elimination studies on rainbow trout indicate that TBT uptake occurs rapidly while elimination occurs slowly. The liver and gall bladder (bile) contain the highest concentration of butyltin metabolites, suggesting that hepatic dealkylation and biliary fecal excretion occur (127).

The half-life of TBT is estimated to be between 14 and 28 days in sheepshead minnow (136), less than three to seven days in carp and goldfish (137), and 10 days in Pacific and European oysters (76). The half-life of TBT in mussels under field conditions is estimated to be 14 days (119).

Information on the bioconcentration potential for other organotin compounds is very limited. The bioconcentration factors for triphenyltin chloride are greater than those for tributyltin chloride in some species of fish and lower in other species. Like tributyltin, triphenyltin is eliminated slowly (130,133,138).

3.1.2.2 Concentrations in Aquatic Organisms³

General

Organotin levels in aquatic organisms are influenced by such factors as species, age, feeding habits, metabolic activity, physiological condition (lipid weight, spawning state) and also the route, concentration and duration of exposure.

3. Data for biota are presented on a wet weight basis.

Organotin concentrations in aquatic species vary with geographic location. Significant differences in environmental levels of organotin compounds can occur between sites in close proximity to one another. The highest concentrations are generally found in organisms from marinas, harbours, and other areas of heavy boat traffic, particularly where these activities occur in confined areas with slow water exchange. Very high concentrations have been observed in biota collected near boatyards (82,139 to 147). In several areas, concentrations in aquatic species have decreased since the introduction of restrictions on the use of TBT antifoulants in marine paints (31,139 to 142).

Bivalves, in particular, accumulate high concentrations of organotin compounds. Oysters and mussels have been used worldwide as indicators of environmental TBT contamination. Concentrations exceeding several hundred ng Sn/g have been detected in oysters and mussels from coastal harbours. TBT concentrations in these species from clean areas are normally in the very low ng Sn/g range (31,82,139 to 145). Significant differences in organotin concentrations occur in various bivalve species collected from the same area. For example, in the Gulf of Mexico, the butyltin concentration in clams was 2.8 times that in oysters and 7.7 times that in mussels (140). Little information is available on organotin concentrations in other invertebrate species.

Seasonal variations in butyltin concentrations in aquatic species have also been reported. Peak concentrations often coincided with the start of boating season and were attributed to the release of TBT from freshly painted boats. In addition, body burdens of contaminants often vary seasonally due to the changing physiological condition of the organism (i.e., spawning state, lipid content) (144,146 to 148).

Butyltin compounds were detected in 50% of the fish collected from the eastern, Pacific, and Gulf coasts of the United States between 1986 and 1990. In fish containing detectable concentrations, a mean of 244 ng Sn/g and a maximum of 727 ng Sn/g total butyltin was detected in the liver. English sole collected from Puget Sound in the United States contained total butyltin concentrations of up to 250 ng Sn/g in the liver and up to 11 ng Sn/g in the muscle tissue (149,150).

Butyltin compounds have also been detected in farmed salmon purchased at public markets in the United States (up to 188 ng Sn/g) and in salmon reared for three to nineteen months in pens treated with TBT antifoulants (up to 369 ng Sn/g) (148,151). Butyltin compounds were not detected in wild salmon caught off the coast of Alaska (148), but TBT was present at concentrations of up to 30 ng Sn/g in wild salmon caught near Seattle (151).

Very little information is available on the concentrations of other organotin compounds in aquatic biota. In Switzerland, triphenyltin was used as a co-toxicant with tributyltin in antifouling paints until 1990. Phenyltin and butyltin compounds have been detected in mussels from Swiss marinas at concentrations of up to 1,338 ng Sn/g and 3,832 ng

Sn/g, respectively. Only butyltin compounds were detected in fish muscle tissue from the same area (9). TPT has also been used in antifouling paints in Japan until recently. Mussels from Tokyo Bay contained a mean concentration of 576 ng Sn/g TPT (up to 2,045 ng Sn/g). Much lower concentrations of MPT and DPT (less than 15 ng Sn/g) were reported. In comparison, mussels from the same area contained a maximum of 98 ng Sn/g of TBT (8).

Methyltin compounds have also been detected in aquatic biota. Fish from Lake Ontario harbours contained monomethyltin ranging from 220 to 880 ng Sn/g (whole fish basis) (104). Dimethyl- and trimethyltin have also been detected in fish and some invertebrates from other areas (59).

Very little information on the presence of butyltin compounds in aquatic species of birds and mammals is available. TBT was detected in ng Sn/g (wet weight) concentrations in the liver and muscle of oystercatchers in the United Kingdom (152) but not in gulls in Japan (153). No information is available on other fish-eating species.

Iwata *et al* (123,154) detected butyltin compounds in the blubber of several species of marine mammals (up to several hundred ng/g) and in a variety of tissues of finless porpoise (up to several thousand ng/g) collected off the coast of Japan.

British Columbia

Environment Canada surveys revealed that concentrations of butyltin compounds in aquatic species were highest in marina and harbour areas of British Columbia, with mussels from these areas containing especially high concentrations.

Total butyltin concentrations were most elevated in mussels collected from marinas in False Creek (70.5 to 9,400 ng Sn/g), Coal Harbour (1,500 to 4,370 ng Sn/g), Crescent Beach (750 to 3,700 ng Sn/g), and Tsehum Harbour (711 to 1,660 ng Sn/g) in the late 1980's (7). Subsequent Environment Canada surveys indicated that concentrations of TBT and total butyltin compounds in mussels from marinas at the False Creek market, Coal Harbour, and Crescent Beach have declined since the late 1980's (refer to Table 1).

The decrease in butyltin concentrations observed in mussels collected from the recreational boat marinas at the False Creek market, Coal Harbour, and Crescent Beach since the 1980's, is probably a result of the regulations on the use of TBT-based antifoulants introduced in 1989. These regulations prohibit the use of TBT-based antifoulants on most recreational boats, but still allow the use on boats greater than 25 metres in length and those with aluminum hulls.

**TABLE 1 Concentrations of Butyltin Compounds in Mussels from South Coastal
Marinas in British Columbia (1987 to 1995) (7)**

LOCATION	YEAR	TBT	TOTAL BUTYLtin (ng Sn/g wet weight)
Crescent Beach:			
Crescent Beach Marina	1987	1,100	1,770
	1988	290-940	750-3,690
	1995	43	115
Coal Harbour Area:			
Bayshore Marina	1987	730	3,530
	1988	420-1,100	1,500-2,240
	1989	740-1,000	1980-2,410
	1991	260-420	550-826
	1995	84-120	161-235
RVYC Marina	1988	410-970	2,000-4,370
	1989	590-680	1,650-1,900
	1991	220	658
	1995	64-74	104-172
False Creek Area:			
Marina at the market	1988	850-1,700	2,400-9,400
	1991	300-630	551-990
	1995	200	564
Government Wharf/ Fisherman's Terminal	1987	630	1,650
	1988	260-870	1,100-4,000
	1995	310-320	820-830

Mussels collected off the government wharf/Fisherman's Terminal in False Creek in the late 1980's also contained elevated concentrations of butyltin compounds (1,500 to 3,530 ng Sn/g). Although both TBT and total butyltin levels appear to have decreased somewhat since the late 1980's (Table 1), the decrease is less dramatic than that observed at other marina sites. Most of the vessels docked at the government wharf/Fisherman's Terminal are commercial fishing vessels. Many of these vessels have aluminum hulls and/or exceed 25 metres in length, therefore, the use of TBT-based antifoulants on these vessels is still permitted. This probably accounts for the continued presence of elevated TBT concentrations at this site.

Several hundreds of ng Sn/g of butyltin compounds were detected in mussels collected from several marinas on Vancouver Island and at Horseshoe Bay in the late 1980's, but information on current levels of butyltin compounds at these sites was not available (7).

Mussels collected off several commercial docks and shipyards in Vancouver Harbour in the late 1980's also contained several hundred ng Sn/g of butyltin compounds. However, in contrast to the declining concentrations of butyltin compounds observed in mussels from False Creek, Coal Harbour and Crescent Beach marinas, concentrations in mussels collected from commercial docks and shipyards in the 1990's had not decreased. The only exception was Allied Shipyards where mussels collected in 1995 contained 289 to 590 ng Sn/g of total butyltin compounds compared to 1,400 ng Sn/g detected in 1988 (7).

Elevated concentrations of butyltin compounds were also detected in mussels collected from Point Grey at the mouth of the Fraser River in 1993 (115), Comox Harbour in 1987 (7), and at the DND facility at Constance Cove in Esquimalt Harbour in 1990. Total butyltin concentrations in mussels from these sites exceeded 400 ng Sn/g.

Butyltin compounds were also detected in mussels collected at aquaculture sites (4.2 to 140 ng Sn/g) and in recreational boating areas (6 to 217 ng Sn/g) (7).

Mussels collected from reference sites including Crescent Beach, Larkin Island and French Beach contained total butyltin concentrations of less than or close to the detection limits (0.9 to 6 ng Sn/g) (7).

Clams collected from Victoria and Esquimalt harbours in 1990, and also from various coastal marinas in 1988, contained total butyltin concentrations in the hundreds of ng Sn/g range. Concentrations of butyltin compounds in clams from the Nanaimo area in 1991 ranged from 14.6 to 75 ng Sn/g, and similar concentrations were detected in clams collected near coastal aquaculture sites (5 to 76 ng Sn/g) and recreational boating areas (11 to 49 ng Sn/g) in 1988. Clams collected at reference sites contained 2.8 to 7.5 ng Sn/g of total butyltin compounds (7).

Concentrations of total butyltin compounds were less than 50 ng Sn/g in oysters collected from Comox Harbour in 1987 and Nanaimo Harbour in 1991 (7). In 1987, oysters

from a southern Vancouver Island oyster farm exhibited shell deformities characteristic of TBT contamination and contained an average of 97 ng Sn/g of butyltin compounds (114). The oyster farm was located near a salmon farm using TBT-based antifoulants on net pens. The use of TBT at the salmon farm was terminated and the oysters collected from this location in 1988 contained much lower levels of butyltin compounds (12 ng Sn/g) (7). Concentrations of butyltin compounds in oysters collected from other aquaculture facilities in 1988 ranged from 14 to 128 ng Sn/g (7). The presence of shell deformities at these facilities was not recorded.

Cullen *et al* (110) reported that oysters collected from the Wreck Beach area of Vancouver in 1989 contained total butyltin concentrations of greater than 250 ng Sn/g. Oysters collected at Fanny Bay on Vancouver Island in 1993 contained 56.6 ng Sn/g (110).

Oysters collected from recreational boating areas contained total butyltin concentrations ranging from 7.6 to 142 ng Sn/g. Seasonally elevated concentrations of butyltin compounds were detected in shellfish from recreational boating areas at Pendrell Sound, Prideaux Haven and Roscoe Bay in 1988. Concentrations in oysters, clams, and mussels were approximately 10 fold higher during peak boating season in August than at the start of boating season in June (7). Although, it is likely that the introduction of regulations on the use of TBT-based antifoulants on recreational boats in 1989 would have reduced such seasonal elevations in butyltin levels, confirmation is required.

Shrimp from the Coal Harbour region of Vancouver Harbour and from Constance Cove in Esquimalt Harbour contained substantially higher concentrations of butyltin compounds (250 to 300 ng Sn/g) than did shrimp collected from Victoria Harbour or from Plumper Bay in Esquimalt Harbour (40 to 60 ng Sn/g). Shrimp collected from outer Vancouver Harbour contained 9 ng Sn/g, while shrimp from the reference site contained approximately 2 ng Sn/g (7).

Elevated levels of total butyltin compounds (97 to 1,028 ng Sn/g) were present in the hepatopancreas of Dungeness crabs collected from the Fraser River estuary, False Creek, and Vancouver Harbour in 1988 and from Victoria Harbour and Esquimalt Harbour in 1990 and 1991. Much lower concentrations of butyltin compounds were found in the muscle tissues of crabs from all sites (less than 5 to 83 ng Sn/g). The hepatopancreas of crabs from the reference sites contained 4.3 to 71 ng Sn/g (7).

Concentrations of butyltin compounds were also elevated in fish from harbour areas. Whole body concentrations were highest in English sole from Constance Cove in Esquimalt Harbour in 1990 (377 ng Sn/g) and in starry flounder collected off Allied Shipyards in Vancouver Harbour in 1988 (962 ng Sn/g). Total butyltin concentrations did not exceed 100 ng Sn/g in whole body analysis of most species of fish collected from False Creek and Vancouver Harbour in 1986, 1988, and 1991 and from Victoria and Esquimalt harbours in 1990 (7).

Fish liver contained much higher concentrations of butyltin compounds than did the muscle tissue. For example, starry flounder from the Port Moody area of Vancouver Harbour contained 910 ng Sn/g in liver tissue compared to 23 ng Sn/g in muscle tissue. Similarly, muscle tissue of rockfish collected from Coal Harbour and from a reference site outside Vancouver Harbour did not contain detectable levels of butyltin compounds. However, rockfish from Coal Harbour contained 68 ng Sn/g in the liver, while the rockfish from the reference site contained 23 ng Sn/g in the liver (7).

Total butyltin concentrations in whole body samples of rockfish collected off two salmon farms in 1988 were somewhat higher (31 to 45 ng Sn/g) than concentrations in rockfish from the reference site (3 to 12 ng Sn/g) (7). Elevated levels of butyltin compounds were also detected in muscle and liver tissue of farmed salmon raised in TBT-treated net pens. Total butyltin concentrations of up to 3,320 ng Sn/g in the liver and 247 ng Sn/g in the muscle tissue were detected. In comparison, wild salmon contained 4 to 16 ng Sn/g in the liver and 0.3 to 5.8 ng Sn/g in muscle. In salmon liver tissue much of the butyltin present was in the form of DBT, while in the muscle tissue virtually all of the butyltin was present as TBT (7). There are no Canadian guidelines for acceptable levels of butyltin compounds in fish or shellfish intended for human consumption. Although more recent information on butyltin levels in fish from coastal salmon farms was not available, it is expected that concentrations would no longer be elevated due to the fact that the aquaculture industry voluntarily terminated the use of TBT shortly after the 1988 survey was completed.

Tricyclohexyltin and triphenyltin were not detected in mussels collected from Vancouver Harbour or in various species of biota collected from False Creek, Victoria Harbour, or Esquimalt Harbour (7). Similarly, with the exception of one oyster sample, clams and oysters from Nanaimo Harbour did not contain detectable levels of tricyclohexyltin or triphenyltin. Dicyclohexyltin was not detected in mussel, crab, and fish samples from False Creek and Vancouver Harbour (7). However, according to Cullen *et al* (110), dicyclohexyltin was present in oysters collected from Fanny Bay (12 ng Sn/g), Jervis Inlet (1 ng Sn/g), and Wreck Beach (34 ng Sn/g) in 1989. Tricyclohexyltin was not detected in these samples. Similarly, Stewart and Thompson (115) did not detect cyclohexyltin or phenyltin compounds in shellfish from five locations in south coastal British Columbia or in flatfish collected from two locations in the Fraser River.

No information was available on the presence of organotin compounds in fish-eating birds and aquatic mammals in British Columbia. However, birds and mammals feeding on fish and shellfish in the vicinity of harbours, marinas, shipyards and commercial docks may accumulate elevated concentrations of butyltin compounds.

3.2 Terrestrial Systems

General

Information on the levels of organotin compounds in the terrestrial environment is lacking.

Cyclohexyltin and triphenyltin compounds have been detected in fruits and vegetables following the agricultural application of pesticides containing these active ingredients. Concentrations of cyclohexyltin in cucumbers, tomatoes, and peppers rarely exceed 0.5 mg/kg. Maximum values in apples and pears on the day of pesticide application were reported to be less than 2 mg/kg. Concentrations decreased by 50% within approximately three weeks due to photodegradation. Concentrations of triphenyltin compounds in potatoes and carrots rarely exceed 0.1 $\mu\text{g/g}$. Washing and peeling vegetables and fruits also removes significant amounts of both cyclohexyltin and phenyltin (2).

Virtually no information is available on the levels of organotin compounds in wildlife or other terrestrial species. However, low concentrations of TPT have been detected in milk obtained from cows fed contaminated sugar beet leaves (2).

Information on birds is very limited. TBT was detected (ng Sn/g wet weight) in the liver and muscle of oystercatchers in the United Kingdom but not in starlings and gulls in Japan (152,153).

The main routes of exposure for terrestrial animals are associated with the use of these compounds as agricultural pesticides and wood preservatives. A microcosm study to examine the effects of TBT oxide treated wood posts on terrestrial species revealed no effects on soil organisms, worms, insects, crickets, snails, and a vole after 77 days of exposure. It was observed that 95% of the TBT oxide remained in the posts over the study period (155).

British Columbia

No information is available on levels of organotin compounds in the terrestrial environment of British Columbia.

4. TOXICITY⁴

4.1 Aquatic Organisms

The toxicity of organotin compounds to aquatic organisms is determined by their structure and is related to the side chain length and their octanol-water partition coefficient. For example, the alkyltin compounds in decreasing order of toxicity are butyltin compounds > propyltin compounds > ethyltin compounds > methyltin compounds. The information on the toxicity of aryltin compounds is limited. However, some studies suggest that phenyltin is comparable in toxicity to butyltin in at least some species of aquatic organisms (156).

Triorganotin compounds are more toxic than tetra-, di-, or mono-organotin compounds. However, toxicity tests with butyltin compounds indicate that the anionic radical (eg. chloride, fluoride, oxide, hydroxide, acetate) has much less influence on toxicity (157,158).

Environmental factors such as temperature, pH, dissolved oxygen, suspended solids, salinity, and water hardness are also important in determining the toxicity of environmental contaminants, including organotin compounds. Greater mortality has been observed in oysters exposed to TBT in seawater at higher salinity levels. Also, it has been demonstrated that the presence of sediment reduces the toxic effects of TBT to grass shrimp and oysters in laboratory situations (137,159 to 161). More information is required on the effects of environmental variables on the toxicity of organotin compounds.

Organotin compounds, and particularly TBT, affect energy production by interfering with the oxidative phosphorylation processes (162 to 166). Organotin compounds also affect the survival, growth, metabolism, and reproduction of aquatic organisms at ng/L to $\mu\text{g/L}$ concentrations. Significant interspecific differences in sensitivity to organotin compounds have been observed in aquatic organisms. Size, age and genetic variations may account for some of these differences. Larval and juvenile life stages of aquatic organisms are often more susceptible to the effects of organotin compounds than are adults. Route and duration of exposure are also important factors in determining uptake and toxicity (119,132,161,167 to 173).

4. Concentrations cited in this section are presented on an organotin cation basis (eg. Bu_2Sn_2^+). To convert the values to a Sn basis, in order to compare with the data presented in the environmental levels sections, divide the values cited by the conversion factors listed in Appendix 1.

Molluscs are particularly sensitive to TBT. This may be due, at least in part, to the very low cytochrome P-450 content and MFO activity in molluscs that limit the detoxifying abilities of these organisms (134,135,174).

Exposure of bivalve species to low concentrations of TBT (less than 1 $\mu\text{g/L}$) in both laboratory and field situations results in adverse effects. These include significant mortality in larval stages, abnormal development of the shell and gonad, and reduced larval settlement and growth (33,174 to 179). TBT in low concentrations can interfere with shell calcification resulting in shell deformities such as chambering, thickening, and balling. The meat yield in affected oysters is usually significantly reduced. This effect has commonly been observed in southern France and England since the 1970's (81,142,180 to 182). In addition, a condition known as imposex (the development of male sex organs in females) is widespread in gastropods from coastal areas of several countries and has been attributed to TBT contamination (183 to 189). In laboratory tests this condition has been observed at concentrations of 20 ng/L TBT and the NOEL (no observed effect level) for the development of imposex is reported to be less than 1 ng/L (183,190).

Recent studies in other areas of the world indicate that mollusc populations have shown signs of recovery since the restrictions on TBT use in antifouling paints were introduced. Oyster populations have shown signs of significant recovery in France (80), Australia (191), and the United Kingdom (99,192). Similarly, Evans *et al* (193,194) reported evidence of recovery of dogwhelk populations from imposex symptoms in the United Kingdom. However, recovery will probably be slow in many areas. Gibbs *et al* (195) reported that a significant incidence of imposex on the French coast was still evident seven years after the ban on TBT antifoulants.

Acute toxicity tests with TBT revealed 96 hr LC_{50} values for marine invertebrate species ranging from 0.42 $\mu\text{g/L}$ for juvenile mysid shrimp to greater than 100 $\mu\text{g/L}$ for adult oysters (168,169,196 to 198). Growth inhibition, reproductive effects, and reduced neonatal survival were observed in marine copepods at concentrations of 0.01 to 0.1 $\mu\text{g/L}$ depending on the species and the duration of exposure (169,170,197 to 200). Growth retardation and deformities in regenerated limbs were observed in fiddler crabs exposed to 0.5 $\mu\text{g/L}$ TBT or greater (201,202). Similarly, regeneration and molting were retarded in shrimp exposed for 14 days to a concentration of 0.1 $\mu\text{g/L}$ of TBT (203). Little information is available for freshwater crustaceans. Effects on behaviour and reproduction occur at TBT concentrations of less than 1 $\mu\text{g/L}$ (204 to 207).

The acute toxicity of TBT to fish is highly variable. Acutely toxic levels (96 hour LC_{50} s) for various species of fish range from 1.5 to over 200 $\mu\text{g/L}$ (129,157,169,172,198, 204,208,209). Numerous sublethal effects have also been observed in fish exposed to TBT concentrations in the low $\mu\text{g/L}$ range. These include the disruption of enzyme activity (210,211); decreased growth (212); behavioural abnormalities (213,214); increased liver weight (212); histopathological changes in the liver, kidney and gill (212,213,215,216); thymus

atrophy (215); reduced hatchability of eggs (217); decreased embryo viability (217); vertebral malformations in larvae and other abnormalities (217). Effects on the eye, swim bladder, skin, mouth and thyroid gland have also been documented (216).

Aquatic plants and phytoplankton exposed to TBT in the ng/L range experienced decreased growth, decreased primary productivity, inhibition of spore settling, degeneration, and mortality (218 to 222). The sensitivity of aquatic vegetation and phytoplankton varies with species and may be related to their ability to degrade TBT into less toxic degradation products. Studies with the diatom *Skeletonema costatum* show that this species can degrade TBT without lethal effects, even at 4 degrees C (223).

Less information is available on the effects of MBT and DBT to aquatic plants. DBT and MBT are less toxic than TBT and, therefore, higher concentrations of these compounds are required to cause similar effects (218 to 223).

Information on the effects of other organotin compounds on aquatic organisms is limited. Some of the reported effects include: inhibition of enzymes in fish brains by tricyclohexyltin (210); inhibition of digestive enzymes in fish by trimethyltin chloride (211); changes in carbohydrate, fat and protein metabolism in fish by triethyltin chloride (224); behavioural changes in fish larvae by phenyltin compounds (225); decreased fecundity in snails by tripropyltin (226); and decreased population growth in aquatic vegetation species by methyltin, ethyltin, propyltin and phenyltin (221,226,227).

Evidence of TBT toxicity has been observed in marine invertebrates from coastal areas of British Columbia. Growth and shell abnormalities characteristic of TBT toxicity were first observed in 1985 in commercially reared oysters from Nanoose Bay on Vancouver Island, following the installation of a salmon farm using TBT net treatments (114). In addition, imposex was reported to be widespread throughout the Straits of Georgia and Juan de Fuca. All six species of gastropods examined were affected (184,186).

Canadian water quality guidelines for the protection of aquatic life recommend that, in freshwater systems, TBT and TPT concentrations not exceed 8 ng/L (3 ng Sn/L) and 20 ng/L (7 ng Sn/L), respectively. The recommended guideline for TBT in marine and estuarine systems is 1 ng/L (0.4 ng Sn/L). There are no Canadian water quality guidelines for other organotin compounds (156).

4.2 Terrestrial Organisms

As with aquatic species, the triorganotin compounds are more toxic to terrestrial species than are mono- and diorganotin compounds. Tetraorganotin compounds have toxic effects similar to triorganotin compounds, but the effects are somewhat milder and usually delayed (156). Trimethyltin (TMT) and triethyltin (TET) are the most toxic of the trialkyltin compounds to mammals (2).

Exposure of mammals to organotin compounds has resulted in effects on the central nervous system, liver, bile duct, and spleen; brain development; oxidative phosphorylation; cytochrome P-450 activity; enzyme activity in the brain; blood lipid levels; endocrine system; growth; and pituitary and thyroid activity (163 to 167, 228 to 235). Immune system impairment, embryotoxicity and fetotoxicity have also been observed (236, 237).

However, not all these effects are elicited by all organotin compounds. For example, neurological damage has been observed following exposure to trimethyl- (TMT) and triethyltin (TET), but not following exposure to dimethyl-, diethyl-, or organotin compounds of higher alkyl groups (229).

There is no conclusive evidence of teratogenicity, carcinogenicity, or mutagenicity in mammals exposed to butyltin compounds. However, teratogenicity was observed in rats exposed to TPT hydroxide (238).

Based on information summarized by Eisler (239), LD₅₀ values (single oral dose) for TMT were 3.0 mg/kg body weight for marmoset and from 9.1 to 30 mg/kg body weight for rats. The LD₅₀ values for TET were between 4 and 10 mg/kg body weight for rats, rabbits, and guinea pigs. In comparison, the LD₅₀ values for these species of experimental animals exposed to TBT ranged from 20 to 380 mg/kg body weight. Acute toxicity information for organotin compounds was also summarized in Moore *et al* (156). LD₅₀ values for rats and mice exposed to TBT ranged from 44 to 234 mg/kg body weight. LD₅₀ values for TPT ranged from 110 to 491 mg/kg body weight for rats, 80 to 1000 mg/kg body weight for mice, 10 to 41.2 mg/kg body weight for guinea pigs, and 30 to 140 mg/kg body weight for rabbits. The LD₅₀ value for rats exposed to tricyclohexyltin was 540 mg/kg body weight (156).

The route by which organotin compounds are administered affects their toxicity to experimental animals. Organotin compounds are less toxic when administered orally than via other routes (intramuscularly, intravenously, etc.), as adsorption from the gut is not efficient (161). Dermal exposure results in a low acute toxicity, although irritation of the skin and eyes has been documented (240 to 242). TBT in aerosol form is highly toxic and results in lesions in the respiratory system, lung congestion, and death (161).

In both mammals and birds, TBT is metabolized to dibutyltin, monobutyltin, and ultimately to inorganic tin (229,243). Organotin compounds concentrate mainly in the liver and kidney (161) but can cross the blood-brain barrier and also enter the fetus via the placenta (161,244).

Little information on toxicity to avian species was available, however, there was some evidence that trimethyltin and triethyltin compounds are the most toxic. A single oral dose of 3 mg/kg body weight of trimethyltin or triethyltin was fatal to domestic chickens in 24 hours, while 50 mg/kg trimethyltin in the diet of mallard ducks was fatal within 60 days. The acute oral LD₅₀ of tricyclohexyltin was between 255 and 390 mg/kg body weight for Japanese quail and 654 mg/kg body weight for domestic chickens (239,245). Many other effects have been observed including impaired motor response, tremors and convulsions, degradation and necrosis of the cerebral cortex by trimethyltin; behavioural changes, muscular weakness, convulsions, decreased food consumption, vacuolization of spinal cord and brain white matter by triethyltin; changes in blood chemistry and central nervous system damage by tetraethyltin (225,245 to 248).

Organotin compounds are toxic to a wide range of insects. TBT is more toxic to house flies than are phenyltin, tricyclohexyltin, diethyltin and dimethyltin, but is much less toxic than trimethyltin. Exposure of honey bees to TBT oxide treated wood has resulted in high mortality (161).

5. REGULATIONS, CONTROLS AND GUIDELINES⁵

The current regulations and guidelines pertaining to the presence or release of organotin compounds in the aquatic environment are as follows.

5.1 Water Quality

Guidelines are provided for reference as one source of information in assessing environmental quality. It must be emphasized that guidelines should not be used in direct isolated comparisons with monitoring data. Site specific factors including local biophysical conditions must also be considered and guideline numbers may need to be modified to suit local aquatic conditions. For example, the toxicity of many chemicals varies with environmental variables including pH, temperature, water hardness, presence of other toxic compounds and also the species and life stage of the organisms.

The Canadian Water Quality Guidelines were developed by the Canadian Council of Ministers of the Environment (CCME). Recommended guidelines for organotin compounds were published in 1992. Interim guidelines for organotin compounds in freshwater systems are 8 ng/L (3 ng Sn/L) for tributyltin and 20 ng/L (7 ng Sn/L) for triphenyltin. Additional toxicity information was considered necessary prior to the acceptance of these interim guidelines as final. The recommended guideline for tributyltin in marine and estuarine systems is 1 ng/L (0.4 ng Sn/L). Toxicity information available for other organotin compounds was considered insufficient for the development of guidelines (156).

Water quality guidelines for organotin compounds were developed for agricultural water supplies. The recommended guidelines for livestock water are 250 µg/L (100 µg Sn/L) for TBT, 800 µg/L (270 µg Sn/L) for TPT, and 250 µg/L (80 µg Sn/L) for tricyclohexyltin (interim level). Available information was not sufficient for the development of guidelines for drinking water, recreational water, agricultural irrigation, and industrial water supplies (156).

5. The concentrations cited in this section refer to the concentrations of the organotin cations (eg. Bu_2Sn_2^+). To convert the data to a Sn basis, divide the values cited by the conversion factors listed in Appendix 1.

The United States Environmental Protection Agency (EPA) proposed water quality criteria for TBT specify a four-day average concentration and a one hour average concentration that should not be exceeded more than once every three years. For freshwater systems, the proposed four-day average concentration is 26 ng/L (10 ng Sn/L) and the one hour average concentration is 149 ng/L (60 ng Sn/L). For marine environments, the proposed four-day average concentration is 10 ng/L (4 ng Sn/L) and the one hour average concentration is 266 ng/L (109 ng Sn/L) (249).

In the United Kingdom an environmental quality target of 20 ng/L (8 ng Sn/L) for marine waters was introduced by the Department of the Environment in 1985. This has since been replaced by an environmental quality standard of 2 ng/L (0.8 ng Sn/L) due to evidence that aquatic organisms could be adversely affected at concentrations below 20 ng/L (8 ng Sn/L) (101).

5.2 Human Health

There are presently no Canadian guidelines for acceptable levels of organotin compounds in fish and shellfish intended for human consumption. Incidents of elevated organotin levels in commercially important species would be reviewed on a case by case basis.

Maximum allowable residue levels for fenbutatin oxide (Vendex ®) in fruits and vegetables are specified under the *Canadian Food and Drug Act* Regulations.

The Food Packaging Materials section of the *Canadian Food and Drug Act* Regulations specifies the permitted uses of certain organotin stabilizers in PVC food packaging materials and also tolerance levels in packaged food.

There are no existing Canadian drinking water guidelines for organotin compounds. Similarly, the United States EPA and the World Health Organization have not proposed drinking water guidelines for these chemicals. However, the United Nations Food and Agriculture Organization (FAO/WHO) has recommended acceptable daily intakes of 0.5 µg/L for triphenyltin and 7.5 µg/L of tricyclohexyltin. Researchers examining mammalian toxicity and human health risks have suggested an acceptable daily intake of 3.2 µg/L for tributyltin (161).

5.3 Ocean Disposal

The ocean disposal of wastes and other materials off the Canadian coast is controlled under the federal *Canadian Environmental Protection Act (CEPA)*, Part VI, Ocean Dumping Regulations. There are currently no criteria for maximum levels of organotin compounds in materials to be ocean disposed.

5.4 Use and Release

Federal and provincial legislation provide controls on the entry of organotin compounds into the environment.

The provincial *Pesticide Control Act* ensures that the sale and use of pesticides in British Columbia comply with label instructions.

The federal *Pest Control Products Act* requires the registration of all pesticides used, manufactured, and sold in Canada. It also regulates these products with respect to composition, packaging, labelling, distribution, and use. All organotin compounds used for pesticidal purposes must be registered. As of 1989, *Pest Control Products Act* regulations have prohibited the manufacturing, importation, distribution, retail sale, and use of all unregistered antifouling paints. In addition, registration requirements for tributyltin-based antifouling paints specified that these products must not be used on vessels under 25 metres in length, with the exception of aluminum hulled vessels and outboard marine fittings. Registered TBT antifouling paints must be of the 'low leaching' type with a maximum tin release rate of $4 \mu\text{g}/\text{cm}^2/\text{day}$ for TBT. The registration requirements for organotin-based antifoulants have very likely resulted in a decrease in the volume of organotin compounds used for antifoulant purposes in Canada.

Non-regulatory actions to reduce the entry of organotin-based paints and antifoulants in the environment have also been initiated. In 1989, Environment Canada, published and distributed a pamphlet entitled "Don't Foul Things Up" which recommends voluntary guidelines for the use of antifouling paints on pleasure craft (14). These guidelines were adapted from guidelines originally published and distributed by the Royal Yachting Association of Great Britain. Adherence to these guidelines during the application of new paint and the removal of old paint would effectively reduce the input of chemical antifoulants into the aquatic environment from pleasure craft. The guidelines were updated and distributed in 1993 and again in 1995. In addition, Environment Canada - Pacific and Yukon Region has developed documents outlining best management practices (BMPs) for ship and boat building and repair facilities and for marinas and small boatyards in British Columbia (12,13). These documents were prepared in cooperation with the provincial Ministry of Environment, Lands and Parks, the Greater Vancouver Regional District, the Department of Fisheries and Oceans, and the Burrard Inlet Environmental Action Program. The recommendations from these documents will be applicable to government and private facilities that service commercial and recreational vessels of any size. Compliance promotion will be initiated and industry's voluntary implementation of the recommendations will be monitored. The recommended practices focus on surface preparation, coatings (storage, application, and disposal), waste fluids, petroleum products and chemical storage, general yard maintenance, spill prevention and response, standards and internal best management practices, monitoring and training.

The federal *Fisheries Act* subsection 36(3) prohibits the deposition of deleterious substances into waters frequented by fish. This legislation has never been used for prosecution of any offences involving organotin compounds.

The *British Columbia Waste Management Act* controls the handling and disposal of industrial and municipal wastes. Regulations under this Act control the transportation and disposal of contaminated waste materials. Levels of chemical contaminants in specific industrial effluents and atmospheric emissions can also be controlled under the provisions contained in this legislation. This legislation has not been used for the control of organotin releases.

The transport of organotin compounds and organotin-contaminated wastes is regulated under the *Transportation of Dangerous Goods Act* (Canada). Regulations under this Act are administered jointly by the Federal, Provincial and Territorial Governments.

REFERENCES

1. Thompson, J.A.J., M.G. Sheffer, R.C. Pierce, Y.K. Chau, J.J. Cooney, W.R. Cullen and R.J. Maguire. 1985. Organotin compounds in the aquatic environment: scientific criteria for assessing their effects on environmental quality. Associate Committee on Scientific Criteria or Environmental Quality. National Research Council of Canada (NRCC) Publ.No. 22494, Ottawa, Canada. 284 pp.
2. World Health Organization (WHO). 1980. Tin and organotin compounds: a preliminary review. Environmental Health Criteria 15. Task Group on Environmental Health Aspects of Tin and Organotin Compounds. 109 pp.
3. Piver, W.T. 1973. Organotin compounds; industrial applications and biological investigation. *Environmental Health Perspect.* **4**: 61-79.
4. Maguire, R.J. 1991. Aquatic environmental aspects of non-pesticide organotin compounds. *Water Poll. Res. J. Canada.* **26**(3): 243-360.
5. Krahn, P. 1985. Characterization and chemical use patterns of the plastics, rubber and resin industry in British Columbia. Regional program report: 85-05, Environmental Protection Service, Environment Canada, Vancouver, B.C., 102 pp.
6. Krahn, P. 1985. Characterization and chemical use patterns of the paints and coatings industry in British Columbia. Regional Program Report: 85-09, Environmental Protection Service, Environment Canada, Vancouver, B.C., 61 pp.
7. Garrett, C.L. and J.A. Shrimpton. In preparation. Organotin compounds in the British Columbia environment. Regional program report 96-01, Environmental Protection, Environment Canada, Vancouver, B.C.
8. Higashiyama, T., H. Shiraushi, A. Otsuki and S. Hashimoto. Concentrations of organotin compounds in blue mussels from the wharves of Tokyo Bay. *Mar. Poll. Bull.* **22**(12): 585-587.
9. Fent, K. and J. Hunn. 1991. Phenyltins in water, sediment and biota of freshwater marinas. *Environ. Sci. Technol.* **25**: 956-963.
10. Lawrence, M., March 1993. Agriculture Canada, Plant Industry Information Service, Ottawa, Canada, Personal communication.
11. Agriculture Canada. 1989. Decision Document: Cyhexatin; Bulletin 89-01, Pesticides Directorate, Agriculture Canada, Ottawa, 18 pp.

12. Environment Canada, 1995. Best Management Practices (BMPs) for Marinas and Small Boatyards in British Columbia. DOE FRAP 1995-16. Prepared for Environment Canada by PCA Consultants., 18 pp.
13. Environment Canada, 1995. Best Management Practices for the Ship and Boat Building and Repair Industry in British Columbia. DOE FRAP 1995-14. Prepared for Environment Canada by PCA Consultants., 26 pp.
14. Environment Canada, 1995. Don't Foul Things Up. Information Pamphlet.
15. Schebek, L., M.O. Andraea and H.J. Tabschall. 1991. Methyl- and butyltin compounds in water and sediments of the Rhine River. *Environ. Sci. Technol.* **25**: 871-878.
16. Fent, K., J. Hunn, D. Renggli and H. Siegrist. 1991. Fate of tributyl-tin in sewage sludge treatment. *Mar. Environ. Res.* **32**: 223-231.
17. Fent, K. 1989. Organotin speciation in municipal wastewater and sewage sludge: ecotoxicological consequences. *Mar. Environ. Res.* **28**: 477-483.
18. Chau, Y.K., S. Zhang and R.J. Maguire. 1992. Occurrence of butyltin species in sewage and sludge in Canada. *Sci. of the Total Environ.* **121**: 271-281.
19. Braman, R.S. and M.A. Tompkins. 1979. Separation and determination of nanogram amounts of inorganic tin and methyltin compounds in the environment. *Anal. Chem.* **51**: 12-19.
20. Fent, K. 1991. Occurrence of organotins in municipal wastewater and sewage sludge and behaviour in a treatment plant. *Environ. Sci Technol.* **25**: 489-493.
21. Waldock, M.J., M.E. Waite and J.E. Thain. 1987. Changes in concentrations of organotins in U.K. rivers and estuaries following legislation in 1986. In: Proceedings of the Oceans '87 Conference, Volume 4: International Organotin Symposium. Halifax, Nova Scotia. 28 September to 1 October 1987. pp. 1352-1356.
22. Bacci, E. and C. Gaggi. 1989. Organotin compounds in harbour and marina waters from the northern Tyrrhenian Sea. *Mar. Poll. Bull.* **20**: 290-292.
23. Randall, L. and J.H. Weber. 1986. Adsorptive behaviour of butyltin compounds under simulated estuarine conditions. *Sci. Total Environ.* **57**: pp. 191-203.
24. Donard, O.F.X. and J.H. Weber. 1985. Behaviour of methyltin compounds under simulated estuarine conditions. *Environ. Sci. Technol.* **19**: 1104-1110.

25. Stang, P.M. and P.F. Seligman. 1987. *In situ* adsorption and desorption of butyltin compounds from Pearl Harbour, Hawaii, sediment. *In: Proceedings of the Oceans '87 Conference, Volume 4: International Organotin Symposium. Halifax, Nova Scotia. 28 September to 1 October 1987. pp.1386-1391.*
26. Weber, J.H., O.F.X. Donard, L. Randall and J.S. Han. 1986. Speciation of methyl- and butyltin compounds in the Great Bay estuary (N.H.), 1986. *In: Proceedings of the Oceans '86 Conference, Volume 4: Organotin Symposium. Washington, D.C. 23 to 25 September 1986. pp. 1280-1282.*
27. Quevauviller, P., R. Lavigne, R. Pinel and M. Astruc. 1989. Organotins in sediments and mussels from the Sado estuarine system (Portugal). *Environ. Poll. 57: 149-166.*
28. Harris, J.R.W. and J.J. Cleary. 1987. Particle-water partitioning and organotin dispersal in an estuary. *In: Proceedings of the Oceans '87 Conference, Volume 4: International Organotin Symposium. Halifax, Nova Scotia. 28 September to 1 October 1987. pp. 1370-1374.*
29. Johnson, W.E., L.W. Hall, Jr., S.J. Bushong and W.S. Hall. 1987. Organotin concentrations in centrifuged versus uncentrifuged water column samples and in sediment pore waters of a northern Chesapeake Bay Tributary. *In: Proceedings of the Oceans '87 Conference, Volume 4: International Organotin Symposium. Halifax, Nova Scotia. 28 September to 1 October 1987. pp. 1364-1369.*
30. Valkirs, A.O., M.O. Stallard and P.F. Seligman. 1987. Butyltin partitioning in marine waters. *In: Proceedings of the Oceans '87 Conference, Volume 4: International Organotin Symposium. Halifax, Nova Scotia. 28 September to 1 October 1987. pp.1375-1380.*
31. Valkirs, A.O., B. Davidson, L.L. Kear, R.L. Fransham, J.G. Grovhoug and P. F. Seligman. 1991. Longterm monitoring of tributyltin in San Diego Bay California. *Mar. Environ. Res. 32: 151-167.*
32. Valkirs, A.O., P.F. Seligman and R.F. Lee. 1986. Butyltin partitioning in marine waters and sediments. *In: Proceedings of the Oceans '86 Conference, Volume 4: Organotin Symposium. Seattle, Washington. 23 to 25 September 1986. pp. 1165-1170.*
33. Thain, J.E., M.J. Waldock and M.E. Waite. 1987. Toxicity and degradation studies of tributyltin (TBT) and dibutyltin (DBT) in the aquatic environment. *In: Proceedings of the Oceans '87 Conference, Volume 4. International Organotin Symposium. Halifax, Nova Scotia, 28 September to 1 October 1987. pp. 1398-1404.*

34. Laughlin, R.B. Jr., H.E. Guard and W.M. Coleman. 1986. Tributyltin in seawater: speciation and octanol-water partition coefficient. *Environ. Sci. Technol.* **20**(2): pp. 201-204.
35. Laughlin, R., W. French and H.F. Guard. 1983. Acute and sublethal toxicity of tributyltin oxide and its putative environmental product, tributyltin sulfide to zoeal mud crabs, *Rhithropanopeus harrisi*. *Water, Air and Soil Poll.* **20**: 69-79.
36. Maguire, R.J. and R.K. Tkacz. 1985. Degradation of tri-n-butyltin species in water and sediment from Toronto Harbour. *J. Agric. Food Chem.* **33**: 947-953.
37. Unger, M.A., W.G. MacIntyre and R.J. Huggett. 1987. Equilibrium sorption of tributyltin chloride by Chesapeake Bay sediments. In: Proceedings of the Oceans '87 Conference, Volume 4: International Organotin Symposium. Halifax, Nova Scotia. 28 September to 1 October 1987. pp. 1381-1385.
38. Laughlin, R.B. Jr. and O. Linden. 1985. Fate and effects of organotin compounds. *Ambio*. **14**(2): 88-92.
39. Stewart, C. and S. J. de Mora. 1990. A review of the degradation of tri(n-butyl)tin in the marine environment. *Environ. Technol.* **11**: 565-570.
40. Maguire, R.J. 1987. Environmental aspects of tributyltin. *Appl. Organomet. Chem.* **1**: 475-498.
41. Seligman, P.F., A.O. Valkirs and R.F. Lee. 1986. Degradation of tributyltin in marine and estuarine waters. In: Proceedings of the Oceans '86 Conference, Volume 4: Organotin Symposium. Seattle, Washington. 23 to 25 September 1986. pp. 1189-1195.
42. Clark, E.A., R.M. Sterritt and J.N. Lester. 1988. The fate of tributyltin in the aquatic environment. *Environ. Sci. Technol.* **22**(6): 600-604.
43. Seligman, P.F. A.O. Valkirs and R.F. Lee. 1986. Degradation of tributyltin in San Diego Bay, California, waters. *Environ. Sci. Technol.* **22**(6): 600-604.
44. de Mora, S.J., N.G. King, and M.C. Miller. 1989. Tributyltin and total tin in marine sediments: profiles and the apparent rate of TBT degradation. *Environ. Technol. Letters* **10**: 901-908.

45. Astruc, M.R., R. Lavigne, R. Pinel, F. Leguille, V. Deauziers, P. Quevauviller, and O. Donard. 1989. Speciation of tin in sediments of Arcachon Bay. *In: the Second International Symposium on Metal Speciation, Separation, Recovery.* J.W. Patterson and R. Passino, Eds., Lewis Publishers, Rome. pp. 263-281.
46. Maguire, R.J., R.K. Tkacz and D.L. Sartor. 1985. Butyltin species and inorganic tin in water and sediment of the Detroit and St. Clair rivers. *J. Great Lakes Res.* 11(3): 320-327.
47. Cardwell, R.D. 1988. Fate and effects of tributyltin in the marine environment: an update on knowledge. Paper presented at Puget Sound Research, First Annual Meeting. Seattle, Washington, March 18-19, 1988.
48. Cardwell, R.D. and A.W. Sheldon. 1986. A risk assessment concerning the fate and effects of tributyltin in the aquatic environment. *In: Proceedings of the Oceans '86 Conference, Volume 4: Organotin Symposium.* Seattle, Washington. 23 to 25 September 1986. pp. 1117-1129.
49. Maguire, R.J. 1986. Review of the occurrence, persistence and degradation of tributyltin in freshwater ecosystems in Canada. *In: Proceedings of the Oceans '86 Conference, Volume 4: Organotin Symposium.* Seattle, Washington. 23 to 25 September 1986. pp. 1252-1255.
50. Seligman, P.F., A.O. Valkirs, P.M. Strong and R.F. Lee. 1988. Evidence for rapid degradation of tributyltin in a marina. *Mar. Poll. Bull.* 19(10): 531-534.
51. Barug, D. 1981. Microbial degradation of bis(tributyltin) oxide. *Chemosphere* 10(10): 1145-1154.
52. Olson, G.J. and F.E. Brinckman. 1986. Biodegradation of tributyltin by Chesapeake Bay microorganisms. *In: Proceedings of the Oceans '86 Conference, Volume 4: Organotin Symposium.* Seattle, Washington. 23 to 25 September 1986. pp. 1196-1201.
53. Lee, R.F., A.O. Valkirs and P.F. Seligman. 1987. Fate of tributyltin in estuarine waters. *In: Proceedings of the Oceans '87 Conference, Volume 4: International Organotin Symposium.* Halifax, Nova Scotia, 28 September to 1 October 1987. pp. 1411-1415.
54. Lee, R.F., A.O. Valkirs and P.F. Seligman. 1989. Importance of microalgae in the biodegradation of tributyltin in estuarine waters. *Environ. Sci. Technol.* 23: 1515-1518.

55. Lee, R.F. 1989. Fate of tributyltin. *In: Proceedings of the Oceans '89 Conference, Volume 2: Ocean Pollution. Seattle, Washington, 18 to 21 September 1989.* pp. 512-515.
56. Maguire, R.J., J.H. Carey and E.J. Hale. 1983. Degradation of the tributyltin species in water. *J. Agric. Food Chem.* **31**: 1060-1065.
57. Slesinger, A.E. and I. Dresser. 1978. The environmental chemistry of three organotin compounds. *In: Good, M. (Ed). Report of the Organotin Workshop. New Orleans, Louisiana, 17 to 19 February 1978.* pp. 115-162.
58. Blunden, S.J. 1983. The ultraviolet degradation of methyltin chlorides in carbon tetrachloride and water. *J. Organomet. Chem.* **248**: 149-160.
59. Tugrul, S., T.I. Balkas and E.D. Goldberg. 1983. Methyltins in the marine environment. *Mar. Poll. Bull.* **14**(8): 297-303.
60. Dahab, A.O., M.A. El-Sabrouti and Y. Halim. 1990. Tin compounds in sediments of Lake Maryut, Egypt. *Env. Poll.* **63**: 329-344.
61. Hallas, L.E., J.C. Means and J.J. Cooney. 1982. Methylation of tin by estuarine microorganisms. *Science.* **215**(4539): 1505-1507.
62. Craig, P.J. and S. Rapsonmanikis. 1985. Methylation of tin and lead in the environmental oxidative methyl transfer as a model for environmental reactions. *Environ. Sci. Technol.* **19**: 726-730.
63. Cooney, J.J. 1988. Microbial transformations of tin and tin compounds. *J. Ind. Microbiol.* **3**: 195-204.
64. Alzieu, C., P. Michel, I. Tolosa, E. Bacci, L.D. Lee and J. W. Readman. 1991. Organotin compounds in the Mediterranean: a continuing cause for concern. *Mar. Environ. Res.* **32**: 261-270.
65. Soderquist, C.J. and D.G. Crosby. 1980. Degradation of triphenyltin hydroxide in water. *J. Agric. Food Chem.* **28**(1): 111-117.
66. Smith, G.N., F.S. Fischer and R.J. Axelson. 1976. Volatilization and photodecomposition of Plictran miticide. *J. Agric. Food Chem.* **24**(6): 1225-1229.
67. Blair, E.H. 1975. Biodegradation of tricyclohexyltin hydroxide. *Environ. Qual. Saf. Suppl.* **3**: 406-409.

68. Getzander, M.E. and H.B. Corbin. 1972. Residues on apples and pears from the use of a Plictran miticide. *J. Agric. Food Chem.* **20**(4): 881-885.
69. Engelhart, J.E. and A.W. Sheldon. Cited in Zuckerman, J.J., R.P. Reisdorf, H.V. Ellis and R.R. Wilkinson, 1978. Organotin. *In: Organometals and Organometalloids: Occurrence and Fate in the Environment*. F.E. Brinkman and J.M. Bellama (Eds.). American Chemical Society Symposium. Series 82, pp. 388-422.
70. Loch, J.P.G., P.A. Greve and S. Van der Berg. 1990. Accumulation and leaching of the fungicide Fentin acetate and intermediates in sandy soils. *Water, Air and Soil Poll.* **53**: 119-129.
71. Muller, M.D. and H.P. Bosshardt. 1987. Degradation and residues of cyclohexyltin compounds in orchard soil and following field application of Cyhexatin. *Bull. Environ. Cont. Toxicol.* **38**: 627-633.
72. Chapman, A.H. and J.W. Price. 1972. Degradation of triphenyltin acetate by ultraviolet light. *Int. Pest Control.* **14**: 11-12.
73. Cenci, P. and B. Cremonini. 1969. Thin layer chromatography of two organotin pesticides and their behaviour in various types of soil. *Ind. sac. Ital.* **69**: 313-316 (as cited Reference #2).
74. Akagi, H. and Y. Sakagami. 1971. On degradation of organotin compounds by ultraviolet ray. *Rep. Public Health Inst.* **20**: 1-4 (as cited in Reference #2).
75. Barnes, R.O., A.T. Bull and R.C. Poller. 1973. Studies on the persistence of the organotin fungicide, fentin acetate (triphenyltin acetate) in the soil and on surfaces exposed to light. *Pestic. Sci.* **4**: 305-317.
76. Waldock, M.J. and D. Miller. 1983. The determination of total and tributyltin in seawater and oysters in areas of high pleasure craft activity. Marine Environmental Quality Committee Report CM 1983/E:12. Ministry of Agriculture, Fisheries and Food, Fisheries Laboratory, Burnham-on-Crouch. U.K. (as cited in Reference #39).
77. Grovhoug, J.G., P.F. Seligman, G. Vafa and R.L. Fransham. 1986. Baseline measurements of butyltin in U.S. harbours and estuaries. *In: Proceedings of the Oceans '86 Conference, Volume 4: Organotin Symposium*. Seattle, Washington. 23 to 25 September 1986. pp. 1283-1288.
78. Seligman, P.F., J.G. Grovhoug, A.O. Valkirs, P. M. Stang, R. Fransham, M.O. Stallard, B. Davidson and R.F. Lee. 1989. Distribution and fate of tributyltin in the United States Marine Environment. *Appl. Organometal. Chem.* **3**: 31-47.

79. Hall, L.W., Jr., S. J. Bushong, W.E. Johnson and W.S. Hall. 1988. Spatial and temporal distribution of butyltin compounds in Maryland waters of Chesapeake Bay. *Mar. Poll. Bull.* **18**: 78-83.
80. Alzieu, C., J. Sanjuan, P. Michel, M. Borel and J.P. Dreno. 1989. Monitoring and assessment of butyltins in Atlantic coastal waters. *Mar. Poll. Bull.* **20**(1): 22-26.
81. Waldock, M.J., J.E. Thain and M.E. Waite. 1987. The distribution and potential toxic effects of TBT in U.K. estuaries during 1986. *Appl. Organometal. Chem.* **1**: 287-301.
82. Ritsema, R., W.P.M. Laane and O.F.X. Donard. 1991. Butyltins in marine waters of the Netherlands in 1988 and 1989; concentrations and effects. *Mar. Environ. Res.* **32**: 243-260.
83. Langston, W.J., G.R. Burt and Z. Mingiling. 1987. Tin and organotin in water, sediments, and benthic organisms of Poole Harbour. *Mar. Poll. Bull.* **18**: 634-639.
84. Cocchieri, A.R., A. Biondi, A. Arnese, and A. Pannaccione. 1993. Total tin and organotin in seawater from the Gulf of Naples, Italy. *Mar. Poll. Bull.* **26**(6): 338-341.
85. Cleary, J.J. and A.R.D. Stebbing. 1985. Organotin and total tin in coastal waters of southwest England. *Mar. Poll. Bull.* **16**(9): 350-355.
86. Ebdon, L., K. Evans and S. Hill. 1988. The variation of tributyltin levels with time in selected estuaries prior to the introduction of regulations governing the use of tributyltin-based antifouling paints. *Sci. Total Environ.* **68**: 207-223.
87. Waldock, M.J., M.E. Waite and J.E. Thain. 1988. Inputs of TBT to the marine environment from shipping activity in the U.K. *Environ. Technol. Letters* **9**: 999-1010.
88. Jensen, A. and Z. Cheng. 1987. Total tin and organotin in seawater from pleasure craft marinas along Danish coast of the Sound. In: Proceedings of the 15th Conference of Baltic Oceanographers (CBO), Copenhagen, 1986. Charlottenlung, Denmark, Marine Pollution Laboratory, Vol. 1, pp. 289-298 (as cited in Reference #2).
89. Seligman, P.F., J.G. Grovhoug and K.E. Richter. 1986. Measurement of butyltins in San Diego Bay, CA: A monitoring strategy. In: Proceedings of the Oceans '86 Conference, Volume 4: Organotin Symposium. Seattle, Washington. 23 to 25 September 1986. pp. 1289-1296.

90. Maguire, R.J. and R.J. Thacz. 1987. Concentration of tributyltin in the surface microlayer of natural waters. *Water Pollut. Res. J. Can.* **22**(2): 227-233.
91. Maguire, R.J., Y.K. Chau, G.A. Bengert, E.J. Hale, P.T.S. Wong and O. Kramar. 1982. Occurrence of organotin compounds in Ontario lakes and rivers. *Environ. Sci. Technol.* **16**(10): 698-702.
92. Dowson, P.H., J.M. Bubb and J.N. Lester. 1992. Organotin distribution in sediments and waters of selected east coast estuaries in the UK. *Mar. Poll. Bull.* **24**(10):492-498.
93. Fortman, T.J. and E.A. Crecelius. 1989. Tributyltin concentrations in sediments of Puget Sound urban bays, non-urban bays and marinas, *In: Proceedings of the Oceans '89 Conference, Volume 2: Ocean Pollution, Seattle, Washington.* 18 to 21 September 1989. pg. 696.
94. Stallard, M., V. Hodge and E.D. Goldberg. 1987. TBT in California coastal waters: monitoring and assessment. *Environ. Monit. Assess.* **9**: 195-220.
95. Makkar, N.S., A.T. Kronick and J.J. Cooney. 1989. Butyltins in sediments from Boston Harbour, U.S.A. *Chemosphere* **18**(9/10): 2043-2050.
96. Krone, C.A., D.W. Brown, D.G. Burrows, S.L. Chan and U. Varanasi. 1989. Butyltins in sediments from marinas and waterways in Puget Sound, Washington State, U.S.A. *Mar. Poll. Bull.* **20**(10): 528-531.
97. Stewart, C. and S.J. de Mora. 1992. Elevated tri(n-butyl)tin concentrations in shellfish and sediments from Suva Harbour, Fiji. *Appl. Organomet. Chem.* **6**: 507-512.
98. Yonezawa, Y., K. Nakata, Y. Miyakozawa, A. Ochi, T. Kowata, H. Fukawa, Y. Sato, S. Masunaga, and Y. Urushigawa. 1993. Distributions of butyltins in the surface sediment of Ise Bay, Japan. *Environ. Toxicol. Chem.* **12**: 1175-1184.
99. Sarradin, P.M., A. Astruc, V. Desauziers, R. Pinel and M. Astruc. 1991. Butyltin pollution in surface sediments of Arcachon Bay after 10 years of restricted use of TBT-based paints. *Environ. Technol.* **12**: 537-543.
100. Waite, M.E., M.J. Waldock, J.E. Thain, D.J. Smith and S.M. Milton. 1991. Reductions in TBT concentrations in U.K. estuaries following legislation in 1986 and 1987. *Mar. Environ. Res.* **32**: 89-111.

101. Cleary, J.J. 1991. Organotin in the marine surface microlayer and sub-surface waters of south-west England: Relation to toxicity thresholds and the U.K. environmental quality standard. *Mar. Res.* **32**: 213-222.
102. Donard, O.F.X., S. Rapsomanikis and J.H. Weber. 1986. Speciation of inorganic tin and alkyltin compounds by atomic absorption spectrometry using eletrothermal quartz furnace after hydride generation. *Anal. Chem.* **58**: 772-777.
103. Randall, L, J.S. Han and J.H. Weber. 1986. Determination of inorganic tin, methyltin and butyltin compounds in sediments. *Environ. Tech. Letters* **7**: 571-576.
104. Maguire, R.J., R.J. Tkacz, Y.K. Chau, G.A. Bengert and P.T.S. Wong. 1986. Occurrence of organotin compounds in water and sediment in Canada. *Chemosphere* **15**(3): 253-274.
105. Hashimoto, S., Y. Koshikawa, Y. Sirizawa and A. Otsuki. 1989. Monitoring of organic tin compounds in inland sea by transplant of reference blue mussels. *In: Proceedings of the Oceans '89 Conference, Volume 2: Ocean Pollution, Seattle, Washington. 18 to 21 September 1989.* pp. 1049-1053.
106. Muller, M.D. 1987. Comprehensive trace level determination of organotin compounds in environmental samples using high-resolution gas chromatography with flame photometric detection. *Analytical Chemistry* **59**: 617-623.
107. Blair, W.R., G.J. Olson, F.E. Brinkman, R.C. Paule, and D.A. Becker. 1986. An international butyltin measurement methods intercomparison: sample preparation and results of analyses. National Bureau of Standards, NBSIR 86-3321.
108. Carter, R.J., N.J. Turoczy and A.M. Bond. 1989. Container adsorption of tributyltin (TBT) compounds: implications for environmental analysis. *Environ. Sci. Technol.* **23**(5): 615-617.
109. Carter, R.J., N.J. Turoczy and A.M. Bond. 1988. Environmental levels of tributyltin (TBT): does container adsorption render the results invalid? *In: Proceedings of the Conference on Organotin Materials in the Marine Environment. Centre for Coastal Management, Feb. 3-4, 1988. Northern Rivers College of Advanced Education, Lismore, N.S.W., Nicholas Holmes, Ed.,* pp. 35-39.
110. Cullen, W.R., G.K. Eigendorf, B. U. Nwata and A Takatsu. 1990. The quantitation of butyltin and cyclohexyltin compounds in the marine environment of British Columbia. *Appl. Organomet. Chem.* **4**: 581-590.

111. Kaye, K., D. Hope and B. Humphrey. 1986. Organotin concentrations in Esquimalt Harbour. Prepared by Seakem Oceanography Ltd. for Research and Development Branch, Department of National Defense. Contractors Report Series 86-35, 29 pp.
112. Stewart, C. and S. J. de Mora. 1991. A study of the efficacy of the 1989 Pesticides (Organotin Antifouling Paints) Regulations. University of Auckland, New Zealand, Report for the Ministry for the Environment (New Zealand), 23 pp.
113. Gabrielides, G.P., C. Alzieu, J.W. Readman, E. Bacci, O. Aboul Dahab and I. Salihoglu. 1990. MEDPOL survey of organotins in the Mediterranean. *Mar. Poll. Bull.* **21**(5): 233-237.
114. Harding, L. and B. Kay. 1988. Levels of organotins in water, sediments and oysters (*Crassostrea gigas*) from Nanoose Bay, B.C. Environmental Protection, Environment Canada, Vancouver, B.C. 9 pp.
115. Stewart, C. and J.A.J. Thompson. 1994. Extensive butyltin contamination in southwestern coastal B.C., Canada. *Mar. Poll. Bull.* **28**(10): 601-606.
116. Swain, L.G. and D. G. Walton. 1993. Chemistry and toxicity of sediments from sloughs and routine monitoring sites in the Fraser River Estuary - 1992. Fraser River Monitoring Program. 234 pp.
117. Blair, W.R., G.J. Olson, F.E. Brinkman and W. P. Iverson. 1982. Accumulation and fate of tri-n-butyltin cation in estuarine bacteria. *Microbiol. Ecol.* **8**: 241-251.
118. Maguire, R.J. 1984. Butyltin compounds and inorganic tin in sediments in Ontario. *Environ. Sci. Technol.* **18**(4): 291-294.
119. Laughlin, R.B. Jr., W. French and H.E. Guard. 1986. Accumulation of bis(tributyltin)oxide by marine mussel *Mytilus edulis*. *Environ. Sci. Technol.* **20**(9): 884-890.
120. Laughlin, R.B., Jr. 1986. Bioaccumulation of tributyltin: the link between environment and organism. In: Proceedings of the Oceans '86 Conference, Volume 4: Organotin Symposium. Seattle, Washington. 23 to 25 September 1986. pp. 1206-1209.
121. Bryan, G.W., P.E. Gibbs, L.G. Hummerstone and G.R. Burt. 1989. Uptake and transformation of ¹⁴C-labelled tributyltin chloride by the dog-whelk, *Nucella lapillus*: importance of absorption from the diet. *Mar. Environ. Res.* **28**: 241-245.

122. Cardwell, R.D. and J.P. Meador. 1989. Tributyltin in the environment: overview and key issues. *In: Proceedings of the Oceans '89 Conference, Volume 2: Ocean Pollution.* Seattle, Washington. 18 to 21 September 1989. pp. 537-544.
123. Iwata, H., S. Tanabe, T. Mizuno, and R. Tatsukawa. 1995. High accumulation of toxic butyltins in marine mammals from Japanese coastal waters. *Environ. Sci. Technol.* **29**: 2959-2962
124. Laughlin, R.B. Jr. and W. French. 1988. Concentration dependence of bis(tributyl)tin oxide accumulation in the mussel, *Mytilus edulis*. *Environ. Toxicol. Chem.* **7**: 1021-1026.
125. Lee, R.F. 1989. Metabolism and accumulation of xenobiotics within hepatopancreas cells of the blue crab *Callinectes sapidus*. *Mar. Environ. Res.* **28**: 93-97.
126. Evans, D.W. and R. B. Laughlin. 1984. Accumulation of bis(tributyltin) oxide by the mud crab, *Rhithropanopus harristii*. *Chemosphere* **13**(1): 213-219.
127. Martin, R.C., D.G. Dixon, R.J. Maguire, P.V. Hodson and R.J. Thacz. 1989. Acute toxicity, uptake, depuration and tissue distribution of tri-n-butyltin in rainbow trout, *Salmo gairdneri*. *Aq. Toxicol.* **15**: 37-52.
128. Martin, R.C., D.G. Dixon, R.J. Maguire, P.V. Hodson and R.J. Thacz. 1988. Acute toxicity, uptake, depuration and tissue distribution of tri-n-butyltin in rainbow trout, *Salmo gairdneri*. NWRI report RRB-88-29, Environment Canada, Burlington, Ontario.
129. Davies, I.M. and J.C. McKie. 1987. Accumulation of total tin and tributyltin in muscle tissue of farmed Atlantic salmon. *Mar. Poll. Bull.* **18**(7): 405-407.
130. Tsuda, T., M. Wada, S. Aoki and Y. Matsui. 1987. Excretion of bis(tri-n-butyltin)oxide and triphenyltin chloride from carp. *Toxicol. Environ. Chem.* **16**: 17-22.
131. Tsuda, T., H. Nakanishi, S. Aoki and J. Takebayashi. 1988. Bioconcentration and metabolism of butyltin compounds in carp. *Water Res.* **22**(5): 647-651.
132. Langston, W.J. and G.R. Burt. 1991. Bioavailability and effects of sediment-bound TBT in deposit-feeding clams, *Scrobicularia plana*. *Mar. Environ. Res.* **32**: 61-77.
133. Tsuda, T., S. Aoki, M. Kojima and H. Harada. 1990. Differences between freshwater and seawater-acclimated guppies in the accumulation and excretion of tri-n-butyltin chloride and triphenyltin chloride. *Water Res.* **24**(11): 1373-1376.

134. Lee, R.F. 1985. Metabolism of tributyltin oxide by crabs, oysters and fish. *Mar. Environ. Res.* **17**: 145-148.
135. Lee, R.F. 1986. Metabolism of bis(tributyltin)oxide by estuarine animals. *In*: Proceedings of the Oceans '86 Conference, Volume 4: Organotin Symposium. Seattle, Washington. 23 to 25 September 1986. pp. 1182-1188.
136. Ward, G.S., G.C. Cramm, P.R. Parrish, H. Trachman and A. Slesinger. 1981. Bioaccumulation and chronic toxicity of bis(tributyltin)oxide (TBTO): Tests with a saltwater fish. *In*: Aquatic Toxicology and Hazard Assessment. Fourth Conference. ASTM Spec. Tech. Publ. 737. D.R. Branson and K.L. Dickson (eds.) American Society for Testing and Materials, Philadelphia, PA. pp. 183-200.
137. Tsuda, T., M. Wada, S. Aoko and Y. Matsui. 1988. Bioconcentration, excretion, and metabolism of bis(tri-n-butyltin) oxide and triphenyltin chloride by goldfish. *Toxicol. Environ. Chem.* **18**: 11-20.
138. Tas, J.W., J.L.M. Hermens, M. Van den Berg and W. Seenen. 1989. Bioconcentration and elimination of triphenyltin hydroxide in fish. *Mar. Environ. Res.* **28**: 215-218.
139. Wade, T.L., B. Garcia-Romero and J.M. Brooks. 1991. Oysters as biomonitors of butyltins in the Gulf of Mexico. *Mar. Environ. Res.* **32**: 233-241.
140. Wade, T.L. and B. Garcia-Romero. 1989. Status and trends of tributyltin contamination of oysters and sediments from the Gulf of Mexico. *In*: Proceedings of the Oceans '89 Conference, Volume 2: Ocean Pollution, Seattle, Washington. 18 to 21 September 1989. pp. 550-553.
141. Uhler, A.D., G.S. Durell, W.G. Steinhauer and A.M. Spellacy. 1993. Tributyltin levels in bivalve molluscs from the east and west coast of the United States; results from the 1988-1990 national status and trends mussel watch project. *Environ. Toxicol. Chem.* **12**: 139-153.
142. Alzieu, C., J. Sanjuan, J.P. Deltreil and M. Borel. 1986. Tin contamination in Arcachon Bay; effects on oyster shell anomalies. *Mar. Poll. Bull.* **17**: 494-498.
143. Short, J.W. and J.L. Sharp. 1989. Tributyltin in bay mussels (*Mytilus edulis*) of the Pacific Coast of the United States. *Environ. Sci. Technol.* **23**(6): 740-743.
144. Uhler, A.D., T.H. Coogan, K.S. Davis, G.S. Durell, W.G. Steinhauer, S.Y. Freitas and P.D. Boehm. 1989. Findings of tributyltin, dibutyltin and monobutyltin in bivalves from selected U.S. coastal waters. *Environ. Toxicol. Chem.* **8**: 971-979.

145. King, N., M. Miller and S. de Mora. 1989. Tributyltin levels for sea water, sediment and selected marine species in coastal Northland and Auckland, New Zealand. *N. Z. J. Mar. F.W. Res.* **23**: 287-294.
146. Wade, T.L., B. Garcia-Romero and J.M. Brooks. 1988. Tributyltin concentrations in bivalves from United States coastal estuaries. *Environ. Sci. Technol.* **22**(12): 1488-1493.
147. Becker, K., L. Merlini, N. de Bertrand, L.F. de Alencastro and J. Tarradelias. 1992. Elevated levels of organotins in Lake Geneva: Bivalves as sentinel organisms. *Bull. Environ. Cont. Toxicol.* **48**: 37-44.
148. Short, J.W. and F.P. Thrower. 1986. Accumulation of butyltins in muscle tissue of chinook salmon reared in sea pens treated with tri-n-butyltin. *Mar. Poll. Bull.* **17**(12): 542-545.
149. Krone, C.A., S.L. Chan and U. Varanasi. 1991. Butyltins in sediments and benthic fish tissues from the east, Gulf and Pacific coasts of the United States. In: Proceedings of the Oceans '91 Conference. Volume 2: Ocean Technologies and Opportunities in the Pacific for the 90's, Honolulu, Hawaii, pp. 1054-1059.
150. Krone, C.A., G. Burrows, D.W. Brown, S.L. Chan and U. Varanasi. 1989. Tributyltin contamination of sediment and English sole from Puget Sound. In Oceans: '89 Conference, Volume 2: Ocean Pollution, Seattle, Washington. 18 to 21 September 1989. pp. 545-549.
151. Sullivan, J.J., Torkelson, J.D. Wekell, M.W. Hollingworth, T.A. Saxon, W.L. Miller, G.A. Panaro, K.W. and A.D. Uhler. 1988. Determination of tri-n-butyltin and di-n-butyltin in fish as hydride derivatives by reaction gas chromatography. *Anal. Chem.* **60**: 626-630.
152. Osborne, D. and D.V. Leach. 1987. Organotins in birds: pilot study. Huntingdon Institute of Terrestrial Ecology, 15 pp. Final report to the U.K. Department of the Environment. Contract No. F3CR/27/D4/01) (as cited in Reference #160).
153. EAJ. 1988. Outline of TBT compounds monitored in Japan. Tokyo Environment Agency of Japan, OECD Clearing House Project on Organotins (as cited in Reference #160).
154. Iwata, H., S. Tanabe, N. Miyazaki, and R. Tatsukawa. 1994. Detection of butyltin compound residues in the blubber of marine mammals. *Mar. Poll. Bull.* **28**(10): 607-612.

155. Gill, J.D., J.C. Collins and J.W. Gillett. 1982. Fate and impact of wood preservatives in a terrestrial microcosm. *J. Agric. Food Chem.* **30**: 295-301.
156. Moore, D.R.J., D.G. Noble, S.L. Walker, D.M. Trotter, M.P. Wong and R.C. Pierce. 1992. Canadian Water Quality Guidelines for Organotins. Scientific Series No. 191. Ecosystem Sciences and Evaluation Directorate, Environment Canada, Ottawa, Ontario. 145 pp.
157. Linden, D., B.E. Bengtsson, O. Svanberg and G. Sundstrom. 1979. The acute toxicity of 78 chemicals and pesticide formulations against two brackish water organisms, the bleak (*Alburnus alburnus*) and the harpactoid (*Nitocra spinipes*). *Chemosphere* **8**(11/12): 843-851.
158. Walsh, G.E., C. H. Deans and L.L. McLaughlin. 1987. Comparison of the EC₅₀s of algal toxicity tests calculated by four methods. *Environ. Toxicol. Chem.* **6**: 767-770.
159. Laughlin, R.B. Jr. and W. French. 1989. Differences in responses to factorial combinations of temperature and salinity by zoeal from two geographically isolated populations of the mud crab, *Rhithropanopeus harrisi*. *Mar. Biol.* **102**: 387-395.
160. Laughlin, R.B. Jr. and W. French. 1989. Interactions between temperature and salinity during brooding on subsequent zoeal development of the mud crab, *Rhithropanopeus harrisi*. *Mar. Biol.* **102**: 377-386.
161. World Health Organization. 1990. Environmental Health Criteria Document 116. World Health Organization, Geneva. pp 273.
162. Rosenberg, D.W. and G.S. Drummond. 1983. Direct effects of bis(tributyl)tin oxide on hepatic cytochrome P-450. *Biochem. Pharmacol.* **32**: 3823-3829.
163. Rosenberg, D.W., G.S. Drummond, H.C. Cornish and A. Kappas. 1980. Prolonged induction of hepatic haem oxygenase and decreases in cytochrome P-450 content by organotin compounds. *Biochem. J.* **190**: 465-468.
164. Rosenberg, D.W., M.K. Sardana and A. Kappas. 1985. Altered induction response of hepatic cytochrome P-450 to phenobarbital, 3-methyl-cholanthene and B. naphthoflavone in organotin treated animals. *Biochem. Pharmacol.* **34**: 997-1005.
165. Evans, W. H., N.F. Cardarelli and D.J. Smith. 1979. Accumulation and excretion of [1-14C] bis (tri-n-butyltin) oxide in mice. *J. Toxicol. Environ. Health* **5**: 871-877.

166. Aldridge, W.N. and B.W. Street. 1971. Oxidative phosphorylation: the relation between specific binding of trimethyltin and triethyltin to mitochondria and their effects on various mitochondrial functions. *Biochem. J.* **124**: 221-234.
167. Widdows, J. and D.S. Page. 1993. Effects of tributyltin and dibutyltin on the physiological energetics of the mussel, *Mytilus edulis*. *Mar. Environ. Res.* **35**: 233-249.
168. Clark, J.R., J.M. Patrick, Jr., L.C. Moore and E.M. Lores. 1987. Waterborne and sediment source toxicities of six organic chemicals to grass shrimp (*Palaemonetes pugio*) and amphioxus (*Branchiostoma caribaeum*). *Arch. Environ. Contam. Toxicol.* **16**: 401-407.
169. Thain, J.E. 1983. The acute toxicity of bis(tributyltin)oxide to the adults and larvae of some marine organisms. Copenhagen, Int'l Council for the Exploration of the Sea (ICES) 5 pp. (Report #CM 1983/E13).
170. Hall, L.W. Jr., S.J. Bushong, W.S. Hall and W.E. Johnson. 1988. Acute and chronic effects of tributyltin on a Chesapeake Bay copepod. *Environ. Toxicol. Chem.* **7**(1): 41-46.
171. Bushong, S.J., W.S. Hall, W.E. Johnson and L.W. Hall. 1987. Toxicity of tributyltin to selected Chesapeake Bay biota. In: Proceedings of the Oceans '87 Conference, Volume 4: International Organotin Symposium. Halifax, Nova Scotia. 28 September to 1 October 1987. pp. 1499-1503.
172. Short, J.W. and F.P. Thrower. 1987. Toxicity of tri-n-butyltin to chinook salmon, *Oncorhynchus tshawytscha* adapted to seawater. *Aquaculture* **61**: 193-200.
173. Weis, J.S. and J. Perlmutter. 1987. Effects of tributyltin on activity and burrowing behaviour of the fiddler crab, *Uca pugilator*. *Estuaries* **10**(4): 342-346.
174. Lee, R.F. 1991. Metabolism of tributyltin by marine animals and possible linkages to effects. *Mar. Environ. Res.* **32**: 29-35.
175. Salazar, M.H. and S.M. Salazar. 1987. Tributyltin effects on juvenile mussel growth. In: Proceedings of the Oceans '87 Conference, Volume 4: International Organotin Symposium, Halifax, Nova Scotia. 28 September to 1 October 1987. pp. 1504-1510.
176. Thain, J.E. and M.J. Waldock. 1986. The impact of tributyltin (TBT) antifouling paints on molluscan fisheries. *Water Sci. Technol.* **18**: 193-202.

177. Stomgren, T. and T. Bongard. 1987. The effect of tributyltin oxide on growth of *Mytilus edulis*. *Mar. Poll. Bull.* **18**: 30-31.
178. Roberts, M.H. 1987. Acute toxicity of tributyltin chloride to embryos and larvae of two bivalve mollusks, *Crassostrea virginica* and *Mercenaria mercenaria*. *Bull. Environ. Contam. Toxicol.* **39**: 1012-1019.
179. Laughlin, R.B. Jr., R.G. Gustafson and P. Pendoley. 1989. Acute toxicity of tributyltin (TBT) to early life history stages of the hard shell clam, *Mercenaria mercenaria*. *Bull. Environ. Contam. Toxicol.* **42**: 352-358.
180. Alzieu, C. 1986. TBT detrimental effects on oyster culture in France - evolution since antifouling paint regulations. *In*: Proceedings of the Oceans '86 Conference, Volume 4: Organotin Symposium. Seattle, Washington. 23 to 25 September 1986. pp. 1130-1134.
181. Waldock, M.J. and J.E. Thain. 1983. Shell thickening in *Crassostrea gigas* - Organotin antifouling or sediment induced. *Mar. Poll. Bull.* **14**(11): 411-415.
182. Alzieu, C. and J. E. Portmann. 1984. The effect of tributyltin on the culture of *Crassostrea gigas* and other species. *In*: Proceedings of the 50th Annual Shellfish Conference, 15 to 16 May 1984. pp. 87-104.
183. Gibbs, P.E. and G.W. Bryan. 1987. TBT paints and the demise of the dog whelk, *Nucella lapillus*. *In*: Proceedings of the Oceans '87 Conference, Volume 4: International Organotin Symposium. Halifax, Nova Scotia. 28 September to 1 October 1987. pp. 1482-1487.
184. Ellis, D.V. and L.A. Pattisina. 1990. Widespread Neogastropod imposex, a biological indicator of global TBT contamination? *Mar. Poll. Bull.* **21**(5): 248-253.
185. Alvarez, M.S. and D.V. Ellis. 1990. Widespread neogastropod imposex in the northeast Pacific: implications for TBT contamination surveys. *Mar. Poll. Bull.* **21**(5): 244-247.
186. Bright, D.A. and D.V. Ellis. 1990. A comparative survey of imposex in northeast Pacific neogastropods related to tributyltin contamination and choice of a suitable bioindicator. *Can. J. Zool.* **68**: 1915-1924.
187. Short, J.W., S.D. Rice, C.C. Broderson and W.B. Stukle. 1989. Occurrence of tri-n-butyltin caused imposex in the north Pacific marine snail *Nucella limi* in Auke Bay, Alaska. *Mar. Biol.* **102**: 291-297.

188. Smith, P. J. and M. McVeagh. 1991. Widespread organotin pollution in New Zealand coastal waters as indicated by imposex in dogwhelks. *Mar. Poll. Bull.* **22**(8): 409-413.
189. Ten Hallers-Tjabbes, C.C., J.F. Kemp, and J.P. Boon. 1994. Imposex in whelks (*Buccinum undatum*) from the open North Sea: Relation to shipping traffic intensities. *Mar. Poll. Bull.* **28**(5): 311-313.
190. Bryan, G.W., P.E. Gibbs, L. G. Hummerstone, and G.R. Burt. 1986. The decline of the gastropod *Nucella lapillus* around southwest England: evidence for the effect of tributyltin from antifouling paints. *J. Mar. Biol. Assoc. U.K.* **66**: 611-640.
191. Batley, G.E., M.S. Scammel, and C.I. Brockbank. 1992. The impact of the banning of tributyltin-based antifouling paints on the Sydney rock oyster, *Saccostrea commercialis*. *Sci. Tot. Environ.* **122**: 301-314.
192. Dyrinda, E.A. 1992. Incidence of abnormal shell thickening in the Pacific oyster *Crassostrea gigas* in Poole Harbour (UK), subsequent to the 1987 TBT restrictions. *Mar. Poll. Bull.* **24**: 156-163.
193. Evans, S.M., A. Hutton, M.A. Kendall, A.M. Samosir. 1991. Recovery in populations of dogwhelks *Nucella lapillus* (L.) suffering from imposex. *Mar. Poll. Bull.* **22**: 331-333.
194. Evans, S.M., S.T. Hawkins, J. Porter, and A.M. Samosir. 1994. Recovery of dogwhelk populations on the Isle of Cumbrae, Scotland following legislation limiting the use of TBT as an antifoulant. *Mar. Poll. Bull.* **28**(1): 15-17.
195. Gibbs, P.E., G.W. Bryan, P.L. Pascoe, and G.R. Burt. 1990. Reproductive abnormalities in female *Ocenebra erinacea* (Gastropoda) resulting from tributyltin-induced imposex. *J. Mar. Biol. Assoc. U.K.* **10**: 639-656.
196. Davidson, B.M., A.O. Valkirs and P. F. Seligman. 1986. Acute and chronic effects of tributyltin on the mysid *Acanthomysis sculpta*. In: Proceedings of the Oceans '86 Conference, Volume 4: Organotin Symposium. Seattle, Washington, 22 to 25 September 1986, pp. 1219-1225.
197. U'Ren, S.C. 1983. Acute toxicity of bis(tributyltin)oxide to a marine copepod. *Mar. Poll. Bull.* **14**: 303-306.
198. Bushong, S.J., L.W. Hall, W.S. Hall, W.E. Johnson and R.L. Herman. 1988. Acute toxicity of tributyltin to selected Chesapeake Bay fish and invertebrates. *Water Res.* **22**: 1027-1032.

199. Bushong, S.J., M. C. Ziegenfuss, M.A. Unger and L.W. Hall, Jr. 1990. Chronic tributyltin toxicity experiments with Chesapeake Bay copepod, *Acartia tonsa*. *Environ. Toxicol. Chem.* **9**: 359-366.
200. Johansen, K. and F. Mohlenberg. 1987. Impairment of egg production in *Acartia tonsa* exposed to tributyltin oxide. *Ophelia* **27**(2): 137-141.
201. Weis, J.S., P. Weis and F. Wang. 1987. Developmental effects of tributyltin on the fiddler crab, *Uca pugilator* and the killifish, *Fundulus heteroclitus*. In: Proceedings of the Oceans '87 Conference, Volume 4: Organotin Symposium. Halifax, Nova Scotia, 28 September to 1 October 1987. pp. 1456-1460.
202. Weis, J.S., J. Gottlieb and J. Kwiatkowski. 1987. Tributyltin retards regeneration and produces deformities of limbs in the fiddler crabs, *Uca pugilator*. *Arch. Env. Contam. Toxicol.* **16**: 321-326.
203. Khan, A.T., J.W. Weiss, C.E. Saharig, and A.E. Polo. 1993. Effect of tributyltin on mortality and telson regeneration of grass shrimp, *Palaemonetes pugio*. *Bull. Environ. Cont. Toxicol.* **50**: 152-157.
204. Brooke, L.T., D.J. Call, S.H. Poirier, T.P. Markee, C.A. Lindber, D.J. McCauley and P.G. Simonson. 1986. Acute toxicity and chronic effect of bis(tributyltin)oxide to several species of freshwater organisms. Centre for Lake Superior Environmental Studies, University of Wisconsin - Superior, WI.
205. Meador, J.T. 1986. An analysis of photobehaviour of *Daphnia magna* exposed to tributyltin. In: Proceedings of the Oceans '86 Conference, Volume 4: Organotin Symposium. Seattle, Washington. 23 to 25 September 1986, pp.1213-1218.
206. Valkirs, A., B. Davidson and P. Seligman. 1985. Sublethal growth effects and mortality to marine bivalves and fish from long-term exposure to tributyltin. Technical Report NOSC-TR-1042 or AD-A162-629-0. Naval Ocean Systems Centre, San Diego, CA.
207. Goodman, L.K., G.M. Cripe, P.H. Moody and D.G. Halsell. 1988. Acute toxicity of malathion, tetrabromobisphenol-A, and tributyltin chloride to mysids of three ages. *Bull. Environ. Contam. Toxicol.* **41**: 746-753.
208. Tooby, T.E., P. A. Hursey and J.S. Alabaster. 1975. The acute toxicity of 102 pesticides and miscellaneous substances to fish. *Chem. Ind.* **12**: 523-526.
209. Cotta-Ramusino, M. Doci and A. Doci. 1987. Acute toxicity of Bresdan and Fentin acetate on some freshwater organisms. *Bull. Environ. Contam. Toxicol.* **38**: 647-652.

210. Desiah, D., L.K. Cutkoomp and R.B. Koch. 1973. Inhibition of spider mite ATPases by Plictran and three organochlorine acaricides. *Life Sc.* **13**(12): 1693-1703.
211. Putintsev, A.I. and N. A. Gameza. 1980. Changes in the biochemical indices of carp during experimental intoxication of trimethyltin chloride. *Biol. Nauki* **8**: 29-34 (in Russian) (as cited in Reference #1).
212. Seinen, W.T., T. Helder, H. Vernij, A. Penninks and P. Leeuwangh. 1981. Short term toxicity of tri-n-butyltin chloride in rainbow trout yolk sac fry. *Sci. Total Environ.* **19**(2): 155-156.
213. Chliamovitch, Y.P. and C. Kuhn. 1977. Behavioural, haematological and histological studies on acute toxicity of bis(tri-n-butyltin)oxide on *Oncorhynchus mykiss* Richardson and *Tilapia rendalli* Boulenger. *J. Fish Biol.* **10**(6): 575-585.
214. Pinkney, A.E., L.E. Hall, M.J. Lenkevich, D.T. Burton and S. Zeger. 1985. Comparison of avoidance responses of an estuarine fish, *Fundulus heteroclitus* and crustacean, *Palaemonetes pugio*, to bis (tri-n-butyltin) oxide. *Water, Air, Soil Poll.* **25**: 33-40.
215. Wester, P.W. and J.H. Canton. 1987. Histopathological study of *Poecilia reticulata* (guppy) after long-term exposure to bis(tri-n-butyltin) oxide (TBTO) and di-n-butyltin dichloride (DBTC). *Aquat. Toxicol.* **10**: 143-165.
216. Wester, P.W., J.H. Canton, A.A.J. Van Iersel, E.I. Krajnc and H.A.M.G. Vaessen. 1990. The toxicity of bis(tri-n-butyltin) oxide (TBTO) and di-n-butyltin dichloride (DBTC) in the small fish species *Oryzias latipes* (medaka) and *Poecilia reticulata* (guppy). *Aquat. Toxicol.* **16**: 53-72.
217. Walker, W.W., C.S. Heard, K. Lotz, T.F. Lytle, W.E. Hawkins, C.S. Barnes, D.H. Barnes, and R.M. Overstreet. 1989. Tumorigenic, growth, reproductive, and developmental effects in medaka exposed to bis (tri-n-butyltin) oxide. In: Proceedings of the Oceans '89 Conference, Volume 2: Ocean Pollution. Seattle, Washington. 18 to 21 September 1989. pp. 156-524.
218. Davies, R.J., R.L. Fletcher and S.E.J. Furtado. 1984. The effects of tributyltin compounds on spore development in the green alga *Enteromorpha intestinalia*. In: Proceedings of the 6th International Congress on Marine Corrosion and Fouling. Athens. September 1984, pp. 557-565 (as cited in Reference #160).
219. Thomas, T.E. and M.G. Robinson. 1986. The physiological effects of the leachates from a self-polishing organotin paint on marine diatoms. *Mar. Environ. Res.* **18**: 215-219.

220. Beaumont, A.R. and P.B. Newman. 1986. Low levels of tributyltin reduce growth of marine micro-algae. *Mar. Poll. Bull.* **17**: 457-461.
221. Wong, P.T.S., Y.K. Chau, O. Kramer and G.A. Bengert. 1982. Structure-toxicity relationship of tin compounds on algae. *Can. J. Fish. Aqu. Sci.* **39**: 483-488.
222. Walsh, G.E., L.L. McLaughlin, E.M. Lores, M.K. Louie and C.H. Deans. 1985. Effects of organotins on growth and survival of two marine diatoms, *Skeletonema costatum* and *Thalassiosira pseudonana*. *Chemosphere* **14**: 383-392.
223. Reader, S. and E. Pelletier. 1991. Biosorption and degradation of butyltin compounds by the marine diatom *Skeletonema costatum* and the associated bacterial community at low temperature. *Bull. Environ. Contam. Toxicol.* **48**: 599-607.
224. Stroganov, N.S., O.V. Parian, and K.F. Sorvachev. 1974. Effect of triethyltin chloride on the uptake of inorganic carbon (NaHCO_3) by carp. *Hydrobiol. J.* **10**: 20-24 (as cited in Reference #156.)
225. Jarvinen, A.W., D.K. Tanner, E.R. Kline and M.L. Knuth. 1988. Acute and Chronic toxicity of triphenyltin hydroxide to fathead minnows (*Pimephales promelas*) following brief and continuous exposure. *Environ. Pollut.* **52**: 289-301.
226. Hall, L.W. Jr. and A.E. Pickney. 1985. Acute and sublethal effects of organotin compounds on aquatic biota: an interpretative literature evaluation. *CRC Crit. Rev. Toxicol.* **14**: 159-209.
227. Duncan, J. 1980. The toxicology of molluscicides. The organotins. *Pharmacol. Ther.* **10**: 407-429.
228. Snoeji, N.J., A.A.J. Van Iersel, A.H. Penninks and W. Seinen. 1985. Toxicity of triorganotin compounds: comparative *in vivo* studies with a series of trialkyltin compounds and triphenyl tin chloride in male rats. *Toxicol. Appl. Pharmacol.* **81**: 274-286.
229. Snoeji, N.J., A.H. Penninks and W. Seinen. 1987. Biological activity of organotin compounds - an overview. *Environ. Res.* **44**: 335-353.
230. Krajnc, E.I., P.W. Westerr, J.G. Loeber, F.X.R. Van Leeuwen, J.G. Vos, H.A.M.G. Vaessen and C.A. Van Der Heijden. 1984. Toxicity of bis (tri-n-butyltin)oxide in the rat. 1. Short term effects on general parameters and on the endocrine and lymphoid systems. *Toxicol. Appl. Pharmacol.* **75**: 363-386.

231. O'Callaghan, J.P. and D.B. Miller. 1988. Acute exposure of the neonatal rat to tributyltin results in decreases in biochemical indicators of synaptogenesis and myelinogenesis. *Pharmacol. Exp. Ther.* **246**: 394-402.
232. Rosenberg, D.W., K.E. Anderson and A. Kappas. 1984. The potent induction of intestinal heme oxygenase by the organotin compound, bis(tri-n-butyltin) oxide. *Biochem. Biophys. Res. Commun.* **119**: 1022-1027.
233. Pieters, R.H., J. Kampinga, M. Bol-Schoenmakers, B.W. Lamb, A.H. Penninks, and W. Seinen. 1989. Organotin-induced thymus atrophy concerns the ox-44+ immature thymocytes: relation to the interaction between early thymocytes and thymic epithelial cells? *Thymus* **14**(1-3): 79-88.
234. Schweinfurth, H.A. and P. Gunzel. 1987. The tributyltins: mammalian toxicity and risk evaluation for humans. *In: Proceedings of the Oceans '87 Conference Records, Volume 4: International Organotin Symposium, Halifax, Nova Scotia, September 28 to October 1 1987.* pp. 1421-1431.
235. Seinen, W., J.G. Vos, I. Van Spanje, M. Snoek, R. Brands. and I. H. Hooykaas. 1977. Toxicity of organotin compounds. II. Comparative *in vivo* and *in vitro* studies with various organotin and organolead compounds in different animal species with special emphasis on lymphocyte cytotoxicity. *Toxicol. Appl. Pharmacol.* **42**: 197-212.
236. Davis, A. R. Barale, G. Brun, R. Forster, T. Gunther, H. Hautefeuille, C.A. Hautefeuille, C.A. Van Der Heijden, A.G.A.C. Knaap, R. Krowke, T. Kuroki, N. Loprieno, C. Malaveille, H.J. Merker, M. Monaco, P. Mosesso, D. Neubert, H. Norppa, M. Sorsa, E. Vogel, C.E. Voogd, M. Umeda and H. Bartsch. 1987. Evaluation of the genetic and embryotoxic effects of bis(tri-n-butyltin) oxide (TBTO), a broad-spectrum pesticide, in multiple *in vivo* and *in vitro* short-term tests. *Mutat. Res.* **188**: 65-95.
237. Crofton, K.M., K.F. Dean. V.M. Boncek, M.B. Rosen, L.P. Sheets, N. Chernoff and L.W. Reiter. 1989. Prenatal or postnatal exposure to bis(tri-n-butyltin)oxide in the rat: postnatal evaluation of teratology and behaviour. *Toxicol. Appl. Pharmacol.* **97**: 113-123.
238. U.S. EPA. 1984. Special review of certain pesticide products. Triphenyltin hydroxide (TPTH): Position document 1.EPA/540/9-84/013. Office of Pesticide Programs. Washington, D.C. (as cited in Reference #156).
239. Eisler, R. 1989. Tin Hazards to fish, wildlife and invertebrates: a synoptic review. U.S. Fish and Wildlife Service. Biological Report 85(1.15), Contaminant Hazard Reviews Report No. 15. 83 pp.

240. Pelikan, Z. 1969. Effects of bis(tri-n-butyltin) oxide on the eyes of rabbits. *Br. J. Ind. Med.* **26**: 165-170.
241. Middleton, M.C. and I. Pratt. 1978. Changes in incorporation of [3H]thymidine into DNA of rat skin following cutaneous application of dibutyltin, tributyltin and l-chloro-2:4-dinitrobenzene and the relationship of these changes to a morphological assessment of the cellular damage. *J. Invest. Dermatol.* **71**: 305-310.
242. Middleton, M.C. and I. Pratt. 1977. Skin water content as a quantitative index of the vascular and histologic changes produced in rat skin by di-n-butyltin and tri-n-butyltin. *J. Invest. Dermatol.* **68**: 379-384.
243. Bridges, J.W., D.S. Davies and R.T. Williams. 1967. The fate of ethyltin and diethyltin derivatives in the rat. *Biochem. J.* **105**: 1261-1266.
244. Iwai, H., M. Manabe, H. Matsui, T. Ono and O. Wada. 1980. Effects of tributyltin and its metabolites on brain function. *J. Toxicol. Science* **5**: 257.
245. Stoner, H.B., J.M. Barnes and J.I. Duff. 1955. Studies on the toxicity of alkyl tin compounds. *Br. J. Pharmacol.* **10**: 16-25.
246. Kimmel, E.C., R. H. Fish and J.E. Casida. 1977. Bioorganotin chemistry. Metabolism of organotin compounds in microsomal monooxygenase systems in mammals. *J. Agric. Food Chem.* **25**(1): 1-9.
247. Idemudia, S.O. and D.E. McMillan. 1986. Effects of chemicals on delayed matching behaviour in pigeons. III. Effects of triethyltin. *Neurotoxicol.* **7**: 109-118.
248. Idemudia, S. O. and D.E. McMillan. 1986. Effects of chemicals on delayed matching behaviour in pigeons. IV. Effects of trimethyltin. *Neurotoxicol.* **7**: 75-88.
249. Federal Register. 1989. Water Quality Criteria: request for comments. Federal Register **54**: 23529-23531.

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APPENDIX 1

CONVERSION FACTORS FOR ORGANOTIN COMPOUNDS¹

To convert concentrations calculated on an organotin cation basis (ng/g or ng/L organotin compound) to equivalent concentrations calculated on a Sn basis (ng/g or ng/L Sn), divide by the conversion factors listed below. To convert concentrations calculated on a Sn basis to equivalent concentrations on a cation basis, multiply by the conversion factors listed below.

<u>COMPOUND</u>	<u>CONVERSION FACTOR</u>
Tributyltin (TBT)	2.44
Dibutyltin (DBT)	1.96
Monobutyltin (MBT)	1.48
Trimethyltin (TMT)	1.34
Dimethyltin (DMT)	1.26
Monomethyltin (MMT)	1.14
Triphenyltin (TPT)	2.95
Diphenyltin (DPT)	2.32
Monophenyltin (MPT)	1.66
Tricyclohexyltin (TCHT)	3.10
Dicyclohexyltin (DCHT)	2.40

1. Conversion factors supplied by Axys Analytical Services, Sidney, British Columbia

Organotin Compounds in the Aquatic Environment of British Columbia

Uses and Sources of Release

Organotin compounds are synthetic organometallic substances whose toxic properties have contributed to diverse and widespread use. These compounds have been used mainly as heat stabilizers in polyvinyl chloride (dimethyl, dibutyl and dioctyltin), industrial cooling water slimicides and agricultural biocides (tributyl, triphenyl-, and tricyclohexyltin), wood preservatives (tributyltin), antifouling agents (tributyl and triphenyltin) and industrial catalysts in chemical reactions (dibutyltin). Organotin compounds are not currently manufactured in Canada but are imported for use.

In British Columbia, current use pattern information is not available, however, surveys conducted by Environment Canada in the 1980's documented the use of more than 100,000 kg/yr of butyltin heat stabilizers by industrial plants producing PVC products, as well as the use of more than 9,000 kg/yr by the resins, paints, and coatings industries. No information on releases to the environment from these sources was obtained.

Organotin-based pesticides have also been used in British Columbia. Plictran®, a tricyclohexyltin compound, was registered between 1971 and 1989 and was the most widely used of these products. It was used in British Columbia to treat hop, strawberry, peach, pear, and apple crops. Only Vendex®, which is used as a miticide on ornamental plants is still registered for use in Canada.

Approximately one third of the salmon farms operating in British Columbia used nets treated with a tributyltin (TBT)-based antifoulant until the late 1980's. Between 1982 and 1987, more than 13,000 litres of TBT-based antifoulants were used by the aquaculture industry. TBT-based antifoulant paints have also been used extensively to treat the hulls of boats and ships. The volume of TBT used in antifoulant paints applied to boats and ships in British Columbia has not been quantified, but it was undoubtedly the largest source of butyltin compounds to the aquatic environment. The use of TBT antifoulants in Canada has been greatly reduced since 1989 when regulations severely restricting their use were introduced.

Shipyards and marinas have been identified as major sources of butyltin compounds to the aquatic environment in British Columbia and elsewhere. Wastewater collection and treatment systems at shipyards can be effective in reducing

TBT releases to the environment but these practices are not currently in widespread use. Environment Canada, in cooperation with other agencies, has developed documents outlining best management practices for ship and boat building and repair facilities and for marinas and small boatyards in British Columbia. Industry compliance with the recommendations in these documents is voluntary but will be monitored. In addition, Environment Canada prepared and distributed an information pamphlet recommending guidelines for the use of antifouling paints on pleasure craft.

Information is lacking on other potential sources of release to the British Columbia environment such as sewage treatment plants, landfills, municipal incinerators, and the use of industrial slimicides and wood preservatives. Butyltin and other organotin compounds have been detected in sewage treatment plant wastewaters and sludges and in landfill leachates in other areas. The use of TBT-based wood preservatives and slimicides in other countries has resulted in the release of TBT to the environment. Releases from such usage in Canada have not been estimated.

Regulations

Federal and provincial legislation provides controls on the entry of organotin compounds into the environment. The provincial **Pesticide Control Act** ensures that the sale and use of pesticides in British Columbia comply with label instructions. The federal **Pest Control Products Act** requires the registration of all pesticides used, manufactured and sold in Canada. It also regulates these products with respect to composition, packaging, labelling, distribution, and use. As of 1989, **Pest Control Products Act** regulations have prohibited the manufacturing, importation, distribution, retail sale, and use of all unregistered antifoulant paints. In addition, registration requirements for tributyltin-based antifoulant paints specify that these products must not be used on vessels under 25 metres in length, with the exception of aluminum hulled vessels and outboard marine fittings. Registered TBT antifoulant paints must be of the 'low leaching' type with a maximum tin release rate of 4 µg/cm²/day for TBT. The registration requirements for organotin-based antifoulants have undoubtedly resulted in a decrease in the volume of organotin compounds used as antifoulants in Canada. The regulations prohibit the use of



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these compounds at aquaculture facilities and on the majority of recreational boats.

Other legislation which could be used to control TBT releases into the environment include the federal Fisheries Act and the Canadian Environmental Protection Act (CEPA) and the British Columbia Waste Management Act. The transport of organotin compounds and organotin-contaminated wastes is regulated under the Transportation of Dangerous Goods Act (Canada).

Environmental Concerns

Fate in the Environment

Organotin compounds entering aquatic systems can be dissolved in water or can adsorb to suspended solids and be deposited in the bottom sediment. The proportion which adsorbs to solids in the water column depends on many factors including pH, salinity, dissolved oxygen content, size and amount of particulate matter, and organic content.

In the aquatic environment organotin compounds can be degraded or removed by microorganisms, aquatic biota, and photolysis (light). Degradation rates are variable and are influenced by environmental conditions such as the presence of oxygen and sunlight, temperature, and the types and numbers of microorganisms present. TBT is degraded to the less toxic compounds, dibutyltin (DBT) and monobutyltin (MBT), and finally to inorganic tin. The relative proportion of TBT compared to its degradation products in the environment is often used as an indicator of local degradation rates and also current inputs of TBT into the area. A strong predominance of TBT suggests a continuing input of TBT.

Lab studies indicate that the half-life of TBT is in the range of several days to a few weeks in water and a few months in bottom sediments. However, profiles of butyltin compounds in sediment cores suggest that, under certain conditions, TBT may persist in sediments for several years. It has also been demonstrated that TBT adsorbed to bottom sediments can be released to overlying waters. Although organotin compounds are less environmentally persistent than PCB and DDT, the high toxicity of these compounds (especially TBT) to aquatic life makes their release to the environment of great concern.

Toxicity to Aquatic Organisms

Organotin compounds, particularly TBT, affect energy production, survival, growth, metabolism, and reproduction in aquatic organisms at ng/L (nanograms per litre) to µg/L (micrograms per litre) concentrations.

Significant differences in sensitivity to organotin compounds have been observed between various species. Size, age, and genetic variations may account for some of these differences. Larval and juvenile life stages are often more susceptible to the effects of organotin compounds than are adults. Other important factors include the route and duration of exposure as well as environmental factors such as temperature, pH, dissolved oxygen, suspended solids, salinity, and water hardness.

TBT concentrations of less than 1 µg/L cause growth retardation, deformities in regenerated limbs, delayed molting, reproductive impairment, and behavioural abnormalities in marine invertebrates. Fish exposed to TBT in the low µg/L range exhibited decreased growth; thymus atrophy; disrupted enzyme activity; behavioural abnormalities; reduced hatching of eggs and survival of embryos; vertebral malformations in larvae; histopathological changes in the liver, kidney and gill; as well as effects on the eye, swim bladder, skin, mouth, and thyroid gland. Aquatic plants and phytoplankton exposed to TBT in the ng/L to µg/L range experienced decreased growth and primary productivity, inhibition of spore settling, and mortality.

Molluscs are particularly sensitive to TBT. Exposure of bivalve species to low concentrations of TBT (less than 1 µg/L), in both laboratory and field situations, has resulted in significant mortality in larval stages; abnormal development of the shell and gonad; and reduced larval settlement and growth. Low concentrations of TBT can interfere with shell calcification and cause shell deformities such as chambering, thickening, and balling. This effect has commonly been observed in southern France and England since the 1970's. In addition, a condition known as 'imposex' (the development of male sex organs in females) has affected gastropods in coastal areas of several countries and has been attributed to TBT contamination. It is estimated that this condition can occur at concentrations as low as 1 ng/L.

In British Columbia, evidence of TBT toxicity has been observed in marine invertebrates from coastal areas. Growth and shell abnormalities characteristic of TBT toxicity were first observed in 1985 in oysters grown commercially adjacent to a salmon farm using TBT-based net treatments. In addition, imposex was reported to be widespread throughout the Straits of Georgia and Juan de Fuca. All six species of gastropods examined were affected. Studies on the incidence of imposex in gastropods from coastal areas of British Columbia are continuing.

Canadian Water Quality Guidelines for the protection of aquatic life were developed by the Canadian Council of Ministers of the Environment (CCME). The recommended interim guidelines for organotin compounds



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in freshwater systems are 8 ng/L (3 ng Sn/L) for tributyltin and 20 ng/L (7 ng Sn/L) for triphenyltin. The recommended guideline for tributyltin in marine and estuarine systems is 1 ng/L (0.4 ng Sn/L). The toxicity information available for other organotin compounds was considered insufficient for the development of guidelines.

Concentrations in the Environment

Concentrations of butyltin compounds in aquatic systems vary greatly and are influenced by tidal effects, seasonal conditions (temperature, water exchange, salinity, suspended solids, boating activity), and proximity to sources. The highest concentrations of butyltin compounds have been found in the vicinity of harbours, marinas, and areas of heavy boating activity, particularly in areas of poor water exchange.

Studies conducted in many parts of the world indicated that surface waters in harbour and marina areas commonly contained more than 100 ng Sn/L, but levels in excess of 1000 ng Sn/L were detected. In comparison, surface waters from well flushed or open coastal areas usually contained butyltin compounds at concentrations of less than 10 ng Sn/L. Bottom sediments often contained organotin compounds at concentrations which were orders of magnitude greater than those in surface waters. Butyltin concentrations in the hundreds to thousands of ng Sn/g range have been detected in the vicinity of marinas, harbours, and shipyards.

Aquatic organisms accumulate organotin compounds from water, sediments, and food. Some species can attain tissue concentrations many thousands of times higher than the surrounding water levels. Factors influencing the uptake and accumulation of organotin compounds in aquatic organisms include level, route and duration of exposure, species, age, feeding habits, reproductive state, and time of year.

The half-lives for TBT have been estimated to be less than one week to several weeks for various fish species, ten days for oysters, and fourteen days for mussels. Until recently most evidence indicated that organotin compounds were not biomagnified through the food chain. However, recent studies in Japan which revealed very high levels of butyltin compounds in several tissues of porpoise, suggest that biomagnification does occur.

Elevated concentrations of other organotin compounds, including methyltin and phenyltin compounds, have also been detected in the aquatic environment but concentrations are usually lower than those of butyltin compounds. Phenyltin compounds were commonly detected in marinas and harbours in countries where these compounds have been used as antifoulants. Methyltin compounds can be produced naturally in

the environment by methylation of inorganic tin compounds or can enter the environment via sewage treatment plant discharges, industrial wastes, and rainwater.

In British Columbia, Environment Canada conducted surveys between 1984 and 1995 to determine the presence of organotin compounds in coastal areas. Most of the environmental levels information obtained from these surveys, and those of other agencies, pertains to TBT, and its less toxic degradation products, DBT and MBT. TBT was the predominant form in most samples, however, DBT and MBT were also commonly detected.

Butyltin compounds have been detected at elevated levels in surface waters, bottom sediments, and/or aquatic organisms collected in the vicinity of some marinas, harbours, shipyards, salmon farms, and recreational boating areas of coastal British Columbia. In some of these areas, concentrations in surface waters have greatly exceeded the Canadian water quality guideline for the protection of marine life (1 ng/L or 0.4 ng Sn/L).

In the 1980's, Environment Canada surveys detected TBT concentrations in the hundreds to thousands of ng Sn/L range in surface water samples from Vancouver area marinas in False Creek and Coal Harbour. Several thousand ng Sn/g of TBT were detected in mussels from these marinas, while mussels collected from marinas on Vancouver Island contained several hundred ng Sn/g TBT. Butyltin compounds at concentrations in excess of 1000 ng Sn/g were detected in sediments from several south coastal marinas.

In Vancouver Harbour, TBT concentrations of up to 26 ng Sn/L in surface water and several thousand ng Sn/g (up to 42,000 ng Sn/g) in sediments were detected at various shipyards and commercial docks in 1988 and 1991. Mussels collected at these facilities contained several hundred ng Sn/g of TBT. Elevated concentrations of butyltin compounds were also detected in other harbour areas. In 1991, water and sediments collected near the Department of National Defense (DND) Base in Esquimalt Harbour on Vancouver Island contained 130 ng Sn/L and up to 26,000 ng Sn/g TBT, respectively. Mussels collected at this facility and contained several hundred ng Sn/g TBT. Butyltin compounds at concentrations of several hundred ng Sn/g were prevalent in sediments collected throughout Victoria Harbour in 1990, with levels exceeding 1000 ng Sn/g at some sites. Concentrations of 100 to 1,000 ng Sn/g TBT were detected in the hepatopancreas of Dungeness crab from the Fraser estuary, False Creek and Vancouver, Victoria and Esquimalt harbours. Crab muscle contained much lower levels. Concentrations of butyltin compounds were also elevated in clams, shrimp, and fish (especially in the liver tissue) from harbour areas.



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In 1988, butyltin compounds were detected in water, sediment, and aquatic biota from some British Columbia salmon farms. Shortly after these samples were collected, salmon farms in British Columbia stopped using TBT antifoulants.

Elevated concentrations of butyltin compounds were also detected in shellfish from some recreational boating areas during peak summer boating season in 1988.

Evidence that butyltin compounds were present in unacceptable concentrations in the Canadian environment resulted in the introduction of regulations restricting the use of TBT-based antifoulants in Canada in 1989. Current regulations prohibit the use of these products on most recreational boats and at aquaculture facilities. However, the use of 'low release' products on many commercial vessels is still permitted.

In 1995, Environment Canada conducted additional surveys at coastal marinas and in Vancouver Harbour in order to determine whether levels of butyltin compounds in these areas had declined since regulations were introduced. The results of these surveys suggest that the current regulations may be effective at reducing environmental contamination originating from recreational boats, but may not be effective at reducing contamination from commercial vessels in harbours and shipyards. TBT concentrations in mussels (and possibly surface waters) from, at least some, recreational boat marinas appear to be declining. However, concentrations in the water and mussels at Vancouver Harbour shipyards and commercial docks remain at 1980's concentrations.

Concentrations of butyltin compounds in mussels from recreational boat marinas in False Creek, Coal Harbour, and Crescent Beach have declined significantly in recent years. In the late 1980's, mussels from these sites contained total butyltin compounds at concentrations of up to 9,400, 4,370, and 3,690 ng Sn/g, respectively. By 1995, concentrations in mussels from these sites had decreased significantly (up to 564, 235, and 115 ng Sn/g, respectively). Mussels collected at Fisherman's Terminal in False Creek also contained lower levels of butyltin compounds in 1995 (up to 830 ng Sn/g) than in the late 1980's (up to 4000 ng Sn/g). However, the decrease was less dramatic at this site, probably due to the continued legal usage of TBT-based paints on fishing vessels more than 25 metres in length and those with aluminum hulls.

TBT concentrations in surface waters from marinas in Coal Harbour were also much lower in 1995 (8.3 to 23 ng Sn/L) than in the late 1980's (17 to 2600 ng Sn/L). However, important factors such as sampling stations, season, and tidal conditions were not consistent from year to year. For this reason, additional monitoring is required to verify that concentrations are

decreasing. Despite the finding that surface water concentrations may be decreasing, all samples collected from Coal Harbour and False Creek in 1995 were in excess of the 1 ng/L (0.4 ng Sn/L) Canadian water quality guideline.

Available data indicate that concentrations of butyltin compounds in sediments from False Creek and Coal Harbour marinas and from Vancouver Harbour have not decreased since the introduction of regulations in 1989. However, trends in sediment concentrations can be difficult to establish. The persistence of TBT in sediments is greater than that in surface waters and aquatic organisms, and reduced inputs to the environment are more rapidly reflected in water and mussels than in the sediments.

Recent information on concentrations of butyltin compounds at salmon farms and boating areas is lacking. However, it is likely that butyltin concentrations have declined at these sites since the 1980's as the current regulations have prohibited the use of TBT-antifoulants at aquaculture facilities and on most recreational boats since 1989.

Other organotin compounds are less frequently detected in the aquatic environment of British Columbia than are butyltin compounds. The past use of cyclohexyltin-based pesticides and the presence of foreign vessels coated with triphenyltin-based paints has not resulted in widespread contamination of the coastal British Columbia environment. Triphenyltin was detected in some sediment samples collected in Vancouver, Victoria, and Esquimalt harbours but at much lower levels than was tributyltin. Tricyclohexyltin concentrations were below the level of detection in virtually all sediment samples collected in Vancouver, Victoria, and Esquimalt harbours and in the lower Fraser River system. With very few exceptions, phenyltin and cyclohexyltin compounds were not detected in various species of aquatic organisms from British Columbia. Methyltin compounds were detected in low concentrations in a few samples from harbour areas.

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