Risk assessment studies on targeted consumer applications of certain organotin compounds

Final Report

prepared for the European Commission

RPA

September 2005

RISK ASSESSMENT STUDIES ON TARGETED CONSUMER APPLICATIONS OF CERTAIN ORGANOTIN COMPOUNDS

Final Report - September 2005

prepared for

the European Commission

by

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EXECUTIVE SUMMARY

1. Background

Organostannic (organotin) compounds are substances composed of tin, directly bound to a number of organic groups. In the context of this Report, consideration is given to di and tri-substituted organotins (with, respectively, two and three organic groups bound to the tin atom). Di-substituted compounds (usually in combination with mono-substituted compounds and, to a lesser extent, tri-substituted compounds) are used as stabilisers for PVC and as catalysts for various products. Historically, tri-substituted organotins were used as biocides and pesticides. The main use was in anti-fouling paints applied to ship hulls. Although the use of tri-substituted organotins in most former applications is now prohibited, small amounts of tributyltin (TBT) are still used as a biocide.

The Commission (DG Enterprise and Industry) contracted Risk & Policy Analysts Ltd. (RPA), working with the Centre for Ecology and Hydrology (CEH), to study possible risks from the application of organostannic compounds in areas outside of their use as a biocide in anti-fouling systems, as well as to describe the broad economic profile of the organotins industry. The Final Report for the study - hereafter referred to as the 2002 Report - was duly prepared and submitted to the Commission. Subsequently, the 2002 Report was considered by the Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) which raised some concerns over the 2002 Report.

In view of some of the concerns expressed by CSTEE, the organotin industry considered that it would be beneficial to all parties to revisit the 2002 Report and provide, where possible, updated information on the uses, quantities involved and associated research reports. To facilitate this process, the industry (through its trade association, ETINSA) with the approval of DG Enterprise and Industry, contracted RPA (with support from CEH) to update the study and, where possible, to address the concerns expressed by CSTEE. The resultant report - hereafter referred to as the 2003 Report - was also considered by CSTEE.

In view of some of the concerns expressed by CSTEE on the 2003 Report, a third study was commissioned by DG Enterprise and Industry and this Report presents its findings.

2. Changes from the 2002 and 2003 Reports

There have been four major changes from the earlier 2002 and 2003 Reports. Specifically, this Report has:

- included consideration of the presence and risks associated with the past use of triphenyltins in anti-fouling paints and, to a lesser extent, as a pesticide;
- extended the consideration of the presence and risks associated with the use of butyltins to include anti-fouling paints;
- focused on the presence and effects of four specific (groups of) organotins - dibutyltin (DBT), tributyltin (TBT), dioctyltin (DOT) and triphenyltin (TPT); and

- adopted a ‘group’ TDI (tolerable daily intake) for the effects on human health of the four listed organotins in combination.

In addition, all the calculations (and associated text) presented in the earlier Reports have been reviewed. Where appropriate, calculations have been refined and presentation improved taking account of new information, where available.

3. Summary of Work Undertaken

An overview of the areas of interest for this study is presented in Table 1.

Table 1: Overview of Organotin Risk Assessment

Organotin of Interest:	**DBT**	**TBT**	**DOT**	**TPT**
Assess risks to environment associated with:				
- organotin production	yes	yes	yes	no
- wood treatment with TBT biocide	no	yes	no	no
- use of wood treated with TBT biocide	no	yes	no	no
- processing of PVC containing organotins stabilisers	yes	yes	yes	no
- use of PVC products containing organotins stabilisers	yes	yes	yes	no
- production of products containing organotin catalysts	yes	yes	yes	no
- application of products containing organotin catalysts	yes	yes	yes	no
- use of products containing organotin catalysts	yes	yes	yes	no
Review environmental concentrations of organotins (and associated risks)	yes	yes	yes	yes
Assess risks to adult/child consumers associated with:				
- consumption of fish/fishery products	yes	yes	yes	yes
- intake of household dust	yes	yes	yes	yes
- intake via the environment (close to major sources)	yes	yes	yes	yes
- use of products containing TBT biocide	no	yes	no	no
- use of PVC products (containing organotin stabilisers)	yes	yes	yes	no
- use of products containing organotin catalysts	yes	yes	yes	no

4. Risks for the Environment

Overview

As outlined above, this report provides a revision of an earlier report prepared for the organotin industry and DG Enterprise and Industry (the 2003 Report which, in turn, represented an update of the 2002 Report). As such, the scenarios considered in the 2003 Report have been revisited. There are, therefore, three sets of scenarios to consider:

- those presented in the 2003 Report;
- those presented in the 2003 Report which have been reassessed (in this Report) as well as some new scenarios not previously considered; and
- those resulting from planned risk reduction measures (as discussed in this Report).

The three specific risk reduction measures considered in this Report are:

- the production and use of TBT as a wood preservative will cease in the near future (voluntary action by industry);
- the use of TBT biocides in other applications will cease by 1 September 2006 (in accordance with the Biocidal Products Directive); and
- the use of organotin catalysts in baking papers (whether imported into the EU or not) will be eliminated (voluntary action by industry).

Presentation of the Results

The derived numerical values for the Predicted Environmental Concentrations (PECs), the Predicted No Effect Concentrations (PNECs) and the associated PEC/PNEC ratios are presented in both the 2003 Report and this Report. However, the item of particular interest to chemical risk managers is whether a particular PEC/PNEC ratio exceeds unity. In the revised Technical Guidance Document (CEC, 2003), guidance is provided as to the three conclusions which may be reached by the 'rapporteur' (i.e. the competent authority designated for a particular risk assessment being undertaken within the context of the Existing Substances Regulations (ESR)) are as follows:

Conclusion (i): there is a need for further information and/or testing;

Conclusion (ii): there is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already; and

Conclusion (iii): there is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

In broad terms, Conclusion (ii) applies where the PEC/PNEC ratio is less than unity and Conclusion (iii) applies where the PEC/PNEC ratio exceeds unity. In cases where the PEC/PNEC ratio exceeds unity and the rapporteur determines that there is a possibility that further information would result in a reduced PEC/PNEC ratio (and reduced uncertainty), a Conclusion (i) may be reached.

This report and the 2002 Report present results of a 'targeted risk assessment' rather than a formal ESR risk assessment. As such, the conclusions of the authors do not carry the same authority as those reached by 'rapporteurs'. Nevertheless, the decision framework presented in the TGD provides an indication of whether the risks examined are likely to be of concern or not.

The Results

Although there have been some changes to the numerical values derived in this report from those presented in the 2003 Report, the conclusions of both reports (see Table 2) are the same (in respect of organotins not used in anti-fouling paints) - the risks to the environment are low (Conclusion (ii)) with the exception of those associated with the treatment of wood with a TBT biocide. This activity results in a PEC/PNEC ratio greater than unity (Conclusion (iii) for the aquatic environment). The use of such treated wood may also result in significant risks to the local soil environment (Conclusion (iii) for the terrestrial environment).

Table 2: Risk Assessment Conclusions for the Aquatic Environment - based on TGD Guidance

Risk Source	**2003 Report**	**This Report**	**With Risk Reduction Measures**	**Comment**
All excluding anti-fouling paints (regional PEC/PNEC)	(ii)	(ii)	(ii)	Risks are primarily associated with the production and use of dibutyltins and dioctyltins.
All including anti-fouling paints (regional PEC/PNEC)	Outside scope of work	(iii)	(iii)	Risks due to levels of TBT in surface waters which in some regions may lead to PEC/PNEC ratios >1.
Anti-fouling paints (local PEC/PNEC)	Outside scope of work	(iii)	(iii)	In some ports, harbours and marinas, levels of DBT, TBT and TPT may be well above PNEC values.
Organotin production (local PEC/PNEC)	(ii)	(ii)	(ii)	Risks are primarily associated with the production of dibutyltins and dioctyltins.
Wood treatment plant using TBT biocide (local PEC/PNEC)	(iii)	(iii)	(ii)	Risks due to TBT. Products to be withdrawn from market - although residual risk (to soil) from previous product use will take time to decay.
PVC processing sites using organotin stabilisers (local PEC/PNEC)	(ii)	(ii)	(ii)	Risks are primarily associated with the use of dibutyltins and dioctyltins.
Product manufacture using organotin catalysts (local PEC/PNEC)	(ii)	(ii)	(ii)	
Application of products with organotins catalysts (local PEC/PNEC)	(ii)	(ii)	(ii)	

Key: *Conclusion (i): PEC/PNEC > 1 but may reduce with further testing*
Conclusion (ii): PEC/PNEC < 1 (risks not of concern)
Conclusion (iii): PEC/PNEC > 1 (risks of concern)

In this Report, consideration has also been given to the levels of butyl and phenyl tins resulting from the use of anti-fouling paints on vessels. Monitoring data confirm that levels of these organotins in some aquatic environments are well above the PNEC values resulting in a Conclusion (iii) for the aquatic environment at a local level and, possibly, at the regional level.

Industry has confirmed that TBT biocides will be withdrawn from the market. When implemented, the risks to the environment associated with wood treatment plants will be eliminated as, in time, will the risks to the local environment associated with the use of such wood. In other words, the implementation of this risk reduction measure will result in a Conclusion (ii) for all the uses of organotins other than anti-fouling paints.

Although the application of organotin anti-fouling paints is now banned within the EU, vessels may still enter EU ports and waters until 2008 with such paint previously applied (i.e. applied prior to 1 July 2003). This, together with past use, ensures that it will be some time before existing levels of organotin contamination decay to acceptable levels.

5. Risks for Consumers

Overview

As for risks to the environment, the scenarios considered in the 2003 Report have been revisited in light of new information. As a result of the comments made by CSTEE, consideration has been given to a number of additional routes by which consumers may be exposed to organotins.

Presentation of the Results

The derived numerical values for the predicted intake, the tolerable daily intake (TDI) and the associated TDI percentage which the predicted intake represents are presented in both the 2003 Report and this Report. As already mentioned, in this Report, risks to consumers are based on a group TDI (in other words, the organotins are considered to act in combination rather than individually). As for the risks to the environment, the item of particular interest to chemical risk managers is whether the %TDI value exceeds 100% (which would result in an ESR Conclusion (iii)).

However, in relation to organotins, risks to consumers may arise from a wide range of products and other risk sources. It is, therefore, possible that the cumulative risk associated with exposure to a number of risk sources would result in a Conclusion (iii) (i.e. the combined organotin intake exceeds the TDI). To assist in determining which risk sources are likely to be significant contributors to the overall cumulative risk, those risk sources which result in an organotin intake in the range 20% to 100% of the TDI have been assigned a Conclusion (ii)*.

With these points in mind, the summary of the risks to consumers, as presented below, is based on the following modified categorisation of the ESR Conclusions:

Conclusion (i): there is a need for further information and/or testing;

Conclusion (ii): there is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already;

Conclusion (ii): although there is no need for further information and/or testing and no need for risk reduction measures when considering this risk source in isolation, when considered in combination with other risk sources, it may be desirable to consider limiting the risks (from this risk source); and*

Conclusion (iii): there is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

The Results

The results for adults and children are presented in Tables 3 and 4 respectively. As discussed above, it is likely that a particular consumer will be exposed to more than one exposure route. For this reason, in addition to the Conclusions (i), (ii) and (iii), a further ‘conclusion’ has been provided for this report and the definition of Conclusion (ii) has been slightly modified as follows. Conclusion (ii)* has been used where the predicted organotin intake is in the range 20-100% TDI and the definition of Conclusion (ii) has been taken to mean where the predicted organotin intake is <20%TDI.

Table 3: Risk Assessment Conclusions for Adult Consumers (modified from TGD Guidance)

Risk Source (Worst Case)	**2003 Report**	**This Report**	**With Risk Reduction Measures**	**Comment**
Tri-substituted Tins (mainly TBT)				
Fish/fishery products (95% intake)	Not considered	(ii)*	(ii)*	Risks associated with anti-fouling paints. Note that median intake is about 10 times lower which would result in a Conclusion (ii)
Via environment (worst local)	(iii)	(iii)	(ii)	Use of TBT in wood treatment to be discontinued
Foot spray	(ii)*	(ii)*	Eliminated	Eliminated with ban on TBT biocides in consumer products
Cycling shorts padding	(ii)	(ii)	Eliminated	
Non-allergenic pillows	Not considered	(ii)	Eliminated	
Insoles	(ii)*	(ii)*	Eliminated	
Di-substituted Tins (DBT and DOT)				
Via environment (worst local)	(iii)	(iii)	(i)	Local DOT emissions lead to significant risks (from organotin production and PVC processing) but uncertainties over leaf-air partition coefficient remain. Note that regional risks about 300 times lower (Conclusion (ii)).
Indoor air./dust	(ii)	(ii)	(ii)	Risks mainly associated with DBT

Table 3: Risk Assessment Conclusions for Adult Consumers (modified from TGD Guidance)

Risk Source (Worst Case)	**2003 Report**	**This Report**	**With Risk Reduction Measures**	**Comment**
Use of Di-substituted Tins in Flexible PVC Products				
Shower curtains, steel coating	Not considered	Not considered in detail but unlikely to present a significant direct risk to consumers suggesting a Conclusion (ii)		
T-shirts	Not considered	(ii)*	(ii)*	
PVC gloves	(ii)*	(ii)*	(ii)*	
PVC bags	Not considered	(ii)	(ii)	
PVC sandals	Not considered	(ii)*	(ii)*	Sandals could also use rigid PVC but consumer uptake likely to be lower
Earplugs	(ii)	(ii)	(ii)	
Use of Di-substituted Tins in Rigid PVC Products				
Profile extrusions (e.g. window frames), foamed sheeting, pipes (other than for drinking water)	Not considered	Not considered in detail but unlikely to present a significant direct risk to consumers suggesting a Conclusion (ii)		
Drinking water pipes	Not considered	(ii)	(ii)	
Rigid film/credit card	Not considered	(ii)	(ii)	
PVC food packaging (97.5% intake)	(ii)	(ii)*	(ii)*	Risk increased due to use of lower TDI value. Note that median intake is 5 times lower (Conclusion (ii))
Use of Di-substituted Tins in Catalysts				
Polyurethane foams	Not considered	Not considered in detail but unlikely to present a significant direct risk to consumers suggesting a Conclusion (ii)		
Female hygiene products	(ii)	(ii)*	(ii)*	Risk increased due to use of lower TDI value
Dental moulding	(ii)	(ii)*	(ii)*	
Silicone sealant	Not considered	(ii)	(ii)	
2-part silicone moulds	Not considered	(ii)*	(ii)*	
Cookies (baking paper)	(iii)	(iii)	Eliminated	Assume measures taken to eliminate organotin catalysts from baking paper

Table 4: Risk Assessment Conclusions for Child Consumers (modified from TGD Guidance)

Risk Source (Worst Case)	**2003 Report**	**This Report**	**With Risk Reduction Measures**	**Comment**
Tri-substituted Tins (mainly TBT)				
Fish/fishery products (95% intake)	Not considered	(iii)	(iii)	Risks associated with anti-fouling paints - based on an assumed intake per kg bodyweight four times that for adults. Note that median intake is about 10 times lower which would result in a Conclusion (ii)*

Table 4: Risk Assessment Conclusions for Child Consumers (modified from TGD Guidance)

Risk Source (Worst Case)	**2003 Report**	**This Report**	**With Risk Reduction Measures**	**Comment**
Via environment (worst local)	(iii)	(iii)	(ii)	Use of TBT in wood treatment to be discontinued
Non-allergenic pillows	(ii)	(ii)	Eliminated	Eliminated with ban on TBT biocides in consumer products
Di-substituted Tins (DBT and DOT)				
Via environment (worst local)	(iii)	(iii)	(i)	Local DOT emissions lead to significant risks (from organotin production and PVC processing) but uncertainties over leaf-air partition coefficient remain. Note that regional risks about 300 times lower (Conclusion (ii)).
Indoor air/dust	(ii)*	(iii)	(iii)	Higher risk due to higher measured values and use of group TDI
Use of Di-substituted Tins in Flexible PVC Products				
T-shirts	(ii)*	(iii)	(iii)	Higher risk due to use of group TDI
Paddling pool	(ii)	(ii)	(ii)	
PVC toys	(ii)	(ii)	(ii)	
PVC sandals	Not considered	(ii)*	(ii)*	Sandals could also use rigid PVC but consumer uptake likely to be lower
Use of Di-substituted Tins in Rigid PVC Products				
Drinking water pipes	Not considered	(ii)	(ii)	
PVC food packaging (97.5% intake)	(ii)	(ii)*	(ii)*	Risk increased due to use of lower TDI value. Note that median child intake is 10 times lower (Conclusion (ii))
PVC squash bottle	Not considered	(ii)	(ii)	
Use of Di-substituted Tins in Catalysts				
Nappies	(ii)	(ii)*	(ii)*	Risk increased due to use of lower TDI value
Cookies (baking paper)	(iii)	(iii)	Eliminated	Assume measures taken to eliminate organotin catalysts from baking paper

Key (to both Tables 3 and 4):

Conclusion (i): Intake > 100% TDI but may reduce with further testing

Conclusion (ii): Intake < 20% TDI (risks not of concern)

Conclusion (ii): 20% TDI < Intake < 100% TDI (risks of possible concern)*

Conclusion (iii): Intake > 100% TDI (risks of concern)

Although there are variations in the numerical values between those presented in the 2003 Report and in this Report, the overall conclusions are broadly similar.

For adults, the incorporation of the identified risk reduction measures (with specific reference to the cessation of TBT biocide production and use and the elimination of organotin catalysts in baking paper) leads to exposures which are all below the TDI with the exception of local exposure via the environment. This is associated with the emissions of DOT from both production plants and, to a lesser extent, PVC processing plants. As detailed in the text, the high uptake values are due to the predicted high leaf-air partition coefficients - which have been subject to considerable debate with industry representatives. Although attempts have been made to model the specific DOT compounds being emitted, there are no measurements to confirm the reliability of such predictions. For this reason, a Conclusion (i) is proposed as further studies may provide a more robust approach to modelling the specific DOT compounds being emitted and their environmental behaviour.

More generally, the adoption of the group TDI and some additional exposure sources leads to several exposure routes being in excess of 20% of the TDI (Conclusion (ii)*).

A Monte Carlo simulation of (largely) assumed exposure distributions for adult consumers suggests that although the overall 'typical' (median) exposure is about 65% of the TDI, about 25% of adult consumers are exposed to more than the TDI.

In general terms, the risks to child consumers are higher than those for adult consumers. Of note is that the use of the group TDI leads (in the worst case) to exposures in excess of the TDI (even after risk reduction measures) for the intake of organotins:

- in fish and fishery products (assuming that the intake per kg bodyweight is four times that for adults);
- via the environment in the proximity of certain production/processing facilities;
- present in household dust; and
- from PVC prints on T-shirts (and other child clothing).

Aggregating the various exposure routes (using a Monte Carlo simulation) suggests that the overall exposure for 70% of young child consumers will exceed the group TDI, while the 'typical' (median) 8kg child consumer is exposed to about 160% of the TDI.

Although arguments can be advanced that there are uncertainties within each of the associated sets of calculations, it would appear that the risks associated with the extensive and varied use of organotins cannot be readily dismissed as negligible.

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7. RISK ASSESSMENT CONCLUSIONS

GLOSSARY OF ACRONYMS

ADI	Acceptable Daily Intake
AFS	Anti-fouling System
ATC	Alkyltin Chloride
DBT	Dibutyltin
DBTC	Dibutyltin Chloride
DBTL	Dibutyltin Laurate
DBTM	Dibutyltin Maleate
DBTO	Dibutyltin Oxide
DMT	Dimethyltin
DMTC	Dimethyltin Chloride
DOT	Dioctyltin
DOTC	Dioctyltin Chloride
DOTO	Dioctyltin Oxide
DPT	Diphenyltin
ECVM	European Council of Vinyl Manufacturers
EDC	Electrodeposition Coating
EHMA	Ethylhexyl Mercaptoacetate
ESD	Emission Scenario Document
E-PVC	Emulsion-polymerised PVC
ERPA	European Rigid PVC-film Association
ESPA	European Stabilisers Producers Association
ETICA	European Tin Catalysts Association
ETINSA	European Tin Stabilisers Association
EU	European Union
EUPC	European Plastics Converters
HDPE	High Density Polyethylene
HPV	High Production Volume
ICCA	International Council of Chemical Associations
IMO	International Maritime Organisation
IOMA	Iso-octyl Mercaptoacetate
ISOPA	European Isocyanate Producers Association
Kemi	National Chemicals Inspectorate, Sweden
LOEL	Lowest Observed Effect Level
MAC	Maximum Allowable Concentration
MBT	Monobutyltin
MBTC	Monobutyltin Chloride
MBTO	Monobutyltin Oxide
MMT	Monomethyltin
MMTC	Monomethyltin Chloride
MOS	Margin of Safety
MOT	Monooctyltin
MOTC	Monooctyltin Chloride
MPT	Monophenyltin
NOAEL	No Observed Adverse Effect Level
NOEC	No Observed Effect Concentration

OECD	Organisation for Economic Co-operation and Development
OEM	Original Equipment Manufacture
ORTEP(A)	Organotin Environmental Programme (Association)
PEC	Predicted Environmental Concentration
PNEC	Predicted No-effect Concentration
PBT	Persistent, Bioaccumulative and Toxic substance
PUR	Polyurethane
PVC	Poly Vinyl Chloride
RCR	Risk Characterisation Ratio (i.e. PEC/PNEC)
RTV	Room Temperature Vulcanisation
SCF	Scientific Committee for Food
Sn	Tin
S-PVC	Suspension-polymerised PVC
TBT	Tributyltin
TBTC	Tributyltin Chloride
TBTO	Tributyltin Oxide
TDI	Tolerable Daily Intake
TGD	Technical Guidance Document
TOTC	Trioctyltin Chloride
tpa	Tonnes per Annum
TPT	Triphenyltin
TPTC	Triphenyltin Chloride
TPTH	Triphenyltin Hydroxide
TTBT	Tetrabutyltin
TTCL	Tin Tetrachloride
TTOT	Tetraoctyltin
UCD	Use Category Document
uPVC	Unplasticised PVC
vPvB	Very Persistent, very Bioaccumulative substance
WHO	World Health Organisation

Examples of Units Used

mg	milligram (= 1 x 10^{-3} g)
µg	microgram (= 1 x 10^{-6} g)
ng	nanogram (= 1 x 10^{-9} g)
pg	picogram (= 1 x 10^{-12} g)
dm^2	10cm x 10cm = 100 cm^2 = 0.01 m^2
kg bw	kg bodyweight
kg dw	kg dry weight
kg fw	kg fresh weight

1. INTRODUCTION

1.1 Background

Organostannic (organotin) compounds are substances composed of tin, directly bound to a number of organic groups. In this Report, particular consideration is given to di and tri-substituted organotins (with, respectively, two and three organic groups bound to the tin atom). Small amounts of tri-substituted organotins are used as pesticides and biocides, whilst the di-substituted compounds are used as stabilisers for PVC, and catalysts for various products.

Commission Directives 1991/51/EC[1] and 2002/62/EC[2] restricted the use of organotin compounds as a biocide in the aquatic environment from 1 January 2003 and EC Regulation 782/2003[3] prohibited the use of organotin compounds in all marine anti-fouling paints with effect from 1 July 2003 (although existing (unsealed) coatings may remain in place until 2008).

However, concerns have also been expressed over the use of tri-substituted organotin compounds as biocides in other applications such as in wood preservation, heavy industrial textiles and consumer products. Additional concerns have been expressed regarding use of di-substituted organotin compounds as stabilisers in certain PVC plastic consumer products and the possibility that tri-substituted organotin compounds are also present as impurities in significant concentrations.

Furthermore, detection of organostannic compounds has been reported in various consumer products, including nappies, carpets, textiles, PVC beach balls and female personal hygiene products.

The Commission (DG Enterprise and Industry) contracted Risk & Policy Analysts Ltd. (RPA), working with the Centre for Ecology and Hydrology (CEH), to study possible risks from the application of organostannic compounds in areas outside of their use as a biocide in anti-fouling systems, as well as to describe the broad economic profile of the organotins industry. The Final Report for the study was duly prepared and submitted to the Commission on 19 July 2002 (RPA/CEH, 2002) - hereafter referred to as the 2002 Report. Subsequently, the 2002 Report was considered by the Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) and a preliminary view was presented to the 37th Plenary Meeting held in Brussels on 1st April 2003. The final

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[1] Commission Directive adapting to technical progress for the fifth time Annex I to Council Directive 76/769/EEC on the approximation of laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations (tin, PCP and cadmium) (OJ L142, 5.6.1999).

[2] Commission Directive adapting to technical progress for the ninth time Annex I to Council Directive 76/769/EEC on the approximation of laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations (organostannic compounds) (OJ L183, 12.7.2002).

[3] Regulation (EC) No 782/2003 of the European Parliament and of the Council of 14 April 2003 on the prohibition of organotin compounds on ships (OJ L115, 9.5.2003).

opinion was adopted at the 38th Plenary Meeting on 12th June 2003 and published on the internet (CSTEE, 2003).

In view of some of the concerns expressed publicly by CSTEE, the organotin industry considered that it would be beneficial to all parties to revisit the 2002 Report and provide, where possible, updated information on the uses, quantities involved and associated research reports. To facilitate this process, the industry (through its trade association, ETINSA) with the approval of DG Enterprise and Industry, contracted RPA (with support from CEH) to update the study on an independent basis and, where possible, to address the concerns expressed by CSTEE. The Final Report for this study was duly prepared and submitted to ETINSA (and the Commission) on 19 December 2003 (RPA, 2003) - hereafter referred to as the 2003 Report. Subsequently, the 2003 Report[4] was considered by CSTEE and its opinion was adopted during the 43rd plenary meeting of 28 May 2004 (CSTEE, 2004).

Against the background of continuing criticisms from CSTEE, a third study was commissioned by DG Enterprise and Industry (with the support of ETINSA) in order to address outstanding issues.

1.2 Objectives of this Study

The full Specifications for this third study are attached as Annex 1. The key features are summarised below:

- the study is to be limited to four organotins - tributyl tin (TBT), dibutyltin (DBT), dioctyltin (DOT) and triphenyltin (TPT);
- these compounds shall be considered as a single group for the purposes of human toxicity;
- estimates shall be made of total exposure for each organotin;
- exposure calculations shall include those associated with:
  - losses from wood treatment plants;
  - PVC processing and recycling plants;
  - waste (with particular reference to landfills);
  - use as stabilisers in a range of consumer products made from PVC;
  - use as catalysts (particularly in polyurethane) in a range of consumer products; and
  - use in biocides;
- the associated degree of risk shall be determined using a ‘group’ tolerable daily intake for the four organotins in combination; and
- to determine how these may change over time.

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[4] To facilitate access to the relevant information, copies of the 2002 and 2003 Reports together with the relevant CSTEE Opinions will (shortly) be available as downloads from www.rpaltd.co.uk. Once approved, the Final Report from this study will also be made available on-line.

1.3 Structure of Report

This Report is similar in structure to the 2002 and 2003 Reports and reproduces relevant material from the earlier reports.

Section 2 provides an overview of the use of organotins, including an overview of the economic profile of the industry. Section 3 outlines the emissions and associated fate of organotins released to the environment. Section 4 provides details of the effects of organotins upon the environment and the environmental risks associated with the emissions considered in Section 3. Section 5 provides an overview of the exposure of consumers (both adults and children) to organotins through the use of a diverse range of everyday products. Section 6 describes the potential health impacts of the organotins under consideration and the associated risks (from both environmental and consumer exposure). The conclusions are summarised in Section 7, with references provided in Section 8.

Further information is contained in the Annexes. This Report does not include the numerous pages of output from the *EUSES2* progam used in the assessment. However, electronic copies (together with an electronic copy of this Report if desired) may be freely downloaded from RPA’s website: www.rpaltd.co.uk.

Finally, the CSTEE comments on the 2003 Report are reproduced in full in Annex 2, together with responses from the Consultants which highlight how the concerns expressed have been addressed in this Report.

2. PRODUCTION, USE AND MARKETS FOR ORGANOTINS

2.1 Introduction

This Section provides an overview of the production and usage of organotin compounds in the EU[5], including the use of the different groups of substances in the various categories. Consideration has also been given to the 'downstream' industries in which the substances are used. For each use category, a description of the reasons for use of organotin compounds is provided, with available information on the size and value of the related markets. This has also been applied to the downstream user sectors, taking account of the relative contribution from organotins, where possible. The information in this Section is mainly drawn from that presented previously in the 2002 and 2003 Reports with some additional material in respect of tri-phenyl tins.

2.2 Production of Organotins

Organotin compounds are produced at seven sites in the EU and one additional site in the European Economic Area (EEA). This production is carried out by seven companies, as detailed in Table 2.1.

Table 2.1: Production of Organotins in the EU and EEA in 2001

Production site	**Tetra-substituted (intermediate)**	**Tri-substituted[1] (biocides/pesticides)**	**Mono/di- (stabilisers, catalysts)**
Akcros - Germany			Yes
Atofina - Holland		Yes	Yes
Baerlocher - Italy			Yes
BNT - Germany	Yes	Yes	Yes
Crompton - Germany[2]	Yes	Yes	
Crompton - Germany			Yes
Reagens - Italy			Yes
Rohm & Haas - Switzerland		Yes	Yes

Source: ORTEPA (2002b).

Notes:

1) ETINSA has advised that as of 2004, only two of the four sites identified in 2001 still produce tri-substituted tins for use in biocidal products. However, the tetra-substituted tins used as an intermediate contain significant amounts of tri-substituted tins. Furthermore, small amounts of tri-substituted tins will still be present as impurities in mono- and di-substituted compounds.

2) On 1st July 2005, Crompton merged with Great Lakes to form Chemtura (www.chemtura.org).

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[5] Within this Report, as for the 2002 and 2003 Reports, reference to the EU should be taken to refer to the EU-15 Member States.

The production sites listed in Table 2.1 used a total of 12,779 tonnes of inorganic tin in 2001 for the production of the various organotin compounds, as well as for production of inorganic tin compounds. It should further be noted that the above data apply only to butyltin and octyltin compounds. Methyltin compounds, whilst used in the EU, are only produced outside the EU and are imported.

2.3 Use of Organotins

There is a wide range of organotin compounds that can be manufactured and placed on the market. The properties of organotin compounds vary significantly, depending upon their structure[6].

Commercially used organotins are characterised by the number of organic groups in the compound. Tetra-substituted compounds are only used as intermediates in synthesis of other organic chemicals. Tri-substituted organotins are used as biocides, pesticides and as intermediates in the production of other chemicals. Mono and di-substituted organotins are generally considered together[7] and are used as PVC stabilisers, as catalysts and in glass coating. Table 2.2 outlines the key uses for organotins in the EU and the quantities sold to the EU market in 2002.

Table 2.2: Organotin Uses and Quantities Sold in the EU (estimates for 2002[1])

	Applications	**Quantity (t/yr)**
Tetra-substituted	Intermediate in synthesis	N/A
Tri-substituted	Biocide	< 100
	Biocide in anti-fouling paints[2]	1,250
	Pesticide	100
	Synthesis[3]	< 150
Mono/di-substituted	PVC stabilisers	15,000
	Catalysts	1,300 to 1,650
	Glass coating	760 to 800
Total (maximum)	***All uses (except tetra-subs)***	***approx 19,000***

Notes:

1) Data from ORTEPA (2002) (biocides, pesticides, synthesis and glass coating), ESPA (2002) (stabilisers) and ETICA (2002) (catalysts) as updated by ETINSA in 2003.

2) As discussed below, use of tributyltins for this application are now prohibited (within the EU).

3) ETINSA has advised that the total quantity of tri-substituted tins for use as an intermediate in 2004 was substantially higher than the estimate for 2002. Although not clarified, this could perhaps be because the quantities present in the tetra-substituted tins were excluded.

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[6] Organotin compounds are characterised by the presence of a carbon to tin bond and have the following general formula: $R_x\ Sn\ L_{(4-x)}$ where R is an organic alkyl or aryl group and L is an organic (or sometimes inorganic) ligand. Whilst the carbon-tin bond is strong, the association with the anionic ligand is less so and has a tendency to undergo dissociation both in use and in the environment.

[7] In most of their applications, a mixture of mainly mono and di-substituted compounds is used, with the relative amounts depending upon the technical requirements of the application in question.

It should be noted that uses of the tri-substituted organotins and uses of the mono/di-substituted compounds do not overlap. Thus, for example, mono/di compounds are not suitable for use as biocides and tri-substituted compounds are not suitable as PVC stabilisers.

Within a commercial organotin product, there will always be some quantity of related substances, in addition to the substance itself. In some cases, the performance of these products relies upon the presence of more than one related substance (e.g. mono and di-substituted octyltin stabilisers), whereas in others, the related substances are present as an inevitable impurity. For example, tributyltin chloride will contain impurities of mono, di and tetra-butyl tins, as well as tin tetrachloride.

Similarly, whilst the main products used as stabilisers in PVC, for example, are mono and di-substituted compounds, due to the chemistry involved in their production, tri-substituted organotin compounds will comprise a small fraction of the total amount (as discussed further in subsequent sections).

However, it should be noted that the R (alkyl or aryl) groups in most organotin compounds are the same. For example, tributyltin will contain other butyl tins but not, for example, octyltins.

2.4 Applications and Markets for Organotins

2.4.1 Overview

This Section provides a discussion of the areas of application for organotin compounds, including:

- further detail on the quantities and specific substances used in each application;
- reasons for the use of organotin compounds;
- the manner in which organotins are used;
- details of the potential end-uses for the products in which organotins are used;
- a discussion of the key markets and economic profile; and
- details of markets for downstream products.

2.4.2 Tetra-substituted Organotins

As indicated above, tetra-substituted organotins are used as an intermediate in the synthesis of other chemicals. They are produced at only two sites in the EU and are used at these and other organotin producing sites, such as for the production of mono/di-substituted organotins through a redistribution reaction to produce organotin chlorides.

Since tetra-substituted organotin compounds are not used commercially, except in synthesis of other chemicals, they will not be considered further in this study.

2.4.3 Tri-substituted Organotins

The situation for tri-substituted organotins is complex and has changed significantly in recent years. Until recently, there were five main uses:

- as a biocide in anti-fouling paints;
- as a biocide in wood preservatives;
- as a biocide in other applications;
- as a pesticide; and
- as an intermediate.

As a Biocide in Anti-fouling Paints

Tributyltin (TBT) and triphenyltin (TPT) compounds have been used as a paint additive since the 1970s to prevent the fouling of ship hulls. Due to effects on marine ecosystems, bans (at national and international levels) have been introduced progressively since the 1980s to prohibit this use for small vessels (less than 25m in length) and, subsequently, for larger vessels.

At its 21st Assembly Meeting in November 1999, the International Maritime Organisation (IMO) agreed that the application of organotins in anti-fouling paint should be banned (globally) from 1 January 2003 and the presence of organotins (unless sealed) should be banned from 1 January 2008. These proposals were subsequently incorporated into the IMO's International Convention on the Control of Harmful Anti-fouling Systems on Ships (the AFS Convention) adopted in October 2001. However, by January 2005, only nine countries had ratified the AFS Convention[8]. Since the AFS Convention will only enter into force 12 months after 25 States representing 25% of the world's merchant shipping tonnage have ratified it, the global ban is not yet (i.e. as of early 2005) in place.

However, and as already indicated, these proposals have been adopted within the EU through EC Regulation 782/2003 which prohibited the use of organotin compounds in all marine anti-fouling paints with effect from 1 July 2003 (although existing (unsealed) coatings may remain in place until 2008). This Regulation applies to the merchant shipping of Member States and to any other ships entering an EU port.

As a Biocide in Wood Preservatives

It is reported that the total amount of treated wood supplied by Western Europe's wood preserving industry is around 6.5 million m^3 per year. This relates to pressure-treated wood, so there will also be an additional quantity of wood that is treated through dipping, for example. There is a variety of possible end uses for treated wood but it has been confirmed by industry that the key uses for wood products treated with trialkyltin compounds were in fences and facades of houses.

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[8] Discussion with IMO, January 2005.

In terms of the overall market for wood preservatives, the types of preservatives used are as follows:

- water-borne wood preservatives constitute approximately 71% of the market;
- solvent-borne products constitute 18%; and
- creosote products constitute the remaining 11% (WEI, 2001).

Tri-substituted organotins are used in ‘light organic solvent’ type wood preservatives, in which petroleum distillate or white spirit is used as a carrier (OECD, 2001). These are used for the treatment of wood in industrial premises through pressure or vacuum impregnation and the substances are not sold to consumers. Until recently, tri-substituted organotin compounds formed a relatively small proportion of the solvent-borne wood preservatives used in the EU.

As of 2001, less than 100 t/yr of tri-substituted organotins were used as biocides in wood preservatives, primarily in the UK, France and Spain, as summarised in Table 2.3.

Table 2.3: Use of Tri-substituted Organotins in EU Biocides in 2001

Substances	Applications	Quantities
Tributyltin oxide	Wood preservatives	< 50 t/yr
Tributyltin naphthenate	Wood preservatives	< 50 t/yr
Total		***< 100 t/yr***

Source: ORTEPA (2002).

However, the (only) company which produces tri-substituted tins for use in wood preservatives has advised the European Commission that it will be withdrawing these products from the market[9].

As a Biocide in Other Applications

It has been reported that TBT has been used as a biocide in a wide range of industrial applications including cooling water, pulp and paper mills, breweries, leather processing and textile mills (WHO, 1999a).

In addition, there are a number of products which tri-substituted organotin compounds are believed to be used in (by companies that are not members of the ORTEPA). These include:

- non-allergenic pillows used in the UK (DTI, 2002);
- insoles for shoes in the UK (DTI, 2002);
- use in the padding of cycling shorts in Germany (BgVV, 2000); and
- use in a spray for the treatment of athlete’s foot in Germany (UBA, 2000).

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[9] Letter from Crompton GmBH to the European Chemicals Bureau dated 26 September 2003.

It is has not been possible, however, to present detailed information on the overall levels of use in these products. In particular, it is thought that a significant proportion of products treated with tri-substituted organotin biocides are imported from outside the EU.

In relation to the use of tri-substituted organotin compounds in sprays to treat athlete's foot, it is indicated that the annual market in Germany is around 7.5 t/yr (as TBT benzoate). No data are available for the other uses.

Information has been received from one company that produces TBT-based anti-microbial products, based on tributyltin oxide and tributyltin maleate (formulated at concentrations around 1% and 25% respectively and generally further diluted by mixing with other ingredients). These products are sold only to industrial customers for use in manufacturing (and are not sold to consumers, nor are they sold for apparel applications). Applications for these products include:

- polyurethane foam, where it is added during the 'blowing' process and is subsequently incorporated into the polymer matrix;
- incorporation into various other polymers that are used for products such as flooring tiles and carpeting;
- back-coating of textiles used in upholstery (co-applied with a polymeric binder on the rear of the fabric); and
- a small amount used in treatment of feather and down.

In the review of the Biocidal Products Directive[10], these 'non-notified' uses will cease before 1 September 2006 (provided they contain one (or more) of the five TBT compounds 'identified' in Annex III of 2032/2003). It should be noted that biocides containing other organotins which have not been notified nor identified have not been permitted within the EU since December 2003.

To minimise risks to consumers associated with TBT biocides (prior to 2006), ORETPA has stated to the European Commission that it would support a 'marketing and use' restriction on all TBT-based biocides (ORTEPA, 2003).

As a Pesticide

Tri-substituted tins are also used as pesticides for a range of edible crops and ornamental plants. The global value for this sector is of the order of €35 million[11].

There are three relevant groups of compounds: triphenyltins (TPT), tricyclohexyltins (TCT) and trineophenyltins (TNT). For the 2003 Report, it was estimated (by industry) that a total of 100 t/yr of tri-substituted organotins (excluding TPT) were used in

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[10] Commission Regulation 2032/2003 on the second phase of the 10-year work programme referred to in Article 16(2) of Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market, and amending Regulation (EC) No 1896/2000 (OJ L307, 24.11.2003).

[11] This figure is based on global sales for 2002 for the main manufacturer (Atofina) as downloaded from www.cerexagri.com.

pesticides (as shown in Table 2.4), but this quantity is expected to continue to decline in the future.

Table 2.4: Use of Tri-substituted Organotins in Pesticides (in the EU as of 2003)

Substances	Applications	Quantities
Triphenyl tins	Mainly as a fungicide (now banned - see below)	n/a
Tricyclohexyl tins	Mainly as acaricides in vineyards	50 t/yr
Trineophenyl tins	Mainly for protection of citrus fruit against mites	50 t/yr
Total		***100 t/yr***

Source: Information supplied by ETINSA for the 2003 Report.

The main TPT (or fentin) pesticides used in recent years within the EU were:

- TPT hydroxide which was used as a fungicide for potato blight and leaf spot on sugar beet - particularly in the UK (at around 50 t/yr) and Belgium; and
- TPT acetate which was used as a fungicide for use on celery and sugar beet.

TPT chloride has also been used as a fungicide for use on sugar beet - but not within the EU in recent years.

The use of TPT (triphenyltin) as a pesticide is no longer authorised in the EU (following Commission Decisions 2002/478/EC and 2002/479/EC dated 20 June 2002) after evaluation of the toxicological, ecotoxicological and environmental-fate data.

TCTH (Tricyclohexyltinhydroxide), TCTT (Tricyclohexyltintriazole), and TNTO (bis-Trineophenyltinoxide) are marketed in Europe. These products are used as acaricides on vines, vegetables, top fruits (mainly citrus) and ornamentals. Although these products are permitted under the Pesticides Directive in the EU, they are now under review. The draft review is expected to be issued by May 2006.

As an Intermediate

The quantity of tri-substituted organotins used in organic synthesis will not be considered for the purposes of this study since this use relates only to an intermediate used in the production of other chemicals. Losses to the environment and exposure of consumers are, therefore, considered to be negligible.

Summary

Within the context of this Report, attention is focused on the residual uses (and exposures associated with past uses) of tributyl and triphenyl tins. These include:

- the use of tributyltin as a biocide in anti-fouling paints;
- the use of tributyltin as a biocide in wood preservatives;
- the use of tributyltin as a biocide in other applications; and
- the past use of triphenyltins in pesticides.

It is acknowledged that bans within the EU do not necessarily mean that there is no on-going production of tri-substituted organotins destined for export and one of the companies has advised that most of its TBT production is for export.

Finally, it is worth noting that numerous TBT (and TPT) chemicals (in relatively small unit sizes) are available within the EU from laboratory chemical suppliers. It has been assumed that these uses do not lead to significant emissions.

2.4.4 Use of Mono/Di-Substituted Organotins in PVC

Quantities Used

The largest use for tin compounds is in the stabilisation of PVC. Stabilisers are used in all PVC products in order to avoid decomposition[12] whilst heating during processing (EVC, 1996). The consumption of tin stabilisers[13] in Europe is about 15,000 t/yr of which about 60% is used for food (and medical) packaging and 40% for technical applications (ESPA, 2002). Tin systems are used for almost all rigid PVC applications in North America whereas the main use in Europe is for rigid[14], transparent applications where rigorous processing conditions require enhanced stabilisation. These consumption levels have remained fairly constant over recent years as illustrated in Figure 2.1.

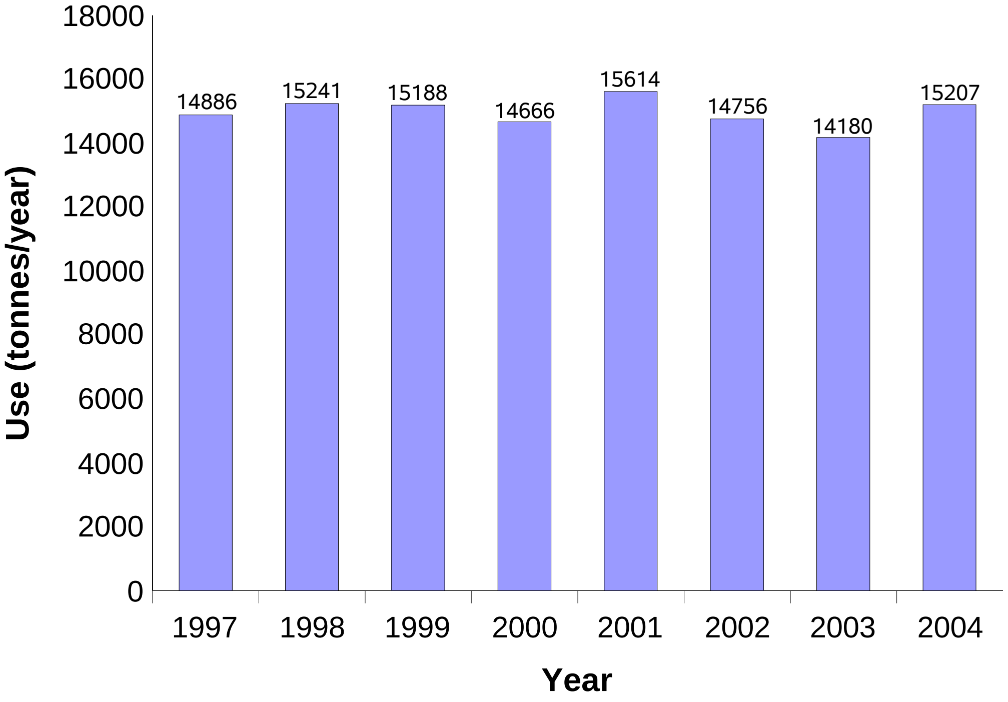

Figure 2.1: Use of Organotin Stabilisers in the EU-15 plus Norway, Switzerland and Turkey (tonnes/year) (based on RPA/CEH, 2002 and Vinyl 2010, 2005)

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[12] Through dehydrochlorination, autooxidation and mechanochemical chain scission (ECVM *et al*, 2001).

[13] As of 2004, tin stabilisers accounted for nearly 9% of the stabilisers (by weight) used in PVC. The dominant stabiliser system is lead (62% of the market). Other stabiliser systems are based on Calcium/Zinc and Barium/Zinc (Vinyl 2010, 2005).

[14] See explanation of rigid and flexible PVC below.

Organotin stabilisers include methyl, butyl and octyltins, all of which are used in both flexible and rigid PVC products.

Tin stabilisers are divided into two main categories: tin mercaptides (stabilisers with tin-sulphur bonds) and tin carboxylates (stabilisers with tin-oxygen bonds). Tin mercaptide stabilisers allow the production of clear, rigid vinyl commodities even under high-demanding processing conditions. Tin mercaptides have a characteristic odour, which might be undesirable during processing. Organotin stabilisers are always mono/di-substituted compounds, the alkyl groups being methyl, butyl or octyl groups[15]. The most common stabilisers are produced by reaction of mono- and di-alkyltinchlorides with mercaptoesters.

Tin carboxylate stabilisers are typically used in outdoor applications (such as transparent panels and translucent double-wall panels for greenhouses) as they are more resilient to light and weathering. However, it is important to note that PVC used in such applications will also have additional (ultra-violet) light and weathering non-organotin stabilisers.

PVC Processing

PVC is generally classified as either ‘rigid’ (unplasticised or uPVC) or ‘flexible’, with the latter softened by incorporation of plasticisers such as phthalates and adipates. About one third of the PVC used in the EU is ‘flexible’.

PVC is processed by techniques such as calendering, injection moulding and extrusion:

- *Calendering* involves processing a mass of material through successive pairs of parallel rolls to form a sheet or a film. This process is generally used in the thermoplastics, rubber, textile, paper and non-woven fabrics industry.
- The process of *injection moulding* allows the conversion of thermoplastic and thermosetting materials into final products. This process permits the manufacture of small PVC parts.
- Finally, the process of *extrusion* consists of forcing a heat softened plastic through a die which determines the cross section of the profile after cooling.

Additionally, plastisol (‘paste’) type PVC compounds are in the form of a thick paste that can be applied by techniques such as coating, dipping or rotational moulding.

Over 90% of organotin stabilisers are used in rigid PVC. Only octyltin and butyltin stabilisers are produced in Europe, with methyltin stabilisers imported from outside the EU. Table 2.5 (overleaf) provides details of the estimated quantities of methyl, butyl and octyltin stabilisers used in rigid and flexible PVC applications.

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[15] Dodecyl compounds were used in the past but it is understood that this is no longer the case.

Table 2.5: Use of Organotin Stabiliser Types in Rigid and Flexible PVC in Europe (t/yr)

Stabiliser	Rigid PVC	Flexible PVC	Total
Methyltin	1,090	94	1,184
Butyltin	3,889	754	4,644
Octyltin	8,922	251	9,173
Total	**13,901**	**1,099**	**15,000**

Source: Based on data for 2001(totalling 15,614 tpa) from ESPA (2002) which has been 'normalised' (i.e. adjusted) to give a total consumption of 15,000 tpa.

As stated in the 2002 Report, industry estimates suggest that, for the two major uses - packaging and rigid construction, accounting for over 85% of use - the products in question are produced at 55 PVC processing plants across the EU. Further data suggest that much of the rigid PVC used in packaging is produced by over 60 large calendering units located at over 20 sites, mainly in Italy and Germany. These large calendering units each produce the order of 7,000 tonnes of PVC per year[16].

For all uses, there are estimated to be 130 major plants and a further 250 smaller users, spread fairly evenly across the EU (ESPA, 2002).

Downstream Markets

Table 2.6 details the overall market for PVC in Western Europe over the period 2000 to 2002 (APME, 2002) and in the EU-25 for the period 2002 to 2004 (PlasticsEurope, 2005). PVC is the only plastic in which organotin stabilisers are used, and as already noted, organotins account for nearly 10% of the stabilisers used in PVC.

As of 2000, the Western European market for PVC was slightly more than 5.5 million tonnes of PVC resin or 8.3 million tonnes of finished product with an estimated worth of €75 billion (ECVM *et al*, 2001). More recent figures for the EU-25 show a continuing expansion with the current market in excess of 6.5 million tonnes of PVC resin.

Table 2.6: European Market for PVC in 2000 to 2004 (1000s of tonnes per year)

	2000	2001	2002	2002	2003	2004
Area Covered	Western Europe			EU-25		
Production	5,579	5,681	6,374	6,530	6,700	7,000
Sales	5,600	5,700	5,787	6,350	6,510	6,655
Source	*APME (2002)*			*PlasticsEurope (2005)*		

Based on the figures presented above, it would be expected that the current EU market for organotin stabilised PVC would be of the order of 600,000 tpa with the majority being used in rigid PVC packaging. Recent figures suggest that perhaps 50% of such packaging would be for food contact applications with an estimated 267,000 tpa (of organotin stabilised PVC) being used in food packaging in Western Europe (EUPC,

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[16] Based on discussions with industry representatives at a meeting hosted by EVC in Verase, Italy on 10 May 2005.

2005). A full picture of this and other uses of PVC products containing organotin stabilisers is presented in Table 2.7.

Table 2.7: Applications for Rigid and Flexible PVC Containing Organotin Stabilisers

Rigid Applications	**Examples**	**Stabiliser Use (tpa)**
Packaging, including food contact	Pharmaceutical – blister packs plus some rigid medical applications. Food-contact plastics: ➢ single layer where PVC is the food-contact surface ➢ laminated composites with PE, where PE is the food-contact surface. General consumer goods for: ➢ transit packaging ➢ sealed containers and profiles for high value electrical and electronic components ➢ tamper-proof and tamper-evident packs for cosmetics, housewares, hardware and DIY goods. ➢ Pre-formed trays for complex shapes and fragile items. Shrink sleeves used on packaging such as bottles. Furniture films.	11,816
Credit cards		
Rigid construction including foamed sheeting	Use in external decking and railing (small in Europe but much larger in the USA). External furniture. Sheeting including foamed panels. Point of Display applications. Vinyl mini-blinds	973
Thin rigid film	Food-contact plastics - blown film, which relates to sweet-wrapping and other items	278
Bottles		278
Pipes and mouldings	Pipes and guttering including all pipe types (and fittings) such as sewer pipes, rainwater goods and drinking water pipes. Electrical conduit profiles and other electrical boxes etc Rigid PVC used in computers (may or may not be tin stabilised). Very small quantities of rigid toy applications	278
Profile extrusions (e.g. windows)	Profiles – windows, door frames and doors, conservatories etc. Architectural in-house applications – decorative profiles.	278
Flexible Applications	**Examples**	**Stabiliser Use (tpa)**
Flooring	Vinyl Flooring – mostly plastisol and mostly do not use tin stabilisers.	314
Wallcovering	Vinyl wallcovering – use of tin stabilisers is effectively non-existent.	314
Steel coating		314
Miscellaneous	PVC gloves – general purpose and surgical goods (but virtually none are tin stabilised in practice). T-shirt and other clothing printing – for children and adults. Plastisol coated leathercloth and various coated fabric applications (note: tin stabilisers are little used except for some automotive uses). Ear Plugs. Paddling pools. Shower Curtains. Toys – rigid mostly in reality. Possibly some beach balls but most flexible toys would not use tin stabilisers. Fishing buoys. Other consumer articles.	157

Source: ESPA (2002) with examples provided in ESPA (2004).
Note: Figures are based on percentages (assuming total use of 15,000 tonnes/year) and have been rounded.

2.4.5 Use of Mono/Di-Substituted Organotins as Catalysts

The concentration of tin catalysts is between 0.001% and 0.5% of the finished polymer. Following production, the catalyst is retained within the polymer (they are homogeneous catalysts) and hence within the finished product (ETICA, 2002), although in some cases, the organotin may be partially degraded by the high temperatures used in the production processes.

There are several key areas of use for organotins as catalysts and a separate discussion, including that for downstream markets, is provided for each of these in the following sections.

Electrodeposition

Dibutyltin oxide (DBTO[17]) is used as a catalyst for the curing of cathodically applied electrodeposition coatings (EDC). The main use for EDCs containing DBTO is as a primer applied for corrosion protection on motor vehicles.

The electrodeposition process involves submerging an uncoated negatively charged vehicle body in a tank containing an aqueous dispersion of the EDC resin system[18]. The resin from the electrodeposition medium is deposited on the metal surface, washed and then baked on in an oven (ETICA, 2002 and Environment Agency, 1997).

In 2000, between 700 and 800 tonnes of organotin catalysts were used in electro-deposition coatings.

Downstream Markets for Use in Electrodeposition

As indicated above, between 700 and 800 t/yr of organotin catalysts were used in electrodeposition coatings in 2000. If it is assumed that the concentration of organotin catalyst in the final electrodeposition coating is as high as 0.5%[19], the total quantity of coating produced would be around 160,000 tonnes.

This can be compared to the quantity of coatings used in automotive 'original equipment manufacture' (OEM[20]) in the EU in 1999, as set out in Table 2.8. This Table also sets out the estimated value of the coatings produced with the value for EDC coatings containing organotins based on the corresponding unit value for all automotive OEM paints.

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[17] This is the only organotin used in Europe for electrodeposition coatings.

[18] Containing a solubilised crosslinkable resin, crosslinking agent, non-soluble catalyst and other additives.

[19] The maximum suggested value for the concentration of organotin catalysts used.

[20] This will include other types of coatings used in automotive OEM (not just the electrodeposited primer coating).

Table 2.8: European Market for Automotive OEM Coatings and Estimated Market for Electrodeposition Coatings Containing Organotins

	Amount (kt)	Value, € million
All automotive OEM paint	280	1,280
Organotin-containing EDC coatings	160	730

Source: CEPE (2001). Data have been rounded.

Note: Data on automotive OEM paint are included to provide a comparison for the estimated value. It should be noted that more recent data for 2001, 2002 and 2003 suggest that the overall OEM paint figures have remained broadly static over the last few year (CEPE, 2005).

Silicones

Organotins are used as catalysts in 'room temperature vulcanisation' (RTV) via a condensation reaction. Dibutyltin laurate is the most commonly used organotin catalyst for this application. It is typically used at between 0.01% and 0.1% by weight.

Between 50 and 100 tonnes of organotin catalysts were used in production of silicones in 2000 (ETICA, 2002).

Downstream Markets for Use in Silicones

It is estimated that the European silicones market is worth €2.5 billion per year and accounts for some 10,000 jobs (CES, 2002). Furthermore, the downstream uses for silicones represent even greater markets. Silicones that have been produced using organotins represent some fraction of this (although the exact amount is not known).

Typical uses for silicones that employ organotin catalysts include:

- one-component sealants for consumer (do-it-yourself) sealant application;
- two-component systems for industrial application; and
- condensation cross-linking of silicone-grafted polyolefins such as polyethylene cable insulation (ETICA, 2002).

More widely, there is a wide range of silicone products on the EU market, some of which will contain organotin compounds as catalysts. ETINSA has advised that, in general terms, manufacturers have worked to minimise the use of organotin catalysts in products which are likely to come into contact with consumers - although this is not entirely borne out by other catalysts uses (see, for example, Table 2.10).

An overview of silicone downstream applications in general and where tin-catalysed silicones may be used is presented in Table 2.9.

Table 2.9: Overview of Downstream Applications for Silicones

Sector	**Applications (All Silicones)**	**Applications (Tin-catalysed Silicones)**
Automotive	Gaskets, adhesives, lubricants, fuel additives, paints	Adhesives
Construction	Sealants, protective coatings	Sealants
Personal care	Shampoos, conditioners, deodorants, creams and gels	None
Sports	Water repellents for sportswear, goggles & masks, gels in running shoes	None
Textiles	Finishes (for durability, abrasion resistance, waterproofing)	None
Other	Paints, pulp & paper, computers, space travel, visual arts, model-making, shipping, railways, medical devices, waste water treatment plants, domestic appliances, machine tools, high voltage insulators	Adhesives in computers and model-making, non-stick coatings for ships, polyethylene cable insulation and pipes. One identified use in which there is direct consumer contact is the use of silicone dental mouldings.
Source:	*CES (2002)*	*ETICA (2003)*

In relation to consumer uses of possible concern for this study, data from the Women's Environmental Network indicate that butyltin stabilisers have been detected in the non-woven polypropylene top sheet of babies' nappies (diapers). It is possible that this could relate to the last of the three key uses described above, in that the top sheet could be of silicone-grafted polypropylene (or, as discussed below, the butyltin may be present due its use as a catalysts in the production of an antioxidant in polyolefin films).

Additionally, organotin-catalysed silicones have been used in products such as coatings on baking paper (for use in food preparation). Information provided for the 2002 Report by the European Silicones Association (CES, 2002a) indicated that organotin-catalysed silicones are only used in a small proportion of baking paper produced in the EU. For the 2003 Report, the European Silicones Association advised that the supply of tin-catalysed silicone coated baking paper ceased at the end of 2002 (CES, 2003).

As noted in the 2003 Report, it is evident that a significant quantity of greaseproof paper (and hence baking paper) is imported from outside the EU. Hence, it is possible that baking paper on the EU market may include silicone-coated paper produced using octyltin or butyltin catalysts. This would appear to be borne out in a 2003 survey of 35 baking papers in Germany which found just one containing DOT but no fewer than 19 containing MBT and/or DBT (DG SANCO, 2005). This issue is considered in more detail in the consumer exposure assessment (Section 5).

Another specialist consumer use, not identified in the earlier 2002 and 2003 Reports, is the making of silicone moulds using a two-part system (such as 'red silicone rubber' and DBT catalyst). Such moulds may be used to produce, for example, chess pieces and casts of fossils[21]. DIY kits for domestic consumers or, indeed, SMEs, are readily available in the EU which, unlike the other consumer uses being considered, expose consumers to pure solutions of DBTs.

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[21] A detailed practical account of making moulds for fossils is to be found in Kuban (2004).

Esterification and Powder Coating

Organotin compounds such as monobutyltin oxide[22], dibutyltin oxide, monooctyltin oxide and dioctyltin oxide are used in certain esterification and transesterification reactions, at a concentration between 0.001% and 0.5% by weight. They are used in the production of substances such as:

- phthalates;
- polyesters;
- alkyd resins;
- fatty acid esters;
- adipates; and
- in transesterifications.

These substances are, in turn, used as plasticisers, synthetic lubricants and coatings. Organotins are used as catalysts to reduce the formation of unwanted by-products and also provide the required colour properties (ETICA, 2002).

Downstream Markets for Use in Esterification and Powder Coating

Organotins are used at a concentration of around 0.3% in the production of polyester resins that are used for powder coating (which accounts for over 50% of the organotins used in this area). This process also involves an esterification reaction, typically using mono or dibutyltin oxide (MBTO or DBTO) as the catalyst. The final coatings consist of the polyester resin, with a curing agent and other additives. They are applied as a dry powder via an electrostatic spray gun and then heating of the coating layer to cause formation of the cured coating. Typical applications include:

- household appliances (washing machines, refrigerators, etc.);
- office furniture;
- architectural uses (e.g. aluminium window frames);
- automotive components (e.g. trim parts, body primers, wheels);
- lawn and garden equipment; and
- heating and air conditioning systems (ETICA, 2002).

These and other applications are listed in Table 2.10 (overleaf). As a first estimate of the downstream value, chemicals produced via the esterification reactions are worth €1,000 per tonne. Data have been provided which indicate that the combined usage of organotins in esterification and in powder coating is 250 to 350 t/yr. Based upon the range of concentrations for these products[23], the quantities of chemicals or powder coating produced could be between 50,000 tonnes and 35 million tonnes per annum, with an associated value of between €50 million and €3.5 billion. Assuming a concentration of 0.1% by weight would give perhaps more realistic results: 300,000 tonnes of chemicals/powder coating, worth €300 million per year.

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[22] The main substance used, accounting for 70% of consumption.

[23] 0.001% to 0.5% by weight.

Table 2.10: Overview of Downstream Applications for Esterification and Powder Coating

Type	Applications
Polyester resins for powder coatings	Coating of metal items (examples listed above)
Other polyester resins	Coil coating inks and toner
Alkyd resins	Paints
Acrylic coatings	Clothing
Plasticisers for PVC	Flexible PVC items (including items which come into direct human contact such as gloves)
Adhesives	Adhesives
Antioxidants for polyolefins	Polyolefin films, could be used in applications such as nappies, hygiene products
Lubricants	Lubricants for industrial processes

Source: ETICA (2003).

It is also possible to provide some indicative estimates of the overall markets for the products of the esterification reactions and powder coating. For example, phthalates and adipates (see above) are primarily used as plasticisers. Data indicate that the overall market for plasticisers is around 1 million tonnes per year, of which 90% is used in PVC. This market could be expected to have a value of around €1 billion per annum, of which chemicals produced using organotin catalysts will form some fraction.

Table 2.11 details the *overall* market for powder coatings, as compared to total paints. These data do not reflect the market associated with organotin compounds.

Table 2.11: European Market for Powder Coatings and Total Paints Market in 1999

	Percent of quantity	Amount (Mt)	Percent of value	Value, €bn	€/tonne
Powder coatings	4 %	0.2	6 %	1.0	4,300
Total European paints market	100 %	5.6	100 %	16.0	2,900

Source: CEPE (2001). Data have been rounded.

Polyurethanes

Organotin catalysts are used in a wide variety of urethane applications, aiding formation of the urethane bond in applications such as:

- urethane modified resins (e.g. alkyd, acrylic and acrylate) for printing inks, adhesives and surface coatings;
- two component polyurethane elastomers for a variety of applications; and
- industrial and automotive two-component coatings (ETICA, 2002).

Although it was originally reported in the 2002 Report that organotin catalysts were not used in flexible cushioning and rigid insulation foams (the main applications of polyurethanes), industry subsequently advised (ETICA, 2003) that this was not correct and this was reflected in the 2003 Report.

The catalyst is reported to be highly compatible with the final polyurethane product and may become chemically bound into the polymer backbone where used in polyester-based urethanes[24].

Downstream Markets for Use in Polyurethanes

Table 2.12 details some of the key types of polyurethanes produced using organotin catalysts, the concentrations of the catalysts used and the types of final applications for the products in question.

Table 2.12: Applications for Polyurethane Catalysed with Organotins

Type	Conc.	Applications
Foams	<0.1%	Upholstered furniture, mattress fillings, car seats, car dashboards, insulation panels.
Urethane modified resin	0.01% - 0.05%	Printing, surface coating, adhesives.
2-component elastomers	0.05% - 0.2%	Engineering components (gaskets, bearings, oil seals, rollers, etc.); Conveyor belts, heavy duty coatings, sealants, vibration/sound insulation; Tyre infill elastomers, stacker-truck and skateboard wheels; Electronic component potting compound; Printing rollers and squeegees; Shoes and shoe soles (outer surface) and Mould making.
Industrial and automotive 2-component coatings	0.01% - 0.1%	Top coatings for: automobiles, boats, planes, wood varnishes, repair coatings, fabrics, heavy duty flooring in industry and sport grounds.

Source: ETICA (2002) and ETICA (2003).

The European Isocyanate Producers Association (ISOPA, 2004) has published data on the quantities and associated market values and employment for polyurethane products used in Europe as summarised in Table 2.13.

Table 2.13: Key Data on the European Polyurethanes Industry

Sector	Volume (kt)	Market Value, €m	
		Direct	Downstream
Adhesives/sealants	267	710	2,240
Appliances	177	220	9,500
Automotive	560	1,400	40,000
Binders	181	300	42,000
Coatings	560	1,700	7,200
Construction	585	1,700	4,100
Elastomers	202	900	1,700
Footwear	250	700	5,300
Furniture/bedding	570	1,900	14,000
Total Polyurethane	**3,352**	**9,530**	**126,040**

Source: ISOPA (2004).

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[24] Polyurethanes are formed through reaction of an isocyanate with either a polyol or a polyester.

By comparing the applications listed in Table 2.13 with those in Table 2.12, some rough estimates can be made regarding the downstream markets for polyurethanes and products containing organotin catalysts as detailed in Table 2.14.

Table 2.14: Estimated Values for Polyurethane (PUR) Containing Organotins

Use	Mass of organotin (t)	Assumed conc.	PUR (kt)	Direct (€m)
Coatings	100	0.05%	200	607
Elastomers	150	0.20%	75	334
Automotive	150	0.10%	150	375
Total	**400**	**-**	**425**	**1,316**

Note: Maximum values for the concentration ranges provided by industry have been taken (thus total markets may be an underestimate).

It will be noted that no attempt has been made to include estimates based on the use of organotins in foam as this has been assumed to be a relatively minor use.

It is evident from the Tables 2.13 and 2.14 that the polyurethane products in which organotin catalysts are used represent a significant proportion of the total polyurethane market: around 13% of the market by tonnage and of the direct market by value. Usage in the individual sectors (coatings, elastomers and automotive) is unknown.

2.4.6 Use of Monobutyltin Chloride in Glass Coating

As discussed in the 2002 and 2003 Reports, approximately 700 tonnes per year of monobutyltin chloride (MBTC) are used in hot-end coating of glass bottles and a further 60 to 100 t/yr used in coating of flat glass. However, monobutyltin compounds are outside the scope of this study and are not considered further.

3. ENVIRONMENTAL EXPOSURE ASSESSMENT

3.1 Overview

3.1.1 Approach to Assessment

This Section considers exposure of the environment to organotin compounds, including the basis for determining the exposure of humans via the environment. There is a wide range of organotin compounds used in the EU, and the commercially used products are generally heterogeneous in that they contain a number of related substances. It is therefore necessary to conduct a number of separate exposure assessments, encompassing the use of the various products and their constituents in the various applications.

The methodology adopted is as follows:

- estimate overall emissions by industry sector (organotin production, stabilisers, catalysts and biocides);
- for each sector, estimate emissions by organotin compound and life-cycle stage (for example, emissions of dibutyltin during PVC processing);
- determine the Predicted Environmental Concentrations (PECs) at a regional level for each of the organotin compounds using the *EUSES2* model[25]; and
- determine local PECs using the TGD equations (with a cross-check being undertaken using *EUSES2*).

3.1.2 Quantities as Chlorides

In determining PECs (and, indeed, PNECs as discussed in Section 4), quantities (and concentrations) of organotins may be expressed as a function of:

- the amount of organotin compound under consideration;
- the amount of tin present; and
- the equivalent amount of the alkyl chloride.

In the environmental assessment (in this and the earlier 2002 and 2003 Reports), quantities (and concentrations) are (generally) expressed in terms of the chloride. The prime reason for this was that, initially at least, there were concerns about the potential impacts upon the aquatic environment and Kemi (2000) indicated that:

> *Organic stabilisers estered, for example, with mercaptoesters or carboxylates are expected to hydrolyse in the aquatic environment, forming complexes of chlorides or hydroxides. The bond between the tin atom and the esters is ionic, with the*

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[25] The *EUSES* model is based on the Technical Guidance Document for risk assessment of new and existing substances and is available from the European Chemicals Bureau, Ispra, Italy. Version 1 of the model was used for the analysis presented in the 2002 and 2003 Reports. This has now been replaced by Version 2 (*EUSES2)* which was used for this study.

> *esters constituting the anionic companion. ...... This dissociation of organotin stabilisers in the aquatic compartment means that the risk assessment can focus on the alkyltin compounds (i.e. mono- and dibutyltins or mono- and dioctyltins) ...*

As indicated in the 2002 and 2003 Reports, such an approach is attractive for three further reasons:

- consideration as such allows for cross-comparison of the exposure due to various sources of some organotin compounds (e.g. tributyltin);
- there are more extensive data available on the physicochemical properties of the chlorides than for most of the other substances; and
- many of the ecotoxicological data relate to effects observed when exposed to the chlorides. Also, ecotoxicological hazards are generally believed to be independent of the anionic species, and are thus focused upon the alkyltin species.

Whilst it is generally accepted that organotins hydrolyse, the precise complexes formed depend on various factors such as pH and chloride concentrations (Foti *et al* (2000), ATSDR (2003), and Yoder (2003)). It is worth noting that typical environmental concentrations of chlorides are 20 g/L in seawater, 20 mg/L in freshwater and 2 µg/m^3 in the atmosphere. Nevertheless, for this Report, greater consideration is given to the probable presence of hydroxides[26] in the aquatic environment. Similarly, in respect of emissions from process plants, greater consideration is given to the nature of the organotins being emitted as this influences the *EUSES2* modelling results.

The overall EU consumption of organotins expressed as alkyltin chlorides (ATC) is summarised in Table 3.1 (and the associated calculations are presented in Annex 3).

Table 3.1: Estimated EU Consumption (t/yr) of Organotins (as chlorides)

Site	DBTC	TBTC	DOTC
PVC stabilisers	1,094	25	2,538
Catalysts	1,253	9	40
Biocides	-	87	-
Totals	**2,346**	**121**	**2,578**

Note: Full names for the substances are given in the glossary.

The total quantity of organotin chlorides from Table 3.1 (around 5,000 t/yr) is significantly lower than the value of 19,000 t/yr from Table 2.2. The main reason is that not all organotins are being considered in this Report. Furthermore, the actual organotin compounds used generally have a greater weight than the respective chloride. For example, a typical compound used in PVC stabilisation is dioctyltin (2-ethylhexyl mercaptoacetate) with a molecular weight of 752 while the corresponding chloride (DOTC) has a molecular weight of 416.

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[26] In the absence of specific data on the various hydroxides which may be formed, reliance has been placed upon the properties of the corresponding oxides.

3.2 Emissions from Organotin Production

3.2.1 Overall Emissions

For the purposes of this risk assessment, industry has provided data on losses of organotin compounds from all of the production sites listed in Table 2.1 (based on ORTEPA, 2002b). The data are summarised in Table 3.2. As most of the data are expressed in terms of the quantity of tin emitted, the corresponding quantity of organotin will be somewhat larger.

Table 3.2: Emissions of Organotins from Production Plants in the EU and EEA

Site	Products	Waste	Air	Water[1]
S	Mono/di butyl and octyl stabilisers and catalysts	0	Not detectable	20.66 kg/yr (as tin) (<10 ng/L TBT)
T	Mono/di stabilisers and catalysts	25% incinerated. Remainder to authorised disposal (90% converted to inorganic tin)	1.67 kg/yr (as tin)	1.38 kg/yr (as tin) (70-100 ng/L TBT)
U	Mono/di/tri for stabilisers, catalysts and biocides	25 kg/yr (as tin) to incinerator	None (passes to process water)	12.5 kg/yr (as tin) (oxidised, filtered and biol. treated)
V	Mono/di butyl and octyl stabilisers and catalysts	Landfill or incineration	Negligible	Max. 4.43 kg/yr (as tin) (<20 ng/L TBT)
W	Mono/di/tri for catalysts, stabilisers, biocides and glass coating	Incinerated (inorganic tin recovered)	All data below MAC values	5.9 kg/yr (as tin) (<2000 ng/L TBT)
X	Mono/di/tri/tetra compounds	Incinerated (to tin oxide)	4 kg/yr (as tin) of which 75% is DOTO in dust	18 kg/yr (as tin) to waste water (7.5 ng/L TBT)
Y	Mono/di/tetra compounds	10 t/yr (as tin) incinerated to tin oxide	9.72 kg/yr (as tin)	9 kg/yr (as tin) (14 ng/L TBT)
Z	Mono/di/tri/tetra compounds	Incinerated (inorganic tin recovered)	0.15 kg/yr (as tin)	0.1 kg/yr (as tin) (<0.1 ng/L TBT)
Totals (as tin)			**15.5 kg/yr**	**18 kg/yr (waste water)** **54 kg/yr (surface water)**

Source: ORTEPA (2002b). Note that these values are the same as in the 2003 Report (Table 3.2).

Note (1): Emissions to water are generally to watercourses after treatment. Site X discharges to waste water which is treated at a municipal treatment works. In addition, ETINSA has provided an indication of measured TBT levels in the process effluent stream which as can be seen are generally below 100 ng/L.

Of the four sites producing tri-substituted tins in 2002, only two produced these compounds in 2004. As such, Table 3.2 and subsequent calculations overstate the associated emissions.

3.2.2 Emissions by Organotin

Based upon the information presented in Table 3.2, estimated losses of each of the organotin chlorides[27] have been estimated assuming that the measured emissions (by organotin) were proportional to the quantities produced. The associated calculations are detailed in Annex 4. The overall emissions are summarised in Table 3.3 and the associated emission factors are presented in Table 3.4. The calculations are conservative as emissions of tin have all been assumed to comprise organotins (in other words, no emissions of inorganic tin have been assumed).

Table 3.3: Production Plant Emissions (kg/yr as ATC) from Eight Sites

Compartment	**DBTC**	**TBTC**	**DOTC**	**Comment**
Air	21.1	0.4	44.3	Estimates (conservatively) assume that detailed figures provided for four sites can be doubled to cover those sites with no quantitative estimates.
Surface Water	45.1	1.8	49.5	Figures based on detailed emissions from seven sites.
Waste Water	3.5	1.2	0.1	Figures based on Site X - but note that the vast majority of emissions involve mono-butyl tin which is outside the scope of this study.
All Compartments	**69.7**	**3.4**	**93.8**	

Note: These values are similar but slightly different from those presented in Tables 3.3-3.5 in the 2003 Report due to use of different simplifying assumptions and focus on fewer organotin compounds (as detailed in Annex 4).

Table 3.4: Average Production Plant Emission Factors

Compartment	**DBTC**	**TBTC**	**DOTC**
Air	9.0E-06	3.7E-06	1.7E-05
Surface Water	1.9E-05	1.5E-05	1.9E-05
Waste Water	1.5E-06	9.6E-06	2.4E-08

Note: The values are derived by dividing the figures from Table 3.3 by the associated production quantities in Table 3.1. For example, for air emissions of DBTC, emission factor = 21.1 kg/yr / 2346 t/yr = 9.0E-06 (i.e. 9.0 x 10^{-6}).

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[27] Thus, DBTC is dibutyltin chloride and where various chlorides are being considered, the collective term ATC (alkyltin chloride) is used.

3.3 Emissions from Use as a Stabiliser in PVC

3.3.1 Overall Emissions

Emissions from the use of organotins as stabilisers in PVC products are associated with product manufacture and subsequent use.

Product Manufacture

ESPA (2002) provided information on the use of organotin stabilisers in PVC processing within the EU-15 as follows:

- 130 major customer plants;
- a further 250 smaller users; and
- of the total, around 55 are involved in the processing of packaging and rigid construction materials.

Although the smaller plants are assumed to be spread fairly evenly across Europe, the large calendering plants are concentrated in Italy and Germany (as discussed in Section 2.4.4).

A range of different additives is added to PVC polymer in order to produce the final PVC product. In the case of rigid PVC and some flexible applications, the various constituents are combined in a closed dry blender, at room temperature, which mixes the components together. The mixing action heats the mixture to around 120°C, forming a ‘dry blend’. The dry blend is processed using a number of techniques but typically through calendering or extrusion[28].

Industry has confirmed that this process is entirely dry and that equipment is never washed out with water (ESPA, 2002). As such, zero emissions to water have been assumed. In the calendering process, the dry blend is passed through an extruder, where it is heated to around 200°C (in a closed process), the molten PVC being passed through the series of calender rolls to form a product of the desired thickness.

For certain applications, a ‘paste’ (plastisol[29]) containing PVC and the relevant additives is produced. Plastisol-type PVC is typically applied to a substrate such as paper or textiles, by coating using rollers or by a technique known as knife-coating. The coated product is then passed through an oven to allow the plastic to solidify (gelation). Again, this process is reported to be carried out in dry areas with no waste water discharges (ESPA, 2002).

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[28] Extrusion involves passing the mixture (‘dry blend’) through a hopper and then a screw forces the melt through a die which shapes the product. Calendering involves passing a PVC formulation through multiple heated rollers to produce either rigid or flexible films or sheets.

[29] Plastisols use emulsion-polymerised PVC (E-PVC), which consists of smaller polymer particles than the typically used suspension-polymerised PVC (S-PVC). A high quantity of plasticiser used makes the blend a paste, rather than a dry-blend.

In the 2002 and 2003 Reports, emission factors were taken from a 2001 Emission Scenario Document (BRE, 2001). OECD has recently published an updated version (OECD, 2004) although the values remain essentially unchanged from those used previously, as shown in Table 3.5. The loss factors used are those given for substances allocated to a 'high' volatility group, as defined by the ESD.

Table 3.5: ESD Emission Factors (% Loss) for PVC Product Manufacture

Process	Air	Waste	Applicable Product Groups	Process Description
Handling	0%	0.01%	All	Raw Material handling (liquid)
Compounding	0.025%	0.035%	All	Dry blending (particle size >40µ)
Calendering	0.125%	0.125%	Packaging, incl. food contact, credit cards; thin rigid film	Calendering
Foamed Articles	0.25%	0.25%	Rigid construction incl. foamed sheeting	Losses are double those for 'open processes'
Blow Moulding	0.125%	0.125%	Bottles	Values for 'blown film'
Extrusion	0.025%	0.025%	Pipes and mouldings; profile extrusions (e.g. windows)	Extrusion
Spread Coating	0.125%	0.125%	Flooring; wallcovering	Spread coating
Other	0.025%	0.025%	Steel coating; misc. (e.g. T-shirt printing)	Closed process

Sources: Section 19 'Heat Stabilisers', OECD (2004) and relevant product groups taken from Table2.6.

Although the ESD document on which Table 3.5 is based may be considered authoritative, further investigation suggests that the emission factors presented for heat stabilisers are based on few, if any, actual measurements. This creates a degree of uncertainty as to the reliability of the numbers quoted. However, as reported in the 2003 Report, some limited monitoring data (of emissions to air) have been provided as summarised in Table 3.6. For completeness, the corresponding 'high' and 'low' factors from the Emission Scenario Document have also been included for comparison.

Table 3.6: Predicted and Measured Loss Factors (%Loss to Air) for PVC Processing

Extrusion	DBT	TBT
ESD - high	0.025	0.025
Upper measurement	0.003	0.006
ESD - low	0.001	0.001
Calendering	**DOT**	
ESD - high	0.125	
Upper measurement	0.013	
ESD - low	0.005	

Source: Summary of relevant results based on measured exhaust gas concentrations from work undertaken by Limnologisches Institut Dr Nowak for ETINSA and reported in September 2003 (as previously reported in Table 3.7, 2003 Report).

These findings suggest that although the use of the low ESD values would underestimate the emissions, the use of the high ESD values would overestimate the emissions. Of course, such limited data are open to question (as noted by CSTEE - see Annex 2), and efforts have been made to provide further assurance on the reliability of these measured values. Specifically:

- the industry (ETINSA) contracted one of the authors of the initial work used in the BRE and OECD ESDs to critically review the measurements and related issues and to report the findings (Willoughby, 2005); and
- DG Enterprise and Industry and RPA met with industry representatives and inspected a major calendering plant in Italy.

These considerations led to the following views:

- PVC processing will be very similar from one plant to the next. In other words, the emissions will largely be a function of the type and scale of processing rather than being dependent on site-specific factors (age of equipment, nature of management, etc.);
- the measurements presented in Table 3.6 are indicative of the scale of the emissions from PVC processing; and
- as PVC plants are not generally provided with fume elimination equipment (although some plants will have local fume exhaust systems), there is no substantive basis on which to increase the emission factors for small plants (contrary to the information provided in the latest ESD).

However, the key issue, which has been discussed at length with industry, is the speciation of organotins used in stabilisers. The most common stabiliser used is the mercaptide DOT-EHMA (dioctyltin bis(2-ethylyhexylmercaptoacetate)). When added to the PVC process, the stabiliser undergoes a chemical reaction which may be represented as follows:

unstabilised PVC + DOT-EHMA → stabilised PVC + DOT Cl EHMA

In other words, one of the two 2-EHMA ligands is replaced with a chlorine atom to produce DOT-Cl-EHMA (dioctyltin monochloride (2-ethylyhexylmercaptoacetate)). As such, the DOT emissions from PVC processing plants are likely to comprise DOT-EHMA and DOT-Cl-EHMA (Willoughby, 2005). There could also be some DOTC present if both EHMA ligands were substituted by chlorine atoms.

Although the choice of compound to be modelled impacts upon the modelling results, it should be noted that, within the ESD definitions, all three compounds fall into the ‘high’ volatility category based on their vapour pressures. Nevertheless, in accordance with the TGD (Section 2.3.3.3, Pt II, CEC (2003)), preference should be given to the use of ‘real’ substance-specific data. With this in mind, the emission factors (where based on volatile losses) used in the subsequent analysis have been taken as 20% of the high ESD values (presented in Table 3.5) to reflect the measured values (presented in Table 3.6) as shown in Table 3.7.

Table 3.7: Emission Factors (% Loss) for PVC Product Manufacture Used in Analysis

Process	Air	Waste	Applicable Product Groups
Handling	0.000%	0.010%	All
Compounding	0.005%	0.007%	All
Calendering	0.025%	0.025%	Packaging, incl. food contact, credit cards; thin rigid film
Foamed Articles	0.050%	0.050%	Rigid construction incl. foamed sheeting
Blow Moulding	0.025%	0.025%	Bottles
Extrusion	0.005%	0.005%	Pipes and mouldings; profile extrusions (e.g. windows)
Spread Coating	0.025%	0.025%	Flooring; wallcovering
Other	0.005%	0.005%	Steel coating; misc. (e.g. T-shirt printing)

Sources: Table 3.6 with a correction factor of 20% applied to volatile losses.

Product Use

Service life figures were provided in the 2003 Report. Similar figures are to be found in the latest Emission Scenario Document (OECD, 2004) and in a comprehensive PVC life-cycle assessment (PE Europe *et al*, 2004). Sample values are provided in Table 3.8.

Table 3.8: Lifetimes for PVC Products

PVC	Application	Indoor/ Outdoor	Lifetime (years)		
			2003[1]	ESD[2]	PE[3]
Rigid	Packaging, incl. food contact, credit cards	Indoor	2	2	<2
	Rigid construction incl. foamed sheeting	Outdoor	20	>10	2-10
	Thin rigid film	Indoor	7	0 to 10	?
	Bottles	Indoor	2	2	<2
	Pipes and mouldings	Outdoor	20	>10	>20
	Profile extrusions (e.g. windows)	Outdoor	10	>10	>20
Flexible	Flooring	Indoor	20	20	10-20
	Wallcovering	Indoor	7	7	2-10
	Steel coating	Outdoor?	10	30	10-20
	Miscellaneous (e.g. T-shirt printing)	Indoor	5	10?	2-10

Sources:

1) Values taken from S3.4, 2003 Report (RPA, 2003).

2) Values taken from Tables 4.3 and 6.2, ESD (OECD, 2004)

3) Values taken from S4, PE Europe et al (2004).

On the basis of the information provided, the values used in the 2003 Report will be retained. Emissions may be derived from the expression: Release = F x Usage; and the associated emission factors (F) for rigid applications are summarised in Table 3.9.

Table 3.9: Service Lifetime and Associated Losses

Product Use	Life (yrs)	Use	Air	Waste Water	Surface Water	Soil
Packaging, incl. food contact, credit cards	2	Indoor	0.05%	0.05%		
Rigid construction incl. foamed sheeting	20	Outdoor	0.05%		1.6%	1.6%
Thin rigid film	7	Indoor	0.05%	0.05%		
Bottles	2	Indoor	0.05%	0.05%		
Pipes and mouldings	20	Outdoor	0.05%		1.6%	1.6%
Profile extrusions (e.g. windows)	10	Outdoor	0.05%		0.8%	0.8%

Source: Based OECD (2004) assuming that 'indoor' water releases enter waste water whilst those outside enter both surface water and soil. Note that outdoor factors have been based on the expression 0.16% x Service Life (as given in OECD, 2004).

For flexible PVC plastics, emission factors have been based on a report by Fabes (2000) which provides empirical data on migration of various organotins from flexible PVC flooring (conducted by several laboratories) from which the following equation was derived:

$$M = 0.2\, C_0\, \rho\, (Dt/\pi)^{1/2}$$

or, rearranged:

$$D = (\pi/t) \times (5M / C_0\, \rho)^2$$

where

M = migration (µg Sn/dm^2)
C_0 = initial stabiliser concentration (µg Sn/kg)
ρ = density of plastic (g/cm^3)
D = diffusion coefficient (cm^2/sec)
t = elapsed time (seconds)

Diffusion coefficients in the range 5×10^{-16} to 5×10^{-13} have been derived empirically for a range of organotins including mono-, di- and tri-butyl and mono-octyl tins. For a PVC floor covering, the losses due to migration are of the order of 1-2% over an assumed 20 year lifetime. For flooring, an additional in-use loss will be associated with abrasion. The draft ESR risk assessment for di-2(ethylhexyl) phthalate (KemI, 2001) suggests an average loss factor of 3.125% over a 20 year lifetime[30] and this value has been used[31].

Disposal

At the end of service, most PVC products will enter the solid waste stream. A portion will be incinerated which will effectively destroy any organotins present. However, the

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[30] This is based upon a loss of 6.25% over a 20 year lifetime, with only half of the area being subject to this loss rate.

[31] As presented below, the total loss is simply the sum of the migration and abrasion losses. Strictly speaking, it could be argued that abrasion will lead to 'new' surfaces being exposed which would be expected to have a higher migration rate (since the migration rate decays with time). However, such refinements have not been incorporated into this assessment.

majority will be disposed of to landfill. It is possible that there will be some residual leachate emissions of organotins and these are discussed in Section 3.8.

3.3.2 Emissions by Organotin

Quantities Used

Based upon the data in Section 2, it is possible to break down the uses for organotin stabilisers in PVC into the various groups of compounds of interest (dibutyl, dioctyl, etc.) according to their use in the various types of products indicated in Table 2.7. The resulting estimates are illustrated in Table 3.10 in which the data have been converted to the relative amounts of the chlorides, rather than the compounds actually used in practice (such as mercaptoacetates).

Table 3.10: Estimated Usage (t/yr as Chlorides) by Substance for PVC Products

	DBTC	TBTC	DOTC
Rigid Applications			
Packaging, incl. food contact, credit cards	779	18	2,098
Rigid construction incl. foamed sheeting	64	1.5	173
Thin rigid film	18	0.4	49
Bottles	18	0.4	49
Pipes and mouldings	18	0.4	49
Profile extrusions (e.g. windows)	18	0.4	49
Flexible applications			
Flooring	51	1.2	20
Wallcovering	51	1.2	20
Steel coating	51	1.2	20
Misc. (e.g. T-shirt printing)	25	0.6	10
All PVC Products	**1,094**	**25**	**2,538**

Emissions from PVC Product Manufacture

Combining data on use (Table 3.10) with emission factors (Table 3.7 and associated text) enables the emissions from the use of organotin stabilisers in PVC product manufacture to be determined, as shown in Table 3.11. Data from Table 3.11 were then used (in *EUSES2*) to estimate 'generic' emissions for PVC processing by calculating an average emission factor for losses from all processing types as compared to the total usage.

Table 3.11: Emissions (t/yr) from Stabilisers in PVC Product Manufacture

	DBTC	TBTC	DOTC
To Air	0.32	0.01	0.78
To Controlled Waste	0.45	0.01	1.08
Total Emissions	**0.77**	**0.02**	**1.86**
Emission Factor (Air)	**2.94E-04**	**2.94E-04**	**3.07E-04**

As already indicated, it is accepted that DOT-EHMA is added to and combines with PVC but the precise nature of the emissions and their subsequent behaviour remains uncertain. By way of example, no measurements have been provided by industry to demonstrate the ratio of DOT-Cl-EHMA to DOT-EHMA in production plant emissions. More generally, due to the generally low levels found in the environment, few studies indicate the precise compounds being detected (since results tend to be presented in relation to the presence of DOT, TBT, etc.). In the *EUSES2* modelling, calculations are based on assuming the presence of DOT as DOTC (dioctyltin dichloride). This may be taken to represent the view that, within the environment, the remaining ligand (of DOT-Cl-EHMA) is replaced by another chlorine atom. In other words:

DOT-Cl-EHMA + environmental chlorine → DOTC + EHMA

However, it is recognised that, for some pathways, use of more robust modelling is required and this is considered in subsequent sections.

Emissions during In-service Use

Combining the data on usage by organotin (Table 3.10) with the emission factors presented for the in-service use of rigid PVC products (Table 3.9) enables the emissions by organotin to be calculated as summarised in Table 3.12.

Table 3.12: Estimated Emissions (as Chlorides) by Substance for Rigid PVC Products

All data given in t/yr	**DBTC**	**TBTC**	**DOTC**
Packaging, incl. food contact, credit cards	0.779	0.018	2.098
Rigid construction incl. foamed sheeting	2.084	0.049	5.616
Thin rigid film	0.018	0.000	0.049
Bottles	0.018	0.000	0.049
Pipes and mouldings	0.596	0.014	1.605
Profile extrusions (e.g. windows)	0.302	0.007	0.815
Total losses (t/yr)	**3.798**	**0.088**	**10.233**
Losses by Compartment			
Loss to air	0.458	0.011	1.234
Loss to waste water	0.408	0.009	1.099
Loss to surface water	1.466	0.034	3.950
Loss to soil	1.466	0.034	3.950
Total losses (t/yr)	**3.798**	**0.088**	**10.233**

The losses presented in Table 3.12 are approximately four times higher than those presented in Table 3.12 of the 2003 Report. The prime reason for this is the use of much higher emission factors for the ‘outdoor’ uses as prescribed in the latest ESD.

For flexible products, the losses were derived using the Fabes expression given above, assuming 2 mm thickness for flooring and steel coating and 1 mm thickness for wallcoverings and miscellaneous items. A sample calculation (for flooring) is presented in Table 3.13 with the full set of results presented in Table 3.14.

Table 3.13: Estimated Emissions (as Chlorides) by Substance for PVC Flooring *(1)*			
Calculation Step	**DBTC**	**TBTC**	**DOTC**
Initial conc. in PVC (mg Sn/kg)	1380	30	1184
D (cm^2/s) *(2,3)*	2.60E-14	9.98E-15	5.67E-15
Thickness (m)	0.002	0.002	0.002
Mass of 1 m^2 (kg)	2.8	2.8	2.8
Mass of 1 dm^2 (kg)	0.028	0.028	0.028
mg Sn in 1 dm^2	38.6	0.8	33.2
Lifetime (yrs)	20	20	20
Lifetime (s)	6.3E+08	6.3E+08	6.3E+08
Migration (µg/dm^2)	882	12	354
%loss (migration)	2.28%	1.42%	1.07%
%loss (abrasion)	3.13%	3.13%	3.13%
% loss (total)	**5.41%**	**4.54%**	**4.19%**

Notes:
(1) All flexible PVC products have been assumed to have a density of 1.4 g/cm^3
(2) 6E-15 is the same as 6.0 x 10^{-15}
(3) The values for DBTC and TBTC (among others) were derived empirically by Fabes (2000). The value for DOTC has been derived from a theoretical equation developed by Fabes (2000).

Table 3.14: Estimated Emissions (as Chlorides) by Substance for Flexible PVC Products			
All data given in t/yr	**DBTC**	**TBTC**	**DOTC**
Flooring	2.746	0.054	0.830
Wallcovering	1.371	0.020	0.250
Steel coating	0.820	0.012	0.149
Misc. (e.g. T-shirt printing)	0.579	0.008	0.106
Total losses (t/yr)	**5.516**	**0.094**	**1.336**

For comparison, the estimated losses for flexible products were also derived using the same approach as used for rigid products. The results were a factor of two to three lower and hence the values derived from the Fabes expression were carried forward in the analysis. The overall losses and associated emission factors are summarised in Table 3.15.

Table 3.15: Estimated Emissions (as Chlorides) by Substance for PVC Products			
All data given in t/yr	**DBTC**	**TBTC**	**DOTC**
Rigid Products	3.798	0.088	10.233
Flexible Products	5.516	0.094	1.336
All Products	**9.314**	**0.182**	**11.569**
Substance Use (t/yr)	1094	25	2538
Emission factor (air)	2.94E-03	2.26E-03	7.49E-04
Emission factor (waste water)	2.89E-03	2.21E-03	6.96E-04
Emission factor (surface water)	1.34E-03	1.34E-03	1.56E-03
Emission factor (soil)	1.34E-03	1.34E-03	1.56E-03
Emission factor (all compartments)	**8.51E-03**	**7.15E-03**	**4.56E-03**

3.4 Emissions from Use as a Catalyst

3.4.1 Overall Emissions

Depending on the particular application, emissions from the use of organotins as catalysts may be associated with product manufacture, application of product, in-service use and disposal as shown in Table 3.16.

Table 3.16: Emissions by Life-cycle Stage for Catalysts

Application	**Product Manufacture**	**Application of Product**	**In-service Use**	**Disposal**
Electrodeposition Coatings	Yes	negligible	Yes	Yes
Silicones	Yes	Yes	Yes	Yes
Esterification and Powder Coating	Yes	Yes	Yes	Yes
Polyurethanes	Yes	n/a	Yes	Yes

Note: For further information on the various applications, see Section 2.4.

Within the *EUSES2* modelling, the 'product manufacture' and 'application of product' were modelled as 'formulation' and 'industrial use' stages respectively. There have been no substantive changes to this section from that presented in the 2003 Report.

Product Manufacture

The emission factors used are generally based on those suggested by the Technical Guidance Document (TGD). For those involving PVC and polyurethane production, the more recent factors suggested by BRE (2001) are used. The values used in the analysis are summarised in Table 3.17.

Table 3.17: Emission Factors (% Loss) for Product Manufacture involving Catalysts

Process	**Air**	**Surface Water**	**Waste Water**	**Soil**	**Waste**	**Source**
Electrodeposition Coatings	0%	0%	0%	0%	1%	TGD
Silicones	0%	0%	0%	0.05%	0%	TGD
Esterification and Powder Coating						
- Plasticisers for PVC	0.025%	0%	0.035%	0%	0%	BRE (2001)
- Paint formulation	0%	0%	1%	0%	2%	TGD
- Powder Coating	0%	0%	0%	0%	1%	TGD
Polyurethanes	0.03%	0%	0.04%	0%	0.21%	BRE (2001)

Application of Product

For electrodeposition coatings, although the TGD emission scenario document gives a 5% loss to soil (landfill), this is assumed to relate to spraying. Since the transfer efficiency for electrodeposition is assumed to be 100%, there will be no losses during application.

For silicones (sealants and adhesives), losses during application are assumed to relate to washing down of residues (in various situations, including houses for example) for waste water and remaining product in containers, etc. being disposed of as solid waste.

For PVC and polyurethanes, there is no 'application' stage as such (i.e. there are no 'industrial use' losses in *EUSES2*) as such. For the application of paints (such as alkyd gloss finishes), the emission factors are based on a draft Emission Scenario Documents for paints, lacquers and varnishes (Environment Agency, 2001). For powder coatings, a transfer efficiency of 99% has been assumed with the remainder entering the solid waste stream. The values used in the analysis are summarised in Table 3.18.

Table 3.18: Emission Factors (% Loss) for Application of Products Containing Catalysts

Process	**Air**	**Surface Water**	**Waste Water**	**Soil**	**Waste**
Electrodeposition Coatings	n/a	n/a	n/a	n/a	n/a
Silicones	0%	0%	3%	0%	3%
Esterification and Powder Coating					
- PVC processing	n/a	n/a	n/a	n/a	n/a
- Paint application	0%	0%	3%	0%	25%
- Powder Coating	0%	0%	0%	0%	1%
Polyurethanes	n/a	n/a	n/a	n/a	n/a

Product Use

For electrodeposition, losses of 1% due to abrasion are assumed over the 7.5 year vehicle lifetime[32] with a further 1% loss due to repairs (of which 98% is assumed to enter the waste stream).

For other products, the emissions are based on the same approach used for PVC stabilisers - i.e. determination of migration factors based on catalyst concentrations (up to 0.2%), lifetimes (assumed to be 5 years) and product thickness (assumed to be 2mm).

In relation to the diffusion coefficients, the Centre Europeén des Silicones (CES), the European trade association representing the silicones industry, commissioned a study to examine water extractability of butyltin catalysts from silicone sealants (Degussa, 2002). This involved extraction of organotins from 500 cm^2 of cured silicone rubber sheets in 1 litre of water at 40°C. The results suggest diffusion coefficients in the range 1.7×10^{-15} to 3×10^{-14} (cf the range 5×10^{-16} to 5×10^{-13} derived for stabilisers). The resulting values used in the analysis are summarised in Table 3.19.

Disposal

Most products containing organotin stabilisers will enter the solid waste stream and the majority will be disposed of to landfill. This aspect is discussed in Section 3.9.

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[32] Data from European Environment Agency (2001).

Table 3.19: Emission Factors for Use of Products Containing Catalysts					
Product Use	**Life (yrs)**	**ATC**	**% Loss over Lifetime to**		
			Air	**Wastewater**	**Soil**
Electrodeposition Coatings [1]	7.5	DBTC/ TBTC	0.01%	0.01%	1%
Silicones [2]	5	DBTC	0.41%	0.41%	-
		TBTC	0.61%	0.61%	-
Esterification and Powder Coating [2]	5	DBTC	0.41%	0.41%	-
		TBTC	1.22%	1.22%	-
		DOTC	0.61%	0.61%	-
Polyurethanes [2]	5	DBTC	0.41%	0.41%	-
		TBTC	0.61%	0.61%	-

Notes: [1] *Losses to soil relate to abrasion during use. Additional losses during removal at vehicle bodyshop assumed as 1% of all usage, of which 98% passes to landfill and 1% to each of air and waste water.*
[2] *Losses calculated using diffusion coefficient data and assumed to be split equally between air and waste water.*

3.4.2 Emissions by Organotin

Quantities Used

Based upon the data in Section 2.4 and associated information provided by industry, it was possible to break down the consumption of catalysts into the various groups of compounds (monobutyl, dioctyl, etc.) according to their use in the various types of products. The resulting estimates are presented in Table 3.20 in which the data have been converted to the relative amounts of the chlorides, rather than the compounds actually used in practice.

Table 3.20: Estimated Usage (as Chlorides) by Substance for Catalysts			
All data given in t/yr	**DBTC**	**TBTC**	**DOTC**
Electrodeposition Coatings	972	4.4	
Silicones	48	0.5	
Esterification and Powder Coating [1]	43	1.5	40
Polyurethanes	191	2.2	
All Products	**1,253**	**9**	**40**

Note: [1] *An equal split amongst PVC applications, paints and powder coating has been assumed for later calculations.*

Emissions from Product Manufacture

Combining data on use (Table 3.20) with emission factors (Table 3.17) enabled the emissions from the use of organotin catalysts in product manufacture to be determined as shown in Table 3.21.

Table 3.21: Emissions (t/yr) from Catalysts in Product Manufacture			
By application:	**DBTC**	**TBTC**	**DOTC**
Electrodeposition Coatings	9.716	0.044	0
Silicones	0.024	0.0003	0
Esterification and Powder Coating	0.575	0.021	0.546
Polyurethanes	0.534	0.006	0
All applications:	**10.849**	**0.071**	**0.546**
By compartment:			
To air	0.061	0.001	0.003
To waste water	0.223	0.006	0.139
To surface water	0	0	0
To soil	0.024	0.0003	0
To solid waste	10.541	0.064	0.403
All compartments:	**10.849**	**0.071**	**0.546**

Emissions from Application of Products

Combining data on use (Table 3.20) with emission factors (Table 3.18) enables the emissions from the application of compounds containing organotin catalysts to be determined as shown in Table 3.22. There are no emissions associated with electrodeposition and polyurethanes during application (no such life-cycle stage is considered for the latter), nor are there emissions to air, surface water and soil for any of the organotins, so these are not included in the table.

Table 3.22: Emissions (t/yr) from Catalysts in Application of Products			
By application:	**DBTC**	**TBTC**	**DOTC**
Silicones	2.863	0.033	0
Esterification and Powder Coating	4.109	0.148	3.898
All applications:	**6.972**	**0.181**	**3.898**
By compartment:			
To waste water	1.856	0.032	0.403
To solid waste	5.115	0.150	3.495
All compartments:	**6.972**	**0.181**	**3.898**

Emissions during In-service Use

Combining the data on usage by organotin (Table 3.20) with the emission factors presented for the in-service use of products containing organotin catalysts (Table 3.19) enables the emissions by organotin to be calculated as summarised in Table 3.23.

Table 3.23: Emissions (t/yr) from In-service Use of Products Containing Catalysts			
By application:	**DBTC**	**TBTC**	**DOTC**
Electrodeposition Coatings	19.431	0.088	0
Silicones	0.391	0.0067	0
Esterification and Powder Coating	0.348	0.038	0.372
Polyurethanes	1.562	0.018	0.000
All applications:	**21.732**	**0.150**	**0.372**
By compartment:			
To air	1.248	0.032	0.186
To waste water	1.248	0.032	0.186
To surface water	0	0	0
To soil	9.716	0.044	0
To solid waste	9.521	0.043	0
All compartments:	**21.732**	**0.150**	**0.372**

Summary of Emission Factors

The results from Tables 3.21, 3.22 and 3.23 were used to generate generic emission factors for the *EUSES2* modelling as shown in Table 3.24.

Table 3.24: Summary of Emission Factors Used in *EUSES2* Modelling				
Stage of Use	**Compartment**	**DBTC**	**TBTC**	**DOTC**
Losses During Production of Catalyst Containing Products (Formulation)	air	4.85E-05	9.07E-05	8.33E-05
	wastewater	1.78E-04	7.13E-04	3.45E-03
	surface water	0	0	0
	soil	1.90E-05	3.16E-05	0
Losses During Application of Catalyst Containing Products (Industrial Use)	air	0	0	0
	wastewater	1.48E-03	3.67E-03	1.00E-02
	surface water	0	0	0
	soil	0	0	0
Losses During Use of Catalyst Containing Products (Private Use)	air	9.96E-04	3.64E-03	4.61E-03
	wastewater	9.96E-04	3.64E-03	4.61E-03
	surface water	0	0	0
	soil	7.76E-03	5.06E-03	0
Total Use (t/yr)		**1,253**	**8.67**	**40.32**

3.5 Emissions from Use in Biocides

Only use as a wood preservative has been considered for the purposes of this analysis. This use represents the greatest potential source (from the products under study in this analysis) of tributyltin (TBT) in the environment. For this Report, as in the 2002 and 2003 Reports, a consumption of TBT for this use is about 87 t/yr (which accounts for about 70% of the TBT being considered in this analysis). Use of TBT-based biocides is understood to be restricted to the United Kingdom, France and Germany.

In relation to timber treatment, tributyltin-based wood preservatives (which are organic solvent-based) are typically applied to wood using a double vacuum process. A typical application rate reported in the literature is around 150 g/m^3 (Kazemi *et al*, 2001), a value confirmed by consultation for the current study, indicating a typical concentration in the solvent of 1% and an application rate of 14 to 15 litres per m^3. The (draft final) OECD ESD (OECD, 2003) suggests loss factors to:

- waste water of 3% for substances with a water solubility over 100 µg/L (BUA (2003) reports TBTO solubilities in the range 0.75 to 75 mg/L); and

- air of 0.1%, for substances with a vapour pressure less than 0.005 Pa at 20°C (the vapour pressure of TBTO is around 0.001 Pa (BUA, 2003)).

These values are used in the exposure assessment conducted in the remainder of this section. However, in certain countries, disposal to waste water will not be permitted, with relevant legislation or codes of practice specifying that such waste should be treated as hazardous/special waste (see for example BWPDA (1998)) and thus the values quoted may not apply[33]. By way of example, in the UK, national legislation requires that plants are built upon floors with no connection to the facility's sewer system.

Losses during in-service use have been calculated using an estimated leaching rate to soil of 15% over an assumed ten year lifetime (Lebow, 1996), giving a value of 1.5% to soil per year. Given that, at any one time, there are assumed to be products in service produced during the past ten years, the total annual loss from all products is estimated as 15% (or 13 tonnes) to soil. Additional losses of 0.25% to air and 0.25% to surface water per year are assumed to occur. Table 3.25 provides a summary of the estimated EU emissions of TBTC during timber treatment and from in-service use (the latter relating to ten years' products).

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[33] Indeed, the draft ESD cautions that "some of the emission pathways and environmental compartments considered here may not apply in certain countries" and that "the strictness and enforcement of the above regulations vary among countries" (paras 72 and 73, OECD, 2003).

Table 3.25: Total EU Emissions from TBT Biocides (87 t/yr as TBTC)

Life-cycle Stage	Parameter	Air	Surface Water	Waste Water	Soil	Waste
Timber treatment [1]	Emission factors	0.1%	0%	3%	0%	0%
Timber treatment	Emissions	0.087 t/yr	0	2.61 t/yr	0	0
In-service use [2]	Emission factors	2.5%	2.5%	0%	15%	0%
In-service use [2]	Emissions	2.175 t/yr	2.175 t/yr	0	13.05 t/yr	0

Sources & Notes: [1] *Emissions based on OECD (2003).*
[2] *Leaching from wooden-clad houses based on losses over 10 years (10 years' products in service at any one time).*

3.6 Environmental Fate and Behaviour

3.6.1 General

As discussed in Section 3.1.2, the alkyltin component of organotin compounds is relatively stable to environmental degradation processes such as hydrolysis, when compared to the association with the relative ligand (such as an iso-octyl mercaptoacetate group). Thus, in water, most of the derivatives are reported to dissociate to the constituent alkyltin (usually as the chloride or hydroxide) and the relevant anion.

There are various data on the environmental fate and behaviour available. A report commissioned by ORTEPA (Summer *et al*, 1996) summarised the key data on environmental fate available at that time and this was a key source for the data presented in the 2002 and 2003 Reports (for a wider range of organotins than those considered here). For this Report, additional data on triphenyltins has been largely drawn from CICAD 13 (WHO, 1999) which suggests that TPTC (and TPT acetate) rapidly hydrolyses to TPT hydroxide (TPTH) in aqueous media. On this basis, data for TPTH are used in the absence of specific data on TPTC. Further supporting data on TPTH is available from OSPAR (2002).

3.6.2 Properties of Organotins

Overview

The modelling of environmental behaviour relies on data on various properties. For organotins, some key data are uncertain and, as a result, it is not always possible to select a definitive value for a particular property. This particularly applies to the water solubility of some of the organotin compounds under consideration for this study. The substances are generally sparingly soluble in water but through hydrolysis of the reactive ligands or ligand exchange, tin compounds of greater solubility may be formed, possibly casting doubt upon some of the data included in the IUCLID datasets. At present, it is reported that there is no analytical technique capable of quantifying the entire organotin compound with its associated ligand in dilute solutions in water (Parametrix, 2004a), although experimental procedures are under development that may allow for determination of the entire organotin compounds in water (see, for example, Yoder, 2003).

Although the 'baseline' modelling has been based on the chlorides, *EUSES2* modelling has also been carried out on the oxides/hydroxides to test the robustness of the results based on chlorides. In addition, additional modelling has been carried out for DOT since the selection of the compound modelled impacts upon the results (particularly in relation to PVC processing).

Butyltins

Table 3.26 presents a summary of the key properties of the butyltins under study (where these have been drawn from the IUCLID data sheets provided by Parametrix and, for TBTO, from BUA (2003)).

Table 3.26: Physicochemical Properties of Butyltins[1,2]

Property	**DBTC**	**DBTO**	**TBTC**	**TBTO**
CAS No.	683-18-1	818-08-6	1461-22-9	56-35-9
EINECS No.	211-670-0	212-449-1	215-958-7	200-268-0
Molecular formula	$(C_4H_9)_2Cl_2Sn$	$(C_4H_9)_2OSn$	$(C_4H_9)_3ClSn$	$(C_4H_9)_6OSn_2$
Mol. weight (g/mol)	303.8	248.9	325.5	596.1
% Tin	39.1%	47.7%	36.5%	19.9%
Melting point (°C)	42	105	-19	-45
Boiling point[3] (°C)	*250*	*250*	*250*	*250*
Vapour pressure @25°C (Pa)	0.15	4.2E-06	1.00 [4]	1.0E-03
Water solubility (mg/L)	33	4.0	10 [5]	35
Source:	*Parametrix, 2004*	*Parametrix, 2004c*	*Parametrix, 2005*	*BUA, 2003*

Notes:

1) *In some cases, the data sources present a range of values and, generally, a geometric mean value (of the 'reliable data') has been taken except where indicated.*
2) *Some values have been (slightly) modified from those presented in the 2002 and 2003 Reports to reflect the more complete data presented in the revised IUCLID data sheets. Significant changes are highlighted below.*
3) *As most organotins decompose, boiling points of 250°C were assumed in the absence of a 'true' boiling point (at atmospheric pressure).*
4) *The measured value of 1Pa (albeit unreliable) was used in the 2002 and 2003 Reports. However the latest IUCLID data sheet suggests that preference should be given to a much higher value of 266Pa derived from the BPMPWIN model. However, this value is derived from a boiling point of 171°C, which was measured not at atmospheric pressure but under partial vacuum (1/3 bar). As such, the suggested vapour pressure of 266 Pa is not considered valid and has not been used in this assessment.*
5) *A value of 0.1 mg/l was used in the 2002 and 2003 Reports. However, the latest IUCLID data sheet suggests a much higher solubility of the order of 10 mg/l and this value has been used in this assessment.*

Octyltins & Phenyltins

Table 3.27 presents a summary of the key properties of the octyltins and phenyltins under study (where these have been drawn from the IUCLID data sheets and CICAD 13 respectively).

Table 3.27: Physicochemical Properties of Octyltins and Phenyltins[1,2]

Property	**DOTC**	**DOTO**	**TPTC**	**TPTH**
CAS No.	3542-36-7	870-08-6	639-58-7	76-89-9
EINECS No.	222-583-2	212-791-1	211-358-4	200-990-6
Molecular formula	$(C_8H_{17})_2Cl_2Sn$	$(C_8H_{17})_2OSn$	$(C_6H_5)_3ClSn$	$(C_6H_5)_3OHSn$
Mol. weight (g/mol)	416.0	361.1	385.5	367.0
% Tin	28.5%	32.9%	30.8%	32.3%
Melting point (°C)	47	230	106	123
Boiling point[3] (°C)	*250*	*250*	*250*	*250*
Vapour pressure @25°C (Pa)	2.63E-04	9.5E-02	2.10E-05	4.7E-03
Water solubility (mg/L)	1.6	0.23	40	1
Source:	*Parametrix, 2004a*	*Parametrix, 2004d*	*CICAD 13 (WHO, 1999)*	*CICAD 13 (WHO, 1999)*

Notes:

1) In some cases, the data sources present a range of values and, generally, a geometric mean value (of the 'reliable data') has been taken except where indicated.

2) Some values have been (slightly) modified from those presented in the 2002 and 2003 Reports to reflect the more complete data presented in the revised IUCLID data sheets.

3) As most organotins decompose, boiling points of 250°C were assumed in the absence of a 'true' boiling point (at atmospheric pressure).

3.6.3 Partition Coefficients

Estimation from Physical Properties and Kow

Based upon the water solubility and vapour pressure data, *EUSES2*[34] estimates the dimensionless Henry's Law constant and the air-water partitioning coefficient. The *EUSES2* model provides an estimate of the organic carbon-water partition coefficient (Koc) based on the octanol-water partition (Kow). The Koc value can then be used to derive solids-water partition coefficients in suspended matter, in sediment and in soil using values of 10%, 5% and 2% of Koc respectively[35].

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[34] The *EUSES1* files generated for the 2003 Report were transferred to *EUSES2* (and an additional file for TPTC was created). As would be expected, the refinement of the model together with changes to some of the input parameters have led to different answers from those derived previously. Significant differenecs are commented upon in the text.

[35] These values represent the typical organic carbon contents of suspended matter, sediment and soil of 10%, 5% and 2% respectively.

Butyltins

The partition coefficients for butyltins are summarised in Table 3.28. Apart from the newly presented values for DBTO and TBTO, the values for DBTC are the same as those used in the earlier reports but those for TBTC are very different due to the use of the significantly greater solubility figure.

Table 3.28: Partition Coefficients (based on data from Table 3.26 and *EUSES2*)

Parameter	**DBTC**	**DBTO**	**TBTC**	**TBTO**
Henry's Law constant (Pa.m^3.mol^{-1})	1.38	2.61E-04	32.5	17
Air-water partition coefficient (m^3.m^{-3})	5.83E-04	1.10E-07	1.37E-02	7.19E-03
Octanol-water partition coefficient (log Kow)	1.89	5.33	4.70	3.57
Kow	77.6	213,796	50,100	3,715
Organic C-water (Koc, l/kg)	42.8	26,200	8,080	982

Notes: The values for Henry's Law constant, air-water partition coefficient and organic carbon-water partition coefficient were all derived from EUSES2 based on inputting the data presented in Table 3.24 together with the values of log Kow derived from the quoted data sources.

As with water solubility data, there is considerable uncertainty associated with some of the log Kow values reported in the IUCLID data sheets, with impurities in the substances possibly contributing to increased water solubility, and hence a lower than expected partition coefficient.

Octyltins & Phenyltins

The partition coefficients for octyltins and phenyltins are summarised in Table 3.29. The values for DOTC have changed (but only slightly) from those used in the earlier reports.

Table 3.29: Partition Coefficients (based on data from Table 3.27 and *EUSES2*)

Parameter	**DOTC**	**DOTO**	**TPTC**	**TPTH**
Henry's Law constant (Pa.m^3.mol^{-1})	0.068	149	2.02E-04	1.72
Air-water partition coefficient (m^3.m^{-3})	2.89E-05	6.29E-02	8.54E-08	7.28E-4
Octanol-water partition coefficient (log Kow)	5.82	*8.0*	3.43	3.43
Kow	660,693	1.0E+08	2,692	2,692
Organic C-water (Koc, l/kg)	65,200	3.81E+06	756	756

Notes: The values for Henry's Law constant, air-water partition coefficient and organic carbon-water partition coefficient were all derived from EUSES2 based on inputting the data presented in Table 3.27 together with the values of log Kow derived from the quoted data sources. For DOTO, the reported log Kow value of 9.26 has been replaced by the advised EUSES2 maximum value of 8. A log Kow value of 3.43 is reported for TPTH (and TPT acetate) in CICAD 13 (and elsewhere) and this value is also used for TPTC.

Measured Koc Values

As indicated in the 2003 Report, some additional data were obtained which suggested that the 'default' Koc values derived from the log Kow values tend to be significantly lower than those measured in laboratory tests as shown in Table 3.30. Although it is acknowledged that this is another area of uncertainty within the risk assessment, reliance was placed upon the geometric mean of the (upper) measured values.

Table 3.30: Organic Carbon-Water Partition Coefficients (Koc l/kg) from Various Sources

Source	DBTC	DBTO	TBTC	TBTO	DOTC	DOTO	TPTC	TPTH
EUSES2 default	42.8	26,200	8,080	982	65,200	3.81E+6	756	756
Berg *et al*, 2001[1]	223,867		293,275					
Terytze *et al*, 2000[2]	61,664				292,556			
ETINSA[3]			96,088					
Margni *et al*, 2002[4]							2,236	
Hansen, 2004[5]							580 - 1,334	
Value used[6]	**117,493**		**167,870**		**292,556**		**1,727**	

Notes:

1) *Berg et al (2001) derived Koc values from measurements in sediments.*
2) *Terytze et al (2000) undertook various tests on soils and the values in the table are not presented in the report but have been provided to ETINSA by the authors.*
3) *As part of its work for ETINSA, Parametrix undertook a review of six studies which had produced Koc values for TBT in soils and sediments from which a mean value was derived.*
4) *Reported Koc value for both TPTH and TPT acetate.*
5) *Reported range of Koc values for TPTH.*
6) *Geometric mean of (upper) measured values.*

3.6.4 DOT Leaf-Air Partition Coefficient

In the 2003 Report, it was found that consumer exposures to organotins were dominated by exposure to DOTC via the environment. The prime reason for the high values for DOTC was found to be the value for the leaf-air partition coefficient which, in turn, is a function of the ratio of Kow to Henry's Law constant (see Equations 3) and 6), Appendix III, Part 1, Revised TGD (CEC, 2003)). DOTC had the highest ratio, by far, of the organotins considered in the 2002 and 2003 Reports.

For a log Kow value of 5.82 (from Table 3.25), *EUSES2* predicts a leaf-air partition coefficient value of 1.17E+08 for DOTC. However, arguments advanced by industry (Vandenbroele *et al*, 2004) suggest that the use of a lower value of 1.28E+05 based on a review of the recent work by Huang (Huang *et al* (2004) and Huang & Klemm (2004)) would be more appropriate.

As already discussed, one area of uncertainty is the precise organotin compound to be modelled. DOT emissions (from PVC processing) are (initially) likely to be dominated by DOT-EHMA and DOT-Cl-EHMA and the associated calculations for the derivation of the leaf-air partition coefficients are summarised below together with those DOTC.

Step 1: Derivation of Henry's Law Constant

As indicated in the revised TGD (Equation 21, Part II):

$$\text{Henry's Law Constant} = (\text{Vapour Press} \times \text{Mol Wt})/\text{Solubility}$$

The associated values are summarised in Table 3.31.

Table 3.31: Derivation of Henry's Law Constant for Dioctyltin Compounds

Parameter	**DOT EHMA**	**DOT Cl EHMA**	**DOTC**
Vap Press (Pa)	2.10E+00	3.49E-02	2.63E-04
Mol Wt	751.80	583.93	416.04
Solubility (mg/L)	8.50	1.16E-06	1.60
Henry's Law Constant	**186**	**1.76E+07**	**0.068**
Source of input parameters	*Parametrix (2004b)*	*ETINSA (2005)*	*Table 3.27*

Step 2: Derivation of Air-Water Partition Coefficient

As indicated in the revised TGD (Equation 22, Part II):

$$K\ \text{air-water} = \text{Henry's Constant} / (R \times \text{Temp})$$

The results are summarised in Table 3.32.

Table 3.32: Derivation of Air-Water Partition Coefficients for Dioctyltin Compounds

Parameter	**DOT EHMA**	**DOT Cl EHMA**	**DOTC**
Henry's Law Constant	186	1.76E+07	0.068
R	8.31	8.31	8.31
Temp (^{O}K)	285	285	285
K air-water	**7.84E-02**	**7.41E+03**	**2.89E-05**

Step 3: Derivation of Plant-Water Partition Coefficient

As indicated in the revised TGD (Equation 3, Appendix III, Part I):

$$K\ \text{plant-water} = \text{Fwater} + \text{Flipid} \times \text{Kow}^{\wedge}b$$

Using the given default values: Fwater = 0.65; Flipid = 0.01; and b = 0.95, the equation becomes:

$$K\ \text{plant-water} = 0.65 + 0.01 \times \text{Kow}^{0.95}$$

The results are summarised in Table 3.33. Within the *EUSES2* model, high log Kow values are entered with a maximum value of 8 and this value is used here.

Table 3.33: Derivation of Plant-Water Partition Coefficients for Dioctyltin Compounds

Parameter	DOT EHMA	DOT Cl EHMA	DOTC
log Kow	15.30	9.66	5.82
log Kow value used	8	8	5.82
Kow (used)	1.00E+08	1.00E+08	660,693
K plant-water	**398,108**	**398,108**	**3,381**
Source of log Kow	*Parametrix (2004b)*	*ETINSA (2005)*	*Table 3.29*

Step 4: Derivation of Leaf-Air Partition Coefficient

As indicated in the revised TGD (Equation 6, Appendix III, Part I):

$$K\ leaf\text{-}air = Fair + K\ plant\text{-}water/K\ air\text{-}water$$

Using the given default value of Fair = 0.3, the results are summarised in Table 3.34.

Table 3.34: Derivation of Leaf-Air Partition Coefficients for Dioctyltin Compounds

Parameter	DOT EHMA	DOT Cl EHMA	DOTC
K plant-water (Table 3.33)	398,108	398,108	3,381
K air-water (Table 3.32)	7.84E-02	7.41E+03	2.89E-05
K leaf-air	**5.08E+06**	**5.40E+01**	**1.17E+08**

As can be seen from Table 3.34, the modelled leaf-air partition coefficients span more than six orders of magnitude. The (relatively) low value for DOT Cl EHMA is driven by its extreme insolubility whereas the (relatively) high value for DOTC is driven by its very low vapour pressure and (relatively) low log Kow.

The question which remains unresolved is which value to use in the risk assessment. One means to address this is to determine the consistency of the predictions with other observations. The industry view is that as Huang has measured DOT in the gas phase, then a higher vapour pressure (than that used for DOTC) must be used. However, analysis of the Huang data suggests that the measurements are more consistent with the presence of DOTC than with DOT-Cl-EHMA or DOT-EHMA.

This argument is summarised in Table 3.35.

Table 3.35: Observed DOT Concentrations (Median Values) in Air and Rainfall

Location	Air (pg Sn/m^3)	Rainfall (ng Sn/l)	Rainfall (pg Sn/m^3)	Implied Air-water partition coefficient
Waldstein	8.91	0.04	4.0E+04	2.2E-04
Bayreuth	2.55	0.22	2.2E+05	1.1E-05
Source: Tables 2 and 3, Huang & Klemm (2004).				

The implied air-water partition coefficients are closest to that of 2.9E-05 for DOTC (as presented in Table 3.32). Although it might be argued that the rainfall concentrations do not represent the ‘true’ water content, it is worth noting that the threshold solubility for the ‘insoluble’ DOT-Cl-EHMA is 1.16E-06 mg/L which is 1.16 ng/L or 0.24 ng Sn/L. In other words, the measured rainfall concentrations are lower than the threshold solubility concentrations for the dioctyltin compounds of interest.

As will be seen in subsequent sections, this issue is important in respect of the ‘local’ exposure close to PVC processing plants and for this reason additional *EUSES2* modelling runs on DOT-EHMA and DOT-Cl-EHMA were undertaken and the results are reported in S5.2.3.

3.6.5 Degradation

Photodegradation

For the purposes of environmental modelling using the *EUSES2* programme, data are available regarding photodegradation of the substances as summarised in Table 3.36. No data on photodegradation of TPT substances have been identified to date.

Table 3.36: Photodegradation of Organotins

Parameter	**DBTC/DBTO**	**TBTC[1] (+TBTO)**	**DOTC/DOTO**	**TPT**
Photodegradation constant (cm3/molecule-sec @25°C)	2.84E-11	4.27E-11	3.97E-11	?
Half-life (days)	0.6	0.4	0.4	?

Source: Data drawn from (revised) IUCLID data sheets.
Note: 1) The value for TBTC is a recent prediction and is higher than that previously reported.

Biodegradation

The (revised) Technical Guidance Document uses the criteria for biodegradation in surface water shown in Table 3.37.

Table 3.37: Biodegradation Criteria for Surface Water

Biodegradation Criterion	**Half-life (days)**
Readily biodegradable	15
Readily, but failing 10 day window	50
Inherently biodegradable	150
Not biodegradable	infinite

Source: Table 7, Revised TGD (CEC, 2003)

There are biodegradation data available for DBTC and DOTC from the IUCLID data sheets as outlined in Table 3.38.

Table 3.38: Results of Biodegradation Tests

Substance	Test	Biodegradation Results	Biodegradation Category
DBTC	OECD 301B	5.5% after 28 days	Inherently biodegradable
DBTO	OECD 301F	0% after 31 days	Not biodegradable
DOTC	OECD 301F	0% after 39 days	Not biodegradable
DOTO	OECD 301F	2% after 31 days	Inherently biodegradable

Source: IUCLID Data Sheets (Parametrix 2004, 2004a, 2004c and 2004d)

It is generally accepted that biodegradation half-lives are longer in both sea water and soil/sediment than in freshwater (CEC, 2003; and OECD, 2003). Although valid data are not presented in the TBTC IUCLID data sheet (Parametrix, 2005), typical half-lives of days, weeks and months are given for TBT biodegradation in freshwater, sea water and soil/sediment respectively and, as such, TBT could be categorised as readily biodegradable in freshwaters (IUPAC, 2003; BUA, 2003; and Japanese Ministry of Environment, 2001). It is of note that BUA (2003) reports that TBT biodegradation is temperature dependent. As a consequence, TBT contamination would be expected to decrease much more rapidly in, say, the Mediterranean than in the Baltic.

Similarly for TPT, typical half-lives of days, weeks and months are given for biodegradation in warm waters, cold waters and soil/sediment respectively (WHO, 1999) and, as such, TPT could be categorised as readily biodegradable under certain circumstances.

More recent work (Stasinakis *et al*, 2005) illustrates some of the uncertainties associated with such results. Tests (in activated sludge batch reactors) on DBTC, TBTC and TPTC indicated half lives of 5, 10 and >18 days respectively. Although the TBT result is consistent with that reported above, those for DBT and TPT are not.

Before continuing, it is important to note that organotin compounds are characterised by the presence of a carbon to tin bond and have the following general formula: R_x Sn $L_{(4-x)}$ where R is an organic alkyl or aryl group and L is an organic (or sometimes inorganic) ligand. Whilst the carbon-tin bond is strong, the association with the anionic ligand is less so and has a tendency to undergo dissociation both in use and in the environment. As such, the measured biodegradation rates reported above are believed to be reflecting the disassociation of the ligand whereas it is the remaining carbon-tin bond(s) which is of interest from an ecotoxicity point of view. For this reason, in the analysis that follows, the biodegradation for all the compounds being considered has been set at ‘inherently biodegradable’ (i.e. 150 day half-life).

In addition, data are available from a study on the degradation of dimethyl, dibutyl and dioctyltin chlorides in soil (Terytze *et al*, 2000) - a copy of which has been provided by industry. It is of note that the results of the degradation testing indicate that the dialkyltin compounds are partially degraded to the corresponding mono compounds[36]. As with the

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[36] By way of example, DOT concentrations were observed to reduce from, say, 40 to 12 ng/L over a three month period while the MOT concentration stayed relatively constant at around 2 ng/L. It is therefore

Koc data outlined above, these degradation data are not included in the IUCLID datasets. The resultant worst-case half-life values (where these relate to the decay of the alkyl group rather than the anionic ligand), as determined from sampling in the lysimeters over a period of six months are detailed in Table 3.39.

Table 3.39: Measured Half-Lives of Dialkyltin Compounds in Soils

	DBT	**DOT**
Half-life (months)	4 ± 1	5 ± 1
Half-life (days)	122	152
Source: Terytze et al (2000)		

The categorisation as ‘inherently biodegradable’ together with the Koc values used (from Table 3.30) and other physical properties enabled estimates of biodegradation half-lives in water, soil and sediment to be made by *EUSES2*. Those for soil and sediment were then reduced to be more consistent with the results of Terytze *et al* (2000) as shown in Table 3.40.

Table 3.40: Biodegradation and Half-lives (t50) in Soils and Sediments

Parameter	**DBTC/O**	**TBTC/O**	**DOTC/O**	**TPTC/H**
Category of biodegradation	Inherently biodegradable			
EUSES2 predicts t50 (days) in:	150			
▪ Freshwater (at 12^0C)				
▪ Soil (at 12^0C)	30,000	30,000	30,000	300
▪ Sediment (at 12^0C)	30,000	30,000	300,000	300
Measured t50 in soil (days)	c120		c150	
t50 values (days) used for soil & sediment in *EUSES2* modelling	**120**	**150**	**150**	**150**

3.6.6 Bioaccumulation

Limited data on bioaccumulation with particular reference to bioconcentration factors in (freshwater) aquatic biota (usually fish) have been located. The results are summarised in Table 3.41.

Table 3.41: Bioconcentration Factors (BCF) used in *EUSES2*

Parameter	**DBTC**	**DBTO**	**TBTC**	**TBTO**	**DOTC**	**DOTO**	**TPTC**	**TPTH**
BCF predicted by E*USES2*	8.06	6,770	1,970	216	17,700	25,100	164	164
BCF found	135		3,388		605		8,200	
Source	*Parametrix (2004)*		*Parametrix (2005)*		*Parametrix (2004a)*		*OSPAR (2002)*	
BCF value used in analysis	**135**		**3,388**		**605**		**8,200**	

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likely that only a fraction of DOT decayed to MOT and/or the biodegradation rate for MOT is significantly greater than for DOT.

Based on the information presented in Table 3.41, it is clear that there is divergence between measured and predicted values. As before, preference is given to the measured values although that for DOT is much lower than the predicted BCF. Although reliance was placed on the measured value of 1 for DOTC in the 2002 and 2003 Reports, a (new) higher value of 605 is used in this Report which is based on an accepted QSAR. This value is consistent with the value of 490 derived by RPA using another QSAR recently developed from measurements of log Kow and log BCF values for 112 pesticides (Hansen, 2004):

$$\log BCF = 0.3324 \log Kow + 0.7545$$

For DOTC, log Kow = 5.82 which gives log BCF = 2.69 and BCF = 490.

3.7 Measured Levels in the Environment

3.7.1 Overview

An overview of various reported concentrations of organotin compounds measured in environmental samples is provided below. The discussion is divided into three parts, relating to the octyl, butyl and phenyl compounds respectively.

In relation to the octyltin compounds, the only source of these substances relates to their use as stabiliser compounds in PVC products (including other relevant life cycle stages such as production). Thus, it can safely be assumed that measured levels in the environment relate to this application.

In relation to butyltin compounds, these substances are only produced anthropogenically. As would be expected, the use of tributyltin compounds in anti-fouling coatings represents a significant source of these substances into the marine and freshwater environments. Hence, many of the measured concentrations reported will relate predominantly to this use, rather than to the other uses considered in this study.

Similarly, measurements of phenyltins tend to be related to their use in anti-fouling paints.

3.7.2 Octyltin Compounds

Atmospheric Compartment

A recent study by Huang & Klemm (2004) reports the presence of MOT and, to a lesser extent, DOT in the atmosphere (at two sites in Germany) as shown in Table 3.42.

Table 3.42: Atmospheric Concentrations of Octyltins (Huang & Klemm, 2004)

	Gas	Aerosol	Rain
Median (max) conc. of MOT	55 (101) pg Sn/m^3	not detected	2.5 (4.5) ng Sn/L
Median (max) conc. of DOT	5.8 (21) pg Sn/m^3		0.1 (1.2) ng Sn/L

Note: ‘Median’ value is average of median values from two sites.

Water Compartment

A number of extensive reviews have concluded that there are no data suggesting the presence of octyltin compounds in water in the environment or in sediment, despite numerous monitoring studies for organotin compounds (including GC (1993), Summer *et al* (1996) and KemI (2000)).

However, in a 2001 monitoring study of 11 rivers in the southwest of France (Bancon-Montigny *et al*, 2004), generally low levels (0-5 ng Sn/L) of DOT (and MOT and TOT) were detected in monthly river samples and DOT and MOT were detected in about half of the associated sediment samples (at concentrations of the order of 1 µg/kg).

Terrestrial Compartment

Further work by Huang *et al* (2004) in upland forested sites in Germany indicates MOT and DOT surface concentrations of up to 10 and 0.6 µg Sn/kg dw respectively which decrease with soil depth.

As discussed further in Section 3.9, a screening test for organotin compounds in European landfill leachates (Mersiowsky *et al*, 2001) indicated maximum levels of approximately 4 µg/L of MOT. As indicated above, the presence of octyltin species can be attributed to its use in PVC products.

Waste Water Treatment

A number of studies have detected octyltin compounds in sewage sludge resulting from waste water treatment. Summer *et al* (1996) report a maximum concentration of DOT in sewage sludge of 0.56 mg DOTC/kg.

A report by KemI (2000) details concentrations found in sewage sludge at Swedish, Danish and Canadian waste-water treatment plants (WWTP), as summarised in Table 3.43.

Table 3.43: Measured Concentrations of Octyltins at WWTP (in KemI, 2000)

Survey	**Measured Concentrations**
Sweden (1993)	Maximum 0.6 mg/kg dw (0.2 mg/kg as Sn)
Sweden (1996-98)	Up to 0.49 mg/kg MOT; 0.14 mg/kg DOT (0.25 and 0.05 mg/kg as Sn) in sludge; <10 to 80 ng/L MOT in effluent (40ng/L as Sn)
Denmark (1993-94)	Up to 1.3 mg Sn/kg dw
Canada (1997)	89 µg Sn/kg MOT; 82 µg Sn/kg DOT; 8 ng/L DOT in effluent (4 ng/L as Sn).

Data on DOT (and MOT) supplied by industry provide further information on the sampling of six Swedish waste water treatment plants in 1997 and 1998, as reported in Table 3.44.

Table 3.44: Sampling in Swedish WWTP Water and Sludge (all values converted to chlorides)

Location	Results from 1997				Results from 1998			
	Water (µg/L)		Sludge (µg/kg dw)		Water (µg/L)		Sludge (µg/kg dw)	
	MOTC	DOTC	MOTC	DOTC	MOTC	DOTC	MOTC	DOTC
Björklinge	<0.015	<0.012	394	181	<0.015	<0.012	540	<12
Kungsängen	<0.015	<0.012	423	157	<0.015	<0.012	292	76
Kungsängen	0.029	<0.012	496	<12	<0.015	<0.012	335	99
Gässlösa	0.12	<0.012	656	<12	<0.015	<0.012	350	89
Linköping	<0.015	<0.012	715	<12	<0.015	<0.012	350	<12
Storvreta	<0.015	<0.012	598	133	<0.015	<0.012	467	111

Source: Work undertaken by Limnologisches Institut Dr Nowak and reported in July 1998. Copies of original report in German together with English translation supplied to RPA by ETINSA.

Biosphere

Given the low levels of octyltins found in the environment, it is not surprising that no measurable levels have been found in fish (EFSA, 2004). Furthermore, in a sample of 91 volunteers across the Netherlands (Meijer *et al*, 2004), only 13 had levels of DOT above the MDL of <0.1 ng DOT/g blood (and 12 had levels of MOT above the minimum detection limit (MDL) of <0.1 ng MOT/g blood).

DOT (and MOT) have been detected in house dust. Santillo *et al* (2003) reports a maximum DOT level of 0.19 mg Sn/kg dust in a UK sample whilst Fromme *et al* (2005) report levels up to 0.12 mg Sn/kg in Berlin apartments. Al Bitar (2004) reports a higher value of 0.31 mg Sn/kg dust from the European Parliament. These results are considered further in Section 5.3.

3.7.3 Butyltin Compounds

Atmospheric Compartment

Huang & Klemm (2004) reports the presence of butyltins in the atmosphere (at two sites in Germany) as shown in Table 3.45.

Table 3.45: Atmospheric Concentrations of Butyltins (Huang & Klemm, 2004)

	Gas	Aerosol	Rain
Median (max) conc. of MBT	10 (23) pg Sn/m^3	66 (461) pg Sn/m^3	9.7 (23) ng Sn/L
Median (max) conc. of DBT	12 (48) pg Sn/m^3	2.8 (11) pg Sn/m^3	2.0 (6.6) ng Sn/L
Median (max) conc. of TBT	14 (83) pg Sn/m^3	0.3 (0.8) pg Sn/m^3	0.1 (1.0) ng Sn/L

Notes: 'Median' values are averages of medians from two sites.

Water Compartment

Summer *et al* (1996), in their review of the available data, refer to measured concentrations of mono and dibutyltin compounds which were thought to relate mainly to degradation of tributyltin from use on boats as an anti-fouling paint.

Hoch (2001) provides a review of concentrations of various organotin compounds found in the environment. A summary of the main results for butyltins is provided in Table 3.46. However further investigation shows that higher values (for sediments) are readily available and an example has been included in the Table (together with the results from Summer *et al* (1996)).

Table 3.46: Maximum Concentrations of Butyltins in Water and Sediment

Parameter	MBT	DBT	TBT	Source
Max. conc. in freshwater (ng Sn/L)	1,900	15,700	-	Summer *et al* (1996)
Max. conc. in coastal waters (ng Sn/L)	2,800	1,300	-	
Max. conc. in water (ng Sn/L)	76	810	3,620	Hoch (2001)
Max. conc. in sediment[1] (mg Sn/kg dw)	3.4	8.5	10.8	Hoch (2001)
Max. conc. in sediment (mg/kg)	6.8	9.6	-	Summer *et al* (1996)
Max. conc. in sediment (mg Sn/kg dw) from Belgian harbours/dry-docks	31	52	53	Ceulemans *et al* (1998)

Note: 1) Includes river, lake, marine and harbour sediments.

In a review of TBT monitoring data (BUA, 2003) from the late 1980s/early 1990s, typical median values of around 50 ng TBT/L were found in rivers, lakes, estuaries and coastal waters at various locations in Germany, UK, France, Italy, Netherlands and Switzerland with typical maximum values of over 1,000 ng TBT/L found in marinas.

More recent data from France for 2001 (Bancon-Montigny *et al*, 2004) shows levels of butyltins (dominated by MBT) to be generally in the range 0-10 ng Sn/L in rivers which have negligible boating. However, considerable monthly variations were observed leading to occasional higher values due, perhaps, to the periodic use of TBT biocides in agriculture and/or the local leather industry[37]. DBT and TBT were also detected in sediment samples at concentrations of, typically, 1-5 µg Sn/kg (together with higher concentrations of MBT).

There is a general consensus that TBT concentrations in surface waters significantly declined in many water bodies following the enactment of TBT legislation in various countries such as Japan (Japanese Ministry of Environment, 2001; Sekizwa *et al*, 2003), Switzerland (Fent & Hunn, 1995), the United States (Hall *et al*, 2000), and the United Kingdom (Waldock *et al*, 1999). Areas where concentrations have not declined as rapidly are generally limited to marinas and other areas where larger ships are permitted to dock.

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[37] Historically (at least), TBT biocides have been used in the leather industry as noted in S2.4.3.

Declining trends in sediment TBT concentrations were also identified after TBT legislation was enacted. However this trend was most pronounced at locations with very high initial TBT concentrations. Nevertheless, there are indications that in many German rivers, TBT sediment concentrations are now below 0.005 mg TBT/kg dry weight (BUA, 2003).

Similar findings for both seawater and sediment are reported for the coastal waters (including harbours and marinas) of Mediterranean countries (UNEP, 2002). Furthermore, UNEP (2002) reports that "*the large predominance of the organotin degradation products over the parent compounds in the Western Mediterranean suggests that there are almost no recent inputs of these compounds*" (referring to TBT and TPT). However, Díez *et al* (2003) report that butyltin sediment concentrations in Spanish ports and harbours increased substantially from 1988 to 1995. Although more recent data from 1999/2000 suggest a decline, levels of TBT were still greater than DBT and MBT with median values of 0.38, 0.13 and 0.13 mg/kg respectively.

Terrestrial Compartment

Work by Huang *et al* (2004) in upland forested sites in Germany indicates MBT, DBT and TBT surface concentrations of up to 30, 0.6 and 0.1 µg Sn/kg dw respectively which decrease with soil depth.

Waste Water Treatment

Concentrations of butyltin compounds in sewage sludge from waste water treatment plants (WWTPs) have also been measured. Values reported are up to 0.77 and 2.22 mg/kg dry weight (Summer *et al*, 1996). Fent (1996) presents results from a number of Swiss plants which demonstrate that butyl organotins are progressively removed during waste water treatment as shown in Table 3.47. Fent (1996) notes that the available data for Switzerland suggest that the concentrations remained constant over the mid-1980s to the mid-1990s.

Table 3.47: Concentrations of Butyltins (ng/L) in Waste Water Treatment (Fent, 1996)

Stage of Treatment	MBT	DBT	TBT
Raw Waste Water	181	456	175
Primary Effluent	69	92	59
Secondary Effluent	30	28	21
Tertiary Effluent	9	6	2
Sludge Concentration (mg/kg dw)	0.5	1.5	1.1

Sampling from 158 German sewage plants in 2001/02 suggests a decline in sludge concentrations from those reported above (as reported in BUA, 2003). The results are summarised in Table 3.48.

Table 3.48: Median Concentrations of Butyltins (mg/kg dw) in Sewage Sludge (BUA, 2003)

Catchment Class	MBT	DBT	TBT
1,2 and 3 (each population 0.3 million)	0.11	0.08	0.01
4 (population 6.5 million)	0.28	0.16	0.04
5 (population 11.7 million)	0.28	0.21	0.03

Biosphere

Numerous studies have reported levels of butyltins in the biosphere particularly in fish and other aquatic organisms.

BUA (2003) summarises a range of studies of TBT levels found in organisms in Europe's rivers, lakes, estuaries and coastal waters during the 1990s with values typically ranging from around 50 to 5,000 µg TBT/kg fw. The highest values were found in bivalves in marines in Switzerland with maximum values 9,000 µg TBT/kg fw.

Lower values are reported by Harino *et al* (2005) for the levels of butyltins found in various organisms taken from the Mersey Estuary (Liverpool) in 1997. In all cases, DBT concentrations were lower than TBT (and MBT). The mean values were 14.4, 4.0 and 10.8 µg/kg fw for MBT, DBT and TPT respectively suggesting that much of the organotin contamination has decayed.

In deep-sea fish from the Mediterranean in 1996, levels of butyltins were measured in various organs (Borghiand & Porte, 2002). Highest levels were found in the liver with total butyltin concentrations of up to 174 µg Sn/kg liver fw. Although there was great variation amongst species, DBT tended to be more prevalent than TBT (and MBT). Bortoli *et al* (2003) report rank concentrations in the order TBT, DBT and MBT among samples of six species from 12 locations in the Lagoon of Venice (in 1999/2000) although there is great variation amongst the results. The highest total butyltin levels were found in the mollusc, *M. galloprovincialis*, with mean/max levels of 2,000/8,000 µg/kg dw.

BgVV (2000) reports levels of up to 15 µg DBT/kg fresh weight in crab (from German samples taken in 2000) and up to 940 µg TBT/kg fw in Zebra mussel (from German samples taken in 1999).

EFSA (2004) reports that samples of fish and fishery products (intended for human consumption) from several EU countries contain higher levels of organotins in "seafood other than fish" than in fish. For DBT, mean values of 52 and 5.1 µg/kg fresh weight were reported for "other than fish" and fish respectively. For TBT, the corresponding mean values are 60 and 17 µg/kg fresh weight respectively. Since much of the underlying data come from Germany and date from 2000 (SCOOP, 2003), this suggests a decline in DBT/TBT concentrations from the earlier data (again with a German focus) reported in BUA (2003).

Willemsen *et al* (2004) report similar results as in EFSA (2004) for TBT levels in fish (and other seafood) from samples taken across 11 of the EU-25 Member States.

Significantly higher levels were found in some samples with median values of 86, 89, 144, 152, 154, 197 µg/kg fresh weight found in Greek sardines, Belgian shrimp, Italian mussels, Portugese cockles, Portugese clams and Italian clams respectively.

Generally low levels of butyltins have been found in humans. Studies in Japan (Takahashi *et al*, 1999) and Denmark (Nielsen and Strand, 2002) produced similar results for butyltins in human livers (although the Japanese concentrations were higher). In both studies, TBT was not detected but significant levels of DBT (up to 76 µg/kg in Japan) and, to a lesser extent, MBT (up to 22 µg/kg in Japan) were detected.

Kannan *et al* (1999) found butyltins (MBT/DBT/TBT) in most of the 32 blood samples from people in Michigan with levels of up to 100 µg/L. However, analysis of more recent eight samples from Germany (Lo *et al*, 2003) found only traces of TBT in human blood (and no MBT/DBT). Similarly, in a sample of 91 volunteers (Meijer *et al,* 2004) across the Netherlands:

- no-one had levels of DBT above the MDL of <0.1 µg DBT/kg blood;
- only 3 had levels of TBT above the MDL of <0.1 µg TBT/kg blood; and
- only 3 had levels of MBT above the MDL of <0.1 µg MBT/kg blood.

DBT and TBT (and MBT) have been detected in house dust. Santillo *et al* (2003) reports maximum DBT and TBT levels in UK samples of 0.66 and 0.31 mg Sn/kg dust respectively whilst Fromme *et al* (2005) report maximum levels of up to 2.85 and 0.03 mg Sn/kg dust for DBT and TBT respectively in Berlin apartments. Al Bitar (2004) reports higher levels from the homes and offices of MEPs in Brussels, with maximum values of 3.11 and 1.02 mg Sn/kg dust for DBT and TBT respectively. These results are considered further in Section 5.3.

3.7.4 Phenyltin Compounds

Water Compartment

Since TPT has been used in anti-fouling paints, it is not surprising that studies focused on TBT in ports and harbours sometimes find TPT (and associated degradation products MPT and DPT) although few data have been identified (see Table 3.49 overleaf). Interestingly, TPT (and degradation products) were found in non-boating rivers in France in 2001 due, perhaps, to uses of TPT pesticides[38] (Bancon-Montigny, 2004).

Unlike the data on butyltin sediment concentrations, data on phenyltins for Spanish ports and harbours (Díez *et al*, 2003) show a significant reduction in the presence of TPT/DPT from 1988 to 1995 (and an associated rise in MPT) with some further reductions from 1995 to 1999/2000 (in DPT and MPT). The median values for the 1999/2000 results are around 0.005 mg Sn/kg. Similarly low levels of phenyltins have been reported for the Lagoon of Venice for 1999/2000 (Bortoli *et al*, 2003) - although one of the 12 sampling locations gave a much higher value for TPT (0.28 mg Sn/kg dw).

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[38] As discussed in Section 2.4.3, the use of TPT pesticides is no longer permitted within the EU.

Table 3.49: Concentrations of Phenyltins in Water and Sediment

Parameter	MPT	DPT	TPT	Source
Max. conc. in Spanish marinas (ng/L)	not reported		68	UNEP (2002)
Max. conc in French non-boating rivers (ng Sn/L)	722	14	7	Bancon-Montigny (2004)
Max. conc in associated sediments (mg Sn/kg)	0.05	0.008	0.004	
Max. conc. in sediment (mg/kg dw) from Belgian harbours/dry-docks	6.5	1.5	5.5	Ceulemans *et al (1998)*
Max. conc in Spanish ports (mg Sn/kg) 1988	<0.005	2.6	4.1	Díez *et al* (2003)
Max. conc in Spanish ports (mg Sn/kg) 1995	3.1	0.2	0.08	
Max. conc in Spanish ports (mg Sn/kg) 1999/2000	0.08	0.06	0.09	
Max. conc in Venice (mg Sn/kg) 1999/2000	not reported		0.28	Bortoli *et al* (2003)

Waste Water Treatment

Fent (1996) reports that in 7 out of 26 sludge samples from Swiss WWTPs, TPT was found with an average concentration of 0.5 mg/kg dw (together with, in some cases, lower concentrations of MPT and DPT). As for the TBT results discussed above, the available data for Switzerland suggest that TPT concentrations remained constant over the mid-1980s to the mid-1990s.

Biosphere

Various studies have reported levels of phenyltins in the biosphere - primarily in the aquatic environment.

Phenyltins (MPT/DPT/TPT) were generally not detected by Harino *et al* (2005a) in mussels and clams taken from the Mersey Estuary (Liverpool) in 1997, although TPT was detected in the digestive gland at levels of up to 10 µg TPT/kg fresh weight.

In contrast, Borghiand & Porte (2002) found phenyltin (MPT/DPT/TPT) levels of up to 1,430 µg Sn/kg fresh weight in the liver of *M. moro* deep-sea fish from the Mediterranean (sampled in 1996). Although there was great variation (in concentrations) amongst species, TPT was by far the most prevalent compound detected. Similarly, Bortoli *et al* (2003) found great variations of phenyltin concentrations by species and location within the Lagoon of Venice (sampled in 1999/2000). The highest concentrations were found in a species of mollusc (*Tapes sp.*) with a mean value of around 1,000 µg/kg dw with a maximum value of over 8,000 µg/kg dw.

EFSA (2004) reports, for TPT in samples of European fish and fishery products, mean values of 21 and 16 µg/kg fresh weight for “other than fish” and fish respectively.

It should be noted that in a sample of 91 volunteers (Meijer *et al*, 2004) across the Netherlands, no traces of phenyltins were found. However, Lo *et al* (2003) found low TPT concentrations (0.17 - 0.67 µg/L) in eight samples from Germany.

Although TPT was not detected in the house dust of Berlin apartments (Fromme *et al*, 2005), traces of TPT were found in one of the ten pooled samples of house dust from the UK (Santillo *et al*, 2003). Similarly, traces of TPT were found in one of 11 pooled dust samples from Belgium and in one of 12 individual samples taken from the homes and offices of MEPs (Al Bitar, 2004).

3.8 Environmental Emissions from Landfills

The current Technical Guidance Document does not provide a basis for risk assessment relating to substances disposed of to landfill. However, some information exists regarding the potential for emissions of organotin compounds from landfills, including laboratory-scale experiments as well as measured concentrations of organotins in landfill leachate - although no new data have been identified from those presented in the 2003 Report.

A study carried out for the European Commission examined the behaviour of PVC products in landfills (Argus, 2000). In this study, landfill simulation investigations were carried out using lysimeters, with PVC products including rigid and flexible types as well as short and long lifetime products. The study concluded that aerobic thermophilic conditions are the most aggressive in relation to degradation of PVC in landfill. However, a change in the weight distribution of PVC was only observed for thin plasticised PVC within the landfill simulations.

In relation to PVC additives, the study concluded that heavy metal additives are more likely to be released under acidogenic conditions (as compared to plasticisers, for example, which are released mainly during the anaerobic and methanogenic phases of landfill development). With respect to landfill emissions, it was concluded that organotin compounds cannot be directly attributed to the presence of PVC in landfills.

Another study (Mersiowsky *et al*, 1999) also undertook laboratory scale landfill simulations of PVC products, with leachate and landfill gas, as well as PVC degradation analysed. It was found that some of the plasticised PVC products exhibited a partial loss of additives into the leachate. Furthermore, Mersiowsky *et al* (2000) also monitored a number of actual landfill sites for leaching of various additives, including organotin compounds. The maximum concentrations reported are as detailed in Table 3.50.

Table 3.50: Concentrations of Organotins in Landfill Leachates (Sweden, Germany and Italy)

Organotin Species	Cation (µg/L)	As Sn (µg/L)	As ATC (µg/L)
DBT	0.92	0.41	1.04
TBT	0.88	0.36	0.99
DOT	0.80	0.25	0.87

Source: Mersiowsky et al (2000).

However, the concentrations found in leachate do not necessarily represent the concentrations that would be found in the environment. Landfill leachate may be treated using on-site water treatment facilities, it may be disposed of direct to municipal sewer, or in some cases - for older facilities - it may leach directly out of the landfill into the environment.

Even in the latter case, there will be a significant dilution of the landfill leachate upon entering the environment. Resulting environmental concentrations are, therefore, likely to be significantly lower than those reported above.

3.9 Estimation of Predicted Environmental Concentrations

3.9.1 Regional PECs

The *EUSES2* model has been run for DBT, TBT and DOT (for both chlorides and oxides). Although TPT has been detected in the environment, this is associated with past uses (primarily in anti-fouling paints). There are no TPT emissions associated with the production and use of other organotins for use in stabilisers, catalysts and biocides.

This involved developing 'use patterns' for each compound, together with appropriate emission factors (based on the results presented earlier) and data on the properties of each of the compounds. The data upon which the analysis is based is the usage of each compound by application as previously shown in Table 3.1.

The 'use patterns' applied in the *EUSES2* modelling are summarised in Table 3.51 together with the fraction (of the total consumption) consumed at each stage.

Table 3.51: *EUSES2* Use Patterns (in Brackets[1]) and Associated Use Fractions

***EUSES2* Stage**	**DBTC**	**TBTC**	**DOTC**
Production (P)			
- Production of Organotins	1 (P1)	1 (P1)	1 (P1)
Formulation (F)			
- Production of Products with Catalysts	0.534 (F3)	0.071 (F3)	0.016 (F3)
Industrial Use (I)			
- Use of Stabilisers in PVC Processing	0.466 (I2)	0.210 (I2)	0.984 (I2)
- Application of Products with Catalysts	0.534 (I3)	0.071 (I3)	0.016 (I3)
- Wood Treatment with Biocide	0	0.719 (I4)	0
Private Use (U)			
- Use of PVC Products with Stabilisers	0.466 (U2)	0.210 (U2)	0.984 (U3)
- Use of Products with Catalysts	0.534 (U3)	0.071 (U3)	0.016 (U3)
- Use of Wood Treated with Biocide	0	0.719 (U4)	0
Recovery (not used)			
Total Consumption (t/yr as chlorides)	**2,346**	**121**	**2,578**
Total Consumption (t/yr as oxides)	***1,922***	***111***	***2,238***

Note: 1) Within EUSES2, uses are modelled by a number of use patterns (1, 2, 3, etc.) and life-cycle stage (production, formulation, etc.). The values given in brackets provide a guide to the relevant EUSES2 results. So, for example, the results associated with the 'application of products with catalysts' for DOTC are to be found in Use Pattern No. 3 under the 'industrial use' stage and those for the production of TBTC are to be found in Use Pattern No. 1 under the 'production' stage.

As previously indicated, for each *EUSES2* stage and compound, generic emissions factors were determined for the three 'product groups' as well as the organotin production using the data presented earlier. These were derived by simply dividing the calculated emissions (per compartment) by the quantity used (see, for example, Table 3.15).

Within *EUSES2*, further data associated with the relative contributions of releases at regional and local levels are required. These are summarised in Table 3.52.

Table 3.52: Further *EUSES2* Input Data

***EUSES2* Stage**	**%Tin[1]**	**Sites[2]**	**F(regional)[3]**	**F(local)[4]**	**E-Days[5]**
P1: Organotin Production	100%	8	0.2	1	300
I2: PVC Processing (Stabilisers)	1.5%	380	0.2	0.1	300
F3: Formulation of Paints, Sealants, etc. (Catalysts)	0.2%	1000	0.1	0.1	300
I3: Application of Silicones, Coatings, etc. (Catalysts)	0.2%	1000	0.1	1E-03	20
Wood Treatment (Biocide)	10%	100	0.2	0.1	300

Notes: 1) Upper limit of % organotin in formulation.
2) Estimated number of processing sites within EU (i.e. at continental level).
3) Proportion of consumption (sites) within a 'region' (10% of continental is EUSES2 default).
4) F(local) is the maximum proportion of regional emissions which could be associated with a single site.
5) E-days represent the emission days per year. For large process sites, 300 days per year is typical (and this value matches data provided by ORTEPA on organotin production sites).

The first results from *EUSES2* as shown in Table 3.53 provide the regional PEC values for the aquatic environment - since this is the compartment of greatest interest for the uses being modelled.

Table 3.53: Regional PECs (Aquatic) with those from the 2003 Report in Brackets

Surface Water	**DBTC**	**TBTC**	**DOTC**
Concentration in Surface Water (ng/L dissolved)	2.9 (2.1)	1.5 (0.5)	2.8 (0.6)
Re-run using oxides (ng/L)	*4.0*	*1.8*	*1.5*
Measured 'background' concentration (ng/L) in surface water (in absence of anti-fouling paints)	0 - 10	0 - 10	0 - 5
Measured 'background' concentration (ng/L) in surface water (with anti-fouling paints)	50	50	0 - 5
Sediment	**DBTC**	**TBTC**	**DOTC**
Concentration in Sediment (µg/kg dw)	54 (20)	43 (6.9)	140 (15)
Re-run using oxides (µg/kg dw)	*77*	*50*	*74*
Measured 'background' concentration (µg/kg) in sediment (in absence of anti-fouling paints)	1 - 5	1 - 5	1
Measured 'background' concentration (µg/kg) in sediment (with anti-fouling paints)	500	500	1

Note: For consistency, the results from the 'oxides' have been converted to the equivalent chloride concentrations so that all the results in the table are directly comparable.

The results show an increase in the regional concentrations from those presented in the 2003 Report. This is mainly due to:

- an increase in the overall emissions from those considered in the 2003 Report due, primarily, to the greatly increased predicted emissions from the 'outdoor' use of PVC products; and
- changes in some of properties (as indicated in Tables 3.26 and 3.27).

Although it is difficult to generate robust regional concentrations from the measured data presented earlier, indicative concentrations have also been included in Table 3.53.

The results form runs of the chlorides and oxides are broadly similar suggesting that the baseline use of the chlorides in the modelling is justified. Although the *EUSES2* predictions and environmental measurements for surface waters are consistent, the predicted concentrations for sediments appear to be on the high side (when compared to the results of environmental monitoring). There are various possibilities for this discrepancy including:

- emissions to surface water (and hence to sediment) have been overestimated;
- the predicted 'continental' (i.e. background) concentrations are about a factor of ten lower than the regional concentrations reported above - in other words, the environmental monitoring results (without anti-fouling paints) should be being compared with the continental rather than the regional predictions; and/or
- the sediment-water partition coefficients (which are derived from the corresponding Koc values) are too high.

3.9.2 Local PECs

Overview

Local PECs for the aquatic environment for each of the organotin groups were derived for six scenarios in the 2002/2003 Reports:

- close to a major organotin production facility;
- close to a major PVC processing facility using organotin stabilisers;
- close to a major formulator (of paints, sealants, etc.) using organotin catalysts;
- close to a site of significant application of sealants (or similar);
- close to a major wood treatment facility using TBT biocide; and
- close to a house clad with TBT treated wood.

The associated calculations, which incorporate some revisions, are summarised below.

Organotin Production Facilities

Local PEC values were derived for production sites V and W (as these gave the highest PEC values) using site-specific data as follows:

- estimate effluent concentration of specific ATCs based on total reported effluent concentration;
- apply a dilution factor (ratio of river flow to effluent flow) to effluent concentration to provide a first order estimate of the local PEC value; and
- apply correction factors for suspended solids (and associated partition coefficients) using Equation 45 (revised TGD).

The results are summarised in Tables 3.54 and 3.55.

Table 3.54: Site-Specific Data used in Derivation of Local PEC Values

Parameter	Plant V	Plant W
Effluent Concentration	10 mg Sn/L	11 µg ATC/L
Dilution Factor (in River)	63,191	10 (default)

Notes: 1) Site specific data obtained from ORTEPA (2002b)

Table 3.55: Local PEC Values in Surface Water (ng diss./L) for Organotin Production Sites

Location	Estimate	DBTC	TBTC	DOTC
Plant V	1st Order	117	1.8	180
	Corrected	99	1.5	125
Plant W	1st Order	267	15	410
	Corrected	227	12	285

As expected, the local PECs are significantly higher than the regional PECs (c2.0 ng/L). It should be noted that the 'corrections' for suspended matter make only a slight difference to the preliminary estimates.

PVC Processing Facilities

Two hypothetical PVC processing sites - a calendering plant and a spread coating plant - have been used to generate local PEC values. Whilst it is acknowledged that PVC processes are generally regarded as 'dry' processes with no liquid effluent, it has been assumed (as a worst-case) that 50% of emissions to air find their way into waste water (for example, due to rainwater flushing local deposition into surface water drains). Such a scenario may apply where a PVC processing plant is located on an industrial estate and the estate drains are connected to a local STP. The site-specific data are shown in Table 3.44. In the 2002/2003 Reports, the emissions from 'small' plants were increased by a factor 10. However, as discussed in Section 3.3.1, this factor is no longer considered valid and has been removed from the calculations for the 'small' spread coating plant in Table 3.56.

Table 3.56: Site-Specific Data used in Derivation of Local PEC Values

Parameter	Calendering Plant	Spread Coating Plant	Source
PVC Consumption (t/yr)	7,046	500	Based on a 'large' and 'small' plant respectively
Stabiliser used (t/yr as EHMA)	105.7	7.5	Industry data
Loss to Air (t/yr as EHMA)	0.032	0.002	Based on emission factors in Table 3.7
% Loss to Waste water	50%	50%	Assumption but consistent with ESD
Emission Days (per year)	300	300	Assumption
Distribution by Compound (as ATC)	MBTC : DBTC : TBTC 42.5% : 56.2% : 1.3%		Based on 0.2% TBT as Sn in stabilisers /catalysts and conversion to chlorides
Emission to STP	Yes	Yes	Assumption
Dilution Factor (in River)	10	10	TGD Default

Similar calculations were undertaken for the mono/di-octyltin compounds. All of the calculations and input data used are the same (in terms of quantities used at a site, losses to air and percentages lost to waste water). It was assumed that the octyltin stabiliser compounds contained 50% each of MOTC and DOTC. The resultant PEC values are presented in Table 3.57 together with a 'generic' local value generated by *EUSES2* for a PVC processing plant.

Table 3.57: Local Aquatic PEC Values (ng dissolved/L) for PVC Processing Sites (Stabilisers)

Location	Estimate	DBTC	TBTC	DOTC
'Large' Calendering Plant	TGD Equations	61	1.2	47
'Small' Spread Coating Plant		4.5	0.1	2.5
Generic Local (=Regional)	*EUSES2*	2.9	1.5	2.8

As can be seen, the site-specific TGD calculations lead to significantly higher results (for the calendering plant at least) than those derived using *EUSES2*. This is mainly due to the assumption that local air emissions will enter the waste water stream - which is not applied to the *EUSES2* calculations. As such, the 'local' concentrations are the same as the 'regional' concentrations.

Formulator (of Paints, Sealants, etc.) using Organotin Catalysts

Two hypothetical sites, a polyurethane plant using butyltin-based products and a paint formulator using either butyltin or octyltin-based products, are used to generate local PEC values. The site-specific data are shown in Table 3.58.

Table 3.58: Site-Specific Data used in Derivation of Local PEC Values

Parameter	Polyurethane Plant	Paint Formulator	
		Butyltins	Octyltins
Catalyst used (t/yr)	0.8 (as laurate) [1]	6.5 (as ATC) [2]	1.4 (as ATC)
% Loss to Waste water [3]	0.04%	1%	1%
Emission Days (per year)	300	300	300
Distribution by Compound (as ATC) [4]	DBTC : TBTC 98.9% : 1.1%	MBTC:DBTC:TBTC 88.7%:10.9%:0.4%	MOTC:DOTC 53%:47%
Emission to STP [5]	Yes	Yes	Yes
Dilution Factor (in River) [5]	10	10	10

Notes: [1] *Based on use of 804 t/yr at one site (BRE, 2001) and catalyst concentration of 0.1%.*
[2] *Based on 5% of total catalyst use in paints at a single large paint formulator.*
[3] *Based on Table 3.17.*
[4] *Based on relative amounts of alkyltin compounds contained in products.*
[5] *TGD defaults.*

The resultant PEC values are presented in Table 3.59 together with 'generic' local values generated by *EUSES2* (for both the chlorides and the oxides) for a site using an organotin catalyst in product manufacture.

Table 3.59: Local Aquatic PEC Values (ng dissolved/L) for Sites using Catalysts

Location	Estimate	DBTC	TBTC	DOTC
Polyurethane Plant	TGD Equations	2.6	0.02	n/a
Paint Formulator		120	3.5	76
Generic Local [1]	*EUSES2*	34 *(42)*	2.2 *(2.6)*	16 *(15)*

Note: [1] *The main values are those derived from the chloride modelling whilst those in the brackets are based on the oxides. As can be seen the two sets of results are very similar.*

As expected, the local PECs are significantly higher than the regional PECs. Although there is considerable variation in local PECs from process to process, the results are not inconsistent with the generic local values generated by *EUSES2*.

Application of Sealants (or Similar)

For the application of a sealant (or similar product) containing catalysts, an indication of the local PEC value has been determined using *EUSES2* as presented in Table 3.60.

Table 3.60: Local Aquatic PEC Values (ng dissolved/L) for the Application of Catalysts (with results from 2003 Report in brackets)

Location	Estimate	DBTC	TBTC	DOTC
Generic Local	*EUSES2*	5.4 (4.7)	1.5 (0.5)	3.2 (1.0)

As with the previous case, the results from the oxide modelling gave very similar results to those for the chlorides.

Major Wood Treatment Facility

The *EUSES2* model was used to generate a local aquatic PEC value for TBTC[39] of 594 ng/L (cf the regional PEC value of 1.5 ng/L). This value is significantly greater than that of 148 ng/L presented in the 2003 Report due (in part) to the higher solubility value used in this Report.

House Clad with TBT Treated Wood

One application for TBT-treated wood is the cladding of buildings and this is used as one of the generic scenarios considered in the Emission Scenario Document (OECD, 2003).

Local PEC values associated with releases from such a building has been evaluated in the following two stages:

1. Determine annual flux of TBT to local soil; and
2. Determine local PEC taking account of soil removal, TBT decay, etc.

The associated calculations are summarised in Tables 3.61 and 3.62.

Table 3.61: Losses of TBT from Treated Wood & Resultant Soil Concentration

Parameter	**Value**	**Note**
Dimensions of Cladded Building (l x w x h)	= 10m x 5m x 2.5m	1
Wood Thickness	= 25 mm	
Treatment Rate	= 0.15 kgTBTO/m^3	
TBTO Present (initially)	= 2 x (10+5) x 2.5 x 0.025 x 0.15 = 0.281kg	
Leaching Rate (based on Lebow, 1996)	= 15% over 10 years = 0.042 kg	2
Soil Area (0.3m wide strip around building)	= 2 x (10+5) x 0.3 = 9m^2	3
Average TBTO Flux to Soil	= 0.42 x 10^6/(9x10x365) = 1.28 mg/m^2/day = 1.40 mg/m^2/day (as TBTC)	

Notes:

1) The OECD ESD (2003) suggests dimensions of 17.5 x 7.5 x 2.5 but the resultant soil concentration is dictated only by the height of the wood, which is the same both above and in the draft ESD.
2) Equivalent to 1.5% per year.
3) The ESD (OECD, 2003) assumes a 0.1m wide strip around the house. This is deemed to be overly conservative.

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[39] As with the other examples, the use of the oxides gave a very similar result of 608 ng/L (expressed as the chloride for ease of comparison).

Table 3.62: Predicting Local Soil TBT Concentrations using TGD Equations		
Parameter	**Value**	**Source**
Aerial Deposition Flux	3.78E-03 mg/kg/d	Equation 44, TGD (using average flux derived above)
Rate Constant for Volatilisation	1.31E-05 /d	*EUSES2* (for grassland soil)
Rate Constant for Leaching	9.52E-07 /d	
Rate Constant for Biodegradation	4.62E-03 /d	
Rate Constant for Removal from Top Soil	4.63E-03 /d	Sum of above
Equilibrium Concentration	0.89 mg TBTC/kg	Equation 55, TGD

The equilibrium PEC value (0.89 mg/kg) for this scenario is reached within three years (and is very slightly higher than that presented in the 2003 Report).

Summary

A summary of PEC values derived above is presented in Table 3.63. Given the similarity between the results from modelling the chlorides and the oxides, only the chloride results have been presented in this table.

By comparison with the data presented in Section 3.7, it can be seen that the local PECs are generally below, or in the order of, the maximum values measured in the aquatic environment. In other words, the higher levels observed in the environment will be associated with the effects of other uses, notably anti-fouling paints.

Table 3.63: Local PEC Values (ng dissolved/L in surface water)			
Activity	**DBTC**	**TBTC**	**DOTC**
Organotin Production			
- Plant V (using TGD)	99	1.5	125
- Plant W (using TGD)	**227**	12	**285**
- Generic Plant (*EUSES2*)	13	4.1	3.0
PVC Processing Sites (using Stabilisers)			
- Large Calendering Plant (using TGD)	61	1.2	47
- Small Spread Coating Plant (using TGD)	4.5	0.1	2.5
- Generic Plant (*EUSES2*)	2.9	1.5	2.8
Product Manufacture (Catalysts)			
- Polyurethane Plant (using TGD)	2.6	0.02	n/a
- Paint Formulator (using TGD)	120	3.5	76
- Generic ‘Formulation’ (*EUSES2*)	34	2.2	16
Product Application (Sealant with Catalysts)			
- Generic Application (*EUSES2*)	5.4	1.5	3.2
Wood Treatment Plant (Biocide)			
- Wood Treatment Plant (*EUSES2*)	-	**594**	-
Maximum Local PEC (from above)	**227**	**594**	**285**

4. ENVIRONMENTAL EFFECTS ASSESSMENT

4.1 Introduction

The effects on the marine environment resulting from the use of TBT (and TPT) as an anti-fouling biocide on sea-going vessels has been extensively studied over the past twenty years. Particular attention has been given to the effects on molluscs, such as dog whelks (with effects including imposex - the expression of male characteristics by female organisms) and oysters (with effects including shell deformities). Such studies led to Commission Directive 1991/51/EC which restricted the use of organotin compounds as a biocide in the aquatic environment and the planned international ban (under the auspices of the International Maritime Organisation) on this use of organotins. This ban is already enforced in the EU through EC Regulation 782/2003 with effect from 1 July 2003.

A substantial volume of information was reviewed for the environmental effects assessment as presented in the 2002 and 2003 Reports. Much of this is in the public domain but various additional, unpublished, documents have been supplied by industry, including:

- draft IUCLID data sheets for 28 organotin compounds (some of which have been updated and referenced in this Report); and

- the ‘GSF Report’ which reviews over 500 references on toxicity and ecotoxicity of various organotin compounds (Summer *et al*, 1996).

It is important to emphasis that the purpose of the review was to establish (and justify) suitable end-points for use in the analysis rather than to provide an exhaustive detailed review of all the studies carried out into the environmental effects of organotins. Nevertheless, it is recognised that there is particular concern over the potential for endocrine effects at very low concentrations. Although endocrine effects (such as imposex) on marine organisms have been observed in both laboratory and field trials and a causal link to TBT exposure has been established, the situation for freshwater organisms is not so clear cut. In particular, although endocrine effects have been observed in the field, the link to (very low levels of) TBT exposure has not been established. Furthermore, whilst some laboratory tests on freshwater snails (albeit on species not found in Europe) exposed to TBT have shown endocrine effects, the concentrations involved are much higher than those which are reported to produce effects amongst marine organisms.

Whilst the focus of this study is on the freshwater environment, considerations of hazards to the marine environment have also been provided (see Section 4.3). However, the exposure calculations in Section 3 should not be considered appropriate for the marine environment without first revisiting the assumptions used.

4.2 Environmental Toxicity

4.2.1 Freshwater Toxicity

Table 4.1 outlines the critical endpoints for the organotin species and the estimated PNEC derived using appropriate uncertainty factors (where these were based on consideration of the data presented in Annex 7 of the 2003 Report). For the purposes of the assessment, all values have been presented as concentrations of both tin and the corresponding chloride.

Table 4.1: Estimated PNECs for use in the Environmental Risk Assessment

Organotin Species	Endpoint (Freshwater)	Uncertainty factor	Estimated PNEC	
			as Sn	as Chloride
DBT	4.1 µg Sn/L chronic NOEC for Daphnia (ABC, 1990)	10	0.4 µg/L	1.0 µg/L
TBT	0.06 µg Sn/L chronic NOEC for Daphnia (Kühn *et al*, 1989)	10	0.006 µg/L	0.016 µg/L
DOT	0.12 mg Sn/L chronic NOEC for Daphnia (Schering AG, 1999)	100	1.2 µg/L	4.2 µg/L
TPT	0.03 µg Sn/L chronic NOEC for Daphnia (FAO, 1991)	10	0.003 µg/L	0.011 µg/L

For each of the organotin groups it is necessary to summarise the reasoning behind the choice of the critical study and endpoint and to justify the uncertainty factor and, therefore, the derived estimated PNEC. In all cases, uncertainty factors are based on the matrix presented in the EU Technical Guidance Document.

DBT

A large dataset exists for DBT, including both acute and long-term test results. The lowest identified endpoint is a chronic NOEC for *Daphnia magna* at 4.1 µg Sn/L. Long-term values are available across three trophic levels and, therefore, an uncertainty factor of 10 is considered appropriate.

TBT

A large database exists for TBT with acute and chronic studies at three trophic levels. The critical concentration has been identified as a chronic NOEC on *Daphnia magna* at 0.06 µg Sn/L. The test was carried out using TBT oxide and so in order to provide a consistent endpoint based on the chloride salt, the test result has been corrected accordingly. A slightly lower endpoint of 0.02 µg Sn/L based on a long-term fish study has been identified; however, it appears (by reference back to the original paper) that when the test was repeated the same endpoint gave an NOEC of 0.07 µg Sn/L. Since the results for the *Daphnia* and fish tests are so similar, the uncertainty factor has been applied to the more reliable test. An uncertainty factor of 10 is felt to be justified based on the wide range of test results available for this group of compounds.

Although endocrine effects have been observed amongst freshwater species, the lowest reported TBT concentration producing such effects in the laboratory is 125 ng/L (Schulte-Oehlmann *et al*, 1995).

DOT

There are limited usable data available for the octyltins. This is largely because many of the tests showed no toxicity at concentrations within the solubility of the compound. Since only one test has been identified that reported a quantified result - a chronic (21 day) NOEC for *Daphnia magna* at 0.12 mg Sn/L, this value has been used to set the PNEC for DOT. As this is based on a rather limited dataset, a precautionary uncertainty factor of 100 is applied to the critical concentration.

TPT

Although not as extensively studied as TBT, there have been numerous studies on triphenyltins. In freshwater species, a chronic (21 day) NOEC for *Daphnia magna* at 0.03 µg Sn/L has been identified and this value has been used.

4.2.2 Marine Toxicity

It is, of course, accepted that very low threshold concentrations have been derived for TBT in laboratory and field studies for effects amongst marine gastropods (and this point is emphasised by CSTEE - see Annex 2). By way of example, threshold concentrations as low as 0.1 ng/L have been reported (Oehlmann *et al*, 1996 and CSTEE, 1999). More generally, it is becoming increasingly apparent that molluscs are hypersensitive to a range of endocrine disruptors, both oestrogens and aromatise inhibitors (see, for example, Jobling *et al*, 2003).

As for TBT, imposex has been observed amongst marine organisms[40] at levels of TPT down to the order of 1 ng/l (WHO, 1999).

However, DBT is not considered to be as toxic as TBT and threshold concentrations for effects are at least two orders of magnitude greater than the corresponding concentrations for TBT (see, for example, HERD (2003)). This implies that the threshold concentration for DBT endocrine effects could be significantly higher, perhaps 10 ng/L.

4.3 PBT Assessment

Under the revised TGD, there is a requirement to undertake a PBT (persistence, bioaccumulation and toxicity) assessment due, primarily, to concerns over the potential long term impacts of chemicals on the marine environment. The revised TGD provides

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[40] Further evidence that TPT could be regarded as a mammalian endocrine disruptor alongside TBT is provided in a review of various TPT reproductive toxicity tests, including those carried out in support of TPT pesticide applications from the mid-1960s onwards (which were obtained under the US Freedom of Information Act) (Golub & Doherty, 2004).

two sets of criteria, one for PBT substances and one for so-called very persistent and very bioaccumulating substances (vPvB). This second category has been developed on the basis that for substances *"that are very persistent and bioaccumulate significantly in the food chain, high but unpredictable levels may be reached in wildlife or man over extended time periods. For such substances it is not necessary to demonstrate toxicity in laboratory testing as long-term effects can be anticipated anyway"* (S4.2.2, Part II, CEC (2003)).

The revised TGD recommends a stepwise approach to considering P, B and T properties in turn against the criteria presented in Table 4.2.

Table 4.2: Criteria for Identification of PBT and vPvB Substances

Criterion	PBT criteria	vPvB-criteria
P	Half-life >60 d in marine water or >40 d in freshwater* or half-life >180 d in marine sediment or >120 d in freshwater sediment*	Half-life >60 d in marine- or freshwater or >180 d in marine or freshwater sediment
B	BCF >2,000	BCF >5,000
T	Chronic NOEC <0.01 mg/L or CMR or endocrine disrupting effects	Not applicable

* For the purpose of marine environmental risk assessment, half-life data in freshwater and freshwater sediment can be overruled by data obtained under marine conditions.

Organotin property data were reviewed in Section 3.6 and, based on these together with further consideration of the marine environment, the following observations may be made:

Persistence: Based on the discussion presented in S3.6.5, it is likely that the four (groups of) organotins being considered in this Report will meet the P and vP criteria.

Bioaccumulation: As discussed in S3.6.6, TPT has a BCF of more than 5,000 (in freshwater species) and, as such, is likely to exceed the B and vB criteria for the marine environment.

TBT has a BCF value of more than 3,000 and would thus meet the B criterion but not the vB criterion. However, it is important to stress that this is a value obtained for freshwater species. With regard to marine species, much higher BCF values are reported with particular reference to an inverse relationship with concentration (in other words, the lower the concentration the higher the BCF value). Values of 10,000 and upwards have been reported (as discussed in BUA, 2003).

For DBT and DOT, the BCF values are significantly below 2,000 (see Table 3.32). Given the differences in effects in freshwater and marine environments, it is possible that the corresponding BCF values in the marine environment might be somewhat higher but no reliable data have been located.

Toxicity: Based on the discussion presented in the previous sub-section, there is no doubt that TBT and TPT would be classified as T. Furthermore, it is likely that DBT would also be classified as T. However, the situation with DOT is less clear. The freshwater NOEC is above the threshold value and there are insufficient data to demonstrate the use of much lower values in the marine environment.

The results of the above discussion are summarised in Table 4.3.

Table 4.3: Potential PBT/vPvB Classification of Organotins

Criterion	DBT	TBT	DOT	TPT
P	yes	yes	yes	yes
B	possibly	yes	possibly	yes
T	probably	yes	possibly	yes
PBT	**possibly**	**yes**	**possibly**	**yes**
vP	yes	yes	yes	yes
vB	unlikely	yes	unlikely	yes
vPvB	**unlikely**	**yes**	**unlikely**	**yes**

Overall, it is concluded that, in relation to the marine environment, TBT and TPT are likely to be classified as both PBT and vPvB substances.

Although DBT and DOT[41] could be classified as PBT substances, they are unlikely to be vPvB substances.

4.4 Risk Characterisation

4.4.1 Introduction

Comparing the PNEC values (as derived above) with the PEC values (as derived in Section 3) provides an indication of whether the risk to the environment is likely to be of significance. In essence, where the PEC/PNEC ratio is:

- much less than one, then the risks are unlikely to be of concern;
- about one, then the risks may be of concern; and
- much greater than one, then the risks are likely to require closer examination and, possibly, risk reduction measures.

4.4.2 Risks to the Environment at a Regional Level

The values at a regional level are shown in Table 4.4. Clearly, from the results presented in the Table, the environmental risks are unlikely to be of concern at a regional level. It should be noted that these findings also applied to soil and sediment.

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[41] It is understood that following the 5th Meeting of the ECB's subgroup on the Identification of PBT and vPvB Substances held at Ispra, November 2004, both DOTC and DOT-EHMA are candidate PBT/vPvB substances subject to further B tests (which industry intend to complete by the end of 2005).

Table 4.4: PEC/PNEC Ratios at a Regional Level for the Aquatic Environment			
Parameter	**DBTC**	**TBTC**	**DOTC**
Regional PEC	2.9	1.5	2.8
PNEC	1,000	16	4,200
PEC/PNEC	0.003	0.095	<0.001
Note: PEC and PNEC values in ng/L (as chloride)			

However, in regions where many of the surface waters are used by vessels, it is possible that typical TBT levels would exceed the PNEC value of 16 ng/L resulting in a PEC/PNEC ratio of greater than unity. However, such arguments would not apply to DBT or DOT.

4.4.3 Risks to the Environment at a Local Level

The risks at a local level are evaluated using the same approach. Various local PECs (for the aquatic compartment) were presented in Table 3.61 and the PEC/PNEC ratios (also referred to as Risk Characterisation Ratios, RCRs) for the higher values were derived, as shown in Table 4.5.

Table 4.5: PEC/PNEC Ratios at a Local Level (for the Aquatic Compartment)			
	DBTC	**TBTC**	**DOTC**
Activity **PNEC:**	1,000	16	4,200
Organotin Production - Plant W (using TGD)	**0.23**	0.75	**0.068**
Product Manufacture (Catalysts) - Paint Formulator (using TGD)	0.12	0.22	0.018
Wood Treatment Plant (Biocide) - Wood Treatment Plant (*EUSES2*)	-	**45**[1]	-
Maximum Local RCR (from above)	**0.23**	**45**	**0.068**
Sediment RCR Values	similar		x10 higher
Soil RCR Values	x10 lower		
Note: 1) For TBTC, it will be noted that the PEC/PNEC ratio (594/16 = 37) is lower than that reported above. The RCR value has been taken from EUSES2 and incorporates other factors (such as regional concentrations).			

By inspection of the *EUSES2* results, the PEC/PNEC ratios for sediment are very similar whilst those for soil are lower. The exception is that the sediment PEC/PNEC ratios for DOTC are about an order of magnitude greater. However, this is simply due to a correction factor of ten being applied to the results[42] since DOTC (only) has a log Kow >5.

There is only one area where the PEC/PNEC ratio (or Risk Characterisation Ratio) exceeds unity - a wood treatment plant using TBT as a biocide. In this case, the

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[42] For further detail, see S3.5.2 of the revised TGD (CEC, 2003).

PEC/PNEC ratio (RCR) is 45. Although the analysis has focused upon the aquatic compartment, an example is provided in Section 3.10 of leaching from a building clad with wood treated with TBT. This results in predicted local soil concentrations (in the immediate vicinity of the building) of about 890 µg TBTC/kg. As a basis for a preliminary estimate, a PNEC for terrestrial organisms of 47 µg/kg has been generated by *EUSES2*. This leads to an RCR of about 19[43].

Finally, it is important to stress that in some ports, harbours and marinas there will be sufficient (residual) levels of DBT, TBT and TPT (but not DOT) which are well above the PNEC value leading to an RCR well above unity.

4.5 Risk Reduction Scenario

In relation to the environmental RCRs, the effects of the cessation of the use of TBT as a biocide will be considered. As indicated in S2.4.3, the main producer of TBT for use in wood preservatives has announced that it will be withdrawing these products from the market. When this occurs, it would be expected that the wood treatment plants which currently use TBT containing preservatives will move to alternatives. In the longer term, the flux of TBT from treated wood to the environment will also decay.

Against this background, it would be expected that the RCR (for the aquatic compartment) of 45 associated with the wood treatment plant (see Table 4.5) would reduce well below unity in the near future. However, it would be some years before the RCR for the soil compartment declined significantly. The impact of the planned removal of TBT in biocides (and the associated TBT production) is incorporated into the revised summary table presented as Table 4.6.

Table 4.6: PEC/PNEC Ratios at a Local Level (for the Aquatic Compartment)

		DBTC	**TBTC**	**DOTC**
Activity	**PNEC:**	1,000	16	4,200
Organotin Production - Plant W (using TGD)		**0.23**	0.21[1]	**0.068**
Product Manufacture (Catalysts) - Paint Formulator (using TGD)		0.12	**0.22**	0.018
Wood Treatment Plant (Biocide)		-	**eliminated**	-
Maximum Local RCR (from above)		**0.23**	**0.22**	**0.068**
Sediment RCR Values		similar		x10 higher
Soil RCR Values		x10 lower		

Note: 1) For TBTC, the RCR value has been reduced by a factor of 0.28 to reflect the removal of the 87 t/yr used in biocide from the total of 121 t/yr (as TBTC).

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[43] The IUCLID Data Sheet (Parametrix, 2005) contains no toxicity data for terrestrial organisms but ETINSA has cited a reference (Schlatter et al, 1993 - but with no further details) suggesting a more realistic PNEC value of 600 µg/kg which would lead to a lower RCR value of 1.5.

5. CONSUMER EXPOSURE ASSESSMENT

5.1 Overview

As has been seen from the preceding sections, organotin compounds in their various forms are used in a wide array of materials which can be utilised in an enormous number of different applications, including many consumer products. As such, consumers within the EU can expect to be in close proximity to a range of different products containing organotin compounds.

However, the presence of a substance in consumer products does not itself provide any indication of possible harm from these substances. Thus, an approach is required to determine the level of consumer exposure to organotin compounds from consumer products in order to estimate the likely level of risk.

This Section provides an overview of various consumer products in which organotin compounds have been detected and reported. The list of products considered is not intended to be exhaustive; however, it is expected that the types of products monitored for these substances are those that were studied due to a potential concern (taking into account the possible level of exposure).

Following this, a number of worst-case exposure scenarios are developed for both adults and children for a range of different consumer products. It is obviously not feasible to conduct an exposure assessment for all potential routes of consumer exposure. Instead, an attempt has been made to include examples of products that either lead to a relatively high level of possible exposure or that are relatively commonplace and with which a consumer is likely to come into frequent contact. The examples chosen, therefore, provide an indication of the types of exposure that may occur.

In addition to the direct exposure to organotin compounds from products, consumers will be exposed to a certain quantity via the environment. Section 4 provided the data for estimating this exposure, based on the environmental exposure assessment using the TGD and the *EUSES2* model.

Finally, the level of exposure to the organotin compounds from the various sources (products and via the environment) are summarised, in order to provide a basis for comparison of the total exposure with the TDI values used in the assessment (Section 6) and also to allow for comparison of the relative importance of the various sources.

5.2 Organotin Compounds in Consumer Products

5.2.1 Review of Results in 2003 Report

Numerous products containing organotins were identified in the 2002 and 2003 Reports, with detailed exposure models provided for a selection of these. The daily intakes[44] reported (in the 2003 Report) for adults and children are summarised in Tables 5.1 and 5.2.

Table 5.1: Worst-Case Adult Consumer Exposure to Organotin Compounds (µg Sn/kg bw/day)

Product	DBT	TBT	DOT	Sum
Food wrapped in PVC			0.057	0.057
Insoles	0.006	0.020		0.026
Foot spray		0.049		0.049
Cycling shorts padding		0.018		0.018
PVC gloves	0.033	<0.001		0.033
Sanitary pantyliners			0.062	0.062
Cookies	0.611	0.010		0.622
Indoor air (inhalation)	0.008	0.001	0.004	0.013
Dental moulding	0.046			0.046
Earplugs	<0.001	<0.001		<0.001
Via env. (worst local)	0.003	0.328	0.533	0.865

Source: Table 5.18, 2003 Report.

Table 5.2: Worst-Case Child Exposure to Organotin Compounds (µg Sn/kg bw/day)

Product	DBT	TBT	DOT	Sum
Nappies	0.013	0.007		0.021
Cookies	2.292	0.038		2.331
Pool water	0.003	<0.001		0.003
Food wrapped in PVC			0.227	0.227
Non-allergenic pillow	0.004	0.015		0.019
T-shirt	0.002	0.015	0.171	0.189
Indoor air	0.019	0.008	0.010	0.036
PVC toys	negligible			<0.001
Via env. (worst local[1])	0.013	1.311	2.134	3.459

Note: 1) The uptake via the (worst local) environment values were derived by multiplying those derived for adults (see Table 5.1) by a factor of four to account for a higher food intake per unit bodyweight.

Source: Table 5.30, 2003 Report.

By inspection of Tables 5.1 and 5.2, the dominant contributor to human uptake is via the environment (close to sources of significant emissions). Other significant source include cookies (adults and children), food wrapped in PVC (adults and children), sanitary pantyliners (adults) and foot spray (adults).

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[44] In this section all intakes are represented as Sn rather than the organotin chloride. This approach simplifies the addition of intakes of different organotins.

In its Opinion on the 2003 Report, CSTEE (2004) comments on several aspects of the consumer exposure calculations (as detailed in Annex 2). These may be paraphrased as follows:

- no account was taken of TPT intakes;
- the exposure model for indoor air was incorrect;
- the intake from PVC toys was incorrect; and
- sources (with specific reference to food) were omitted.

As discussed in Annex 2, the scope of the 2003 (and 2002) Report specifically excluded consideration of anti-fouling paints (the major source of TBT and TPT). However, in accordance with the Specification (see Annex 1), consideration is given to all potential consumer exposure routes in this Report. The issue of organotins in food (with particular reference to fish and fishery products) has been addressed by EFSA (2004) and this is considered in the next sub-section. Further discussion on other issues raised by CSTEE and other exposure routes are considered later in this Section.

5.2.2 Intake of Organotins via Fish and Fishery Products

EFSA (2004) reports the intakes DBT, TBT and TPT via fish and fishery products as shown in Table 5.3. For comparison, the Table also includes the *EUSES2* results for intake via fish at a regional level.

Table 5.3: Daily Intake of Organotins via Fish & Fishery Products

Population	**Daily Intake (expressed as µg Sn/per kg bodyweight)**				
	DBT	**TBT**	**DOT**	**TPT**	**Sum**
Median (Europe)	0.002	0.004	not detected	0.002	0.007
Mean-based High Intake (95% - based on Norway)	0.024	0.032		0.016	0.071
EU Region (*EUSES2*)	<0.001	0.003	0.001	not modelled	0.004

Source: Table 1, EFSA (2004) with supporting information from SCOOP (2003).

As would be expected, Table 5.3 suggests that the intake of organotins via fish (and fishery products) is higher than that predicted by *EUSES2* (since some sources such as anti-fouling paint have not been included in the modelling).

Furthermore, by inspection of Tables 5.1-5.3, it is clear that although the intake of organotins via fish (and fishery) products is significant, there are other sources of greater concern.

5.2.3 Uptake via the Local Environment

Tables 5.1 and 5.2 indicate that uptake via the local environment is very significant for TBT and DOT. The associated results from *EUSES2* for adult uptakes of organotins from the local environment are summarised in Table 5.4.

Table 5.4: Daily Intake of Organotins via the Environment (µg Sn/kg bw/day)

Life Cycle Stage	DBT	TBT	DOT	TPT	Sum
Production	0.002	0.009	0.342	not modelled	0.353
Stabiliser in PVC - processing	0.001	0.003	**0.605**		0.609
Catalyst - formulation	**0.003**	0.005	0.016		0.024
Catalyst - processing	0.001	0.003	0.054		0.058
Wood pres. - timber treatment	-	**1.273**	-		**1.273**
Wood preservative - use	-	0.003	-		0.003
Maximum local intake (2003 Results)	**0.003 (0.003)**	**1.273 (0.328)**	**0.628 (0.533)**		**1.273 (0.536)**
Regional intake (2003 Results)	<0.001 (<0.001)	0.003 (0.001)	0.001 (<0.001)		0.005 (0.001)

The uptake for TBT has increased - largely due to the use of an increased solubility value. Table 5.5 details the key routes of exposure for TBT and DOT based upon the *EUSES2* modelling (for the worst-case local exposure routes).

Table 5.5: Key Exposure Routes via the Environment (*EUSES2*) for TBT and DOT

Substance and Use Pattern	Key Exposure Routes
TBT - timber treatment	Nearly 95% through fish and 5% through root crops.
DOT - PVC processing	69% through leaf crops (> 99% of plant uptake is through air); 19% through meat and 11% through milk (cattle's intake is >99% through grass which, in turn, is taken up at >99% through air).

As already discussed (Section 3.6.4), the modelling of DOT for exposures close to PVC processing plants may be better represented using DOT-EHMA and DOT-Cl-EHMA rather than DOTC. Accordingly, two further *EUSES2* runs were undertaken for these compounds using the data presented in S3.6.4 (as well as further data from the referenced sources). The results are summarised in Table 5.6.

Table 5.6: Local Human Intake for PVC Processing by Organotin Modelled

Intake Parameter	DOT-EHMA	DOT-Cl-EHMA	DOTC
Daily intake (µg ATC/kg bw/day)	4.6	0.006	2.1
Daily intake (µg Sn/kg bw/day)	0.73	0.001	0.61
%Intake via leaf crops	32%	<1%	69%
%Intake via meat	43%	11%	19%
%Intake via milk	25%	7%	11%
%Intake via air	<1%	76%	<1%
%Intake via other routes	<1%	6%	<1%

Although, as reported in S3.6.4, the leaf-air partition coefficient varies widely from DOT compound to compound, this variation is less marked when comparing the resultant human intakes. In particular, the results for DOTC and DOT-EHMA are very similar. It is acknowledged that considerable uncertainty remains as to the reliability of the derived leaf-air partition coefficients and that much of the DOT emissions from PVC processing plants will be in the form of DOT-Cl-EHMA. In an attempt to take this into account, the local human intake (via the environment) for PVC processing has been estimated as follows:

Intake = 80% DOT-Cl-EHMA + 10% DOT-EHMA + 10% DOTC
= 0.001 + 0.073 + 0.061
= 0.135 μg Sn/kg bw/day

With reference to Table 5.4, the second most important local source of DOT uptake is organotin processing with an uptake of 0.342 μg Sn/kg bw/day. As for PVC processing, it is unlikely that the DOT compound being emitted is DOTC. The most likely DOT compound to be emitted is DOT-EHMA (as this is the main stabiliser in use). The associated local uptake is estimated (by *EUSES2*) as 2.6 μg DOT-EHMA/kg bw/day which is equivalent to 0.411 μg Sn/kg bw/day (i.e. slightly more than if calculated using DOTC).

Using these adjusted DOT values then enables Table 5.4 to be reconstructed as shown in Table 5.7.

Table 5.7: Daily Intake (Adjusted) of Organotins via the Environment (μg Sn/kg bw/day)

Life Cycle Stage	**DBT**	**TBT**	**DOT**	**TPT**	**Sum**
Production	0.002	0.009	**0.411**	not modelled	0.422
Stabiliser in PVC - processing	0.001	0.003	0.135		0.139
Catalyst - formulation	**0.003**	0.005	0.016		0.024
Catalyst - processing	0.001	0.003	0.054		0.058
Wood pres. - timber treatment	-	**1.273**	-		**1.273**
Wood preservative - use	-	0.003	-		0.003
Maximum local intake (2003 Results)	**0.003 (0.003)**	**1.273 (0.328)**	**0.411 (0.533)**		**1.273 (0.536)**
Regional intake (2003 Results)	<0.001 (<0.001)	0.003 (0.001)	0.001 (<0.001)		0.005 (0.001)

5.2.4 Intake via Indoor Air

As indicated in Section 3.7, octyl and butyl tins have been detected in house dust (see, for example, Santillo *et al* (2003), Al Bitar (2004) and Fromme *et al* (2005)) with traces of phenyltins being found in a few samples. There are no data on measured levels of organotins in indoor air (in other words, there are no available direct measurements of organotins in indoor air as the very low concentrations are below the limits of detection). In the absence of monitoring data, two approaches were adopted in the 2003 Report. Firstly, an estimate for intake via inhalation was based on the following:

- derive emissions from migration/abrasion for a room with PVC flooring and wall coverings;
- assume 1% of emissions are airborne; and
- derive daily intake based on continuous occupancy of the room.

The second approach was based on assuming an intake of 200 mg/day of household dust and the highest value from each approach was taken forward in the analysis.

Although CSTEE (2003) has criticised this approach, it is difficult to envisage that the intakes of organotins via indoor air/household dust would be underestimated by ‘two orders of magnitude’. Indeed, if this assertion was correct, the expected indoor concentrations would be of the order of 1 μg/m^3 which would be measurable. The calculations from the 2003 Report have been revised in light of further information as outlined below.

Air Inhalation

The key input parameters are:

- Floor: area 10 m^2, weight of 2mm thick PVC flooring: 28 kg
- Wall: area 25 m^2, weight of 1mm PVC wall covering: 35kg
- Ventilation rate = 50% of room volume (25m^3) per hour = 300 m^3/day

For each organotin compound, the following calculation was carried out:

- daily emission = weight of item x organotin concentration x loss factor
- air concentration = 1% x daily emission / ventilation rate
- adult intake = air concentration x 20 m^3/day / 60 kg bodyweight
- child intake = air concentration x 6.5 m^3/day / 8 kg bodyweight

The results are summarised in Table 5.8.

Table 5.8: Indoor Air - Uptakes via Inhalation (Worst Case)

	Note	**DBT**	**TBT**	**DOT**	**TPT**	**Sum**
C (Sn) mg/kg	*1*	1380	30	1184	negligible	2594
%Loss/year from floor	*2*	0.27%	0.23%	0.21%	0	
%Loss/year from wall	*3*	0.39%	0.24%	0.18%	0	
Loss (mg Sn)/day:						
• from 28kg floor		0.29	0.01	0.19	0	0.48
• from 35kg wall		0.41	0.01	0.16	0	0.58
Daily emission (mg Sn/day)		0.69	0.01	0.35	0	1.06
Air concentration (μg Sn/m3)	*4*	0.023	<0.001	0.012	0	0.035
Adult Intake (μg Sn/kg/day)	*5*	**0.008**	**<0.001**	**0.004**	**0**	**0.012**
Child Intake (μg Sn/kg/day)	*6*	**0.019**	**<0.001**	**0.010**	**0**	**0.029**

Notes:
1. *From Table 5.1.*
2. *Total %Loss (includes abrasion) from Table 3.13/Lifetime (20 years).*
3. *Total %Loss from Table 3.14/Lifetime (7 years).*
4. *Assume1% airborne (Fabes (2000) suggests air emissions are 1% of losses to water).*
5. *Assuming an inhalation rate of 20 m3/day for a 60kg adult.*
6. *Assuming an inhalation rate of 6.5 m3/day for an 8kg child.*

As noted in the 2003 Report, organotin compounds will be transferred from inside a building to the outside environment through transport via clothes, shoes or through waste products disposed of after use. Only a proportion of the compounds emitted from PVC floors and walls (or other applications) would be inhaled, most probably through the loading of household dust.

Exposure via Household Dust

Samples of house dust were collected from 100 UK households and all the (pooled) samples contained organotin compounds, with the most abundant compound being MBT, followed by DBT and MOT (Santillo *et al*, 2003). The results of this study reflected results obtained from samples of dust collected from Parliament buildings across Europe (Santillo *et al*, 2001). In another study, samples were taken from 28 Berlin apartments (in 2000) and MBT/DBT were found in most samples with MOT/DOT/TBT being found in about half the samples (Fromme *et al*, 2005). Al Bitar (2004) reports on results from Belgian homes and from the offices and homes of MEPs in Brussels. DBT/TBT/DOT (and MBT/MOT) were found in all samples while traces of TPT (and tetrabutyl tin) were found in a few samples.

Assuming an intake of 200 mg dust/day, the resultant intake of organotins via ingestion of dust can be determined as shown in Table 5.9. To err on the side of caution, reliance has been placed upon the maximum reported concentrations. Although the 95% values will be slightly lower, it should be noted that the use of pooled sample will mask the presence of high levels in individual samples.

Table 5.9: Indoor Air - Uptakes via Dust Ingestion (Worst Case)

Parameter	***Note***	**DBT**	**TBT**	**DOT**	**TPT**	**Sum**
Median (max) measured dust concentration (mg Sn/kg)	*1*	0.29 (0.66)	0.06 (0.31)	0.04 (0.19)	n.d. (0.02)	
Median (max) measured dust concentration (mg Sn/kg)	*2*	0.02 (0.76)	<0.01 (0.61)	<0.01 (0.52)	n.d	
Median (max) measured dust concentration (mg Sn/kg)	*3*	0.25 (3.11)	0.02 (1.02)	0.02 (0.31)	n.d. (0.01)	
Max Concentration (mg Sn/kg)		3.11	1.02	0.52	0.02	
Max. intake (μg Sn/day) with a dust intake 200 mg/day		0.62	0.22	0.10	<0.01	0.93
Adult Intake (μg Sn/kg/day)		**0.010**	**0.003**	**0.002**	**<0.001**	**0.016**
Adult Intake (via inhalation)	*4*	0.008	<0.001	0.004	0	0.012
Child Intake (μg Sn/kg/day)		**0.078**	**0.026**	**0.013**	**0.001**	**0.117**
Child Intake (via inhalation)	*4*	0.019	<0.001	0.010	0	0.029

Sources:
1) Organotin concentrations in dust taken from Santillo et al (2003). Note that values for DBT, TBT and DOT were based on 10 samples whereas TPT was only found in one sample.
2) Organotin concentrations in dust taken from Fromme et al (2005).
3) Organotin concentrations in dust taken from Al Bitar (2004). TPT was found in 2 of 23 samples.
4) Intake via inhalation from Table 5.8.

Although Table 5.9 illustrates some convergence between the DOT values derived through these two approaches, those for the butyltins are much greater using the dust intake approach.

5.2.5 Migration from PVC Products

With reference to Tables 5.1 and 5.2, migration of organotins from food packaging was found to be a significant source of consumer exposure to DOT in the 2003 Report. The associated calculations were based on actual measurements of organotin concentrations found in olive oil which was in contact with PVC. It is acknowledged that various forms of PVC are used in food packaging and that migration rates may vary by the type of PVC being used. Originally it was envisaged that further information would be provided by DGSANCO and/or EFSA for this study (as detailed in Annex 1) but, in the event, industry arranged for a series of laboratory migration tests to be undertaken and associated exposure modelling to be undertaken. Results from these studies have been made available and incorporated into this Report. However, it should be noted that these results have not been approved (or otherwise) by either DGSANCO or EFSA. Intake via food and food contact materials is discussed in S5.2.10.

In the 2002 and 2003 Reports, consumer exposure to flexible PVC products was considered. Although reference was made to measured concentrations, use was also made of predicted migration rates. Although such calculations carry a degree of uncertainty, attempts were made to ensure consistency between actual measurements and predictions. For this Report, no significant new information has been identified and, as such, the 2003 calculations are carried forward - albeit with some changes to improve their robustness and presentation.

5.2.6 PVC Stabilisers

Scope

As detailed in Sections 2 and 3, mono and di-substituted organotin compounds are used in a wide range of PVC products. The Specification (see Annex 1) requires further consideration to be given to the emissions of DBT and DOT and TBT-impurities from PVC articles when used as a stabiliser in both flexible and rigid PVC articles.

The flexible PVC articles to be considered are:

- flooring and wall covering;
- shower curtains;
- bags;
- steel coating;
- T-shirt printing (can also contain TBT to provide a deodorant effect);
- paddling pools;
- toys in general (add a specific scenario for children under three years old);
- PVC gloves; and
- earplugs.

The rigid PVC articles to be considered are:

- profile extrusions (window frames);
- foamed sheeting;

- pipes, distinguishing between drinking water pipes and other pipes;
- thin rigid film;
- credit cards;
- fencing;
- electrical conduit; and
- PVC sandals.

Flexible PVC Products

General emissions from the use of PVC products containing organotin stabilisers are considered in Section 3.4 (and these were also considered in the earlier 2002 and 2003 Reports). In addition, more detailed consumer exposure models (for flexible products only) were previously considered in detail in the 2002 and 2003 Reports as shown in Table 5.10.

Table 5.10: Exposure Scenarios for Organotin Stabilisers in Flexible PVC Products

Article	Comment
Flooring and wall covering	Adult/child exposure via indoor air/dust considered in 2003 Report and reconsidered in S5.2.4 above.
Shower curtains	Not previously considered in detail
Bags	
Steel coating	
T-shirt printing (can also contain TBT to provide a deodorant effect)	Child exposure considered in 2002/2003 Reports
Paddling pools	Child exposure considered in 2002/2003 Reports
Toys in general (add a specific scenario for children under three years old)	Child exposure (mouthing) considered in 2003 Report
PVC gloves	Adult exposure considered in 2002/2003 Reports
Earplugs	Adult exposure considered in 2003 Report

With reference to Table 5.10, the items not previously considered include shower curtains and steel coating. Whilst it is accepted that such PVC products may contain organotin stabilisers, it is difficult to envisage that direct consumer exposure will be significantly greater than for the other items already considered. As such, these products are not considered further. The remaining calculations from the 2003 Report, revised as appropriate, are presented below. It should be noted that bags are considered along with PVC gloves.

T-shirts (and Pyjamas)

Organotin compounds have been detected in T-shirts from a number of sources. In some cases, their presence relates to PVC printing on the shirts (using mono/di organotin stabilisers), whereas in others, T-shirts imported from outside the EU have reportedly been treated with tri-substituted organotin compounds in order to provide a preservative/deodorant effect.

Maximum concentrations reported in T-shirts (RIVM, 2000) are detailed in Table 5.11, including di and tributyltin, as well as dioctyltin. More recently (TNO, 2003), in an analysis of nine samples (a shampoo, three toys and five printed child pyjamas), organotins (MOT, DOT and traces of TBT) were detected in just one set of pyjamas at concentrations ten times lower than those presented in Table 5.11.

For this analysis, the consumer is assumed to be exposed to an area of 0.3m^2 of a T-shirt with a mass of 1 kg/m^2. Again, migration to the skin is taken as 1% with dermal absorption of 10%, leading to exposure as calculated in Table 5.11. The associated daily consumer exposures are derived based on an 8 kg child and a 60 kg adult

Table 5.11: Concentrations of Organotins in T-Shirts

Parameter	**DBT**	**TBT**	**DOT**	**TPT**	**Sum**
Conc. in product (µg cation/kg)	100	990	13,300	0	
Conc. as tin (µg Sn/kg)	50.9	405	4,573	0	5029
Mass per T-shirt (µg Sn) [a]	15.3	122	1372	0	1509
Estimated daily uptake (µg Sn) [b]	0.015	0.122	1.37	0	1.509
Child Exposure (µg Sn/kg bw/day)	**0.002**	**0.015**	**0.171**	**0**	**0.189**
Adult Exposure (µg Sn/kg bw/day)	**<0.001**	**0.002**	**0.023**	**0**	**0.025**

Notes: [a] *Surface area of area of T-shirt for exposure assumed 0.3m^2 with mass of 1kg/m^2.*
[b] *Assumed migration to skin of 1% and dermal uptake of 10%.*

Paddling Pools

Butyltin stabilisers have been detected in paddling pools made from PVC. The typical concentration of organotin stabilisers may be up to 2% of the plastic weight in PVC products (ORTEPA, 1997), and was assumed at 1.5% for the environmental exposure assessment in this Report. However, it has been indicated by industry for the type of products in question, the maximum amount of stabiliser used would be 1phr[45], equating to 0.62%. Using the latter concentration, the concentrations of mono, di and tri butyltin compounds in PVC paddling pools can be estimated. These are assumed to be used in a paddling pool of 0.3m depth, 2m diameter and 5 mm thickness, and the density of the plastic is assumed to be 1,400 kg/m^3.

Using the migration data from Fabes (2000) reported in preceding sections, it is possible to estimate a worst-case migration from the PVC into the water within the pool. Table 5.10 presents the concentrations of butyltin stabilisers used in the analysis, the migration per unit area into the water[46], the percentage of the stabiliser that migrates and the resultant concentration in the water. As a worst-case, it is assumed that a child drinks 0.33L of the water in the pool to give the resulting exposure presented in Table 5.12.

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[45] This refers to parts per hundred resin. An assumed plasticiser content of 60phr gives a stabiliser content of 0.62% (assumed to be mono, di and tributyltin (2-ethylhexyl) mercaptoacetates).

[46] It is worth noting that the predicted migration rates are more than a factor of ten higher than those measured by the Danish EPA on a single PVC paddling pool (DEPA, 2000).

Table 5.12: Migration of Butyltin Stabilisers from PVC Paddling Pool[1] into Water

Parameter	DBT	TBT	DOT	TPT	Sum
Concentration in PVC (mg Sn/kg) [2]	571	12.4	0	0	583
Migration per area (µg Sn/dm^2) [3]	2.46	0.033	0	0	2.49
Percentage of stabiliser migrated	0.0062%	0.0038%	0	0	0.01%
Mass lost into pool (µg Sn)	1239	16.7	0	0	1255
Concentration in water (µg Sn/L)	1.31	0.018	0	0	1.33
Ave. exposure (µg Sn/kg bw/day) [4]	**0.003**	**<0.001**	**0**	**0**	**0.003**

Notes:

[1] Pool (2m id x 0.3m h) is assumed to be 5mm thick PVC (density=1,400 kg/m^3)

[2] Stabiliser compounds are 3,074, 3,074 and 52 mg/kg respectively (total 6,200 mg/kg or 0.62%).

[3] Based on empirical relationships derived in Fabes (2000), assuming 40°C exposure for eight hours.

[4] Assume child drinks 0.33L on worst-case day on 20 days in year (values given as annual average)

Mouthing PVC Toys

Some toys contain rigid and/or flexible PVC. Organotins are used as stabilisers in rigid and, to a lesser extent, flexible PVC[47]. Although the use of PVC (containing phthalate plasticisers) has been banned for use in soft toys intended to be put into the mouth for the under-threes (Commission Decision 1999/815/EC which is currently renewed on a quarterly basis), it is possible that other plastic toys containing PVC may lead to the ingestion of organotins by children through mouthing activities.

At the outset, it must be stressed that although organotins are not specifically listed as being prohibited for use in toys, Annex II to the Toy Safety Directive (88/378/EEC) states that "*Toys must not contain dangerous substances or preparations ... in amounts which may harm the health of children using them*". Furthermore, industry representatives have advised that organotins would not normally be used in PVC in toys.

However, EU suppliers of organotins have no influence over the use of stabilisers in PVC toys imported from outside the EU. Of note is that in Germany, the Federal Institute for Risk Assessment (BfR) has recommended that toys containing flexible PVC[48] should not contain organotin stabilisers. It is nevertheless possible that some plastic toys contain PVC with organotin stabilisers - as illustrated by the examples of beach balls and paddling pools found by the Danish EPA (2000).

The exposure calculation is based on two key factors - mouthing time and leach rate. In the 2003 Report, reference was made to the key finding from a major US study (US CPSC, 2002) that mouthing times were considerably shorter than previously assumed. The mean mouthing time for soft plastics toys (which could contain flexible PVC with organotin stabilisers) was found to be 1.3 minutes per day with a 95th percentile of 7.1 minutes amongst children aged 3-12 months. As CSTEE notes (see Annex 2), Norris and Smith (2002) report that mean times for mouthing of toys peak at 39 minutes for children

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[47] About 70% of PVC is 'rigid' but this accounts for over 90% of the organotins used as PVC stabilisers.

[48] This recommendation applies to all toys which are intended to be placed in the mouth and all toys for the under-threes which can be expected to be placed in the mouth.

aged 6-9 months. Whilst this figure is higher than that from the US, it encompasses all kinds of toys (flexible and rigid, plastic and non-plastic). A compromise value of 10 minutes is suggested for this analysis.

In this Report, data have been provided on leach rates from flexible PVC items (based on Fabes, 2000) as well as work by the Danish EPA (DEPA, 2000). These data suggest that leach rates are of the order of 1 ng/cm^2/hr although, as CSTEE notes, the leach rates could well be higher under mouthing action. It is therefore proposed that the leach rate is increased by a factor of 10 for this analysis to give a higher 'active' leach rate.

The associated (revised) exposure calculation (for DBT, the dominant stabiliser in flexible PVC) could then appear as follows:

- 'active' leach rate = 10 ng/cm^2/hr
- contact area = 10 cm^2
- mouthing time = 10 minutes/day
- intake = 17 ng/day
- exposure = 2 ng/kg bw/day (for 8kg child less than 1 year in age)

However, this calculation does not preclude the possibility that there are other PVC items containing organotins (but not phthalates) which are intended to be placed in the mouth by the under-threes - in which case, the intake may be significantly greater. Without further research it is not possible to determine whether such items are available on the market.

PVC Gloves (and Plastic Bags)

Concentrations of butyltin stabilisers in PVC gloves have been reported by the Danish Environmental Protection Agency (DEPA, 2002). However, it is thought that these concentrations may not be representative of the likely maximum concentrations in these types of flexible PVC products. Instead, if it is assumed that the concentration of stabiliser in the PVC product is 1phr then the resultant concentrations used in this assessment are significantly higher, as reported in Table 5.13.

Migration from flexible PVC products was discussed in S3.4.1, based upon formulae developed from migration tests on flexible PVC flooring (Fabes, 2000). It is assumed that PVC gloves are 0.2mm thick and are worn for eight hours in a day. The percentage migration from the gloves can then be calculated and, assuming a dermal uptake of 10% and an area of contact of 0.08m^2 (two hands each at 400 cm^2) the uptake by a person can be estimated. These values are presented in Table 5.13.

Table 5.13: Calculation of Uptake of Organotin from PVC Gloves

Parameter	DBT	TBT	DOT	TPT	Sum
Conc. used in analysis (mg Sn/kg)	571	12.4	0	0	583
DEPA (2002) concentration (mg Sn/kg)	*0.018*	*0.023*	*0*	*0*	*0.040*
Migration from gloves during wearing [1]	0.0154%	0.0096%	0	0	
Uptake per wearing (µg Sn) [2]	1.973	0.027	0	0	2.000
Average migration rate (ng Sn/cm^2/hr)	0.308	0.0042	0	0	0.312
Adult uptake (µg Sn/kg bw/day)	**0.033**	**<0.001**	**0**	**0**	**0.033**

Notes: [1] *Calculations based on empirical relationships derived from Fabes (2000), assuming PVC density of 1,400 kg/m^3, thickness of 0.2mm, gloves worn for eight hours per day and starting concentrations of organotins as in previous table.*

[2] *Assumed area of exposure is 0.08m^2 with dermal uptake of 10%.*

The Danish EPA (DEPA, 2000) analysed migration of MBT, DBT and TBT from two flexible PVC items (a beach ball and a paddling pool). Although the results are based on a sample of just two items, migration rates to 'artificial skin grease' of 0.14, 1.43 and 0.004 ng Sn/cm^2/hr for MBT, DBT and TBT respectively were observed which are of a similar order to those predicted in Table 5.13 (although it should be noted that the organotin concentrations were significantly lower than those assumed).

Busy shoppers may clutch plastics bags (possibly made of PVC containing butyltin stabilisers) for several hours. As a worst case, bags will be assumed to be carried for eight hours per day with a total contact area of 160 cm^2 to give an (adult) intake 20% of that derived for PVC gloves i.e. 0.007 µg Sn/kg bw/day for DBT.

Earplugs

Earplugs are usually made from flexible PVC or polyurethane foam both of which may contain organotins. For the purposes of this analysis, it will be assumed that the earplugs are 1.5 cm in length and 1.0 cm in diameter which equates to a contact area (for two ears) of 3.9 cm^2 which is equivalent to about 0.5% of the contact area assumed for PVC gloves (see S5.3.6). Assuming (as for the PVC gloves), a daily wearing of eight hours per day, the average daily uptake will be 0.5% of that presented in Table 5.13 as shown in Table 5.14.

Table 5.14: Calculation of Uptake of Organotins from (PVC) Earplugs

Parameter	DBT	TBT	DOT	TPT	Sum
Uptake per wearing (µg Sn) [1]	0.009	<0.001	0	0	0.010
Daily uptake (µg Sn/kg bw/day)	**<0.001**	**<0.001**	**0**	**0**	**<0.001**

Notes: [1] *Values 0.5% of those presented in Table 5.10 based on a contact area approaching 4 cm^2 and a daily exposure of 8 hours. Further detail on nature and sizes of earplugs may be found at: www.aearo.com/html/industrial/pdf/TipsTools2001.pdf*

Rigid PVC Products

General emissions from the use of PVC products containing organotin stabilisers are considered in Section 3.4 (and these were also considered in the earlier 2002 and 2003 Reports). Further comments on the specific products to be considered are listed in Table 5.15.

Table 5.15: Exposure Scenarios for Organotin Stabilisers in Rigid PVC Products

Article	**Comment**
Profile extrusions (window frames)	Exposure from window frames considered in general emissions to the environment. Not considered to present a significant direct consumer exposure route (beyond those already considered)
Foamed sheeting	Considered below
Pipes, distinguishing between drinking water pipes and other pipes	Considered below
Thin rigid film	Considered below
Credit cards	Considered below
Fencing	As for profile extrusions, not considered to present a significant direct consumer exposure route
Electrical conduit	
PVC sandals	Considered below

Foamed Sheeting

PVC foamed sheeting is used in a range of specialist industries (such as aerospace, marine transport and wind energy) due to its rigidity, light weight and moisture resistance. It is also used in more common applications such as notice boards.

However, no particular consumer use has been identified with significant contact areas and/or times which would lead to significant uptakes (in comparison to those already being considered).

Drinking Water and Other Pipes

More than half of all pipes (and fittings) are now plastic. The major use of plastic pipes (which is increasing) is in drainage and sewerage (more than 50%), followed by service applications including gas/water distribution and heating/cooling systems (approaching 30%). The EU plastic pipe market is of the order of 2,500 kt/yr of which PVC accounts for over 60% (Raynaud, 2004). Against this background, there is a reasonable chance that the drinking water from a domestic tap will have passed through a PVC pipe.

Although only organotin stabilisers are used for PVC pipes and fittings in North America, the dominant stabiliser throughout the rest of the world is lead which accounts for an estimated 92% of the European stabiliser use in PVC pipes and fittings (Schiller & Fischer, 2004). However with the declared industry aim of reducing the use of lead stabilisers, there will be a need for replacement stabilisers systems which could include organotins (Vinyl 2010, 2005). ETINSA has advised that although butyltin stabilisers are used in North America for PVC drinking water pipes, octyltin stabilisers are used in Europe.

The migration of stabilisers from PVC pipes to drinking water is much lower for organotins than for other stabilisers. The organotin migration rate is reported to be less than 0.2 ng/cm^2/hr (Schiller & Fischer, 2004) (cf around 1 ng/cm^2/hr for flexible PVC).

Sadiki & Williams (1999) report butyltin levels of up to 52.5 ng Sn/L in Canadian drinking water conveyed through PVC pipes. More generally, measurements of organotins in tap water in Canada were found to be below the detection limit of 0.5 ng/L (WHO, 2004). McLellan (2002) reports that although, in the US, much higher levels of up to 71 µg Sn/L (mean 5.6 µg Sn/L) in CPVC[49] pipes can be measured in new pipes and fittings, these levels decay rapidly after a few days exposure to potable water.

In those (relatively few) areas served by drinking water passing through organotin stabilised PVC pipes, a concentration of 1 ng Sn/L will be assumed. It is therefore perhaps not surprising that organotins were not detected during a survey of European tap water (Fraunhofer Institute, 2003). With an assumed concentration of 1 ng Sn/L and a daily water intake of two litres, the organotin uptake can be derived as shown in Table 5.16.

Table 5.16: Calculation of Uptake of Organotins from (PVC) Drinking Water Pipes

Parameter	**DBT**	**TBT**	**DOT**	**TPT**	**Sum**
Daily intake (µg Sn/day)	0	0	0.002	0	0.002
Adult uptake (µg Sn/kg bw/day)	**0**	**0**	**<0.001**	**0**	**<0.001**
Child uptake (µg Sn/kg bw/day)	**0**	**0**	**<0.001**	**0**	**<0.001**

Thin Rigid Film and Credit Cards

Clear rigid PVC film is used in a wide range of packaging (including that for food products as considered further below). Layers of rigid PVC film are also extensively used for credit (and similar) cards. Although the typical contact time between consumers and such products is very unlikely to exceed, say, two hours/week, it is possible to conceive of some people with greater contact times. For example, people working in the warehouses and retail outlets may handle large numbers of products packaged in PVC. Similarly, staff manning busy check-outs at retail stores could handle a few hundred cards per day.

For credit cards, the contact area is relatively small at, say, 3cm^2, and the overall contact time may be two hours/day (for some workers). For people handling products packaged in PVC, the contact area could be significantly greater at, say, 400 cm^2 (both hands). Taking this as a worst case with an assumed contact time of two hours/day and a migration rate of 0.2 ng Sn/cm^2/hr, the daily uptake (for some workers) could be as high as 160 ng Sn/day. The resultant daily uptakes are shown in Table 5.17.

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[49] McLellan (2002) distinguishes between PVC and chlorinated PVC (CPVC) pipes with CPVC pipes having higher butyltin concentrations.

Table 5.17: Calculation of Worst-Case Uptake of Organotins from Thin Film (Credit Cards)					
Parameter	**DBT**	**TBT**	**DOT**	**TPT**	**Sum**
Daily intake (µg Sn/day)	0.053	0.001	0.106	0	0.160
Adult uptake (µg Sn/kg bw/day)	**0.001**	**<0.001**	**0.002**	**0**	**0.003**
Note: Distribution of intake by individual organotins based on relative usage of compounds (for this use) as shown in Table 3.10					

PVC Sandals

Rigid PVC can be used in sandals (and other footwear). However, it would be expected that greater degrees of direct contact and exposure would be associated with the use of flexible PVC sandals. The associated uptake (per kg bw) will be of a similar order for that calculated for PVC gloves and this result will be used for both adults and children (since the uptake will vary with foot size).

5.2.7 Catalysts

The Specification (see Annex 1) requires further consideration to be given to the emissions of TBT and DBT, DOT, and TBT-impurities when used as a catalyst in:

- PU Technology including:
  - PU Foam used in upholstered furniture, mattress filling, car seats, car dashboards, insulation panels;
  - PU Adhesives as used in car windscreens, two-component household adhesives, composite door panels;
  - PU Coatings as used in top coatings for automobiles, boats, planes, wood varnishes, repair coatings, industrial outdoor flooring, heavy duty flooring in industry and sports; and
  - PU Elastomers as used in shoes, shoe soles (outer contact);
- antioxidants for polyolefins as used in nappies and hygiene products;
- any silicones used in automotives, computers, construction, sealants, dental mouldings or adhesives; and
- alkyd resins as used in paints.

General emissions from the use of products containing organotin catalysts are considered in Section 3.5 (and these were also considered in the earlier 2002 and 2003 Reports). In addition, more detailed consumer exposure models were previously considered in detail as shown in Table 5.18.

Table 5.18: Exposure Scenarios for Products containing Organotin Catalysts	
Article	**Comment on Scenarios in Earlier Reports**
PU articles	Not considered in detail
Nappies	Child exposure considered in 2002/2003 Reports
Female hygiene products	Adult exposure considered in 2002/2003 Reports
Cookies & baking paper	Adult/child exposure considered in 2002/2003 Reports
Dental mouldings	Adult exposure considered in 2003 Report
Silicone sealants	Not considered in detail
Silicone moulds	Not considered in detail

PU Articles

The general use of organotin catalysts in PU articles and associated emissions to the environment has been accounted for in earlier analysis. Although used in a wide range of consumer articles, very few are associated with extensive direct contact areas and/or times. For this reason, no specific additional consumer exposure calculation is required.

Nappies

Butyltin compounds have been measured in nappies and reported in a number of sources. The maximum values reported are taken here for the worst-case exposure assessment. As indicated above, it is understood that the concentrations in nappies may relate to their presence in the nonwoven topsheets of nappies. It is thus assumed that the concentration in the topsheet (in contact with the skin) is ten times the reported values.

It is estimated that the area of topsheet is 0.15m^2 (all assumed in contact with the skin) and that the topsheet has a density of 800 kg/m^3 and a thickness of 1mm. The resultant amount of organotin compounds in a single nappy is thus as reported in Table 5.19.

Table 5.19: Estimation of Total Butyltins in a Nappy

Parameter	**DBT**	**TBT**	**Sum**
Reported concentration (µg cation/kg)	34.7	24	
Concentration in topsheet (µg Sn/kg) [1]	177	98	275
Mass in nappy (µg Sn) [2]	21.2	11.8	33.0

Notes: [1] *Assumed ten times concentration in topsheet compared to whole nappy.*
[2] *Assumed area of 0.15m^2 with density of 800 kg/m^3 and thickness of 1mm.*

As a maximum, it is assumed that 1% of the organotin catalyst migrates to the skin at each wearing[50] and that dermal absorption is 10%. Nappies may be estimated to be changed 5 times per day and worn every day of the year. The total exposure for the 8kg child can thus be estimated as in Table 5.20.

Table 5.20: Calculation of Uptake of Butyltins from Nappies

Parameter	**DBT**	**TBT**	**DOT**	**TPT**	**Sum**
Exposure per nappy (µg Sn) [1]	0.021	0.012	0	0	0.033
Average daily exposure (µg Sn) [2]	0.106	0.059	0	0	0.165
Average uptake (µg Sn/kg bw/day)	**0.013**	**0.007**	**0**	**0**	**0.021**

Notes: [1] *Assumed 1% migration of catalyst from nappy and dermal uptake of 10%.*
[2] *Based on five nappies worn per day.*

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[50] This is expected to be much higher than would be expected under normal conditions of wearing, since the catalyst is generally well bound within the polymeric structure.

Female Hygiene Products

A report by the Dutch National Institute for Public Health and the Environment (RIVM, 2000) indicates that a concentration of 33.1 mg/kg of dioctyltin has been measured in sanitary pantyliners. This equates to a concentration expressed as tin of 11,381 µg/kg.

It was estimated in the source document (RIVM, 2000) that the mass of product is 10g, giving a mass of dioctyltin per product of 103.2 µg/product as Sn. The RIVM report also indicates that a maximum of 4% of the fluid from such products may resurface, giving a maximum quantity in contact with the skin of 4.1 µg Sn/product. As a very worst-case, it is assumed that the dermal absorption is 50%. It is further assumed that five such products are used on 60 days in the year. The results of the exposure calculation are presented in Table 5.21.

Table 5.21: Calculation of Uptake of Dioctyltin from Sanitary Pantyliners

Parameter	DOT	Sum (DBT/TBT/DOT/TPT)
Concentration in product (µg Sn/kg)	11,381	11,381
Mass dioctyltin in 10g product (µg Sn)	114	114
Uptake per event (µg Sn) [1]	4.6	4.6
Daily uptake for whole person (µg Sn/day) [2]	22.8	22.8
Adult uptake (average) (µg Sn/kg bw/day) [3]	**0.062**	**0.062**

Notes: [1] *Maximum 4% to skin and dermal absorption assumed at 50% as worst-case .*
[2] *Assumed worn five times per day*
[3] *Assumed worn for 60 days in the year.*

Baking Paper & Cookies

This issue is considered in Section 5.2.10.

Dental Mouldings

For some dental treatments (such as preparing for a crown), the dentist will take a dental impression using a moulding material which may be a silicone containing organotin catalysts[51] (usually dibutyltin laureate). Mouldings may involve 50g of material of which organotins would account for 50mg Sn (at 0.1% Sn concentration). Loss, and resultant ingestion, of 1% of this material would lead to an intake of 0.5mg Sn per impression. This analysis (as previously presented in the 2003 Report) has recently been reviewed and accepted by industry (CES, 2005).

Although there will be groups of patients with an average of two impressions/year[52], it is highly unlikely that such a rate would be sustained throughout a lifetime. Industry analysis of national dental statistics from Germany suggests that a more 'reasonable' figure to use would be 0.43 impressions/year (CES, 2005). However, at this stage, the

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[51] In Germany, over 40% of dental impressions utilise silicones containing organotins (CES, 2005).

[52] By way of example, a local Norfolk dentist has 500 patients and does 1,000 impressions/year.

focus is on the worst-case analysis and consideration is therefore given to those at higher risk as shown in Table 5.22.

Table 5.22: Calculation of Uptake of Dibutyltin from Dental Moulding Material

	DBT	**Sum (DBT/TBT/DOT/TPT)**
Mass dibutyltin[1] in moulding (mg Sn)	50	50
Intake of material per moulding[2]	1%	1%
Intake per year (for 2 mouldings/year) (mg Sn)	1.0	1.0
Average daily uptake (µg Sn/day)	2.74	2.74
Adult uptake (average) (µg Sn/kg bw/day)	**0.046**	**0.046**

Notes: 1) For simplicity, all the tin catalyst present has been assumed to be dibutyltin.

2) Although ETICA suggests up to 5%, it is considered that 1% is a more reasonable worst case (for repeated exposures). The intake will be primarily due to the ingestion of residual material left in the mouth rather than from migration.

Silicone Sealants

A wide range of one-part silicone sealants are used in the home by DIY (do-it-yourself) consumers. These may contain organotin catalysts - such as DBT laurate - at low concentrations (0.01-0.1%) as evidenced by the results of a recent survey of sealants (Nilson *et al*, 2004). The mass in a typical DIY sealant tube (for use in caulking guns) is 500g which could therefore contain up to 0.5g DBTL (or 94 mg Sn). It will be assumed that the (unskilled) DIY consumer directly handles about 5% of the product applied which, together with an assumed 1% migration to the skin and 10% dermal uptake, enables the resultant intake to be determined as shown in Table 5.23.

Table 5.23: Calculation of Uptake of Dibutyltin from Silicone DIY Sealants

	DBT	**Sum (DBT/TBT/DOT/TPT)**
Mass of DBTL (as mg Sn) in 500 g sealant	94	94
Mass of DBTL handled (as mg Sn)	4.7	4.7
Uptake per use [1] (µg Sn)	4.7	4.7
Average daily uptake (µg Sn/day) for 20 uses/yr	0.26	0.26
Adult uptake (average) (µg Sn/kg bw/day)	**0.004**	**0.004**

Notes: 1) Assuming 1% migration and 10% dermal uptake.

Silicone Moulds

As indicated in S2.4.5, DIY kits for domestic consumers (or, indeed, SMEs) are readily available in the EU for the making of silicone moulds using a two-part system (such as the 'red silicone rubber' and DBT catalyst). Unlike the other consumer uses being considered, such kits expose consumers to pure solutions of DBTs. Such specialised uses may be compared with artists handling paints containing hazardous materials (such as cadmium and lead) or with collectors of antique barometers handling mercury.

However, within the context of this assessment, a few drops of pure DBTL (or similar compound) could result in a significant uptake. Assuming one or two drops represent 0.2

mL, this would equate to about 200 mg DBTL (38 mg Sn). If this was to come into contact with the skin on a regular basis, an estimate of the resultant uptake for the frequent user of such products can be made as presented in Table 5.24.

Table 5.24: Calculation of Uptake of Dibutyltin from 2-Part Silicone Moulds

	DBT	Sum (DBT/TBT/DOT/TPT)
Mass of DBTL handled (as mg Sn)	38	38
Uptake per use [1] (µg Sn)	38	38
Average daily uptake (µg Sn/day) for 50 uses/yr	5.2	5.2
Adult uptake (average) (µg Sn/kg bw/day)	**0.087**	**0.087**

Notes: 1) Assuming 1% migration and 10% dermal uptake.

5.2.8 Biocides and Other Uses

The Specification (see Annex 1) requires further consideration to be given to the emissions of TBT, and also of TPT if found reasonable, when used as a biocide in:

- wooden articles (impregnated);
- heavy industrial textiles;
- foot spray;
- cycling shorts padding;
- non-allergenic pillows; and
- shoe insoles.

General emissions from the use of products containing organotin biocides are considered in Section 3.6 (and these were also considered in the earlier 2002 and 2003 Reports). In addition, more detailed consumer exposure models (for TBT) were previously considered in detail in the 2002 and 2003 Reports as shown in Table 5.25.

Table 5.25: Exposure Scenarios for Products containing Organotin Biocides

Article	Comment on Scenarios in Earlier Reports
Wooden articles (impregnated)	Not considered in detail
Heavy industrial textiles	Disregarded in 2002/2003 Reports as use discontinued
Foot spray	Adult exposure considered in 2002/2003 Reports
Cycling shorts padding	Adult exposure considered in 2002/2003 Reports
Non-allergenic pillows	Child exposure considered in 2002/2003 Reports
Shoe insoles	Adult exposure considered in 2002/2003 Reports

The environmental risk associated with a wooden building treated with TBT has already been examined (see Section 3.9.2). There is no indication that there are further significant direct risks to consumers associated with such articles and the same applies to heavy industrial textiles. On this basis, these issues are not considered further.

Whilst TPT may still be detected in the aquatic compartment, primarily as a result of its use in anti-fouling paints, and in fish and fishery products, current information suggests that TPT is not used in consumer products. As such, TPT is not considered further in relation to biocides.

The remaining issues are outlined below - where these reproduce (with minor revisions) the calculations from the 2003 Report.

Foot Spray

The 2003 Report stated that a foot spray for prophylaxis of athlete's foot is sold in Germany (FGG, 2001). Although the Consultants have since been advised that such a product was withdrawn from the German market in 2003, the identified product was found (in June 2005) to be readily available in the new Member States. With this in mind, the calculations presented in the 2003 Report have been retained.

The foot spray contains TBT benzoate at a concentration of 83 mg/kg. The resultant concentration expressed as tin is 23,900 µg/kg.

It is assumed that 1g of the foot spray is applied to each foot twice per day with 20% dermal absorption (as a worst-case estimate taking into account the potential for use on damaged skin). It is further assumed that the spray will be used twice per day for up to eight weeks in the year. An annualised average uptake can thus be derived, as indicated in Table 5.26.

Table 5.26: Calculation of Uptake of Tributyltin from Foot Spray

Parameter	**TBT**	**Sum (DBT/TBT/DOT/TPT)**
Mass of TBT benzoate in foot spray (mg/kg)	83	83
Mass of TBT in foot spray (µg Sn/kg)	23,900	23,900
Mass of TBT on skin per application (µg Sn)	47.8	47.8
Daily uptake of TBT whole person (µg Sn/day) [1]	19.1	19.1
Adult uptake (average) (µg Sn/kg bw/day) [2]	**0.049**	**0.049**

Notes: [1] *Assumed 1g applied to each foot twice per day with dermal uptake of 20%.*

[2] *Assumed that spray is applied for eight weeks in the year.*

Cycling Shorts Padding

TBT has been detected in the padding of cycling shorts, used to prevent odour after use (BgVV, 2000). Reported concentrations were 110 mg/kg as TBT cation, equal to 45 mg/kg expressed as tin.

In order to estimate exposure, it is assumed that the padding has a mass per unit area of 1.2 kg/m^2, following the approach adopted in the source document (BgVV, 2000). It is further assumed that the migration rate to skin will be 1% per wearing. Although, in the BgVV document absorption into skin was assumed at 20%, the value of 10% derived above is used. It is assumed that the area of padding in contact with the body is 0.02 m^2 (200 cm^2) and that the person cycles every day. Table 5.27 reports the resulting exposure calculations.

Table 5.27: Calculation of Uptake of Tributyltin from Cycling Shorts Padding

Parameter	TBT	Sum (DBT/TBT/DOT/TPT)
Concentration of TBT in padding (µg Sn/kg)	45,015	45,015
Mass of TBT in area exposed (µg Sn) [1]	1,080	1,080
Exposure per person per wearing (µg Sn) [2]	1.1	1.1
Average Adult daily uptake (µg Sn/kg bw/day)	**0.018**	**0.018**

Notes: [1] *Based on material weight of 1.2 kg/m^2 and exposure area of 0.02 m^2.*
[2] *Assumed that migration to skin is 1% with dermal absorption of 10%.*

Non-allergenic Pillows

Information from the Department of Trade and Industry (DTI, 2002) on sampling of tributyltin and dibutyltin in consumer products indicates that these substances have been detected in the goose feathers used in non-allergenic pillows. Table 5.25 reports the concentrations.

It is assumed that the total mass of such a pillow is 1 kg and that, in use, a maximum of 1% migrates to the skin. Using the 10% dermal absorption utilised above and assuming that such an exposure occurs once a day, the estimated exposure in Table 5.28 has been calculated.

Table 5.28: Calculation of Uptake of Organotin Compounds from Non-Allergenic Pillow

Parameter	DBT	TBT	Sum (DBT/TBT/DOT/TPT)
Reported concentration in pillow (µg cation/kg) [1]	63.1	285	
Concentration expressed as tin (µg Sn/kg)	32.1	117	149
Total mass in 1kg pillow (µg Sn)	32.1	117	149
Uptake per person (µg Sn/day) [2]	0.032	0.117	0.149
Adult uptake (µg Sn/kg bw/day)	**0.001**	**0.002**	**0.002**
Child uptake (µg Sn/kg bw/day)	**0.004**	**0.015**	**0.019**

Notes: [1] *DTI (2002).*
[2] *Assumed migration to skin of 1% and dermal uptake of 10%.*

Shoe Insoles

Dibutyltin and tributyltin have been measured in samples taken from shoe insoles sold in the UK (DTI, 2002). The samples taken relate to the upper part of the insole, that which comes into contact with the foot. The maximum concentrations measured were as detailed in Table 5.29.

Table 5.29: Concentration of Organotins in Shoe Insoles

	DBT	TBT
Concentration in insole (µg cation/kg)	4,790	19,701
Concentration in insole (µg Sn/kg)	2,440	8,060

Source: DTI (2002)

It is assumed that the mass of one insole is 0.15kg, based upon an assumed density of 500 kg/m^3 and a thickness of 5mm. The area of contact with the feet will be around 0.06m^2 (600 cm^2) and thus the total mass of organotin to which the consumer is exposed can be calculated.

In order to estimate the uptake of the organotin compounds, it is assumed that 1% of the TBT in the product migrates to the skin at each wearing. In the 2002 Report, it was estimated that the subsequent dermal absorption would be a maximum of 10%. For the 2003 Report, further data on measured absorption rates were provided by industry as summarised in Table 5.30.

Table 5.30: Measured Organotin Skin Absorption Rates

Substance	**Ref**	**Exposure (mg/cm^2)**	**Test duration**	**Skin absorption (μg tin/cm^2/hr)**		**Max% absorbed by human skin**	**Max % not accounted for**
				Human	**Rat**		
DBTC	1	0.5 (as DBTC)	24hrs	1.0 (1-8 hrs) 0.56 (24 hrs)	2.85 (1-4 hrs) 1.28 (24 hrs)	6.6%	more than 50%
DBT bis(2-EHMA)	2	21.1 (as tin)	24hrs	0.013 (16-24 hrs) 0.007 (24 hrs)	3.88 (16-24 hrs) 2.17 (24 hrs)	0.001%	more than 45%
DOTC	3	1.0 (as DOTC)	24hrs	0.001 (24 hrs)	4.3 (1st hour) 0.014 (24 hrs)	c0.015%	more than 45%
DOT bis(2-EHMA)	4	17.0 (as tin)	24hrs	<0.001	0.033 (max)	0.0001%	75%
TBT0	5	0.3 (as TBTO)	8hrs	c0.28 (8hrs)	not tested	2.2%	not given
TBTN	5	0.6 TBTN	8hrs	c0.15 (8hrs)	not tested	0.6%	not given
TBTM/ MA	6	9.62	8 hrs	0.01 (8hrs)	not tested	0.003%	not given

References:

1) CTL (2003): Report CTL/JV1698/Regulatory/Report dated 9 January 2003.

2) CTL (2003): Report CTL/JV1699/Regulatory/Report dated 8 January 2003.

3) CTL (2003): Report CTL/JV1700/Regulatory/Report dated 8 January 2003.

4) CTL (2003): Report CTL/JV1701/Regulatory/Report dated 8 January 2003.

5) Inveresk Research (not dated): Report No 12617 (1 page summary only).

6) Inveresk Research (not dated): Report No 15347 (1 page summary only).

Based on the data presented, three observations can be made:

- the skin absorption rates for humans are significantly lower than for rats;
- the results need to be treated with caution since, in many cases, much of the test material was unaccounted for; and
- the original estimate of a maximum of 10% absorption as used in the 2002 Report appears robust and has therefore been retained in both the 2003 Report and in this analysis.

If it is assumed that the insoles are worn each day in order to provide a maximum value for the annualised uptake of the organotin compounds, the results presented in Table 5.31 are obtained.

Table 5.31: Calculation of Uptake of Organotin Compounds from Insoles

Parameter	**DBT**	**TBT**	**Sum (DBT/TBT/DOT/TPT)**
Total mass in insoles (µg Sn) [1]	366	1209	1575
Uptake per person (µg Sn/day) [2]	0.37	1.21	1.58
Relative uptake (µg Sn/kg bw/day)	**0.006**	**0.020**	**0.026**

Notes: [1] *Assumed insole density of 500 kg/m*^{3} *and a thickness of 5mm. Area of contact with feet estimated at 0.06m*^{2}.

[2] *Assumed migration of 1% to skin at each wearing, with dermal absorption of 10%.*

5.2.9 Human Exposure to TPT

The Specification (see Annex 1) requires the study to:

- identify possible sources of exposure (of TPT) to humans, via products, articles, food intake or environment; and
- if appropriate, quantify the levels of exposure.

Although residual amounts of TPT have been detected in the environment, these are associated with its past use in anti-fouling paints. Although TPT compounds are available in the marketplace, it is understood that these are intended for use in laboratories. No reports have been identified which suggest that significant amounts of TPT are currently used in any consumer/industrial products within the EU.

The prior use of TPT in anti-fouling paint (which may still be present on some hulls) leads to TPT being found in aquatic organisms which, in turn, are destined for human consumption as discussed below.

5.2.10 Intake from Food and Food Contact Materials

The Specification (see Annex 1) envisaged the following exposure scenarios to be provided by DG SANCO and EFSA:

- DOT used as a catalyst for baking papers;
- TBT biocide as used in marine anti-fouling paints – effectively consumer intake through fish and shell-fish consumption;
- DOT as a stabiliser in single-layer PVC for food contact applications;
- DOT as a stabiliser in PVC for food contact, when the food contact material is laminated with polyethylene; and
- any other identified food contact application.

These are discussed in turn below.

Baking Paper & Cookies

In the 2002 Report, estimates were provided for the intake of mono, di and tributyltin compounds in cookies baked in silicone coated baking paper (based on data from Japan). Since this led to significant risks to consumers, this issue was reviewed by the Scientific Committee on Food. Its findings (SCF, 2003) may be summarised as follows:

- the daily intake of MBT, DBT and TBT (based on the consumption of 100g of cookies per day by a 60kg adult) would be equivalent to 0.29, 0.61 and 0.01 µg Sn/kg bw/day respectively[53];
- there is no production of silicone coated baking paper containing butyl tins within the EU (although such paper could be imported) but 1.5% of the market does use dioctyl tins; and
- industry has advised SCF that the supply (globally) of tin-catalysed silicone coatings for baking paper would cease by the end of 2005 at the latest.

Subsequent to the publication of the SCF review, industry (CES, 2003) advised that the EU production of tin-catalysed silicone coatings for baking paper ceased at the end of 2002.

As already noted, the finding from Germany that 50% of baking paper sampled in 2003 contained butyltins (DG SANCO, 2005) does not provide assurance that the SCF findings (in relation to the use of organotins in baking paper) are robust. It also raises questions as to the validity of some of the views expressed by industry.

With these points in mind, it is proposed that the example of cookies cooked on silicone baking paper is retained (with butyltins rather than DOT) as shown in Table 5.32.

Table 5.32: Calculation of Uptake of Organotins from Cookies

Parameter	DBT	TBT	DOT	TPT	Sum
Adult uptake (µg Sn/kg bw/day)	**0.610**	**0.010**	**0**	**0**	**0.720**
Child uptake (µg Sn/kg bw/day)	**2.287**	**0.037**	**0**	**0**	**2.325**

Note: Uptakes based on daily consumption of 100g of cookies by a 60kg adult and 50g by an 8 kg child.

Consumer Intake (Fish & Fishery Products)

EFSA (2004) reports the intakes DBT, TBT and TPT via fish and fishery products and these have been presented in Section 5.2.2.

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[53] It should be noted that these values are very similar to those of 0.21, 0.53 and 0.01 µg Sn/kg bw/day presented in the 2002 Report (Table 6.11) for MBT, DBT and TBT respectively.

Intake via PVC Food Packaging

Migration from organotin-stabilised PVC that is intended to come into contact with foodstuffs has been measured according to the required test protocols (Pira International, 2001). In an opinion on fatty food intakes, the Scientific Committee on Food (2002) states that 200g per day is the 'realistic maximum' intake. Thus, by reducing the figures derived for an intake of 1 kg/day by a factor of 0.2 provides a realistic worst case. For the child exposure assessment, it has been assumed that the amount eaten per kg bodyweight is four times higher than for an adult giving a proportionally higher level of intake. The associated uptake calculation presented in the 2003 Report is reproduced in Table 5.33.

Table 5.33: Calculation of Intake of Organotins from Food Packaged in PVC (2003 Report)

Intake	**Fat intake**	**DOT**	**Sum (DBT/TBT/DOT/TPT)**
Intake per adult[1] (µg Sn/day)	1 kg/day	17	17
Adult intake (µg Sn/kg bw/day)	1 kg/day	0.28	0.28
Adult intake (µg Sn/kg bw/day)	**200 g/day**	**0.057**	**0.057**
Child intake[2] (µg Sn/kg bw/day)	**n/a**	**0.227**	**0.227**

Notes: [1] Based on migration into olive oil(10 days at 40^{o}C, Pira International, 2001).
[2] Child intake (per kg bw) taken as four times adult intake.

For this Report, further migration tests have been undertaken by Fabes (2005) using 12 different PVC samples stabilised with MOT/DOT-EHMA. The most striking finding is that the nature of the PVC and whether or not it was laminated with polyethylene (PE) had very little influence on the migration rates[54]. In other words, the migration was governed by the food simulant and the results are summarised in Table 5.34.

Table 5.34: Migration of DOT-EHMA from PVC Samples

Simulant Class	**Simulant**	**Duration**	**Temp.**	**N samples**	**Migration (µg Sn/kg)**	
					Median	**Max**
Aqueous	3% acetic acid	10d	40°C	3	n.d. (<0.7)	n.d. (<0.7)
	10% ethanol	10d	40°C	12	n.d. (<0.7)	1.2
Fatty	Tenax	10d	40°C	4	0.2	0.4
	Iso-octane	2d	20°C	12	2.0	10.3
	95% ethanol	10d	40°C	5	8.8	31.3

Source: Fabes (2005) with migration results adjusted to correct molecular weight of DOT-EHMA.

Using the maximum value of 31.3 (µg Sn/kg) as the worst case, the associated intake can be determined using the simple approach used previously as shown in Table 5.35.

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[54] Four of the 12 sampels contained a PE layer of approximately 50 µm thickness and Fabes (2005) concludes that the: *PE Layer in PVC/PE laminates has no barrier properties for the transfer of organotin into food.*

Table 5.35: Revised Calculation of Intake of Organotins from Food Packaged in PVC			
Intake	**Fat intake**	**DOT**	**Sum (DBT/TBT/DOT/TPT)**
Intake per adult[1] (µg Sn/day)	1 kg/day	31.3	31.3
Adult intake (µg Sn/kg bw/day)	1 kg/day	0.52	0.52
Adult intake (µg Sn/kg bw/day)	**200 g/day**	**0.104**	**0.104**
Child intake[2] (µg Sn/kg bw/day)	**n/a**	**0.417**	**0.417**
Notes: [1] Based on migration into 95% ethanol (10 days at 40°C, Fabes, 2005). *[2] Child intake (per kg bw) taken as four times adult intake.*			

Using the Fabes data, industry commissioned the UK Central Science Laboratory to undertake a comprehensive analysis (CSL, 2005) across a wide range of foodstuffs (together with estimates of the associated percentages of those packaged in rigid PVC, contact areas and amounts consumed) in order to determine an overall intake of DOT for consumers. The results are summarised in Table 5.36.

Table 5.36: DOT Uptake from Food Packaged in PVC			
Consumer	**Median Intake (µg Sn/kg bw/day)**	**97.5% Intake (µg Sn/kg bw/day)**	**Major Contributors (by food group)**
Child	0.005	0.054	Bakery 34%, Dairy 18%, Meat 11%
Adult	0.004	0.022	Bakery 23%, Dairy 20%, Meat 19%
Source: CSL (2005).			

Since the purpose of this Report is provide an estimate of the risks to the environment and to consumers, preference has been given to the results of the CSL work on the grounds that an attempt has been made to model the actual patterns of food usage packaged in rigid PVC (albeit based on UK dietary habits).

Other Food Contact Applications

The analysis of intakes via foodstuffs discussed above does not extend to drinks. As reported in Table 2.6, an estimated 278 t of organotin stabilisers are used in PVC bottles. Although the vast majority of plastic bottles are PET (polyethylene terephthalate) or HDPE, PVC bottles are used for a range of domestic products (such as shampoo and cleaners). In relation to drinks, the use of PVC bottles tends to be restricted to the larger squash bottles with handles[55]. An associated intake calculation is presented in Table 5.37 for a young child regularly drinking squash.

Table 5.37: DOT Intake from PVC Squash Bottle (Child)		
Parameter	**Value**	**Comment**
Squash content/bottle	2kg	Standard 2L PVC bottle
DOT content (µg Sn/kg)	1.2	Maximum ‘aqueous’ value from Table 5.34
Child intake of concentrate (kg/day)	0.1	0.5 litre consumed with a 1:5 dilution ratio
DOT intake per child (µg Sn/day)	0.12	
Child intake (µg Sn/kg bw/day)	**0.015**	8kg child

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[55] See, for example, *recycling specifics* page on www.recycle-more.co.uk

5.3 Summary of Exposure Assessments

The results for the adult and child exposure assessments are summarised in Tables 5.38 and 5.39 respectively.

Table 5.38: Daily Uptakes for Adult Consumers (µg Sn/kg bw/day)

Source	Ref.	DBT	TBT	DOT	TPT	Sum
Fish/fishery products (median)	S5.2.2	0.002	0.004	0	0.002	0.007
Fish/fishery products (high)		0.024	0.032	0	0.016	0.071
Via environment (regional)	S5.2.3	<0.001	0.003	0.001	0	0.005
Via environment (worst case)		0.003	1.273	0.411	0	1.273
Household dust (worst case)	S5.2.4	0.010	0.003	0.004	<0.001	0.017
T-shirts (worst case)	S5.2.6	<0.001	0.002	0.023	0	0.025
PVC gloves (worst case)		0.033	<0.001	0	0	0.033
PVC bags (worst case)		0.007	<0.001	0	0	0.007
Earplugs (worst case)		<0.001	<0.001	0	0	<0.001
Drinking water pipes (worst case)		0	0	<0.001	0	<0.001
Rigid film (worst case)		0.001	<0.001	0.002	0	0.003
PVC sandals (worst case)		0.033	<0.001	0	0	0.033
Female hygiene products (worst case)	S5.2.7	0	0	0.062	0	0.062
Dental mouldings (worst case)		0.046	0	0	0	0.046
Silicone sealant		0.004	0	0	0	0.004
2-part silicone moulds		0.087	0	0	0	0.087
Foot spray (worst case)	S5.2.8	0	0.049	0	0	0.049
Cycling shorts (worst case)		0	0.018	0	0	0.018
Non-allergenic pillows (worst case)		0.001	0.002	0	0	0.002
Shoe insoles (worst case)		0.006	0.020	0	0	0.026
Baking paper/cookies (worst case)	S5.2.10	0.610	0.010	0	0	0.720
PVC food packaging (median)		0	0	0.004	0	0.004
PVC food packaging (high)		0	0	0.022	0	0.022

Table 5.39: Daily Uptakes for Child Consumers (µg Sn/kg bw/day)

Source	Ref.	DBT	TBT	DOT	TPT	Sum
Fish/fishery products (median)[1]	S5.2.2	0.008	0.016	0	0.008	0.028
Fish/fishery products (high)[1]		0.096	0.128	0	0.064	0.284
Via environment (regional)[1]	S5.2.3	0.001	0.012	0.005	0	0.018
Via environment (worst case)[1]		0.012	5.092	1.644	0	5.092
Household dust (worst case)	S5.2.4	0.078	0.026	0.013	0.001	0.117
T-shirts (worst case)	S5.2.6	0.002	0.015	0.171	0	0.189
Paddling pool (worst case)		0.003	<0.001	0	0	0.003
Mouthing PVC toys (worst case)		0.002	<0.001	0	0	0.002
Drinking water pipes (worst case)		0	0	<0.001	0	<0.001
PVC sandals (worst case)		0.033	<0.001	0	0	0.033
Nappies (worst case)	S5.2.7	0.013	0.007	0	0	0.021
Non-allergenic pillows (worst case)	S5.2.8	0.004	0.015	0	0	0.019
Baking paper/cookies (worst case)	S5.2.10	2.287	0.037	0	0	2.325
PVC food packaging (median)		0	0	0.005	0	0.005
PVC food packaging (high)		0	0	0.054	0	0.054
PVC squash bottle (worst case)		0	0	0.015	0	0.015

Note: [1] *Child uptakes (per kg bw) for food intakes(and via the environment) have been derived by increasing the corresponding adult intakes (per kg bw) by a factor of four.*

6. HUMAN HEALTH ASSESSMENT

6.1 TDI Values used in this Analysis

As stated in the Specifications (see Annex 1), a 'group' Tolerable Daily Intake (TDI) is to be used in this Report in accordance with the view of CSTEE (see Annex 2):

> *As the common endpoint of thymus atrophy is affected at similar dietary level of these compounds, the CSTEE again proposes that a group TDI value 0.27µg/kg bw/day for TBT, DBT, DOT and TPT as chloride should be adopted, or 0.1 µg/kg bw/day as Sn. Furthermore, assuming a similar mode of action and in the absence of data that contradict it, it seems rational to consider the effects of these chemicals as additive.*

It should be noted that the effects of particular levels of organotin intake have (conservatively) been taken to be the same irrespective of the nature of the organotin containing material and route of uptake by the body.

6.2 Risk Characterisation for Consumers

6.2.1 Worst-Case Analysis (Adults)

The exposure assessment for adults (worst-case) was presented in Table 5.38 which enables the %TDI to be directly derived as shown in Table 6.1.

Table 6.1: Worst-Case Analysis for Adult Consumers

Source	**Sum**[1]	**%TDI**	**>20%TDI?**
Fish/fishery products (high)	**0.071**	**71%**	**Yes**
Via environment (worst case)	**1.273**	**1273%**	**Yes**
Household dust (worst case)	0.017	17%	No
T-shirts (worst case)	**0.025**	**25%**	**Yes**
PVC gloves (worst case)	**0.033**	**33%**	**Yes**
PVC bags (worst case)	0.007	7%	No
Earplugs (worst case)	<0.001	<1%	No
Drinking water pipes (worst case)	<0.001	<1%	No
Rigid film (worst case)	0.003	3%	No
PVC sandals (worst case)	**0.033**	**33%**	**Yes**
Female hygiene products (worst case)	**0.062**	**62%**	**Yes**
Dental mouldings (worst case)	**0.046**	**46%**	**Yes**
Silicone sealant	0.004	4%	No
2-part silicone moulds	**0.087**	**87%**	**Yes**
Foot spray (worst case)	**0.049**	**49%**	**Yes**
Cycling shorts (worst case)	0.018	18%	No
Non-allergenic pillows (worst case)	0.002	2%	No
Shoe insoles (worst case)	**0.026**	**26%**	**Yes**
Baking paper/cookies (worst case)	**0.720**	**720%**	**Yes**
PVC food packaging (high)	**0.022**	**22%**	**Yes**

Note: 1) Sum expressed as µg Sn/kg bw/day.

Using the ‘group’ TDI of 0.1 µg Sn/kg bw as a basis for determining whether consumers are exposed to significant risks from particular sources, two exposure routes (via the environment and baking paper) exceed the TDI. As discussed earlier, exposure via the environment is dominated by ‘local’ emissions from a timber treatment plant.

However, there are a number of other products which, in a worst case analysis, will lead to intakes in excess of 20% of the TDI (and these have been highlighted in bold in Table 6.1). Clearly, it is possible that some consumers may be exposed to more than one product under ‘worst case’ conditions which could lead to a combined intake in excess of the TDI.

6.2.2 Worst-Case Analysis (8kg Child)

The exposure assessment for an 8kg child (worst-case) was presented in Table 5.39 which enables the %TDI to be directly derived as shown in Table 6.2.

Table 6.2: Worst-Case Analysis for Child Consumers

Source	Sum[1]	%TDI	>20%TDI?
Fish/fishery products (high)	**0.284**	**284%**	**Yes**
Via environment (worst case)	**5.092**	**5092%**	**Yes**
Household dust (worst case)	**0.117**	**117%**	**Yes**
T-shirts (worst case)	**0.189**	**189%**	**Yes**
Paddling pool (worst case)	0.003	3%	No
Mouthing PVC toys (worst case)	0.002	2%	No
Drinking water pipes (worst case)	<0.001	<1%	No
PVC sandals (worst case)	**0.033**	**33%**	**Yes**
Nappies (worst case)	**0.021**	**21%**	**Yes**
Non-allergenic pillows (worst case)	0.019	19%	No
Baking paper/cookies (worst case)	**2.325**	**2325%**	**Yes**
PVC food packaging (high)	**0.054**	**54%**	**Yes**
PVC squash bottle (worst case)	0.015	15%	No

Note: 1) Sum expressed as µg Sn/kg bw/day.

Using the same ‘group’ TDI of 0.1 µg Sn/kg bw as a basis for determining whether very young consumers are exposed to significant risks from particular sources, several exposure routes exceed the TDI. These are (in decreasing order of importance): exposure via the environment (as for adults); baking paper/cookies (as for adults); fish and fishery products; T-shirts and household dust.

As for adult consumers, there are a number of other products which, in a worst case analysis, will lead to intakes in excess of 20% of the TDI (and these have been highlighted in bold in Table 6.2).

6.3 Risk Reduction Scenarios

6.3.1 Overview

In light of information presented in this Report (much of which was previously presented in the 2002 and 2003 Reports), it is likely that further actions will be taken to:

- cease the production and use of TBT biocides both in wood treatment and in consumer products (such as foot sprays); and
- cease the use of organotin catalysts in baking papers.

6.3.2 Uptake via the Local Environment

EUSES2 was re-run without the production and use of TBT biocides. The associated results for the revised adult uptakes of organotins from the local (and regional) environment are summarised in Table 6.3.

Table 6.3: Daily Intake of Organotins via the Environment (μg Sn/kg bw/day) after Removal of TBT Biocide Production and Use

Life Cycle Stage	DBT	TBT	DOT	TPT	Sum
Production	0.002	**0.002**	**0.411**	not modelled	**0.415**
Stabiliser in PVC - processing	0.001	<0.001	0.135		0.136
Catalyst - formulation	**0.003**	**0.002**	0.016		0.021
Catalyst - processing	0.001	<0.001	0.054		0.055
Wood pres. - timber treatment	-	0	-		0
Wood preservative - use	-	0	-		0
Maximum local intake	**0.003**	**0.002**	**0.411**		**0.415**
Regional intake	<0.001	<0.001	0.001		0.001

6.3.3 Removal of Organotins from Specific Products

The removal of TBT biocides from products marketed within the EU-25 would, in this Report, lead to the elimination of organotin uptakes associated with foot sprays, cycling shorts, non-allergenic pillows and shoe insoles.

There remains uncertainty as to whether imported baking papers contain organotin catalysts. If action was taken to ban such a use, the associated intakes would be eliminated.

6.3.4 Revised Worst-Case Analysis

The worst-case analysis presented in Table 6.1 is re-presented in Table 6.4, based on the elimination of TBT biocides and removal of organotin catalysts from baking paper.

Although the risks have been reduced from those presented in Table 6.1, in the worst case of uptake via the environment close to an organotin production facility, the TDI is still exceeded.

Table 6.4: Revised Worst-Case Analysis for Adult Consumers after Specified Risk Reduction

Source	Sum	%TDI	>20%TDI?
Fish/fishery products (high)	**0.071**	**71%**	**Yes**
Via environment (worst case)	**0.415**	**415%**	**Yes**
Household dust (worst case)	0.017	17%	No
T-shirts (worst case)	**0.025**	**25%**	**Yes**
PVC gloves (worst case)	**0.033**	**33%**	**Yes**
PVC bags (worst case)	0.007	7%	No
Earplugs (worst case)	<0.001	<1%	No
Drinking water pipes (worst case)	<0.001	<1%	No
Rigid film (worst case)	0.003	3%	No
PVC sandals (worst case)	**0.033**	**33%**	**Yes**
Female hygiene products (worst case)	**0.062**	**62%**	**Yes**
Dental mouldings (worst case)	**0.046**	**46%**	**Yes**
Silicone sealant	0.004	4%	No
2-part silicone moulds	**0.087**	**87%**	**Yes**
Foot spray (worst case)	0	Risks eliminated	
Cycling shorts (worst case)	0		
Non-allergenic pillows (worst case)	0		
Shoe insoles (worst case)	0		
Baking paper/cookies (worst case)	0		
PVC food packaging (high)	**0.022**	**22%**	**Yes**

For an 8kg child, the revised analysis as shown in Table 6.5 shows an improved picture but a number of exposure routes still lead to the TDI being exceeded.

Table 6.5: Revised Worst-Case Analysis for Child Consumers after Specified Risk Reduction

Source	Sum	%TDI	>20%TDI?
Fish/fishery products (high)	**0.284**	**284%**	**Yes**
Via environment (worst case)	**1.660**	**1660%**	**Yes**
Household dust (worst case)	**0.117**	**117%**	**Yes**
T-shirts (worst case)	**0.189**	**189%**	**Yes**
Paddling pool (worst case)	0.003	3%	No
Mouthing PVC toys (worst case)	0.002	2%	No
Drinking water pipes (worst case)	<0.001	<1%	No
PVC sandals (worst case)	**0.033**	**33%**	**Yes**
Nappies (worst case)	**0.021**	**21%**	**Yes**
Non-allergenic pillows (worst case)	0	Risk eliminated	
Baking paper/cookies (worst case)	0		
PVC food packaging (high)	**0.054**	**54%**	**Yes**
PVC squash bottle (worst case)	0.015	15%	No

6.4 Exposure of the Typical Consumer

6.4.1 Overview

Although the above analysis has focused on the 'worst-case', there is also interest in the likely exposure of the 'typical' consumer across a range of sources. For each individual source, the 'typical' exposure will be much lower than the corresponding 'worst-case'.

In some cases, such exposures have already been presented (see Tables 5.38 and 5.39). By way of example, the median[56] intakes of organotins from fish and fishery products are about 10% of the 'high' intakes and, for intakes from PVC food packaging, the median intakes are about 20% and 10% of the 'high' intakes for adults and children respectively.

Similarly, the regional intake via the environment (i.e. away from 'local' sources) is about 400 times lower than the maximum local intake (see Tables 6.3).

For other sources, where specific data have not been obtained, the following assumptions have been made:

- for sources to which large numbers of consumers are exposed, the median value is assumed to be 10% of the 'worst-case' value; and
- for sources to which relatively few consumers are exposed, the median value (across all consumers including those with no exposure to the source in question) is assumed to be 1% of the 'worst-case' value.

6.4.2 Typical Adult Exposures (after Specified Risk Reduction Measures)

Based on the approach outlined above, the resultant 'median' and 'high' adult consumer exposures by source are summarised in Table 6.6.

Table 6.6: Adult Exposures (after Specified Risk Reduction Measures)

Source	%TDI (Median)	%TDI (High)	Median/High
Fish/fishery products	7.00%	71%	10%
Via environment	1.00%	415%	0.24%
Household dust	1.70%	17%	10%
T-shirts	0.25%	25%	1%
PVC gloves	0.33%	33%	1%
PVC bags	0.07%	7%	1%
Rigid film	0.03%	3%	1%
PVC sandals	0.33%	33%	1%
Female hygiene products	0.62%	62%	1%
Dental mouldings	4.60%	46%	10%
Silicone sealant	0.04%	4%	1%
2-part silicone moulds	0.87%	87%	1%
PVC Food Packaging	4.00%	22%	18%

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[56] The median is the mid-point. As such, 50% of the population will be above the median and 50% will be below.

In order to derive the overall 'typical' consumer exposure, the data presented in Table 6.6 were used to derive probability distribution functions for use in a Monte Carlo simulation. The reliability of these functions is shown in Table 6.7 in which some example predictions are compared with the original 'target values' (as listed in Table 6.6).

Table 6.7: Examples of Monte Carlo Simulation Values (expressed as %TDI)

Source	**Target Values**		**Monte Carlo Predictions (after 2,500 trials)**			
	Median	**High**	**Median**	**95%**	**97.5%**	**100%**
Fish/fishery products	7.00%	71%	7.10%	68%	92%	264%
Via environment	1.00%	415%	1.05%	159%	239%	836%
Household dust	1.70%	17%	1.67%	10%	12%	26%
T-shirts	0.25%	25%	0.24%	11%	17%	63%

In general, the target 'high' value has been set to be equivalent to a worst case value in excess of the predicted 97.5% value. In the case of fish/fishery products, the 'high' value corresponds to the 95% value (as outlined in S5.2.2) and the probability distribution function has been adjusted accordingly. The Monte Carlo simulation (based on 2,500 trials) was used to provide a probability distribution of the overall exposure as summarised in Table 6.8.

Table 6.8: Overall Adult Consumer Exposure (based on Monte Carlo Simulation)

%Population	35%	50%	75%	90%	95%
%TDI	50%	65%	106%	172%	245%

Although this analysis is inherently uncertain, it does indicate that about 35% of adult consumers are exposed to less than 50% of the TDI while the 'typical' (median) adult consumer is exposed to about 65% of the TDI. About 25% of the adult consumers are exposed to more than the TDI although less than 10% are exposed to more than twice the TDI.

6.4.3 Typical 8kg Child Exposures (after Specified Risk Reduction Measures)

Based on the same approach for adults, the 'median' and 'high' 8kg child consumer exposures by source are summarised in Table 6.9.

Table 6.9: 8kg Child Exposures (after Specified Risk Reduction Measures)

Source	**%TDI (Median)**	**%TDI (High)**	**Median/High**
Fish/fishery products	28.0%	284%	10%
Via environment	4.0%	1660%	0.24%
Household dust	11.7%	117%	10%
T-shirts	18.9%	189%	10%
Paddling pool	0.30%	3%	10%
Mouthing PVC toys	0.20%	2%	10%
PVC sandals	3.3%	33%	10%
Nappies	2.1%	21%	10%
PVC food packaging	5.4%	54%	10%
PVC squash bottle	1.5%	15%	10%

As for the adult exposures, probability distribution functions were derived to reflect the median and high values presented in Table 6.9. These were then used in a Monte Carlo simulation to provide a probability distribution of the overall exposure as summarised in Table 6.10.

Table 6.10: Overall 8kg Child Consumer Exposure (based on Monte Carlo Simulation)

%Population	30%	50%	75%	90%	95%
%TDI	104%	159%	294%	541%	846%

Although this analysis is inherently uncertain, it does indicate that about 70% of the 8kg child consumers are exposed to more than the TDI while the ‘typical’ (median) 8kg child consumer is exposed to about 160% of the TDI. Nearly 25% of these young consumers are exposed to more than three times the TDI. By inspection of Table 6.9, the key contributors are fish/fishery products and (PVC printed) T-shirts.

7. RISK ASSESSMENT CONCLUSIONS

7.1 Risks to the Environment

7.1.1 Risk Conclusions

The item of particular interest to chemical risk managers is whether a particular PEC/PNEC ratio exceeds unity. In the revised Technical Guidance Document (CEC, 2003), guidance is provided as to the three conclusions which may be reached by the 'rapporteur' (i.e. the competent authority designated for a particular risk assessment being undertaken within the context of the Existing Substances Regulations (ESR)) are as follows:

Conclusion (i): there is a need for further information and/or testing;

Conclusion (ii): there is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already; and

Conclusion (iii): there is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account. (CEC, 2003, Ch3, p175).

In broad terms, Conclusion (ii) applies where the PEC/PNEC ratio is less than unity and Conclusion (iii) applies where the PEC/PNEC ratio exceeds unity. In cases where there the PEC/PNEC ratio exceeds unity and the rapporteur determines that there is possibility that further information would result in a reduced PEC/PNEC ratio (and reduced uncertainty), a Conclusion (i) may be reached.

This Report and the earlier 2002 and 2003 Reports present results of a 'targeted risk assessment' rather than a formal ESR risk assessment. As such, the conclusions of the authors do not carry the same authority as those reached by 'rapporteurs'. Nevertheless, the decision framework presented in the TGD provides an indication of whether the risks examined are likely to be of concern or not.

7.1.2 Risks to the Environment

The results are presented in Table 7.1.

Although there have been some changes to the numerical values derived in this report from those presented in the 2003 Report, the conclusions of both reports are the same (in respect of organotins not used in anti-fouling paints) - the risks to the environment are low (Conclusion (ii)) with the exception of those associated with the treatment of wood with a TBT biocide. This activity results in a PEC/PNEC ratio greater than unity (Conclusion (iii) for the aquatic environment). The use of such treated wood may also result in significant risks to the local soil environment (Conclusion (iii) for the terrestrial environment).

In this Report, consideration has been given to the levels of butyl and phenyl tins resulting from the use of anti-fouling paints on vessels. There is no doubt that levels of these organotins in some aquatic environments are well above the PNEC values (as discussed in Section 4.4) resulting in a Conclusion (iii) for the aquatic environment at a local level and, possibly, at a regional level.

Table 7.1: Risk Assessment Conclusions for the Environment - based on TGD Guidance

Risk Source	2003 Report[1]	This Report[2]	With Risk Reduction Measures[3]	Comment
All excluding anti-fouling paints (regional PEC/PNEC)	(ii)	(ii)	(ii)	
All including anti-fouling paints (regional PEC/PNEC)	outside scope of work	(iii)	(iii)	Risks due to levels of TBT in surface waters which in some regions may lead to PEC/PNEC ratios >1.
Organotin Production	(ii)	(ii)	(ii)	
PVC Processing Sites (using Stabilisers)	(ii)	(ii)	(ii)	
Product Manufacture (Catalysts)	(ii)	(ii)	(ii)	
Product Application (Sealant with Catalysts)	(ii)	(ii)	(ii)	
Wood Treatment Plant (Biocide)	(iii)	(iii)	(ii)	Risks due to TBT. Products to be withdrawn from market - although residual risk (to soil) from previous product use will take time to decay.
Anti-fouling paints (Biocide)	outside scope of work	(iii)	(iii)	In some ports, harbours and marinas, levels of DBT, TBT and TPT may be well above PNEC values.

Key: Conclusion (i): PEC/PNEC > 1 but may reduce with further testing
Conclusion (ii): PEC/PNEC < 1 (risks not of concern)
Conclusion (iii): PEC/PNEC > 1 (risks of concern)

Sources:
1) Table 7.1, 2003 Report (for column entitled '2002 Report revisited').
2) Sections 4.4.2 and 4.4.3
3) Table 4.6, this report - with specific reference to cessation of TBT biocide production and use

Industry has confirmed that TBT biocides will be withdrawn form the market in accordance with the provisions of the Biocides Directive. When implemented, the risks to the environment associated with wood treatment plants will be eliminated as, in time, will the risks to the local environment associated with the use of such wood. In other words, the implementation of this risk reduction measure will result in a Conclusion (ii) for all the uses of organotins other than anti-fouling paints.

Although the application of organotin anti-fouling paints is now banned within the EU, vessels may still enter EU ports and waters with such paint previously applied (i.e. prior to 1 July 2003). This, together with past use, ensures that it will be some time before existing levels of organotin contamination decay to acceptable levels.

7.2 Risks for Consumers

7.2.1 Background

The approach to the consumer risk assessment has involved consideration of worst-case exposure scenarios for a number of consumer products known to contain organotin compounds. These include products both widely used (such as PVC stabilised with mono/di organotin compounds) and those that are likely to represent the highest levels of exposure (such as textiles treated with TBT-based products as anti-microbial agents). Exposure via the environment was also taken into account based on the outputs of the *EUSES*2 model.

Worst-case exposure was considered both for a 60kg adult and for an 8kg child and exposure to organotin compounds is expressed as a percentage of the group TDI value used in this Report.

7.2.2 Scenarios Considered

As for risks to the environment, the scenarios considered in the 2003 Report have been revisited in light of new information. As a result of comments by CSTEE (see Annex 2), further consideration has been given to a number of additional routes by which consumers may be exposed to organotins.

7.2.3 Presentation of the Results

As for the environmental risks, the three conclusions which may be reached by the 'rapporteur' (i.e. the competent authority designated for a particular risk assessment being undertaken within the context of the Existing Substances Regulations (ESR)) are as follows:

Conclusion (i): there is a need for further information and/or testing;

Conclusion (ii): there is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already; and

Conclusion (iii): there is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

In broad terms, Conclusion (ii) applies where the %TDI is less than 100% and Conclusion (iii) applies where the %TDI exceeds 100%. In cases where there the %TDI exceeds 100% and the rapporteur determines that there is possibility that further information would result in a reduced PEC/PNEC ratio (and reduced uncertainty), a Conclusion (i) may be reached.

This Report presents the results of a 'targeted risk assessment' rather than a formal ESR risk assessment. As such, the conclusions of the authors do not carry the same authority as those reached by 'rapporteurs'. Nevertheless, the decision framework presented in the TGD provides an indication of whether the risks examined are likely to be of concern or not.

However, in relation to organotins, risks to consumers may arise from a wide range of products and other risk sources. It is, therefore, likely that consumers will be exposed to a combination of risk sources. Furthermore, whilst the risk from each individual risk source may be determined to result in a Conclusion (ii) (i.e. the organotin intake associated with the risk source is less than the TDI), it is possible that the cumulative risk associated with exposure to a number of risk sources would result in a Conclusion (iii) (i.e. the combined organotin intake exceeds the TDI).

To assist in determining which risk sources are likely to be significant contributors to the overall cumulative risk, those risk sources which result in an organotin intake in the range 20% to 100% of the TDI have been assigned a Conclusion (ii)*.

In practice, this means that, if consumers are likely to be exposed to several risk sources, including several which are designated as Conclusion (ii)* but none are designated as Conclusion (iii), then there is a possibility that the combined exposure to these risk sources will result in an organotin intake in excess of the TDI (which would attract a Conclusion (iii)). In such cases, the focus of the risk reduction measures would be on the major contributors to the combined risk - i.e. those risk sources which are determined to be Conclusion (ii)*.

With these points in mind, the summary of the risks to consumers, as presented below, is based on the following categorisation:

Conclusion (i): there is a need for further information and/or testing;

Conclusion (ii): there is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already;

Conclusion (ii): although there is no need for further information and/or testing and no need for risk reduction measures when considering this risk source in isolation, when considered in combination with other risk sources, it may be desirable to consider limiting the risks (from this risk source); and*

Conclusion (iii): there is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account.

7.2.4 Risks for Adults

The results for adults are presented in Table 7.2. As discussed above, it is likely that a particular adult consumer will be exposed to more than one exposure route. For this reason, in addition to the Conclusions (i), (ii) and (iii), a further 'conclusion' has been provided for this report and the definition of Conclusion (ii) has been slightly modified as follows. Conclusion (ii)* has been used where the predicted organotin intake is in the range 20-100% TDI and the definition of Conclusion (ii) has been taken to mean where the predicted organotin intake is <20%TDI.

Although there are variations in the numerical values between those presented in the 2003 Report and in this Report, the overall conclusions are broadly similar.

Table 7.2: Risk Assessment Conclusions for Adult Consumers (modified from TGD Guidance)

Risk Source (Worst Case)	**2003 Report[1]**	**This Report[2]**	**With Risk Reduction Measures[3]**	**Comment**
Fish/fishery products (‘high’)	not considered	(ii)*	(ii)*	Risks associated with anti-fouling paints.
Via environment (worst local)	(iii)	(iii)	(i)	Use of TBT in wood treatment discontinued but still some risks associated with DOT
Indoor air./dust	(ii)	(ii)	(ii)	
T-shirts	not considered	(ii)*	(ii)*	
PVC gloves	(ii)*	(ii)*	(ii)*	
PVC bags	not considered	(ii)	(ii)	
Earplugs	(ii)	(ii)	(ii)	
Drinking water pipes	not considered	(ii)	(ii)	
Rigid film	not considered	(ii)	(ii)	
PVC sandals	not considered	(ii)*	(ii)*	
Female hygiene products	(ii)	(ii)*	(ii)*	Risk increased due to use of lower TDI value
Dental moulding	(ii)	(ii)*	(ii)*	
Silicone sealant	not considered	(ii)	(ii)	
2-part Silicone moulds	not considered	(ii)*	(ii)*	
Foot spray	(ii)*	(ii)*	eliminated	Eliminated with assumed ban on TBT biocides in consumer products
Cycling shorts padding	(ii)	(ii)	eliminated	
Non-allergenic pillows	not considered	(ii)	eliminated	
Insoles	(ii)*	(ii)*	eliminated	
Cookies (baking paper)	(iii)	(iii)	eliminated	Assume measures taken to eliminate organotin catalysts from baking paper
PVC food packaging	(ii)	(ii)*	(ii)*	Risk increased due to use of lower TDI value

Key: Conclusion (i): Intake > 100% TDI but may reduce with further testing
Conclusion (ii): Intake < 20% TDI (risks not of concern)
Conclusion (ii): 20% TDI < Intake < 100% TDI (risks of possible concern)*
Conclusion (iii): Intake > 100% TDI (risks of concern)

Sources: 1) Table 7.2, 2003 Report (column entitled 2002 Report revisited); 2) Table 6.1, this Report; and 3) Table 6.4, this Report (with specific reference to removal of TBT biocide production/use and removal of organotin catalysts from baking papers).

For adults, the incorporation of the risk reduction measures leads to exposures which are all below the TDI with the exception of local exposure via the environment. This is associated with the emissions of DOT from both production plants and, to a lesser extent, PVC processing plants. As detailed in the text, the high uptake values are due to the predicted high leaf-air partition coefficients - which have been subject to considerable debate with industry representatives. Although attempts have been made to model the specific DOT compounds being emitted, there are no measurements to confirm the reliability of such predictions. For this reason, a Conclusion (i) is proposed as further studies may provide a more robust approach to modelling the specific DOT compounds being emitted and their environmental behaviour.

More generally, the adoption of the group TDI and some additional exposure sources leads to several exposure routes being in excess of 20% of the TDI (Conclusion (ii)*).

A Monte Carlo simulation of (largely) assumed exposure distributions suggests that although the overall 'typical' (median) exposure is about 65% of the TDI, about 25% of adult consumers are exposed to more than the TDI.

7.2.5 Risks for Child Consumers

The results for child consumers are presented in Table 7.3 using the same 'risk assessment conclusions' as for adults.

Table 7.3: Risk Assessment Conclusions for Child Consumers (modified from TGD Guidance)

Risk Source (worst case)	**2003 Report[1]**	**This Report[2]**	**With Risk Reduction Measures[3]**	**Comment**
Fish/fishery products (high)	not considered	(iii)	(iii)	Risks associated with anti-fouling paints
Via environment (worst local)	(iii)	(iii)	(i)	Use of TBT in wood treatment discontinued but still some risks associated DOT
Indoor air/dust	(ii)*	(iii)	(iii)	Higher risk due to higher measured values and use of group TDI
T-shirt	(ii)*	(iii)	(iii)	Higher risk due to use of group TDI
Paddling pool	(ii)	(ii)	(ii)	
PVC toys	(ii)	(ii)	(ii)	
Drinking water pipes	not considered	(ii)	(ii)	
PVC sandals	not considered	(ii)*	(ii)*	
Nappies	(ii)	(ii)*	(ii)*	Higher risk due to use of group TDI
Non-allergenic pillow	(ii)	(ii)	eliminated	TBT biocides eliminated
Cookies (baking paper)	(iii)	(iii)	eliminated	Baking papers discontinued
PVC food packaging (high)	(ii)*	(ii)*	(ii)*	
PVC squash bottle	not considered	(ii)	(ii)	

Key: *Conclusion (i): Intake > 100% TDI but may reduce with further testing*
Conclusion (ii): Intake < 20% TDI (risks not of concern)
Conclusion (ii): 20% TDI < Intake < 100% TDI (risks of possible concern)*
Conclusion (iii): Intake > 100% TDI (risks of concern)

Sources:

1) *Table 7.3, 2003 Report (column entitled 2002 Report revisited)*
2) *Table 6.2, this Report.*
3) *Table 6.5, this Report (with specific reference to removal of TBT biocide production/use and removal of organotin catalysts from baking papers).*

In general terms, the risks to child consumers are higher than those for adult consumers. Of note is that the use of the group TDI leads to exposures in excess of the TDI (even after risk reduction measures). Specifically, the presence of butyltins in fish and fishery products may lead to the group TDI being exceeded in some cases. As for the adult exposure, there are local risks via the environment associated with DOT (both in production and in PVC processing). The presence of DOT stabilisers in PVC may also lead to the TDI being exceeded in relation to the worst-case analyses of the intake of household dust and of the PVC-printed clothing (such as T-shirts and pyjamas).

Aggregating the various exposure routes (using a Monte Carlo simulation) suggests that the overall exposure for 70% of young child consumers will exceed the group TDI, while the ‘typical’ (median) 8kg child consumer is exposed to about 160% of the TDI.

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ANNEX 1:

SPECIFICATIONS FOR THIS STUDY

CONSULTANT STUDY UNDER FRAMEWORK CONTRACT LOT 1

Risk assessment studies on targeted consumer applications of certain organotin compounds

TECHNICAL SPECIFICATIONS

1. General information and objectives

Tin-organic compounds find widespread industrial uses as stabilizers, biocides, and catalysts. Exposure to excessive amounts of tri-substituted organotin compounds can disrupt the endocrine system and cause harm to human health and the environment. Consequently, restrictions have been imposed at EU level on certain of their uses. Use in antifouling paints is restricted in Directive 76/769/EEC, as amended by Directive 2002/62/EC. Use in food contact materials is regulated in Directive 90/128/EEC, as amended by Directive 2002/17/EC. The authorization of uses in biocides is regulated by Directive 98/8/EC and for pesticides by the Plant Protection Directive 91/414/EEC.

Concern remains that the uses of other, unregulated, tin-organic compounds may also cause harm, especially to children. DG Enterprise contracted Risk and Policy Analysts (RPA) to assess the remaining uses. The Commission's scientific committee (SCTEE) assessed the RPA report from 2002 and concluded that it contained weaknesses and data gaps that undermined the reliability of the conclusions on the risks posed by tin-organic compounds. A revised RPA report from 2003, incorporating addition data provided by industry, was also found to be inadequate by the SCTEE. Hence, data to properly assess these uses and to form the scientific basis for possible risk management measures are still not sufficient. An objective of this third study is to focus the scope on those substances that appear to pose the greatest risk and to remedy the associated deficiencies identified by the SCTEE.

The information to be provided for through this contract shall be focused on closing information gaps on exposure scenarios related to tributyltin (TBT), dibutyltin (DBT), dioctyltin (DOT) and triphenyltin (TPT) with the objective of satisfying the SCTEE concept of a group tolerable daily intake (TDI). The purpose of the study is to confirm whether or not human health or environment is at risk from the combined effects of these four compounds. If deemed necessary, it shall form the base for a selection of candidate applications to be targeted in a further study on the advantages and drawbacks of possible risk management measures and use of alternatives.

2. Subject of the study

The study is limited to the four organotin compounds TBT, DBT, DOT and TPT, which effects shall be viewed as additive both for the target organs (thymus) and for the modes of action (immunotoxicity). The levels of exposure to each of those compounds shall be added to form a daily intake (DI) and the risk assessed against a value for the group TDI of 0.27 microgram/kg body weight expressed as TBT-Cl.

A review of the methodology and assumptions for the assessment of exposure scenarios as presented in earlier RPA reports shall be carried through. In addition, some additional exposure scenarios as described in section 3 need to be assessed to predict an overall DI. Applicable comments expressed in the two SCTEE Opinions shall be taken into account in all aspects of the study.

For clarity, and to ensure that identified applications are taken into account, all required exposure routes are listed in section 3. This is for the purpose of presenting a sum of the daily exposure to the four organostannic compounds. It should however be noted that a majority of theses emission scenarios already have been performed by RPA in the two earlier studies.

Special attention shall be paid to indoor air exposure including household dust, exposure to toys, and to the possible presence of TBT as impurities. Exposure routes for children should carefully be identified and evaluated.

For the assessment of the level of risk, the group TDI mentioned above shall be applied. This shall be accompanied by information on exposure measurements and a discussion of uncertainty in the data, applied quality control, and uncertainty in covering various possible exposure routes.

The starting points for the study shall be:

- the SCTEE Opinions on organotins of 2003 and 2004;
- The EFSA Opinion on organotins when available;
- Information reviewed by RPA in previous studies;
- The report from the Danish Toxicology Centre (2003), commissioned by DG SANCO;
- Information on emissions from landfills as reported in “Life Cycle Assessment of PVC and of principal competing material (April 2004)” and “The behaviour of PVC in landfill (2000)”.

General requirements

Problems that are encountered which hinder a proper assessment shall be spelt out clearly. The consultants shall fill the remaining data gaps. Should it not be possible to obtain the data required, a full description shall be provided of actions taken to obtain the data.

The references of studies and information used and consulted by RPA shall be listed.

Kick-off meeting

The methodology to be used for the study shall be based upon the guidance in these technical specifications. The consultants’ proposed methodology to achieve this shall be presented to the Commission at the kick-off-meeting. The methods that will be used to assess and/or to incorporate required exposure scenarios shall comply with the related comments expressed in the SCTEE Opinions on Organostannic Compounds of 12 June 2003 and 28 May 2004.

2.1 Principal objective

For each application, the consultant shall give a conclusion of what the total exposure is to these four substances combined. These will be tabulated to provide an indication of the potential overall exposure from all applications although it is acknowledged that it is highly improbable that any individual (or geographical area) will actually experience such exposure since the maximally exposed targets will vary from application to application. A limited number of worst-case and average-case scenarios will therefore be calculated for illustrative purposes.

For later potential risk management purposes, the consultant will also give an assessment of the individual exposures to the four substances, which shall be further broken down to the different applications as described in part 3. Where the consultant believes that it would help to show further breakdowns within these categories to aid future risk reduction studies, he should do so.

2.2 Additional exposure data to be included

Exposure to the targeted organotin compounds via food intake should be taken into account. The Scientific Panel on Contaminants at the European Food Safety Agency (EFSA) is preparing a consolidated opinion on that exposure route. The application of the group TDI shall include these exposure sources. Further and when provided by DG SANCO, exposure to food contact material, and exposure through drinking water pipes, shall be added.

In case data on exposure to food, food contact material, or drinking water pipes are not available by the time the consultants have completed their work on the assessments required by this contract**,** the DI via these sources shall be calculated on the basis of clearly stated assumptions. The requested calculation of a DI including the other sources might then be performed in a further contract as soon as all necessary data become available.

2.3 Modelling exposures during service life

It is recognised that there are many applications of organotins which fall under the present study, and that therefore, it is difficult to provide detailed individual models for all applications. However, it is also important that all applications are considered in this study.

The European tin stabiliser industry association, ETINSA, will provide a list of all applications where they have exposure data, generally in the form of migration data. ETINSA will also propose criteria for how data from one application can be used to model exposure from another application. This information will be provided to the consultants in due time for the start of the study and shall be considered together with other relevant information.

The exposure levels for the environment and for adult and child consumers shall be assessed separately.

2.4 Assumption of future scenarios based on existing EU regulatory measures

The consultant shall take the following future scenarios into account.

1. Treatment of timber with TBT biocide will cease in Europe in 2006 under the provisions of the EU Biocides Directive. Therefore, the consultant shall present a temporal trend analysis of exposure to environment and consumer, starting with a scenario post-2006, when the emissions from ongoing production have been removed, and finishing when this exposure is negligible. For each main environmental compartment a temporal curve shall be presented, as for consumer exposure via the environment.

Exposure from wooden articles treated with TBT shall be handled as requested under 3.1.2 and 3.1.3.3.

2. Given that approvals for the use of TPT in pesticides in the EU were phased out in 2002 (with an exemption for Greece till 2003), the consultant shall present a temporal trend analysis of exposure to environment and consumer, starting with current levels of exposure to TPT-containing pesticides, and finishing when this exposure is negligible. For each main environmental compartment a temporal curve shall be presented, as for consumer exposure via the environment.

Exposure from articles treated with TPT shall be handled as requested under 3.1.2 and 3.1.3.3.

3. Organotins (i.e. TBT) were prohibited for use in antifouling preparations for all crafts and other marine and fresh-water applications from 2003 by 76/769/EEC. Further, from 2008 the presence of organotin compounds on ships shall be eliminated. To estimate future exposure to TBT through the consumption of fish and shell-fish, the consultant shall set out a temporal trend analysis of exposure to environment and consumer, starting with current levels of exposure and finishing when this exposure is negligible. For each main environmental compartment a temporal curve shall be presented, as for consumer exposure via the environment. The value for current exposure shall be based upon the opinion given by EFSA in September 2004.

2.5 Resolving previous differences of exposure estimates

In the two major analyses of consumer exposure to organotins within this risk assessment, there are a number of discrepancies between the two reports. Where this discrepancy is based upon a difference of opinion based upon hazard, i.e. the level of TDI, the consultant shall accept as a basis the CSTEE opinion of 2004. Where a discrepancy is based upon different interpretations of exposure scenarios, the consultant shall comment on both current estimates in RPA and DTC reports, and shall give a detailed opinion as to the correct assessment for these exposures. Where CSTEE has also given a view with regard to certain exposure scenarios, CSTEE's opinion shall be included in the comparative analysis mentioned above.

2.6 Resolving previous disunity on modelling losses from PVC processing and recycling plants

Industry has raised serious doubts on the modelling of the emissions of octyltins from PVC calendering plants as presented in previous studies. Its own modelling gives quite different results. The industry believes that a particular part of the EUSES model is causing this discrepancy – the partition coefficient between leaves and air. Industry will therefore contribute to obtain an opinion from modelling experts on what a more realistic input to the model should be. Accordingly, and regarding the reliability of using the BRE guidance document and OECD document to estimate losses from PVC plants, experts on plastics processing shall be consulted via industry. The consultant shall conclude on the most realistic partition coefficient. This is to ensure analysis that can be agreed upon by all stakeholders.

If available emission data are inadequate, further measurements of losses can be requested from ETINSA and incorporated in the assessment.

3. Description of tasks to be performed

3.1 Exposure scenarios to be assessed and incorporated into a Group DI

Emission scenarios and calculations of DI for each of the four organotin compounds shall be analysed and described separately for the target groups, e.g. child and adult consumers.

3.1.1 LOSSES FROM WOOD TREATMENT PLANTS

- Estimate emissions of TBT from wood preservation plants to the environment
- Estimate emissions of TBT from wood preservation plants to humans via the environment

3.1.2 LOSSES FROM PVC PROCESSING AND RECYCLING PLANTS

- Estimate emissions of DBT and DOT and TBT-impurities from plants processing and recycling rigid PVC
- Estimate emissions of DBT and DOT and TBT-impurities from plants processing and recycling flexible PVC
- Estimate emissions of DBT, DOT and TBT to humans via the environment from plants processing and recycling rigid PVC
- Estimate emissions of DBT, DOT and TBT to humans via the environment from plants processing and recycling flexible PVC

3.1.3. EMISSIONS TO THE ENVIRONMENT FROM WASTE

Based on available information, the Consultants should attempt to estimate emissions from waste as requested below:

- Estimate emissions at landfills of DBT and DOT and TBT from products and articles made of flexible PVC
- Estimate emissions at landfills of DBT and DOT and TBT from products and articles made of rigid PVC
- Estimate emissions at landfills of TBT and TPT from products and articles as covered in 3.1.4.3 and 3.1.4.4.
- Estimate emissions of DBT and DOT from waste in the environment made of flexible PVC
- Estimate emissions of DBT and DOT from waste in the environment made of rigid PVC

3.1.4. EXPOSURE TO CONSUMERS – DIRECT AND VIA THE ENVIRONMENT

3.1.4.1. Stabilisers

Estimate emissions of DBT and DOT and TBT-impurities from PVC articles when used as a stabiliser in following flexible PVC-articles**:**

- Flooring and wall covering,
- Shower curtains
- Bags
- Steel coating
- T-shirt printing (can also contain TBT to provide a deodorant effect)
- Paddling pools
- Toys in general (add a specific scenario for children under three years old)
- PVC gloves
- Earplugs
- Any other identified flexible PVC applications

Estimate emissions of DBT, DOT and TBT-impurities from PVC articles when used as a stabiliser in following rigid PVC-articles:

- Profile extrusions (window frames),
- Foamed sheeting
- Pipes, distinguishing between drinking water pipes and other pipes
- Thin rigid film
- Credit cards
- Fencing
- Electrical conduit
- PVC sandals
- Any other identified rigid PVC applications

3.1.4.2. Catalysts

Estimate emissions of TBT and DBT, DOT, and TBT-impurities when used as a catalyst, from:

- PU Technology including:
- PU Foam used in upholstered furniture, mattress filling, car seats, car dashboards, insulation panels
- PU Adhesives as used in car windscreens, two-component household adhesives, composite door panels
- PU Coatings as used in top coatings for automobiles, boats, planes, wood varnishes, repair coatings, industrial outdoor flooring, heavy duty flooring in industry and sports
- PU Elastomers as used in shoes, shoe soles (outer contact)
- Antioxidants for polyolefins as used in Nappies and hygiene products
- Any silicones used in automotives, computers, construction, sealants, dental mouldings or adhesives
- Alkyd resins as used in paints
- Any other identified catalyst applications

3.1.4.3. Biocides

Estimate emissions of TBT, and also of TPT if found reasonable, when used as a biocide from:

- Wooden articles (impregnated)
- Heavy industrial textiles
- Foot spray
- Cycling shorts padding
- Non-allergenic pillows
- Shoe insoles
- Any other identified biocide applications

3.1.4.4. Human exposure to TPT

- Identify possible sources of exposure to humans, via products, articles, food intake or environment
- If appropriate, quantify the levels of exposure

Those substances seem to work as fungicides, which means that they can also be used as biocides, e.g. in consumer products. They have however not been identified as existing biocides within the program of work pursuant to directive 98/8/EC.

3.1.4.5 Exposure scenarios performed by DG SANCO and EFSA

- DOT used as a catalyst for baking papers
- TBT biocide as used in marine anti-fouling paints – effectively consumer intake through fish and shell-fish consumption
- DOT as a stabiliser in single-layer PVC for food contact applications
- DOT as a stabiliser in PVC for food contact, when the food contact material is laminated with polyethylene
- Any other identified food contact application

3.2. Application of the group TDI on assessed exposure levels for adult and child consumers

- Apply the group TDI of 0.27 microgram/kg body weight expressed as TBT-Cl to the results of studied human exposure scenarios as requested under 3.1.1 till 3.1.2.4 above.
- If available, include exposure information reported by EFSA and DG SANCO as requested under 3.1.2.5 above.
- Conclude on risks for adult and child consumers separately
- If and when applicable, conclude on specific risks for children under three years old
- Calculate the future impacts over time of assessed levels of exposure originating from already restricted uses as requested under 2.4
- Explain levels of uncertainties and the outcome of applied quality control
- Explain approaches to the exposure measurements concerning the coverage of possible exposure routes and data gaps and how these could be closed

ANNEX 2:

CSTEE COMMENTS ON THE 2003 REPORT AND RPA RESPONSES

Specific comments from CSTEE on the 2003 Report (CSTEE, 2004)	**RPA Response**
The compounds covered in the report do not include the phenyltin species. This is explained by several restrictions on the use of these substances. Nonetheless in a recent paper (Lo et al., 2003), describing the concentrations of organotin compounds in human serum samples, it was shown that triphenyltin was by far the most common organotin compound in the samples. The CSTEE therefore wishes to stress the importance of including this substance in the assessment.	Further consideration has been given to triphenyltin (TPT) compounds in this report.
Environmental exposure The production/use data are less detailed in the new report than in the first version, and often qualified by terms such as “indicated”, “believed”, “thought”, “estimated” and “information from one company”. This gives an overall impression of uncertainty in the basic collection and use of data.	***Environmental exposure*** The wording in the 2003 Report was intended to realistically reflect the uncertainties inherent in the collection and analysis of usage data. It is to be hoped that one of the benefits of REACH will be to reduce such uncertainties in the future.
The emission from one of the producers (site X) is in the new report reduced by an order of magnitude, on the basis that the water is sent to WWTP. TBT seems to be the major tin compound in this emission, and this compound may be degraded to mainly DBT in the plant, and consequently the emission of that compound has to be taken into account.	TBT is not the major compound emitted to water from Site X. The TBT figures relate to measured values in the process effluent (7.5 ng/l for Site X) and the text in Table 3.1 has been amended for improved clarity.
The measurements of loss factors for PVC processing are welcomed, but need to be supported by a sound evaluation before the reduction of the BRE loss factors by a factor of five can be accepted. It must be stressed that the use of this factor will lower all predicted values of PECs where evaporation is playing an important role.	Agreed - but it should be noted that the ESDs are also based on limited data. This issue is considered in some depth in S3.3 in this Report.
The emission factors for formulation and processing of polymers taken from the BRE document is substances with “high” vapour pressure, which in this document correspond to BBP (some 10^{-3} Pa). The organotin compounds have higher vapour pressures (around 1 Pa) and the loss through evaporation may thus be much bigger.	Agreed in principle - but there is no evidence to support the use of much higher emission rates. Indeed, the available evidence is to the contrary as discussed in S3.3 in this Report.
The loss of organotins to water from PVC during outdoor use has been given an emission factor of 0.15 % per year in the BRE (1998) document. This corresponds to a loss of 3 % over the 20 years, not 0.05 % (see table 3.9). This will change the estimated emissions in Table 3.16 significantly. This comment goes for both versions of this report, but was not identified by the CSTEE before.	Agreed and the service life losses have been reviewed and increased in light of the latest ESD (OECD, 2004).
The biodegradation categories assigned to the organotin compounds in Table 3.29 are not obvious. MMT is readily biodegradable, but not necessarily MBT and the experimental data seem to classify both DBT and DOT as inherently biodegradable. The BCF value (1) used for the prediction of DOTC distributions is too low, considering that the Kow is over 600,000 according to Table 3.25. More realistic values for both degradability and BCF would have changed the indirect exposure from the environment considerably.	The P, B and T properties have been reviewed and revised for the organotins considered in this Report. The associated PBT assessment has been revised (S4.3, this Report) and highlights some of the differences in values used for freshwater and marine compartments.

Specific comments from CSTEE on the 2003 Report (CSTEE, 2004)	RPA Response
Human exposure *Inhalation* The section on consumer exposure is not transparent in the revised report. In several of the tables it is difficult to see the origin of the used data, especially for loss or emission factors. For example, the estimation of exposure via indoor air is apparently based on diffusion constants derived by Fabes, and the lifetime loss (20 years) obtained in Table 3.14 (not 3.12 as mentioned in the text) was 2.28 % for DBTC. In Table 5.12 the corresponding value is 0.27 % per year, which is 5.4 % over 20 years. This seems to correspond to migration plus abrasion in Table 3.14, but all the abraded particles will not contribute to the air concentration. The paragraph following Table 5.12 then says that the emission rates used are based on migration to water, and that all values are divided by a factor of 100 to compensate for this. This is not right and the inhalation exposure is underestimated by two orders of magnitude. This indeed may be one of the major sources for human intake of organotin compounds. Several investigations have also shown organotin compounds in household dust (e.g. Al Bitar, 2004), and this is also a possible exposure pathway, especially for children, although it is more difficult to estimate quantitatively.	***Human exposure*** ***Inhalation*** The interpretation of the figures is correct. It is agreed that not all migration (including abrasion) will go into the air (hence the adjustment factor of 1%). In this Report (see S5.2.4), account has been taken of various dust measurements (including Al Bitar) to provide an estimate of human uptake from indoor air/dust.
Oral It is correct that the exposure from mouthing of toys depend on two factors, mouthing time and leach rate. The CSTEE is aware of the US CPSC study that found mouthing times of about 70 minutes for children between 3 months and 1 year for all objects except pacifiers. The time these children spent mouthing soft plastic items was about 4.5 minutes per day, but this figure is very variable since it is affected by a number of factors, such as the availability of such items. There is also a mouthing study published by the UK Department of Trade and Industry (Norris and Smith, 2002), where the mean daily mouthing of toys for 6 to 9 month children was estimated to be about 39 minutes (maximum 3 hours 47 minutes). It is also correct that the value used by CSTEE for the leaching rate was an assumption, but it is not correct that the result from the Fabes study can be applied. There is a big difference between a passive migration and what is happening in the mouth of a child, where there is a substantial mechanical component. The CSTEE found that the migrations of the phthalates were much higher than could be expected from ordinary leaching data. The fact that the organotin compounds have much higher water solubility may also increase the migration compared to the more lipophilic phthalates. This has been shown in a study of migration of organotin compounds from swimming pools and beach balls, where the migration to artificial saliva and water was about equal as that to artificial skin fat (Miljø-Kemi, 2000).	*Oral* These points have been addressed in a revised analysis presented in this Report (see S5.2.6).
Total exposure In the tables (6.7 and 6.8) describing the total consumer exposure, the contributions from insoles, foot spray, cycling shorts and baking paper are described as “eliminated”. This may be true for products produced within the EU, but it gives a false description of the exposure situation as imported products may contain such compounds. A Danish report (Boyd HB, and Höglund L, 2003) has calculated the consumer exposure based on worst case situations and identifies these applications as major contributors. That report is further reviewed in Annex 1.	*Total exposure* This point is exemplified in this Report with reference to continued use (within the EU-25) of baking papers with organotin catalysts and foot spray with TBT biocide.
The total exposure to organotin compounds is very complex including many sources not discussed in this opinion	This is acknowledged in the main text but an attempt has been made to identify and quantify the most significant sources.

Specific comments from CSTEE on the 2003 Report (CSTEE, 2004)	RPA Response
Effects in the environment In the revised report, the issue of imposex in gastropods by TBT is mentioned briefly. Nonetheless in setting a threshold level for freshwater species the daphnia NOEC of 60ng Sn/L is used with an uncertainty factor of 10. In marine gastropods a threshold level of 0.1ng/L has been reported. The lowest reported TBT concentration producing imposex in a freshwater gastropod is 125ng/L. The CSTEE considers that the proposed value could be insufficient for covering potential ED effects on freshwater organisms.	***Effects in the environment*** All the available evidence suggests a marked difference in thresholds between freshwater and marine organisms - as clearly stated in the 2003 Report. This is clearly re-stated in this Report.
Effects in humans *Use of a group exposure standard* The CSTEE considers that a group exposure standard for health protection should be employed if: i) Exposure to several members of a structurally related series of chemicals is likely to occur frequently. ii) Several members of the series have been demonstrated to have a common target organ(s)/cell type and the same mode of action. If these criteria are met individual members of the series for which there is very limited toxicological data should be assumed to make an additive contribution. Toxicological equivalence factors (TEF) should be introduced where the potencies span 3-5 fold or more. If this is not the case the most potent member of the series should be assumed to be representative for the purposes of standard setting; *Application of the group TDI* In the revised report, a group TDI for DOT, DBT, TBT and TPT is not considered, although it is mentioned in the report that a conservative approach has been taken by regarding **all** organotins as immunotoxic, based on their common ability to cause thymus atrophy. The report continues that 'On this basis it is reasonable to consider the effects of the butyl tins as possibly additive but not across the whole group'. The CSTEE does not agree with this conclusion and proposes in line with its earlier opinion (CSTEE, 2003) a group TDI for dioctyltin (DOT), dibutyltin (DBT), tributyltin (TBT) and triphenyltin (TPT) as these compounds have a similar profile of action in terms of immunotoxicity (lymphocyte depletion in the thymus and peripheral lymphoid tissues). In comparative toxicity studies that investigated the structure activity relationship for thymus toxicity in the rat, DBT and DOT were the most potent dialkyltin compounds producing dose-related thymus atrophy at 50 and 150 ppm in the diet (Seinen et al., 1977a). In a subsequent comparative study, DBT and DOT both significantly suppressed the thymus-dependent immunity (retarded rejection of skin transplants) at the 150 ppm dietary level (but no significant effect was found at 50 ppm) (Seinen et al., 1977b). In a later comparative study significant thymus atrophy was noted with TBT and TPT at similar levels (TBT at 50 and 150 ppm; TPT at 15, 50 and 150 ppm) (Snoeij et al., 1985). A function assessment showed that TPT suppressed the thymus-dependent immunity (Vos et al., 1984) like TBT, DBT and DOT. The mechanism of toxicity at the level of the thymus appears to be selective inhibition of the proliferation of immature thymocytes (Penninks et al., 1985; Snoeij et al., 1988; Pieters et al., 1994; Gennari et al., 1997). Regarding TBT, it is likely that the thymus atrophy is produced by the metabolite DBT (Snoeij et al., 1988). In the report a TDI of 0.27 µg/kg per day TBT as chloride is used (WHO, 1999) based on a NOAEL of 0.5 mg TBTO/kg diet derived from the chronic immunotoxicity study in rats where reduced resistance to *Trichinella spiralis* was noted (Vos et al., 1990). Using this same study the US EPA has calculated a benchmark dose (10% benchmark response, with a 95% confidence limit) at 0.68 ppm, i.e. 0.03 mg.kg BW/day (USEPA Integrated Risk Information System). TBT is more extensively studied than DBT, DOT and	***Effects in humans*** *Use of a group exposure standard* In this third report, a group TDI of 0.1 µg Sn/kg bw/day has been used in order to determine the risks to consumers associated with the combined exposure to DBT, TBT, DOT and TPT.

Specific comments from CSTEE on the 2003 Report (CSTEE, 2004)	**RPA Response**
TPT and consequently several endpoints, notably the resistance to infectious disease, have not been investigated for these latter compounds. **As the common endpoint of thymus atrophy is affected at similar dietary level of these compounds, the CSTEE again proposes that a group TDI value 0.27μg/kg bw/day for TBT, DBT, DOT and TPT as chloride should be adopted, or 0.1 μg/kg bw/day as Sn. Furthermore, assuming a similar mode of action and in the absence of data that contradict it, it seems rational to consider the effects of these chemicals as additive.** Finally, the CSTEE considered two recent publications (Cooke et al., 2004; Tryphonas et al., 2004), in which the effect of tributyltin chloride was investigated in rats following in utero, lactational and post-weaning exposure. Regarding thymus toxicity, the study confirmed the thymus as the target organ with a comparable NOAEL as observed in the chronic immunotoxicity study (Vos et al., 1990). Unfortunately, in the study the *Trichinella spiralis* host resistance model was not used to investigate the thymus-dependent immunity, whereas the current TDI is based on this most sensitive parameter.	
Conclusions The CSTEE has been pleased to receive some additional information on human exposure to various organotin compounds and on their toxicological properties. This has helped with one or two of the issues raised by the CSTEE in its opinion on organotin compounds of the 12th of June 2003.	**Conclusions** Noted.
The CSTEE is concerned however that most of the important information gaps it identified in its opinion of 2003 have not been narrowed by this additional information. The CSTEE therefore considers that there is no scientific reason to change the answers it gave in June 2003 to the five questions raised by the Commission.	Further efforts have been made in this Report to address these concerns.
The CSTEE wishes to reiterate the importance of taking into account all sources (food and nonfood) and routes (oral, inhalation and dermal) of exposure in the assessment of the risks to human health from current exposure to organotin compounds. It also would like to emphasise that the effects of TBT, DBT, DOT and TPT should be viewed as additive since they have common target organs/modes of action.	This has been done to the extent possible within the timeframe/budget for this study.
Completion of the assessment of the total risks from the exposure of the public to organotin compounds must await the conclusions of EFSA on exposure through consumption of fish. This information is expected to be available in the next few months.	The opinion of EFSA has been incorporated.

ANNEX 3:

CALCULATIONS FOR CONVERTING USAGE FIGURES INTO USAGE FIGURES BY ATC

A3 Calculations for Converting Usage Figures into Usage Figures by ATC

A3.1 Overview of Uses to be Considered

From Table 2.2, the uses ranked by tonnages are as follows:

Use	**t/yr**	**Organotin**	***Comment***
PVC Stabilisers	15000	Mono/di-substituted	
Catalysts	1650	Mono/di-substituted	
Anti-fouling paints	1250	Tri-substituted tins	*Now banned – not considered further*
Glass coating	800	Monobutyltin chloride	*Outside scope of study – not considered further*
Synthesis	150	Tri-substituted	*Could be higher – but not considered further*
Pesticide	100	Tri-substituted	*No longer use TBT/TPT – not considered further*
Biocide	100	Tri-substituted	
Total (All)	**19050**		

Three uses (stabilisers, catalyts and biocides) are considered further below.

A3.2 PVC Stabilisers

From Table 2.5, the relative usage of mono-di-substituted tins are as follows:

Organotin	**t/yr**	***Comment***
Methyl	1184	*Outside scope of study – not considered further*
Butyl	4644	
Octyl	9172	
Total	**15000**	

It has been assumed that there is a 50:50 split between mono- and di-substitutes
Furthermore, butyltin stabilisers are assumed to have 0.2% (as tin) tributyltin
equivalent to 0.83% TBT (EHMA)

Compound	**t/yr**	***Comment***
MBT (EHMA)	2302.7	*Outside scope of study – not considered further*
DBT (EHMA)	2302.7	
TBT (EHMA)	38.6	
MOT (EHMA)	4586.0	*Outside scope of study – not considered further*
DOT (EHMA)	4586.0	

	Molecular Weights:		
Compound	**Compound**	**ATC**	**Sn**
DBT (EHMA)	639.6	303.8	118.7
TBT (EHMA)	493.4	325.5	118.7
DOT (EHMA)	751.8	416.0	118.7

	Equivalent Tonnages as:		
Compound	**Compound**	**ATC**	**Sn**
DBT (EHMA)	2302.7	1093.7	427.3
TBT (EHMA)	38.6	25.5	9.3
DOT (EHMA)	4586.0	2537.6	724.1

A3.3 Catalysts

A3.3.1 Catalysts – Overview

As discussed in Section 2.4.5, the use of organotin catalysts may be summarised as follows:

Catalyst Use	**t/yr**	**Organotin**
EDC	800	Dibutyl
Silicones	100	Dibutyl
Esterification	350	Butyl/Octyl
Polyurethanes	400	Dibutyl
Total	**1650**	

A3.3.2 Catalysts – EDC

Butyltin catalysts are assumed to have 0.2% (as tin) tributyltin
equivalent to 0.50% TBTO

Compound	**t/yr**	***Comment***
DBTO	796.0	
TBTO	4.0	

	Molecular Weights:		
Compound	**Compound**	**ATC**	**Sn**
DBTO	248.9	303.8	118.7
TBTO	298.0	325.5	118.7

	Equivalent Tonnages as:		
Compound	**Compound**	**ATC**	**Sn**
DBTO	796.0	971.6	379.6
TBTO	4.0	4.4	1.6

A3.3.3 Catalysts – Silicones

Butyltin catalysts are assumed to have 0.2% (as tin) tributyltin
equivalent to 0.82% TBTL

Compound	**t/yr**	***Comment***
DBTL	99.2	
TBTL	0.8	

	Molecular Weights:		
Compound	**Compound**	**ATC**	**Sn**
DBTL	631.5	303.8	118.7
TBTL	489.3	325.5	118.7

	Equivalent Tonnages as:		
Compound	**Compound**	**ATC**	**Sn**
DBTL	99.2	47.7	18.6
TBTL	0.8	0.5	0.2

A3.3.4 Catalysts – Esterification and Powder Coating

The relative usage of butyl/octyl tin catalysts are as follows

Organotin	**%**	**t/yr**	***Comment***
Monobutyl	70%	245	
Dibutyl	10%	35	
Mono-octyl	10%	35	
Di-octyl	10%	35	
Total	**90%**	**350**	

As before, butyltin catalysts are assumed to have 0.2% (as tin) tributyltin
equivalent to 0.50% TBTO

Catalyst Type	**Compound**	**t/yr**	***Comment***
Monobutyl	MBTO	243.8	*Outside scope of study – not considered further*
	TBTO	1.2	
Dibutyl	DBTO	34.8	
	TBTO	0.2	
Mono-octyl	MOTO	35.0	*Outside scope of study – not considered further*
Di-octyl	DOTO	35.0	

	Molecular Weights:		
Compound	**Compound**	**ATC**	**Sn**
DBTO	248.9	303.8	118.7
TBTO	298.0	325.5	118.7
DOTO	361.1	416.0	118.7

	Equivalent Tonnages as:		
Compound	**Compound**	**ATC**	**Sn**
DBTO	34.8	42.5	16.6
TBTO	1.4	1.5	0.6
DOTO	35.0	40.3	11.5

A3.3.5 Catalysts – Polyurethanes

Butyltin catalysts are assumed to have 0.2% (as tin) tributyltin
equivalent to 0.82% TBTL

Compound	**t/yr**	***Comment***
DBTL	396.7	
TBTL	3.3	

	Molecular Weights:		
Compound	**Compound**	**ATC**	**Sn**
DBTL	631.5	303.8	118.7
TBTL	489.3	325.5	118.7

	Equivalent Tonnages as:		
Compound	**Compound**	**ATC**	**Sn**
DBTL	396.7	190.8	74.6
TBTL	3.3	2.2	0.8

A3.3.6 Catalysts – Summary

Usage of Organotin Catalysts (t/yr ATC)

Use	DBTC	TBTC	DOTC
EDC	971.6	4.4	
Silicones	47.7	0.5	
Esterification	42.5	1.5	40.3
Polyurethanes	190.8	2.2	
All Catalysts	**1252.6**	**8.7**	**40.3**
Equivalent as Sn	**489.4**	**3.2**	**11.5**

A3.4 Biocides

From Table 2.3, the relative usage of tri-substituted tins is assumed as follows:

Compound	t/yr	*Comment*
TBTO	50.0	
TBTN	50.0	

	Molecular Weights:		
Compound	**Compound**	**ATC**	**Sn**
TBTO	298.0	325.5	118.7
TBTN	500.0	325.5	118.7

	Equivalent Tonnages as:		
Compound	**Compound**	**ATC**	**Sn**
TBTO	50.0	54.6	19.9
TBTN	50.0	32.6	11.9
All Biocides	100.0	87.2	31.8

A3.5 Summary

The overall use (expressed as t/yr ATC) of the organotins of interest is summarised below

Use	DBTC	TBTC	DOTC
PVC Stabilisers	1094	25	2538
Catalysts	1253	9	40
Biocide		87	
All Uses	**2346**	**121**	**2578**

The overall use (expressed as t/yr Sn) of the organotins of interest is summarised below

Use	DBT	TBT	DOT
PVC Stabilisers	427	9	724
Catalysts	489	3	12
Biocide		32	
All Uses	**917**	**44**	**736**

ANNEX 4:

SIMPLIFIED CALCULATIONS FOR ESTIMATING PRODUCTION PLANT LOSSES BY ATC

A4 Plant Losses (Simplified)

A4.1 Production by Site

Based on Table 3.2, production by site is as follows:

Site	Stabilisers	Catalysts	Biocides
S	y	y	
T	y	y	
U	y	y	y
V	y	y	
W	y	y	y
X	y	y	y
Y	y	y	
Z	y	y	y

The total quantities (t/yr as Sn) of the organotins of interest are:

Organotin	Stabilisers	Catalysts	Biocide	All
DBT	427	489		**917**
TBT	9	3	32	**44**
DOT	724	12		**736**
All	**1161**	**504**	**32**	**1697**

Note: figures taken from Annex 3

The ‘average’ production (t/yr as Sn) for each site may be summarised as follows:

Site	Stabilisers	Catalysts	Biocides	All
S, T, V, Y	145	63	0	**208**
U, W, X, Z	145	63	8	**216**
Total (all sites)	**1161**	**504**	**32**	**1697**

Site	DBT	TBT	DOT	All
S, T, V, Y	115	2	92	**208**
U, W, X, Z	115	10	92	**216**
Total (all sites)	**917**	**44**	**736**	**1697**

A4.2 Air Emissions

As shown in Table 3.2, four sites provided quantitative estimates of air emissions.
Clearly, not all emissions are associated with DBT, TBT and DOT.
By inspection of the figures presented in Annex 3, it would appear that
about 40% of emissions would be associated with MBT and MOT.

For this reason, the air emission figures have been adjusted by a factor of 0.6.
The resultant emissions have been distributed by organotin (based on quantities given above)

Air Emission (kg/yr as Sn)

Site	**kg/yr**	**60%**	**DBT**	**TBT**	**DOT**	*Check?*
T	1.7	1.00	0.55	0.01	0.44	*1.00*
X (general)	1.0	0.60	0.32	0.03	0.26	*0.60*
X (DOT)	3.0	*3.00*	-	-	3.00	*3.00*
Y	9.7	5.83	3.21	0.04	2.58	*5.83*
Z	0.2	0.09	0.05	0.00	0.04	*0.09*
Four sites	**15.5**	**10.52**	**4.13**	**0.08**	**6.31**	*10.52*

These four sites include two for stabiliser/catalysts (Sites T and Y)
and two with additional TBT production (Sites X and Z).

Although perhaps unduly conservative, the figures presented above will be doubled
to generate the following emissions and average emission factors for all sites.

Parameter	**DBT**	**TBT**	**DOT**	*Comment*
Air Emissions (kg/yr)	8.26	0.16	12.63	*from all 8 production sites (as Sn)*
Production (t/yr)	917	44	736	*from all 8 production sites (as Sn)*
Air Emission Factor	**9.01E-06**	**3.68E-06**	**1.72E-05**	

For completeness, the air emission figures were converted to kg/yr as ATC

Parameter	**DBTC**	**TBTC**	**DOTC**	*Comment*
MW (ATC)	303.8	325.5	416	*MW for SN is 118.7*
Air Emissions (kg/yr)	21.1	0.4	44.3	*from all 8 production sites (by ATC)*

A4.3 Surface Water Emissions

As shown in Table 3.2, seven sites (not Site X) provided figures for surface water emissions.
As before, not all emissions are associated with DBT, TBT and DOT and,
for this reason, the surface water emission figures have been adjusted by a factor of 0.6.
The resultant emissions have been distributed by organotin (based on quantities given above)

Surface Water Emission (kg/yr as Sn)

Site	**kg/yr**	**60%**	**DBT**	**TBT**	**DOT**	*Check?*
S	20.7	12.40	6.83	0.09	5.48	*12.40*
T	1.4	0.83	0.46	0.01	0.37	*0.83*
U	12.5	7.50	3.98	0.33	3.19	*7.50*
V	4.4	2.66	1.46	0.02	1.17	*2.66*
W	5.9	3.54	1.88	0.16	1.51	*3.54*
X	0.0	0.00	0.00	0.00	0.00	*0.00*
Y	9.0	5.40	2.97	0.04	2.39	*5.40*
Z	0.1	0.06	0.03	0.00	0.03	*0.06*
All sites	**54.0**	**32.4**	**17.6**	**0.6**	**14.1**	**32.4**

As for the air emissions above, these values provide a basis for estimating an average emission
factor as well as the overall emissions in kg/yr as ATC

Parameter	**DBT**	**TBT**	**DOT**	*Comment*
Emissions (kg/yr)	17.61	0.65	14.13	*from all 8 production sites (as Sn)*
Production (t/yr)	917	44	736	*from all 8 production sites (as Sn)*
Emission Factor	**1.92E-05**	**1.46E-05**	**1.92E-05**	

For completeness, the emission figures were converted to kg/yr as ATC

Parameter	**DBTC**	**TBTC**	**DOTC**	*Comment*
MW (ATC)	303.8	325.5	416	*MW for SN is 118.7*
Emissions (kg/yr)	45.1	1.8	49.5	*from all 8 production sites (by ATC)*

A4.4 Waste Water Emissions

As shown in Table 3.2, only Site X discharges to waste water.
However, further detail on the emissions suggest that the butyl:octyl ratio is 99:1 and more than 90% of the emissions are associated with mono-substituted tins.
The di:tri ratio was found to be 3.2.

The estimated (maximum) emission calculation is as follows:

Overall emission	18.00	kg/yr (as Sn)
Excluding mono-tins	1.80	kg/yr (as Sn)
DOT emissions	0.02	kg/yr (as Sn)
Butyl emissions	1.78	kg/yr (as Sn)
DBT emissions	1.36	kg/yr (as Sn)
TBT emissions	0.42	kg/yr (as Sn)

As before, these values provide a basis for estimating an average emission factor as well as the overall emissions in kg/yr as ATC

Parameter	**DBT**	**TBT**	**DOT**	*Comment*
Emissions (kg/yr)	1.36	0.42	0.02	*from all 8 production sites (as Sn)*
Production (t/yr)	917	44	736	*from all 8 production sites (as Sn)*
Emission Factor	**1.48E-06**	**9.59E-06**	**2.45E-08**	

For completeness, the emission figures were converted to kg/yr as ATC

Parameter	**DBTC**	**TBTC**	**DOTC**	*Comment*
MW (ATC)	303.8	325.5	416	*MW for SN is 118.7*
Emissions (kg/yr)	3.5	1.2	0.1	*from all 8 production sites (by ATC)*

A4.5 Summary

The overall emissions and associated emission factors are summarised below.

Emissions to	**DBTC**	**TBTC**	**DOTC**
Air	21.1	0.4	44.3
Surface Water	45.1	1.8	49.5
Waste Water	3.5	1.2	0.1
All Compartments	**69.7**	**3.4**	**93.8**

Emission Factors for	**DBTC**	**TBTC**	**DOTC**
Air	9.0E-06	3.7E-06	1.7E-05
Surface Water	1.9E-05	1.5E-05	1.9E-05
Waste Water	1.5E-06	9.6E-06	2.4E-08