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Canadian Environmental Protection Act, 1999

Risk Assessment of New and Transitional Organotin Substances

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Synopsis

Between August 1994 and March 2000, notifications pertaining to the organotin substances listed in Table 1 were received by the Minister of Environment pursuant to subsection 26(2) of the 1988 *Canadian Environmental Protection Act* and subsection 81(1) of CEPA 1999. The companies submitting the new substances notifications (hereafter referred to as “notifiers”) proposed to manufacture or import these substances into Canada for a number of uses, namely as stabilizers for polyvinyl chloride products, as intermediates used in the manufacture of organotin stabilizers, and as fungicides¹ or preservers for building material formulations.

Information used in this assessment was supplied in the various new substances notifications submitted to Environment Canada. In addition, the Vinyl Council of Canada (VCC) provided results of an industry survey they conducted which addressed handling practices of organotin stabilizer users (VCC, 2002). Based on the information, the largest environmental releases are expected to occur as a result of loss of liquid residues from shipping containers with smaller releases occurring from storage tanks and transfer lines during formulation and manufacturing processes. Releases from these operations result in predicted environmental concentrations (PECs) in the receiving waters up to 2.0 µg/L. The PEC in sediment for a tributyltin-substituted substance ranged up to 7.8 mg/kg.

Toxicity data from scientific literature indicate that the notified substances are expected to show high levels of acute and chronic toxicity to freshwater organisms. The predicted no effect concentration (PNEC) for the water column was determined to range from 0.008 to 0.45 µg/L for organotins. The PNEC for tributyltin (TBT) in sediment was calculated to be 0.015 mg/kg.

Various physical-chemical properties were reviewed to determine the substances' behaviour in the environment. The available bioconcentration factor (BCF) and log octanol-water partition coefficient (log Kow) values indicate that the notified substances (excluding a tributyltin-substituted compound) and their lower molecular weight degradation products, are not expected to result in BCF values exceeding 5000 or log Kow values in excess of 5. Furthermore, these substances are expected to degrade in the freshwater environment with half-lives of less than a few months. Consequently, these substances do not exceed the criteria for problematic bioaccumulation and persistence under the Persistence and Bioaccumulation Regulations (Government of Canada, 2000).

In contrast, based on the measured data from Maguire (2000), tributyltin is anticipated to have a high potential for bioaccumulation in biota. In addition, measured half-lives in

¹ Although fungicides used in Canada fall under the jurisdiction of the Pest Control Products Act (PCPA), the notified fungicide is manufactured in Canada for export-only, and consequently falls outside PCPA's jurisdiction. New substances which are not addressed by another Federal statute are, by default, addressed by the new substance notification requirements of CEPA.

sediment are in the order of months, and estimated half-lives from sediment core data are in the order of years. Consequently, TBT meets the criteria for problematic bioaccumulation and persistence under the Persistence and Bioaccumulation Regulations (Government of Canada, 2000). Furthermore, by analogy to TBT, the notified tributyltin-substituted substance is also expected to exceed the criterion for problematic bioaccumulation as indicated by a BCF greater than 5000.

In conclusion, available data indicates that substances in Table 1 are entering or may enter the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity. Therefore, these substances are suspected to be toxic under paragraph 64(a) of CEPA 1999. However, in the case of stabilizers, if industry wide stewardship practices are implemented during use, releases can be minimized to levels that are not of concern to the environment.

1.0 Introduction

The *Canadian Environmental Protection Act, 1999* (CEPA 1999) authorizes the Ministers of Environment and Health to assess all Substances New to Canada for their effects on the environment and on human health. Subsection 83(2) of the Act states:

... the Ministers shall assess information provided under subsection 82(1) or otherwise available to them in respect of a substance in order to determine whether it is toxic or capable of becoming toxic.

Under Section 64 of CEPA 1999, a substance is considered toxic if:

... it is entering or may enter the environment in a quantity or concentration or under conditions that

- a. have or may have an immediate or long-term harmful effect on the environment or its biological diversity;
- b. constitute or may constitute a danger to the environment on which life depends;
or
- c. constitute or may constitute a danger in Canada to human life or health.

The general approach to risk assessment of new substances occurs in three main phases. The first phase called pre-screening and prioritization provides a means for triaging new substances so that they may be prioritized for further assessment. The second phase, called the assessment phase, involves characterizing the human and environmental exposure and the potential effects of a substance to humans and biota. The final phase is the risk characterization phase and involves determining the risk potential of a new substance according to a weight of evidence for exposure and effects. Throughout the risk assessment process, data are collected to support the assessment. Most data are collected during the pre-screening and prioritization phase and the assessment phase. Dialogue with interested parties (e.g., regulatory managers, industry, and public) is also conducted throughout the risk assessment process as needed and may result in the re-iteration of the assessment approach as a result of new considerations or data.

Between August 1994 and March 2000, notifications of the organotin substances listed in Table 1 were received by the Minister of Environment pursuant to subsection 26(2) of the 1988 *Canadian Environmental Protection Act* (CEPA 1988) and subsection 81(1) of CEPA 1999. Review of the assessments led to the conclusion that the substances were suspected of being toxic based on ecological considerations. The following is a compilation of the information supplied in the original notifications between 1994 and 2000 that led to these conclusions. As previously mentioned, newer information has also been included in the preparation of this report.

2.0 Regulatory Background on the Substances

The substances will hereafter be referred to as Chemical # 1 through Chemical # 9, as designated in Table 1. To protect confidential business information, in some cases a masked name has been used. Table 1 also includes the regulatory status of these substances in Canada and in the U.S., as indicated in the National Chemical Inventories (NCI) database (2005, Issue 2). The substances are all listed on the confidential or non-confidential portion of the Canadian Non-domestic Substances List (NDSL) and on the confidential or non-confidential portion of the U.S. Toxic Substances Control Act (TSCA) Inventory. All substances were “grandfathered” onto the original TSCA Inventory in 1979 with the exception of Chemical #1 which was the subject of a Pre-manufacture Notification (PMN). The EPA did not make a regulatory finding for this substance which is now on the TSCA Inventory.

Table 1. Notified Organotin Substances and Regulatory Status.

Chemical No.	Substance Identity	CAS No.	Regulatory Status (Canada)	Regulatory Status (US)
1	Tin, butyl mixed thio complexes	Confidential	Confidential NDSL	Confidential TSCA
2	Monoalkyltin (alkyl' thioglycolate)	Confidential	Confidential NDSL	Confidential TSCA
3	Monoalkyl tin tris(alkyl" thioglycolate)	Confidential	Confidential NDSL	Confidential TSCA
4	Dialkyltin bis(alkyl" thioglycolate)	Confidential	Confidential NDSL	Confidential TSCA
5	Dialkyltin bis(alkyl' thioglycolate)	Confidential	Confidential NDSL	Confidential TSCA
6	Stannane, (benzoyloxy)tributyl-	4342-36-3	NDSL	TSCA
7	Stannane, tetrabutyl-	1461-25-2	NDSL	TSCA
8	Stannane, tetraoctyl-	3590-84-9	NDSL	TSCA
9	Stannane, butyltris(dodecylthio)-	15666-28-1	NDSL	TSCA

3.0 Summary of Information Critical to the Conclusion of “Suspected of Being Toxic” under CEPA

3.1 Identity and Physical and Chemical Properties

Because of the technical challenges associated with testing this class of compounds, some of the physical and chemical properties values could not be determined using common test methods (OECD, EEC). These challenges were mainly associated with low water solubility. Consequently some properties were estimated using a number of physical-chemical estimation software programs. Compilations of experimental and estimated property data are provided below:

3.1.1 Chemical # 1

Substance Identity (masked)	Tin, butyl mixed thio complexes
State (at room temperature)	Liquid
Vapor Pressure (in Pa at 25°C)	1.65×10^{-3}
Octanol/Water partition coefficient (log Kow)	>7
Water solubility (mg/L at 20°C)	42
Adsorption/desorption (log Koc)	9.3
Density (g/mL at 25°C)	1.21

3.1.2 Chemical # 2

Substance Identity (masked)	8-Oxa-3,5-dithia-4-stannaeicosanoic acid, 4-alkyl-4-[[2-(dodecyloxy)-2-oxoethyl]thio]-7-oxo-, dodecyl ester.
State (at room temperature)	Liquid
Vapor Pressure (in Pa at 25°C)	$< 8.0 \times 10^{-5}$
Octanol/Water partition coefficient (log Kow)	>7
Water solubility (mg/L at 20°C)	< 50
Adsorption/desorption (log Koc)	12.6
Density (g/mL at 20°C)	1.1

3.1.3 Chemical # 3

Substance Identity (masked name)	Acetic acid, 2,2',2''-[(alkylstannylidyne)tris(thio)]tris-, tritetradecyl ester.
State (at room temperature)	Liquid
Vapor Pressure (in Pa at 25°C)	$< 8.0 \times 10^{-5}$
Octanol/Water partition coefficient (log Kow)	>7
Water solubility (mg/L at 20°C)	<50
Adsorption/desorption (log Koc)	14.2
Density (g/mL at 22°C)	1.1

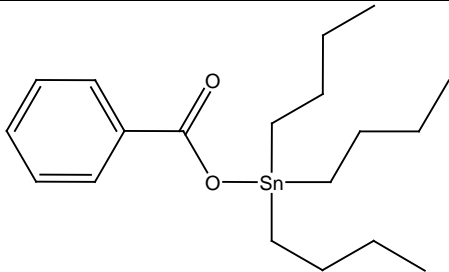
3.1.4 Chemical # 4

Substance Identity (masked)	8-Oxa-3,5-dithia-4-stannadocosanoic acid, 4,4-dialkyl-7-oxo-, tetradecyl ester.
State (at room temperature)	Liquid
Vapor Pressure (in Pa at 25°C)	$< 8.0 \times 10^{-5}$
Octanol/Water partition coefficient (log Kow)	>7
Water solubility (mg/L at 20°C)	<50
Adsorption/desorption (log Koc)	10.3
Density (g/mL at 22°C)	1.1

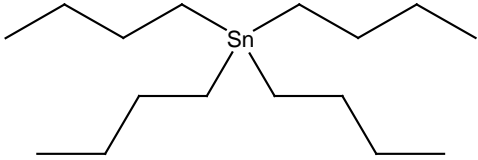
3.1.5 Chemical # 5

Substance Identity (masked)	8-Oxa-3,5-dithia-4-stannaecosanoic acid, 4,4-dialkyl-7-oxo-, dodecyl ester.
State (at room temperature)	Liquid
Vapor Pressure (in Pa at 25°C)	$< 8.0 \times 10^{-5}$
Octanol/Water partition coefficient (log Kow)	>7
Water solubility (mg/L at 20°C)	<50
Adsorption/desorption (log Koc)	9.2
Density (g/mL at 22°C)	1.1

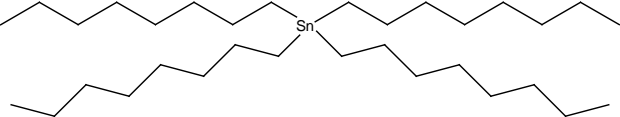
3.1.6 Chemical # 6

Substance Identity	 Stannane, (benzoyloxy)tributyl-
State (at room temperature)	Liquid
Vapor Pressure (in Pa at 20°C)	< 67
Octanol/Water partition coefficient (log Kow)	3.2
Water solubility (mg/L at 20°C)	262
Adsorption/desorption (log Koc)	5.1
Density (g/mL at 25°C)	1.2


3.1.7 Chemical # 7

Substance Identity C ₁₆ H ₃₆ Sn molecular weight of 347 g/mol	 Stannane, tetrabutyl-
State (at room temperature)	Liquid
Vapor Pressure (in Pa at 25°C)	2467
Octanol/Water partition coefficient (log Kow)	> 7
Water solubility (mg/L at 20°C)	86
Adsorption/desorption (log Koc)	5.0
Density (g/mL at 21°C)	1.067

3.1.8 Chemical # 8

Substance Identity C ₃₂ H ₆₈ Sn molecular weight of 572 g/mol	 Stannane, tetraoctyl-,
State (at room temperature)	Liquid
Vapor Pressure (in Pa at 25°C)	893
Octanol/Water partition coefficient (log Kow)	> 7
Water solubility (mg/L at 20°C)	3.0
Adsorption/desorption (log Koc)	9.3
Density (g/mL at 21°C)	0.9669

3.1.9 Chemical # 9

Substance Identity CAS Registry C ₄₀ H ₈₄ S ₃ Sn molecular weight of 780 g/mol	 Stannane, butyltris(dodecylthio)-,
State (at room temperature)	Liquid
Vapor Pressure (in Pa at 25°C)	0.008
Octanol/Water partition coefficient (log Kow)	> 7
Water solubility (mg/L at 22°C)	< 6.0
Adsorption/desorption (log Koc)	12.2

3.2 Entry into the Environment

The substances are imported into Canada as tin stabilizers (Chemicals #1-5, and #9) and tin intermediates (Chemicals #7 and #8). They are used as components of formulations and as stabilizers for polyvinyl chloride (PVC) products, including pipe, vinyl siding, vinyl window frames and in food packaging. One substance (Chemical #6) is manufactured for use as a fungicide or preserver component in building products. Although differences in release and use patterns exist, for the purposes of this assessment each substance will not be addressed individually but within a usage group, for example, stabilizers or intermediates. When a range of releases occur, the highest reasonable value will be used.

3.2.1 Release to Air

In general, the reported vapour pressures and literature data (Maguire, 1992) for analogues indicate that the notified substances have limited potential to volatilize into the atmosphere.

3.2.2 Release to Water

3.2.2.1 Losses from Processes in Formulation and Manufacturing Facilities

Use information from the notifications indicates that the substances are imported or manufactured in liquid forms at concentrations ranging from 11.4 to 96%. In Canada, the largest releases to the environment are expected to be from release of liquid residues remaining in shipping containers with lower releases from residues in storage tanks and from cleaning transfer lines. Potential releases could result in significant concentrations in local receiving waters and sediments. Predictions of environmental releases are detailed in section 3.6.

3.3 Exposure related Information

3.3.1 Bioaccumulation

The log Kow values reported for the notified substances are all greater than 7 except for substance #6 which had a value of 3.2. Due to low water solubility, predictive modeling programs produce unrealistically high estimated values. Consequently, other sources and Bioaccumulation Factor (BAF) and BCF values, thought to be more reliable indicators of bioaccumulation, have been investigated for all the substances.

Analogue BAF/BCF and log Kow values from scientific literature and available databases suggest a range of bioaccumulation/bioconcentration potentials for organotins. Variations can be attributed to factors including impurities in the sample and different testing concentrations.

Data for monobutyltin trichloride, dibutyltin dichloride and tributyltin chloride indicate log Kow values of 0.09, 0.05 and 2.2, respectively (Maguire, 1992). Data from the PSL (Priority Substance List) 1 document (Government of Canada, 1993) reported BCF values in carp, *Cyprinus carpio* to be 126, 10, and 3162, for monobutyl-, dibutyl- and tributyltins, respectively. Tetrabutyltin BCF values were in the range of 38.0-309; dibutyltin dilaurate (CAS # 77-58-7) in the CHEMFATE database has a reported BCF value of 117. The data suggest that short chain mono, di and trialkyl organotin compounds show limited tendencies to bioaccumulate/bioconcentrate in aquatic biota. Only tributyltin had a higher bioconcentration potential. In addition to the bioaccumulation potential of the parent compounds, tetrabutyltin has the potential to degrade to tributyltin which will influence substantially the bioaccumulation profile (see *Bioaccumulation of Chemical # 6*).

The higher molecular weights of Chemicals #1 through 5 and Chemical #9 may hinder bioaccumulation. In addition to the high molecular weights, based on the above BCF and log Kow values, the notified substances (excluding Chemical #6) are not expected to exceed the criteria for bioaccumulation ($BCF \geq 5000$ and $\log Kow \geq 5$) as specified in the Persistence and Bioaccumulation Regulations (Government of Canada, 2000). Furthermore, bioaccumulation of lower molecular weight organotin compounds resulting from degradation of the notified substances via de-alkylation mechanisms is not expected to result in BCF values ≥ 5000 or log Kow values ≥ 5 .

Based on the above information, Chemicals #1-5 and #7-9 are not expected to exceed the criteria for problematic bioaccumulation (BCF values ≥ 5000 and $\log Kow \geq 5$) as specified in the Persistence and Bioaccumulation Regulations (Government of Canada, 2000).

3.3.1.2 Bioaccumulation of Chemical # 6

Based on measured data from Maguire (2000) for TBT, by extrapolation, Chemical # 6 is anticipated to have a high potential for bioaccumulation in biota. Maguire has concluded that bioconcentration/accumulation of tributyltin (TBT) by organisms occurs from food and water and total accumulations may be higher than predicted from water only exposures. Therefore, log Kow is not always a good predictor of bioaccumulation potential for TBT. More recent data from Maguire (2000) for tributyltin shows that total accumulations in freshwater organisms can range up to 330 000 for algae, 900 000 for mussels and 46 000 for fish compared to concentrations in the water.

Based on the above information, Chemical # 6 is expected to exceed the criterion for problematic bioaccumulation ($BCF \geq 5000$) in the Persistence and Bioaccumulation Regulations (Government of Canada, 2000).

3.3.2 Persistence

3.3.2.1 Biotic Degradation

The notifications did not contain any information concerning the biodegradation of the notified substances. Information from the PSL 1 report indicates that organotin compounds with methyl and butyl alkyl chains will undergo biodegradation in aquatic environments fairly rapidly, with half-lives of less than a few months at 20°C.

Further information from the PSL Supporting Document (Maguire, 1992) indicates that, by analogy with the butyltin species, biodegradation of octyltins is known to result in the removal of the entire alkyl chains at the tin atom and are expected to have a similar half-life based on the methyl and butyltin analogues. Consequently, half-lives would be less than a few months.

Based on the above, the notified substances (excluding Chemical # 6) are not expected to exceed the criteria for persistence as specified in the Persistence and Bioaccumulation Regulations (Government of Canada, 2000).

3.3.2.2 Degradation of Chemical # 6

Half-lives of a few days to a few months have been reported for TBT in water depending upon such factors as latitude, the presence or absence of TBT degrading microorganisms, temperature, degree of insolation (which enhances algal degradation of TBT), and season of the year (Maguire, 2000). Other recent information indicates a much longer half life than what had been initially reported, with sediments serving as both a sink and a source of organotins. Measured half-lives in sediment are in the order of months and estimated half-lives from sediment core data are in the order of years. The available data indicate that the half-life of TBT in sediments is greater than one year, and the half life of Chemical #6 would be expected to be the same.

Based on the above information and by analogy to TBT, Chemical # 6 is expected to exceed the criterion for persistence in sediment (half-life = 365 days) as specified in the Persistence and Bioaccumulation Regulations (Government of Canada, 2000).

3.3.2.3 Abiotic Degradation

The notified substances include alkyltins, tin thiolates (mercaptides), and tin esters. Aryl- and alkyl-tin bonds are usually stable to air and moisture (Davies, 2004). However, organotin compounds are known to undergo pH-dependent hydrolysis in water with cations forming at $\text{pH} < \text{pKa}$ (Fent, 1996). For example, the dominant tributyltin species at $\text{pH} < \text{pKa}$ (6.51) is the cation, whereas at $\text{pH} > 6.51$, tributyltin is present as the neutral hydroxide. Organotin cations have a strong tendency to hydrolyze as was demonstrated by Tobias & Freidline (1965).

According to Davies (2004), Sn-S bonds are less easily cleaved in substitution (e.g. hydrolysis) and addition reactions. He also reports that both organotin sulfides ($R_3\text{-Sn-S-Sn-R}'_3$) and thiolates ($R_x\text{-Sn-(SR)'}_{4-x}$) are usually stable towards water and air.

The Organotin Environmental Programme (ORTEP) Stabilizer Task Force provided Environment Canada with preliminary results of three hydrolysis tests conducted on organotin thiolates.

The first study “Analytical Aspects Related to the Determination of the Solubility of Organotin Compounds” (Schultze, circa 2002), provided hydrolysis data for dibutyltin ethylhexylmercaptoacetate (DBT(EHMA)_2). The analytical method employed was electrospray ionization mass spectrometry (ESI/MS).

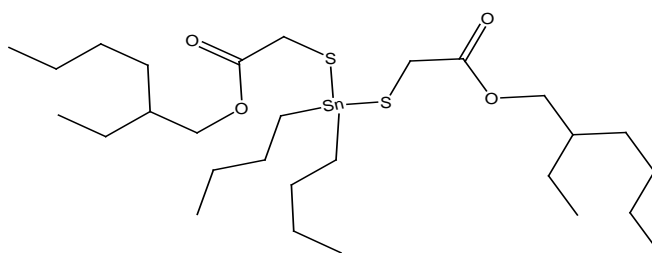


Figure 1. Structure of DBT(EHMA)_2 .

For this study it appears that the compound was dissolved in water and held for a specified amount of time before mixing with acetonitrile (50:50) for analysis by MS. However, no details were provided on sample preparation or compound purity. An initial analysis of the solution was performed after ~ 5 minutes followed by a second analysis after 24 hours. A summary of peaks in the mass spectra of the unfiltered solutions, adjusted for relative peak intensity can be found in Table 2.

Table 2. Relative Peak Intensities of Major Ions Observed in the Mass Spectrum of $\text{Bu}_2\text{Sn(EHMA)}_2$ (Schultze Study).

Observed Ion	m/z	Relative Peak Intensity % (~ 5 min water contact)	Relative Peak Intensity % (1 day water contact)
$[\text{Bu}_2\text{Sn(EHMA)}_2 + \text{Na}]^+$	663	67.6	29
$[\text{Bu}_2\text{Sn(EHMA)} + \text{ACN}]^+$	477	10.1	21.8
$[\text{Bu}_2\text{Sn(EHMA)}]^+$	437	4.3	7.8
$[\text{Bu}_2\text{Sn(SCH}_2\text{COONa)} + \text{ACN}]^+$	388	3.6	4.7
$[\text{Bu}_2\text{Sn(SCH}_2\text{COOH)} + \text{ACN}]^+$	366	2.9	2.6
$[\text{Bu}_2\text{Sn(SCH}_2\text{COONa)}]^+$	347	2.9	12.4
$[\text{Bu}_2\text{Sn(SCH}_2\text{COOH)}]^+$	325	8.6	21.8
Total		100 %	100 %

The results suggest that the substance is reacting with either water, acetonitrile or both resulting in loss of one of the mercapto ligands and subsequent formation of the mercapto acid or mercapto-sodium salt. Definitive conclusions regarding the hydrolysis of this chemical in natural waters are difficult to make since significant amounts of acetonitrile were used in the analysis.

The second study provided by ORTEP was titled “The Simulated Gastric Hydrolysis of Tin Mercaptide Stabilizers” (Gillard-Factor & Yoder, 2000). In this study, hydrolysis testing was conducted on a mixture of methyltin mercaptides as well as several thiolates (dioctyltin and dibutyltin based). A summary of the results of the dibutyltin thiolate are presented in Table 3, while those for the dioctyltin thiolate are presented in Table 4.

The mercaptide stabilizers were tested three ways using solutions of a) 1:1 acetonitrile: water, b) acetonitrile: pH 1 HCl and, c) acetonitrile: pH 4 HCl. The analytical method employed was electrospray ionization mass spectrometry (ESI/MS). For the acetonitrile: pH 1 HCl experiments, neither the parent compound nor any lower molecular weight ions could be detected in any of the solutions studied.

Table 3. Relative Peak Intensities of Major Ions Observed in the Mass Spectrum of $\text{Bu}_2\text{Sn}(\text{EHMA})_2$ (Gillard-Factor & Yoder, 2000).

Observed Ion	m/z	Relative Intensity (ACN/ H_2O)	Peak %	Relative Intensity % (ACN/HCl pH 4)	Peak %
$[\text{Bu}_2\text{Sn}(\text{EHMA})_2 + \text{Na}]^+$	663	52.8		19.4	
$[\text{Bu}_2\text{Sn}(\text{EHMA}) + \text{ACN}]^+$	477	9.7		3.0	
$[\text{Bu}_2\text{Sn}(\text{EHMA})]^+$	437	7.2		14.5	
$[\text{HSn}(\text{EHMA}) + \text{ACN} + \text{Na}]^+$	388	2.4		0.8	
$[\text{HSn}(\text{EHMA}) + \text{ACN}]^+$	366	10.0		16.7	
$[\text{HSn}(\text{EHMA}) + \text{Na}]^+$	347	1.4		4.6	
$[\text{HSn}(\text{EHMA}) + \text{H}]^+$	325	16.6		41.1	
	Total	100 %		100 %	

Table 4. Relative Peak Intensities of Major Ions Observed in the Mass Spectrum of $\text{Oct}_2\text{Sn}(\text{EHMA})_2$ (Gillard-Factor & Yoder, 2000).

Observed Ion	m/z	Relative Intensity (ACN/ H_2O)	Peak %	Relative Intensity % (ACN/HCl pH 4)	Peak %
$[\text{Oct}_2\text{Sn}(\text{EHMA})_2 + \text{Na}]^+$	775	51.5		18.8	
$[\text{Oct}_2\text{Sn}(\text{EHMA})]^+$	549	7.0		12.8	
$[\text{OctSn}(\text{EHMA}) + \text{H} + \text{ACN}]^+$	478	18.7		22.6	
$[\text{OctSn}(\text{EHMA}) + \text{H}]^+$	437	12.0		22.6	
$[\text{OctSn} + 2 \text{ACN}]^+$	315	6.7		10.5	
$[\text{OctSn} + \text{ACN}]^+$	274	4.0		12.8	
	Total	100 %		100 %	

Similar to the Schultz study, the Gillard-Factor study suggests that these substances could be hydrolyzing in either water, acetonitrile, or the acid solution resulting in loss of a mercapto ligand and subsequent formation of other products. It is interesting that for $\text{Bu}_2\text{Sn}(\text{EHMA})_2$, the results of the two authors are different although both experiments used solutions of acetonitrile/water for the analysis. As can be seen in Table 3, there are differences in the ‘observed ion’ assignments by the authors for the lower mass to charge (m/z) range 388-325 when compared to Table 2. This shows that there is uncertainty regarding the identity of the actual products formed during the experiments and that further work would be needed to actually map the hydrolysis reactions of this chemical. Overall, due to the use of significant amounts of acetonitrile in all experiments it is not possible to make any definitive conclusions regarding hydrolysis in natural waters. One noteworthy observation from the Gillard-Factor study is that the reactions of tin stabilizers in acidic acetonitrile solutions produced higher quantities of reaction products than in non-acidic (i.e., acetonitrile-water) solutions.

The results of a third hydrolysis study conducted on dioctyltin stabilizers and chlorides was submitted by the ORTEP group in a document titled “Electrospray Ionization Mass Spectrometry (ESI/MS) Study of Dioctyltin Compounds in Solution,” (Yoder, 2003). Prepared concentrations of the stabilizers were mixed with water and analyzed using ESI/MS. The results obtained for a 1000 ppb (as Sn) solution of $(\text{Oct})_2\text{Sn}(\text{EHTG})_2$ analyzed over time (i.e., 10 min, 6 h, 24 h) are presented in Table 5.

Table 5. Relative Peak Intensities of Major Ions Observed in the Mass Spectrum of $\text{Oct}_2\text{Sn}(\text{EHMA})_2$ (Yoder Study).

Observed Ion	m/z	Rel. Peak Inten. T = 10 min, %	Rel. Peak Inten. T = 6 hr, %	Rel. Peak Inten. T = 24 hr, %
$(\text{Oct})_2\text{Sn}(\text{EHTG})_2$	775	26.7	20.2	12.9
$(\text{Oct})_2\text{Sn}(\text{EHTG})^+ + \text{ACN}$	590	4.8	2.1	2.0
$(\text{Oct})_2\text{Sn}(\text{EHTG})^+$	549	11.7	6.4	3.6
$(\text{Oct})_2\text{Sn}(\text{SCH}_2\text{COO}) + \text{H}^+ + \text{ACN}$	478	22.1	15.6	10.6
$(\text{EHTG})_2 + \text{Na}^+ + \text{ACN}$	470	6.4	13.8	22.1
$(\text{Oct})_2\text{Sn}(\text{SCH}_2\text{COOH}) + \text{Na}^+$	460	5.1	4.6	3.6
$(\text{Oct})_2\text{Sn}(\text{SCH}_2\text{COO}) + \text{H}^+$	437	11.7	10.7	7.6
$(\text{EHTG})_2 + \text{Na}^+$	429	8.5	23.0	33.7
$(\text{Oct})_2\text{SnO} + \text{H}^+ + \text{ACN}$	404	2.9	3.4	4.0
	Total	100 %	100 %	100 %

From these results, the substance appears to be hydrolyzing in 1:1 acetonitrile: water; however, since significant amounts of acetonitrile were used it is not possible to make any definitive conclusions regarding hydrolysis in natural waters.

The Yoder study also included the results of a “water contact” experiment. A 1000 ppb (as Sn) solution of $(\text{Oct})_2\text{Sn}(\text{EHTG})_2$ in acetonitrile was subjected to evaporation via

nitrogen purge. Water was added to the dry residue and the aqueous solution allowed to sit for 24 hrs before analysis. The solution was then mixed 1:1 with acetonitrile and analyzed. The results are shown in Table 6.

Table 6. Relative Peak Intensities of Major Ions Observed in the Mass Spectrum of Oct₂Sn(EHMA)₂ during Water Contact Experiments (Yoder Study).

Observed Ion	m/z	Rel. Peak Intensity at T = 24 hrs, %
(Oct) ₂ Sn(EHTG) ₂	775	0
(Oct) ₂ Sn(EHTG) ⁺ + ACN	590	3.4
(Oct) ₂ Sn(EHTG) ⁺	549	3.4
(Oct) ₂ Sn(SCH ₂ COO) + H ⁺ + ACN	478	11.1
(EHTG) ₂ + Na ⁺ + can	470	8.5
(Oct) ₂ Sn(SCH ₂ COOH) + Na ⁺	460	8.5
(Oct) ₂ Sn(SCH ₂ COO) + H ⁺	437	15.4
(EHTG) ₂ + Na ⁺	429	27.4
(Oct) ₂ SnO + H ⁺ + can	404	22.3
	Total	100 %

Based on the results, there is uncertainty as to whether or not the tin compounds were stable in acetonitrile. In addition, there is no information on the distribution of these chemical species in the original test material relative to the sample analyzed after 24 hours; consequently it is difficult to extrapolate these results to behaviour in the natural environment.

Overall, there is uncertainty regarding the hydrolytic stability of the Sn-S bond under environmentally relevant conditions. The studies presented by ORTEP have demonstrated the susceptibility of tin thiolates to hydrolysis when dissolved in organic solvents, however there is still uncertainty concerning potential hydrolysis of these chemicals under natural environmental conditions, and across a full spectrum of environmental pHs.

3.4 Multi-Media Fate

3.4.1 Water and Sediment Compartmentalization

If released into receiving waters, the substances are likely to partition into the water column and eventually settle into the sediment compartment. Based on moderate to high predicted adsorption coefficients (log K_{oc}) (see below), the substances are expected to have a moderate to high affinity for sediments and suspended particulate matter in the water column.

A Level III multi-media fate simulation was performed for two organotin substances (Chemicals #6 and 7). These substances are expected to represent the range of significant differential partitioning behaviour in the environment for a release to water

based on Koc, Henry's Law Constant and degradation potential in water. Air-water partition coefficients were calculated using estimated values of the Henry's Law Constant. Solid-water partition coefficients were derived using the surrogate Koc values for TBT or estimated values from KOCWIN when judged reliable and adjusting organic carbon content for specific solids. Fish-water partition coefficients (i.e., BCF) were derived using surrogate data for analogous substances (e.g. TBT). Aerosol-water partition coefficients were derived using a default value. Solid and liquid phase half-life estimates were extrapolated from the BIOWIN Ultimate Survey Model predictions using the biodegradation extrapolation procedure recommended by Boethling (2000). In air, the half-life generated using the AOPWIN program was used.

Results of the Level III modeling for the representative organotin substances at steady-state suggest, that when released to water, organotins at the lower end of the range for adsorption potential (log Koc ~5.0, i.e. #6 and #7) will partition between the water column (49.5% bulk water, 7.5% suspended solids) and sediments (43%). The less soluble, higher adsorptive compounds (log Koc >6.0, i.e., all compounds except #6 and #7) will almost completely partition to sediments (~95%), with little partitioning to the water column (~5%). Most of the 5% mass fraction remaining in the water column for the high Koc compounds will be associated with suspended particles. The high solids partition coefficients indicate that sediments will be the sink for the majority of the organotin compounds. It has been shown that there is a significant flux from sediment to water demonstrating that the sediments serve as both a sink and a source of organotins.

The Level III simulation shows that little exchange with the atmosphere from an aquatic release of these organotins will occur. Also, the short half-life of the substances in air reduces residence time in this compartment. Consequently, for all organotins, less than 1% is expected to partition to the atmosphere and as a result no deposition to soil from the atmosphere is expected.

Loss of the substances from the aquatic environment at steady state will be a result of degradation and transport (i.e. advection). Degradation is thought to play an important role in the removal of most substances from local releases to aquatic systems.

In conclusion, the multi-media fate simulation suggests that aqueous releases could result in exposures to aquatic biota inhabiting pelagic zones and sediment-dwelling biota. Consequently, the effects and exposure to this biota will be considered in this assessment.

Level III V 2.70

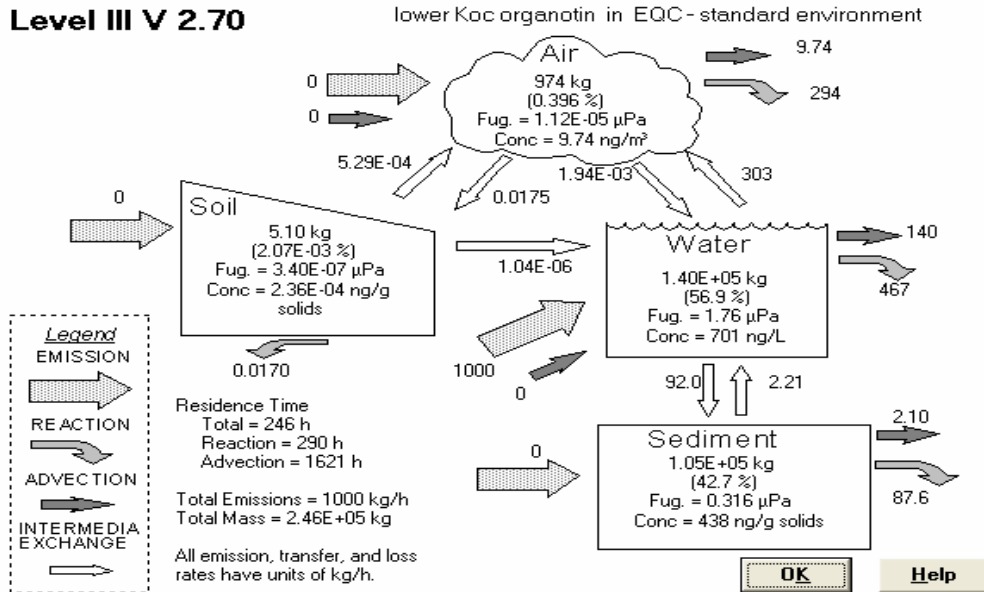


Figure 2. Level III Fugacity Model for Lower Koc Substances (Chemicals # 6 and # 7).

Level III V 2.70

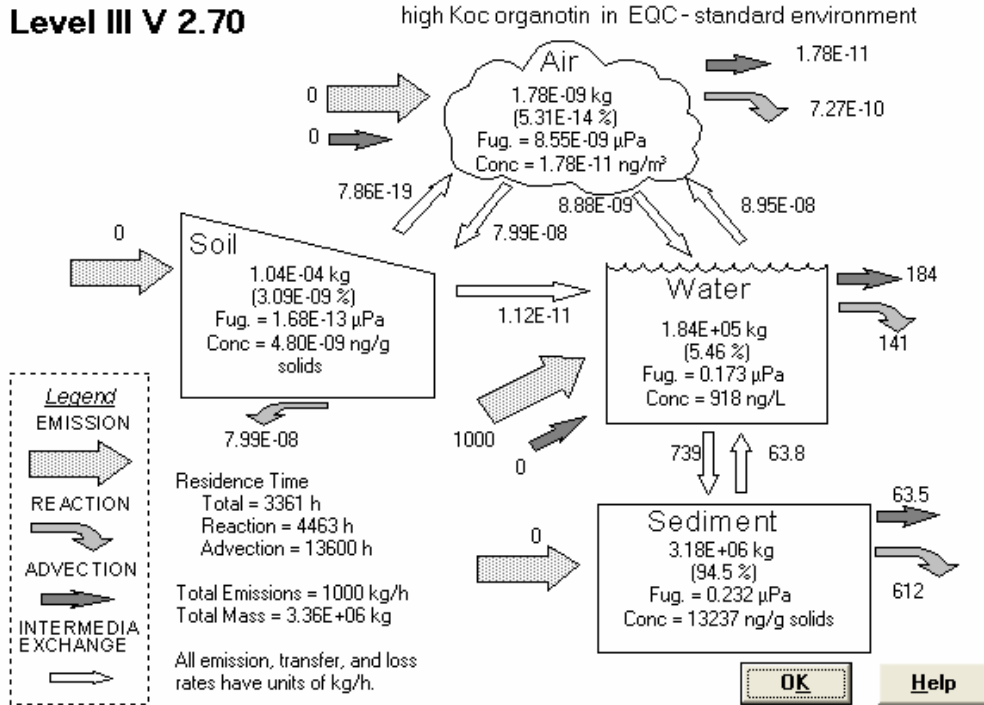


Figure 3. Level III Fugacity Model for Higher Koc Substances (Chemicals # 1-5, 8, 9).

3.4.2 Air Compartmentalization

The experimental vapour pressures and scientific literature (Government of Canada, 1993) for analogue substances indicate that the notified substances are unlikely to volatilize. Some of the experimental vapour pressures (e.g., for Chemicals # 1, 7) are significantly higher than experimental values located for surrogate substances. It was indicated for one substance that this is likely due to impurities present in the product.

Information available for Chemical #9 indicates an atmospheric lifetime for the substance of 1.5 hours to 2.4 hours.

Information on the volatilization of organotins contained in the CEPA PSL 1 report for "Non-pesticidal Organotin Compounds" indicates that long range transport of organotins is a possible route of entry into the Canadian environment as a result of releases in other jurisdictions, but that more hydrophilic organotins would not volatilize.

3.4.3 Soil Compartmentalization

Releases to the soil compartment would likely lead to some binding to the organic matter component of the soil matrix, reducing transport via groundwater to surface water bodies. The main exposure will be to soil-dwelling invertebrates from contact with the substances or ingestion of the compounds sorbed to organic matter. In the overall fate assessment, the soil compartment is not expected to be a significant medium of direct exposure to the substances.

3.5 Waste Treatment Removal

It is expected that the primary removal mechanism for organotin compounds in wastewater treatment will be via adsorption. Information obtained from the PSL 1 Report (Government of Canada, 1993) indicates that there is a wide variation in adsorption coefficients of butyltin species: Stang and Seligman (1987) determined sediment to water partition coefficients in the following ranges: monobutyltin - 1700 to 29 000; dibutyltin - 2100 to 26 000; and tributyltin - 6200 to 55 000. Further information from the Supporting Document on the Assessment of Non-Pesticidal Organotin Compounds (Maguire, 1992) indicates that about 90% of butyltin species may be associated with particles, and removed by sedimentation during wastewater treatment. However, Berg et al, 2001 demonstrated that sorption by organotins compounds to sediment was a fast and reversible process. He indicated that although organotins adsorb, they readily desorb and resuspension of contaminated sediments would lead to increased concentrations in the overlying water column. Since wastewater treatment facilities are a perturbed system, desorption is expected to occur. Modeling the notified substances in EPI indicated a 90-94% removal rate in an undisturbed system. Based on the study and predicted information, it was concluded that 90% removal of the notified substances during wastewater treatment was a reasonable assumption.

3.6 Predicted Environmental Concentration

An aquatic predicted environment concentration (PEC) has been calculated for release of liquid formulations resulting from manufacturing, reaction syntheses, cleaning of shipping containers, storage tanks and transfer lines. A sediment PEC has also been calculated since it has been identified as a compartment to which partitioning is likely to occur.

3.6.1 Aquatic Predicted Environmental Concentration

The aquatic PECs are calculated using conservative exposure release scenarios. The primary source of release of the notified substances is assumed to be effluent release resulting from rinsing of residues left in shipping containers (US EPA Assumptions for PMN Assessments), storage tanks and transfer lines. Available information from the VCC survey indicates that drums, totes and tanker cars are mainly used to ship the substances, although the substances can also be shipped in pails and kegs. In all cases, discharges were calculated for a suite of Canadian rivers (ranging from low to average flow rates), including rivers associated with notifiers' facilities, when such information was available.

3.6.1.1 Releases: Tin Stabilizers (2001 Standard Handling Practices)

Exposure scenarios were examined for tin stabilizers based on handling practices in 2001. These scenarios employed typical volumes in the range of 100 000 to 400 000 kg; these use volumes are considered reasonable for annual use at a single facility based on volume information available in the notifications and information from the Tin Stabilizers Association (TSA, 2001).

The VCC survey indicates that users either manually or automatically transfer the organotin stabilizers from shipping and storage containers to compound mixers. Transfer lines are cleaned, in some cases, on a monthly to infrequent basis, with rinsate either being recycled or directed to wastewater treatment facilities prior to being discharged to receiving waters.

Based on typical washout operations, New Substance Notification (NSN) experience and knowledge of standard industry practices, the likely source of releases of wastes containing the notified substances (Chemical #1-5 and 9) would be from the cleaning of shipping containers, storage tanks and associated transfer lines. Release resulting from the usage of bulk, tote and drum for shipping tin stabilizers are addressed below.

3.6.1.2 Bulk and Tote Shipments

Releases based on use of bulk and tote shipments were examined using the following assumptions:

- Industry provided information which indicated that 0.08% of a product was typically retained in emptied containers.

- A typical use volume of 400 000 kg/year will be used.
- Based on the adsorption potential information for the various organotins, a 90% removal rate is expected during wastewater treatment (refer to Section 3.5).
- Releases are determined over 250 days per year.

Considering these assumptions, the total daily discharge to aquatic systems for stabilizers shipped in bulk or totes is determined as follows:

$$\begin{aligned}
 \text{Predicted Release} &= \text{Daily contribution from bulk/tote use} \times \text{percent remaining in effluent after wastewater treatment} \\
 &= (400\,000 \text{ kg/yr} \div 250 \text{ days/yr} \times 0.08\%) \times 10\% \\
 &= 0.13 \text{ kg/day}
 \end{aligned}$$

3.6.1.3 Drum Shipments

While most of the stabilizers are shipped in bulk or semi-bulk containers in Canada, in 2001 approximately 7% were shipped in drums. Drums are containers that generally present the largest potential for release of the substance to the environment. While it is apparent that a range of stewardship practices exist, it is also generally true that drums are difficult to totally drain and so the “heels” left in drums can result in significant releases. The following release scenario is based on information industry has provided in the last 4 years. It is considered to be an accurate representation of releases occurring from an actual facility.

Releases based on use of drum shipments were examined using the following assumptions:

- As a consequence of drum rinsing, 1% of the total amount is assumed to be released to the plant’s effluent system. The 1% value is a low assumed value for drum residues (Standard US EPA Assumption: default pouring method 1% - 4%).
- It is assumed that annually one facility could use up to 100 000 kg of stabilizer supplied in drums. This quantity is viewed as a reasonable estimate since the average use at a single facility was greater than 65 000 kg/year in 2001.
- Based on the adsorption potential information for the various organotin, a 90% removal rate is expected during wastewater treatment.
- Releases are determined over 250 days per year.

The total daily discharge to aquatic systems at each site of formulation for the various stabilizers described above was calculated as follows:

$$\begin{aligned}
 \text{Predicted Release} &= \text{Daily contribution from drum use} \times \text{percent remaining in effluent after wastewater treatment} \\
 &= (100\,000 \text{ kg/yr} \div 250 \text{ days/yr} \times 1\%) \times 10\% \\
 &= 0.40 \text{ kg/day}
 \end{aligned}$$

Given that tin stabilizers can contain up to 0.5% of tributyltin as an inevitable technical impurity, it is appropriate that this be addressed with a separate release scenario. The total daily discharge to aquatic systems at each site of formulation for the tributyltin technical impurity was calculated as follows:

$$\begin{aligned}\text{Predicted release} &= \text{predicted release of tin stabilizer} \times \text{percent of impurity} \\ &= 0.40 \text{ kg/day} \times 0.5\% \\ &= 0.002 \text{ kg/day}\end{aligned}$$

Combining the above bulk, tote and drum calculations with data for typical Canadian receiving waters, PECs for tin stabilizers (Chemical #s 1, 2, 3, 4, 5 and 9) and for the tributyltin technical impurity were respectively calculated to range from 1.2×10^{-3} to $2.0 \mu\text{g/L}$ and 2.0×10^{-5} to $1.9 \times 10^{-2} \mu\text{g/L}$ for average and low flow rate Canadian river systems. For purposes of risk quantification, the most conservative value will be employed in calculations. In addition, the receiving water associated with these values serves as receiving water for a tin stabilizer facility.

3.6.1.4 Releases: Tin Stabilizers (Post Implementation of Stewardship Practices)

Product stewardship practices initiated by selected facilities led to a decrease in the risk of organotins potentially released to the environment. In order to implement industry wide stewardship practices, the VCC and Tin Stabilizer Association (TSA) recently finalized a guideline for environmental management of tin stabilizers in Canada (Draft Guideline, 2004). One facility practicing these safety measures essentially reduced its discharge of organotins to zero release.

The drum shipment scenario is re-examined at a similar size facility after implementation of proposed stewardship practices. Stewardship practices strive to prevent any release of tin stabilizer to the environment, as well as discourage the use of drums. However, assuming a 100 000 kg/year facility was supplied using drums, the estimated releases would drop to 0.004%, a value identified for a low release scenario for different manufacturing process (US EPA) but is considered to be an accurate estimate for release under stewardship practices for tin stabilizers.

Using 90% adsorption removal rate and reasonable potential releases over 250 days per year, the total daily discharge to aquatic systems at each site of formulation for the various stabilizers described above was calculated as follows:

$$\begin{aligned}\text{Predicted Release} &= \text{Daily contribution from drum use} \times \text{percent remaining in effluent} \\ &\quad \text{after wastewater treatment} \\ &= (100\,000 \text{ kg/yr} \div 250 \text{ days/yr} \times 0.004\% \text{ release}) \times 10\% \\ &= 0.0016 \text{ kg/day}\end{aligned}$$

Using the percentage of tributyltin technical impurity of 0.5%, the total daily discharge to aquatic systems at each site of formulation for the tributyltin technical impurity was calculated as follows:

$$\begin{aligned}\text{Predicted release} &= \text{predicted release of tin stabilizer} \times \text{percent impurity} \\ &= 0.0016 \text{ kg/day} \times 0.5\% \\ &= 8.0 \times 10^{-6} \text{ kg/day}\end{aligned}$$

Under Stewardship practices, the drum-use PECs for tin stabilizers (Chemical #s 1, 2, 3, 4, 5 and 9) and for the tributyltin technical impurity were respectively calculated to range from 1.6×10^{-5} to $8.1 \times 10^{-3} \mu\text{g/L}$ and 8×10^{-8} to $4.0 \times 10^{-7} \mu\text{g/L}$ for average and low flow rate Canadian river systems.

3.6.1.5 Releases: Manufacturing

Chemical #6 is manufactured in Canada for export only; however release scenarios used to evaluate the risk to the Canadian environment took into consideration potential releases from blending operations in Canada. Once exported, it is mainly used as a fungicide component in building materials (sealants, grout, and tape joint cement).

The primary source of release of the notified substance is liquid residues from blending vessels and transfer lines (US EPA Standard Assumptions). It is assumed that 0.1% of a total manufactured volume of 150 000 kg/year is released, and predicted that approximately 90% of the substance will be removed during wastewater treatment.

The total discharge to aquatic systems is thus calculated to be:

$$\begin{aligned}\text{Predicted Release} &= \text{Daily contribution from manufacturing} \times \text{percent remaining in effluent after wastewater treatment} \\ &= (150\,000 \text{ kg/yr} \div 250 \text{ days/yr} \times 0.1\% \text{ release}) \times 10\% \\ &= 0.06 \text{ kg/day}\end{aligned}$$

Because the surrogate used to derive a toxicity value for chemical #6 is the tributyltin moiety, the predicted release for chemical #6 is recalculated on a TBT base.

$$\begin{aligned}\text{Predicted release}_{\text{TBT}} &= \text{Predicted release}_{\text{CHEMICAL\#6}} \times (\text{Mw TBT} / \text{Mw Chemical \#6}) \\ &= 0.06 \text{ kg/day} \times (290.05 \text{ g/mol} / 411.7 \text{ g/mol}) \\ &= 0.04 \text{ kg/day}\end{aligned}$$

Combining the above figure with data for typical Canadian receiving waters, PECs for chemical # 6 were calculated to be in the range of 4.1×10^{-4} to $2.2 \times 10^{-1} \mu\text{g/L}$ for average and low flow rate Canadian river systems.

3.6.1.6 Releases: Tin Intermediates

Tin intermediates (Chemicals #7 and 8) are imported for use in reaction synthesis of stabilizers. Tributyltin can be an impurity in intermediates at concentrations less than 20%. Notifiers have indicated that losses are low during handling and reaction processes. Using a conservative assumption for volume, 1 000 000 kg/year, releases equivalent to those from totes of 0.08%, and a predicted STP removal rate of 90%, the estimated release would be:

Predicted Release of tin intermediates:

$$\begin{aligned} &= (1\,000\,000 \text{ kg/yr} \div 350 \text{ days/yr} \times 0.08\%) \times 10\% \\ &= 0.23 \text{ kg/day} \end{aligned}$$

Predicted Release of tributyltin impurity:

$$\begin{aligned} &= (200\,000 \text{ kg/yr} \div 350 \text{ days/yr} \times 0.08\%) \times 10\% \\ &= 0.05 \text{ kg/day} \end{aligned}$$

Combining the above releases with data for typical Canadian receiving waters, the aquatic PEC for tin intermediates (Chemicals # 7 and 8) ranged from 2.2×10^{-3} to $1.2 \mu\text{g/L}$ for average and low flow rate Canadian river systems. For the tributyltin impurity, the aquatic PEC was calculated to range from 4.5×10^{-4} to $2.3 \times 10^{-1} \mu\text{g/L}$.

3.6.2 Sediment PEC

A $\text{PEC}_{\text{sediment}}$ was calculated for TBT as a surrogate for chemical #6 and tributyltin impurities based on equilibrium partitioning relationship introduced by Di Toro et al. (1991) as follows:

$$\text{PEC}_{\text{sediment}} = \text{Highest PEC}_{\text{pelagic}} \times (K_{\text{suspended sediments}})$$

Where:

- $\text{PEC}_{\text{sediment}}$ = predicted environmental concentration for sediment (mg/kg)
- Highest $\text{PEC}_{\text{pelagic}}$ = highest predicted environmental concentration for surface waters for either chemical #6 or TBT impurities (mg/L)
- $K_{\text{suspended sediments}}$ = the water-suspended sediment partition coefficient (L/kg)²

$$\begin{aligned} \text{The } \text{PEC}_{\text{sediment}} &= 0.00031 \times (25\,180) \\ &= 7.8 \text{ mg/kg dry weight} \end{aligned}$$

The $\text{PEC}_{\text{sediment}}$ is therefore 7.8 mg/kg dry weight

² $K_{\text{susp. sediment}} = K_{\text{oc}}$ of notified substance x dry weight fraction organic carbon of suspended sediments (20%)

Table 7 outlines the predicted environmental concentrations (PEC) for the aquatic and sediment compartments, considering a range of flow rates for receiving waters and a 90% removal rate.

Table 7. The highest PECs for aquatic and sediment compartments.

Chemical #	Compartment	PEC
1-5, 9	water	2.0 µg/L
6 (impurity in tin stabilizers)	water	1.9×10^{-2} µg/L
1-5, 9	water	8.1×10^{-3} µg/L (stewardship)
6 (impurity in tin stabilizers)	water	4.0×10^{-7} µg/L (stewardship)
6 (manufacturing)	water	2.2×10^{-1} µg/L
6 (impurity in tin intermediates)	water	2.3×10^{-1} µg/L
6	sediment	7.8 mg/kg
7, 8	water	1.2 µg/L

Based on estimated releases from rinsing, storage, transfers and manufacture, the upper range PECs for the organotins in the receiving waters range from 4.0×10^{-7} to 2.0 µg/L and the upper PEC in sediment is 7.8 mg/kg dry weight.

3.6.2.1 Disposal

Information available from the Tin Stabilizer Association (TSA, 2001) indicates empty packaging material is either returned to the supplier or disposed of into regular and regulated landfills. Waste organotin substance is recycled back into the reactor, disposed into regular or regulated landfill or stored. Waste intermediate is often reclaimed from waste fluids prior to being shipped for disposal.

3.7 Effects-related Information

3.7.1 Ecotoxicity

3.7.1.1 Effects Overview

Trends

In general, the ecotoxicity of organotins is maximized in tri-substituted compounds, decreasing with both fewer and greater substitutions (Government of Canada, 1993). Further, based on existing data, butyl substituted tins are the most toxic, with both increases and decreases in alkyl chain length resulting in a decrease in toxicity relative to butyl. Variation of the anionic moiety (e.g., chloride, acetate, laurate) is believed to have little effect on biological activity (Maguire, 1992).

Non-lethal Effects

Shorter alkyl chain organotins (tributyltin, dibutyltin, monobutyltin) have been reported to cause high levels of acute sublethal (e.g., weight gain, enzymatic, histopathological) and lethal effects in marine and freshwater invertebrates (Government of Canada, 1993).

In addition, a number of studies have been conducted to investigate the effect of alkyl tins on the development of imposex or the imposition of male characteristics onto females in aquatic life. Horiguchi *et al.* (1997) tested various organotin compounds on the development of imposex in the rock shell, *Thais clavigera*. Mono and dibutyl and phenyl tins had little effect on the promotion of imposex in *T. clavigera*. However, tributyl and phenyl tins showed strong imposex development effects. In another study, tetrabutyltin and tetraoctyltin were shown to not influence the development of imposex in the *Thais clavigera* (Horiguchi, 2005). Bryan *et al.*, (1988) also reported that the effectiveness of tetrabutyltin on the development of imposex in the dogwhelk (*Nucella lapillus*) was negative.

Aquatic Effects

Majority of effects testing involves effects to pelagic organisms. The substances notified were typically not supplemented with toxicity information. Consequently, surrogate information was identified to act as critical studies in the respective effects assessment.

The following table lists the surrogates or substances that were used to predict aquatic and sediment ecotoxicity for the nine notified organotin substances, since ecotoxicity data for the notified substances were not provided in the notification packages. Although variations in toxicity exist between substances (even within a category), the surrogate selected is considered to represent the ecotoxicity profile of the substance being addressed. When multiple values exist for a particular endpoint, the most sensitive study will be used. All studies used have been performed under GLP or equivalent quality assurance systems.

Table 8. List of notified organotin substances (#1 through 9) and associated substance used for predicting toxicity.

Chemical #	Surrogate or Notified Substance
1,2,3,9	Butyltin tris (EHMA)
4,5	Dibutyltin bis (EHMA)
6	Tributyltin / Tributyltin chloride
7	Tetrabutyltin
8	Tetraoctyltin

Data were obtained from the scientific literature, internal databases, information generated for the High Production Volume (HPV) Challenge Program and from the ORTEP Association (ORTEPA, 1996, 2002a, 2002b). The data are summarized below:

3.7.1.2 Aquatic Toxicity Critical Studies

Butyltin tris (2-ethylhexylmercaptoacetate)

The following acute toxicity results were generated by ORTEP in 2002.

Fish 96 hour LC50 > 2.3 mg/L
 Algae 72 hour LC50 > 0.36 mg/L

Both these values exceeded the limit of water solubility and are not considered appropriate for estimating a PNEC. However, a ORTEP sponsored chronic daphnia study was also conducted; the lowest observed effect concentration (LOEC) was determined to be 0.114 mg/L and the no observed effect concentration (NOEC) was 0.048 mg/L. No additional studies for this substance were found in the literature.

The critical study concentrations identified for MBT(EHMA) is the ORTEP chronic daphnia study which indicated a LOEC of 0.114 mg/L and NOEC of 0.048 mg/L.

Dibutyltin bis(2-ethylhexylmercaptoacetate)

A 72 hour algae LC50 result was determined by ORTEP in 2002 to be > 0.65 mg/L. An industry generated 48 hour EC50 for daphnia was reported at > 1.2 mg/L.

Similar to the MBT(EHMA), these values are not considered appropriate for estimating a PNEC as they exceed the limit of water solubility. However, the chronic daphnia lowest observed effect concentration (LOEC) for DBT(EHMA) was determined to be 0.574 (NOEC = 0.098 mg/L).

Further IUCLID generated studies for DBT (EHMA) were as follows:

Daphnia magna 48 hr EC50 = 0.035 mg/L
Algae 72 hr EC50 = 0.56 mg/L
Zebrafish 96H LC50 = 11.7 mg/L

The critical study concentrations identified for DBT(EHMA) is the ORTEP chronic daphnia study which indicated a LOEC of 0.574 mg/L and NOEC of 0.098 mg/L.

Tributyltin

There are numerous studies which demonstrate that TBT is highly toxic to aquatic organisms. Crisinel *et al.* (1994) reports a 48 hour EC50 *daphnia magna* value of 0.018 mg/L and Vighi and Calamari (1985) determined a value of 0.0098 for the endpoint. Walsh *et al.* (1985) report a 72 hour EC50 for algae *Skeletonema costatum* of 0.987 µg/L.

Due to its persistence in sediment, there is concern about impact on benthic organisms as well. Data for adverse effects due to sediment exposure are much less abundant. The toxicity of tributyltin to the freshwater benthic invertebrates *Tubifex tubifex* (tubeworm), *Chironomus riparius* (midge larvae), *Hyalella azteca* (amphipod) and *Hexagenia* sp. (mayfly larvae) was investigated by Day *et al.* (1998). The results showed that *Hexagenia* sp. was the most sensitive of the invertebrates tested with an IC50 (growth) of 0.6 µg Sn/g dry weight. This amount is equal to 1.5 µg TBT/g dry weight (or 1.5 mg TBT/kg dry weight).

Fent and Hunn (1995) found that clams were not present in areas where sediment TBT exceeded 0.8 µg/g dry weight, and Meador and Rice (2001) noted moderate to severe reduction in growth for the polychaete *Armandia brevis* for sediment concentrations in the range of 0.1 - 1.0 µg/g dry weight.

Toxicity data for tributyltin chloride (CAS # 1461-22-9), acetoxytributyltin (CAS # 56-36-0), tributyltin (CAS # 688-73-3) and tributyltin fluoride (CAS # 1983-10-4) found in AQUIRE database generally indicate high acute and chronic lethal and sublethal toxicity in aquatic biota. The lowest reported acute median lethal values for tributyltin chloride were for a rainbow trout 96hr LC50 of 11.2 µg/L and a daphnid 24hr EC50 of 3.4 µg/L. Further ecotoxicity data obtained from the IUCLID dataset indicates algae 96h IC50 = 12.4 µg/L.

The Canadian Water Quality Guideline for Tributyltin is “0.008 µg/L” (CEQG, 2003). This is the concentration that should not be exceeded in order to protect and maintain freshwater aquatic life. It is based on the most sensitive lowest-observed-effect-level (LOEL) found for an acceptable study with a native freshwater species.

The Predicted No-effect Concentration identified for TBT is the CEQG value of 0.008 µg/L.

Tetrabutyltin

An important consideration for interpreting ecotoxicity information of tetrabutyltin, is the significant presence of tributyltin chloride (CAS # 1461-22-9) as an impurity (see above for ecotoxicity data of tributyltin chloride).

The following toxicity data were available from the AQUIRE database for tetrabutyltin (CAS # 1461-25-2):

Fish 96h LC50 = 0.045 mg/L and Daphnia 24h EC50 = 1.55 mg/L.

Further ecotoxicity data obtained from the IUCLID dataset is as follows:

Algae 72h EC50 = 0.05 mg/L.

The critical study concentration identified for Tetrabutyl tin is the IUCLID acute fish 96 hour LC50 value of 0.045 mg/L.

Tetraoctyltin

Data from the ORTEP Association for tetraoctyltin indicated a Fish (*Leuciscus idus*) 24h LC50 = 0.4 µg/L.

The following toxicity data were available from Steinhauser et al. (1985) for tetraoctyltin:

- Daphnid 48h LC50 > 1.0 µg/L
- Fish 96h LC50 = 0.4 µg/L
- Marine Bacterium (*P. phosphoreum*) 30min EC50 = 0.63 µg/L

Data from the ORTEP Association for tetraoctyltin indicated a Fish (*Leuciscus idus*) 24h LC50 = 0.4 µg/L.

The critical study concentration identified for Tetraoctyl tin is the IUCLID acute fish 96 hour LC50 value of 0.4 µg/L.

The above toxicity data from the scientific literature and surrogate data from internal databases indicate that the notified substances and impurities are expected to show high levels of acute and chronic toxicity in aquatic organisms.

3.7.2 Mammalian Toxicity

Based on the available information, the notified organotin compounds have low acute oral and dermal toxicity, are not irritating to the eyes or skin and are not genotoxic. Acute inhalation studies performed on three surrogate organotin compounds indicate that this class of substances have the potential to induce moderate to high acute toxicity via inhalation exposure (LC50 = 59 mg/m³, 941 mg/m³, 1286 mg/m³).

There is a broad range of literature investigating reproductive/developmental effects of organotins in animals. Waalkens-Berendsen (2004 a) reported reduced offspring and pup survival in rats at the high dose of 2000 mg/kg/day diet of tetrabutyltin; a NOAEL of 16-24 mg/kg/day (mid dose) was reported for these effects. In another reproductive/developmental study in rats, a NOEL of 168 mg/kg/day was reported for dibutyltin (Noda et al. 1992). However, concern for these effects is mitigated as these NO(A)ELs are more than 3 to 30 million times greater than the upper bound estimate of intake of butyltin from Canadian tap water and food (Follow-up Report on PSL 1 Substance, 2002). In addition, a number of studies investigating reproductive/developmental effects have reported negative results. Waalkens-Berendsen (2004 b) reported no adverse reproductive effects or effects on the pups when rats were treated with tetraoctyltin at the highest dose of 426 – 624 mg/kg/day. Health concerns regarding chronic neurotoxicity (primarily associated with tri- and tetra-substituted organotins) and immunotoxicity have been raised for organotin compounds.

A review of the acute toxicity studies submitted with the previously assessed organotins indicates that, while certain substances evoked some signs of potential neurotoxicity such as ataxia, exophthalmos, and sedation, in all cases the symptoms were minor and were shown to be completely reversible within the 14 day observation period. The Existing Substances Division at Health Canada reported that the lowest effect level observed for neuropathological effects was 0.79 mg/kg/day of methyltin in a 13-week study. However, concern for neurotoxicity is mitigated as this LOEL was 15 000 times greater than the upper bounding estimate of intake from tap water, based on a maximum concentration in drinking water survey in Canada (Follow-up Report on PSL 1 Substance, 2002). A number of studies indicate that organotins such as dioctyltin, dibutyltin, and tributyltin can cause lymphocyte depletion in the thymus and peripheral lymphoid tissue, resulting in thymus dependent immune suppression. The lowest effect level reported for immunotoxicity was 0.24 mg/kg/day for butyltin. However, concern for immunotoxicity is mitigated as this LOEL was 43 000 to 104 000 times greater than the upper bounding estimate of intake of butyltin from tap water and food (Follow-up Report on PSL 1 Substance, 2002).

Based on the available information, the notified organotin substances are not expected to pose a risk to the general population. Similarly, in a follow-up assessment on the PSL 1 Substance, non-pesticidal organotin compounds, Health Canada concluded that non-pesticidal organotin compounds not be considered “toxic” as defined in Paragraph 64(c) of the Canadian Environmental Act, 1999.

Based on the experimental data, the notified substances are expected to have low toxicity to humans.

4.0 Assessment of “Toxic” under CEPA

4.1 Predicted No Effect Concentration (PNEC)

4.1.1 Aquatic PNEC

A “chronic” PNEC (the concentration above which chronic toxic effects may be observed in the aquatic environment) is used to estimate risk when the substance is anticipated to be released to the environment a minimum of 20 days/year.

PNECs were calculated for the aquatic and sediment compartments, using measured data and surrogate data for the notified substances. The surrogate substances are butyltin tris (EHMA), dibutyltin bis(EHMA) and tributyltin. These surrogates were used as structural analogues for the particular notified substances under investigation.

Butyltin tris (EHMA) and Dibutyltin bis(EHMA) (Surrogates for Chemical # 1,2,3,4,5,9)

The critical toxicity studies identified for Chemicals # 1, 2, 3, 4, 5, 9 were based on the surrogates mono and di butyl (EHMA) compounds. Threshold concentrations were developed using available acute and chronic data for mono and di butyl (EHMA), which were combined to form one data set for each substance. For mono and di butyl (EHMA), the Maximum Acceptable Toxicant Concentration³ (MATC) was calculated, which were 0.07 and 0.24 mg/L respectively. The PNEC was derived by dividing the MATC by an uncertainty factor of 300. The uncertainty factors accounts for quality of the critical study, inter/intraspecies variation, acute to chronic extrapolation and lab to field extrapolation. The calculation of the uncertainty factor can be found in Appendix 2.

Therefore, the PNEC_{chronic} for the water column is 0.2 µg/L for monobutyltins and 0.8 µg/L for dibutyltin.

Tributyltin (Surrogate for Chemical # 6)

The Canadian Water Quality Guideline for the Protection of Freshwater Aquatic Life for tributyltin is used for the PNEC.

Therefore, the PNEC_{chronic} for the water column is 0.008 µg/L.

Tetrabutyltin (Chemical # 7)

An assessment factor of 100 was applied to the Fish 96h LC50 of 0.045 mg/L. This factor represents factors of 10 for each of the following: (1) estimating a chronic

³ Maximum Acceptable Toxicant Concentration is calculated as the geometric mean of the NOEC and LOEC values.

"maximum acceptable toxicant concentration" (MATC) from the base set and (2) extrapolating from the MATC to the PNEC.

Therefore, the PNEC_{chronic} for the water column is 0.45 µg/L.

Tetraoctyltin (Chemical # 8)

An assessment factor of 100 was applied to the acute fish LC50 value of 0.4 µg/L to account for lack of a chronic base set and for extrapolation to field conditions.

Therefore, the PNEC_{chronic} for the water column is 0.004 µg/L.

4.1.2 Sediment PNEC

Tributyltin (Surrogate for Chemical # 6)

As sediments constitute a significant medium of exposure, the predicted no effect concentration was determined using the chronic benthic toxicity data from Day et al. (1998). An assessment factor of 100 was applied to the chronic mayfly *Hexagenia sp.* 21-d IC50 (growth) of 0.6 µg Sn/g dry weight. The assessment factor of 100 represents, a) a factor of 10 to extrapolate from a single benthic study to a base-set of benthic species, and b) a factor of 10 to extrapolate from the base set to the MATC. When corrected to the molecular weight of TBT (290 g/mol), the resulting PNEC_{sed} is 0.015 mg_{TBT}/kg (rounded) dry weight sediments.

Therefore, the PNEC_{chronic} for sediment is 0.015 mg_{TBT}/kg.

4.2 Risk Estimation/Quotient Comparison

The ratio of the PEC to the PNEC is the quantification of the risk to the environment posed by a substance. A ratio greater than 1 indicates that the PEC exceeds the PNEC, and hence that the substance poses a risk to the environment.

Tables 7 and 8 outline the PEC:PNEC ratios for use of the substances in reaction intermediates, blending/formulation of products and manufacturing. PECs were based on a range of usage volumes and considered a range of flow rates for receiving waters. The PECs were then compared to PNECs for both the sediment and aquatic compartments. The PNECs were derived using measured and surrogate data for the notified substances.

Table 9. Aquatic PEC:PNEC ratios for chemicals in intermediates, stabilizers and manufacturing.

Chemical #	Surrogate	PNEC (µg/L)	PEC (µg/L)	PEC/PNEC
1,2,3,9	MBT EHMA	0.2	2.0	10
4,5	DBT EHMA	0.8	2.0	2.5
1,2,3,9 (under stewardship practices)	MBT/DBT EHMA	0.2	0.008	0.04
4,5 (under stewardship practices)	DBT (EHMA)	0.8	0.008	0.01
6 (manufacturing)	Tributyltin	0.008	2.2 x10 ⁻¹	27.5
6 (impurity in tin intermediates)	Tributyltin	0.008	2.3 x10 ⁻¹	29
6 (impurity in tin stabilizers, under 2001 standard handling practices)	Tributyltin	0.008	1.9 x10 ⁻²	2.4
6 (impurity in tin stabilizers, under stewardship practices)	Tributyltin	0.008	4.9 x10 ⁻⁷	6.1 x10 ⁻⁵
7	Tetrabutyltin	0.45	1.2	2.6
8	Tetraoctyltin	0.004	1.2	290

Table 10. Sediment PEC/PNEC ratio for manufacturing tributyltin.

Chemical #	Surrogate	PNEC (mg/kg)	PEC (mg/kg)	PEC/PNEC
6	Tributyltin	0.015	7.8	520

In summary, it is predicted that the use of the substances may result in release to the environment in concentrations exceeding the PNECs, except in instances where industry wide stewardship practices are put in place for use of mono and dibutyl stabilizers.

4.3 Overall Conclusion

Based on the available data, the organotin substances listed in Table 1 are expected to enter the environment in a quantity or concentration or under conditions that have or may have an immediate or long-term harmful effect on the environment or its biological diversity. Therefore, these substances are suspected to be toxic under paragraph 64(a) of CEPA 1999. However, in the case of stabilizers, if industry wide stewardship practices are implemented during use, releases can be minimized to levels that are not of concern to the environment.

The environmental assessment of organotin compounds revealed a number of data uncertainties for these chemicals, namely within the areas of environmental fate and exposure (see Appendix 1).

The available BCF and log Kow values indicate that the notified substances (excluding Chemical #6) and their lower molecular weight degradation products are not expected to result in BCF values ≥ 5000 or log Kow values ≥ 5 . These substances are not expected to exceed the criteria for bioaccumulation as specified in the Persistence and Bioaccumulation Regulations (Government of Canada, 2000).

Based on information available in the scientific literature, the notified substances (excluding Chemical #6) are expected to degrade in the aquatic environment with half-lives of less than a few months at 20 °C. Ultimate degradation of the notified substances (excluding Chemical # 6) will result in the formation of smaller alkyl tin compounds and elemental tin. These substances are not expected to exceed the criteria for persistence as specified in the Persistence and Bioaccumulation Regulations (Government of Canada, 2000).

In contrast, based on the measured data from Maguire (2000), TBT is anticipated to have a high potential for bioaccumulation in biota. In addition, measured half-lives in sediment are in the order of months and estimated half-lives from sediment core data are in the order of years. TBT exceeds the persistence and bioaccumulation criteria under the Persistence and Bioaccumulation Regulations (Government of Canada, 2000).

Based on the available information relevant to the assessment of risk to human health, the manufacture or use of the substances will not constitute a danger to human life or health, and consequently the substances are not suspected to be toxic under paragraph 64(c) of CEPA 1999.

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Appendix 1. Organotin Assessment Uncertainties.

The environmental assessment of new and transitional organotin compounds involved an evaluation of available scientific data for this chemical class. The available information includes a number of uncertainties for these chemicals, namely within the areas of environmental fate and exposure.

Fate

The assessment of the environmental fate of organotin compounds has been limited by the amount of information available on hydrolysis and biodegradation of these compounds. Noteworthy issues regarding the fate of organotins include the following:

1) Hydrolysis

- a. According to the literature, organotins are susceptible to hydrolysis as follows:



Recent information submitted by the ORTEP Association indicates that methyl-, butyl-, and octyltins undergo hydrolysis at neutral pH yielding various degradation products. However, for the time-frames studied, complete hydrolysis did not occur as per the above reaction.

- b. In several studies submitted by the ORTEP Association, details were not provided on the purity of the test substances. Consequently, we cannot distinguish whether the presence of certain species is the result of the formation of hydrolytic products, or whether these species were formed during the manufacturing process. This uncertainty makes it difficult to draw definitive conclusions on the results of hydrolysis studies.
- c. The ORTEP Association hydrolysis studies were conducted at pHs 1, 4, and 7 (ACN/H₂O) with a maximum test duration of 24 hrs. There is uncertainty with respect to whether or not the reactions were complete, and whether hydrolysis was expected to occur under alkaline conditions.

In summary, hydrolysis testing would be of much greater utility if it was conducted following the 4 day OECD screening test and using a continuation period if necessary to monitor the full reaction. In addition, the effect of pH on organotin hydrolysis should be examined by utilizing a test range of pH 1-10. Lastly, in addition to monitoring the hydrolysis rate, monitoring of products with a view to identifying the completeness of the reaction, and the potential for any stable hydrolytic products should be examined. The determination of whether or not stable hydrolytic products are formed is key to developing an understanding of the impact these materials have on the environment, as well as determining which compounds would be most appropriate for chronic toxicity testing.

2) Biodegradability.

- a. Currently there are no empirical data on the biodegradability of the notified organotin compounds. Any planned biodegradation testing should ensure that hydrolysis reactions do not interfere with the results of a biodegradation study (e.g. by monitoring for CO₂ evolution, rather than disappearance of parent compound). Nonetheless, such information in combination with hydrolysis data and potential hydrolytic products would shed light on how the substance is expected to behave in the environment.
- b. Under the High Production Volume (HPV) test program of the U.S. EPA, biodegradation tests will be conducted on many organotin chemicals. However, the program does not include testing on representatives from the mercapto tin category. The results of this testing program should shed some light on the biodegradability of alkyl tin compounds, but testing will be needed on mercapto based stabilizers to determine if they behave similarly.

Exposure

Although some exposure information has been supplied by notifiers and ORTEPA, a number of data gaps remain. Consequently, where information is unavailable, exposure assessments include a number of reasonable, conservative assumptions.

1. Quantity of Organotin Used Relative to Container Type.

Because of limited information concerning use of organotin stabilizers, assumptions were made concerning amount of substance used at a site, as well as the containers used to ship the substance. In the case of organotins shipped by drum, the maximum usage was assumed to be 100 000 kg/site. This scenario agrees with industry data from 2001 that indicates a number of sites used stabilizers shipped in drums, and that the average usage per site was greater than 65 000 kg/year. For this assessment it was assumed that any one site could use 50% more than an average value.

For organotin intermediates, the 1 000 000 kg/year assumption is based on a reasonable volume considering the total market in Canada. In addition, the assumption that the material would be released in quantities of 0.08% is based on an industry figure for totes, and is considered reasonably conservative.

2. Plant Locations and Receiving Waters.

Canada has a wide range of water systems, the size of which affects their ability to assimilate contaminants. A comprehensive listing of organotin related facilities is not available, and information is not available concerning how wastewater would be treated at these sites. Therefore, select representative treatment facilities and receiving water parameters were employed in the assessment.

In addition, it is also not known if two or more facilities are located near the same location, the result of which could be higher predicted environmental concentrations. Consequently, a range of rivers was employed in the assessment. Information on all organotin locations, quantities used, waste water treatment processes, and receiving waters, would reduce uncertainty in the exposure assessment.

3. Drum Recyclers

If drums are shipped to a drum recycling facility for disposal, then the drum recycler's site is another potential release location. In addition, a single recycler could receive drums from more than one location resulting in higher residue releases than described in the assessment. Uncertainty would be reduced with additional information about the use of drum recyclers, the quantities of tin stabilizer drums received, the container residues received, and their stewardship practices. For this assessment, it is assumed that drum recyclers would have equivalent releases to a user of 100,000 kg stabilizer/year with the material supplied in drums, and as a result, a separate assessment was not conducted.

Appendix 2. Uncertainty Factor Calculations: mono/di butyl (EHMA)

The uncertainty factor applied to the critical toxicity values for water was based on calculating and summing component uncertainties according to the procedure outlined in Bonnell (2004). Each component uncertainty is scaled and weighted according to the degree to which it contributes to the overall uncertainty of extrapolating from toxicity tests conducted under laboratory conditions to multispecies populations in the field. The component uncertainties are summed to determine the Total Uncertainty Factor (TUF). The TUF cannot exceed 1000. The order of importance of component uncertainty to the TUF is as follows:

Inter/Intraspecies variation > Quality of the Critical Study > Acute to Chronic Ratio =
Laboratory to Field Extrapolation

Component Uncertainties:

1. Quality of the Critical study

- Test reports were available for review and were of good quality
- Measured concentrations
- Tests were conducted according to GLP
- Critical test conditions maintained throughout tests (DO, pH, Temp, DOC)
- Acceptable CV for study
- NOEC/LOEC endpoints are less preferable than EC10/EC25.
- Scaling Factor = 4 Weighting Factor = 30 $UF_{\text{pivotal study}} = 120$

2. Inter/Intraspecies variation

- Sensitive endpoint: reproduction
- Sensitive lifestage included: hatching of eggs
- Base set of species
- Acute and chronic data combined for weight of evidence
- Most sensitive species determination difficult due to data variability
- Equal sensitivity assumed for all three species

Scaling Factor = 3, Weighting Factor = 50 $UF_{\text{inter/intraspecies variation}} = 150$

3. Acute to Chronic extrapolation

- have chronic MATC study so no need for ACR

Scaling Factor = 0, Weighting Factor = 10, $UF_{\text{acute to chronic}} = 0$

4. Lab to Field extrapolation

- lab conditions expected to approximate field, hydrolysis, photolysis and biodegradation expected to occur under chronic exposures, thus exposures in lab also account for degradation products
- possibility of more bioavailable MBT and DBT forming after 21 days which is not accounted for in test; lack of water solubility not a suitable rationale for low toxicity

Scaling Factor = 3, Weighting Factor = 10, $UF_{\text{lab to field}} = 30$

Calculation of Total Uncertainty Factor (TUF)

TUF = Sum of component UFs

TUF = 120 + 150 + 0 + 30

TUF = 300