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FRAMEWORK FOR QUALITY ASSESSMENT OF ORGANOTIN IN SEDIMENTS IN VIEW OF RE-USE ON LAND

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LIST OF ABBREVIATIONS

ADI	Acceptable Daily Intake
AVS-SEM	Acid Volatile Sulphide - Simultaneously Extracted Metal
BCF	bioconcentration factor (concentration in plant divided by concentration in soil or water)
DBT	dibutyltin
dm	dry matter
DOT	di-n-octyl tin
D_{pe}	diffusion coefficient through polyethylene pipes
EAC	Environmental (Ecotoxicological) Assessment Criteria
EC	Effect Concentration
fw	fresh weight
GWL	groundwater level
H	Henry’s law coefficient
K_D	soil to water partition coefficient
Koc	organic carbon to water partition coefficient
Kow	octanol to water partition coefficient
LoD	limit of detection
LOEC	Lowest Observed Effect Concentration
L/S	liquid to solid ratio
LoQ	limit of quantification
MBT	monobutyltin
NOEC	No Observed Effect Concentration
OVAM	Public Waste Agency of Flanders
P	vapour pressure
PCB	polychlorinated biphenyl
PE	polyelectrolyte
PNEC	Predicted No Effect Concentration
POC	Point of Compliance
PRG	Preliminary Remediation Goal
R value	limit for re-use of excavated soil as soil in land-use classes II-V
R’ value	limit for re-use of excavated soil as soil in land-use class I
S	solubility
SLV	sediment leaching value
SRV	soil remediation value
TBT	tributyltin
TBTO	tributyltin oxide
TCA	Tolerable Concentration in Air
TDI	Tolerable Daily Intake
TPT	triphenyltin
Vlarea	Flemish Regulation on Prevention and Management of Waste
Vlarebo	Flemish Regulation on Soil Remediation
WHO	World Health Organization

0 MANAGEMENT SUMMARY

0.1 Introduction

The study to develop a 'framework for quality assessment of organotin in sediments in view of re-use on land as granular building material' was undertaken within the TBT CLEAN project. The TBT CLEAN project is funded by the European Commission within the Life-Environment program (LIFE02 ENV/B/000341).

In Flanders, the re-use of waste as secondary (granular) material is regulated by Vlarea (Flemish Regulation on the Management and Prevention of Waste). For inorganic contaminants, both a total concentration limit and an emission limit are given. The total concentration limit is indicative, whereas the emission limit (or immission limit in case of applications deviating from the default scenario) is binding. For organic contaminants, only a total concentration limit applies; the values are binding. The total concentration limits for organic contaminants equal the soil remediation values for residential land-use. Vlarea has no quality criteria for organotin compounds in its regulation on re-use as secondary building material.
Work is currently undertaken to modify the Vlarea framework. The background to start this revision was the publication of the European Landfill Directive and its Technical Background Document, and the lack of an adequate method for the estimation of the impact of leaching of organic contaminants.

The objective of the work, presented in this report, was to derive quality criteria for butyltin compounds (tributyltin, dibutyltin and monobutyltin) in a scenario of re-use of treated harbour sediment as granular building material. The framework should take account of the present legislation and ongoing developments. The present legislation provides quality criteria for – what is called here – free re-use. This means that no restrictions with regard to containment, coverage, contact possibilities, … apply. In parallel to this, quality criteria were developed for two restricted re-use scenarios: application with coverage and above groundwater level, and application under groundwater level.

An initial framework was developed, which looked as follows:

- free re-use: upper limit equal to the soil remediation value for residential land-use (SRV(III));
- restricted re-use: upper limit and emission limit based on leaching to groundwater; the emission limit should be receptor-based with either human health or ecosystem health as the endpoint.

During the project, the framework was modified and finally looks as:

- free re-use: upper limit (SedUL) equal to the soil remediation value for residential land-use (SRV(III)); total concentration limit (SedLV) based on leaching to groundwater with a human-health based criterion as endpoint;
- restricted re-use: upper limit (SedUL) equal to the soil remediation value for industrial land-use (SRV(V)); total concentration limit (SedLV) based on leaching to groundwater

with a human-health based criterion as endpoint and based on default scenarios for re-use with coverage above groundwater level and re-use below groundwater level.

The reasons for these changes were:

- the leaching test applied does not allow to calculate an emission limit; the limits have to be expressed on a total concentration basis in the sediment and are calculated from the results of the leaching test;
- leaching limits were also needed for free re-use to keep consistency in the framework and its application;
- a human-health based criterion is a logical condition for groundwater as a receptor (drinking-water use); an ecosystem based criterion is a valid condition for surface water (under the influence of groundwater discharge) as a receptor; for the latter situation only some indicative simulations were done because no default scenario could be determined due to large variability in possible scenarios.

In order to reach the project goals, following phases were distinguished:

- literature review on environmental fate; effects on human health; background exposure of the population and terrestrial ecotoxicity;
- experiments consisting of leaching tests on treated sediment samples; development of an adequate aquatic ecotoxicity test and application of the ecotoxicity test on the leachates;
- derivation of the quality criteria.

0.2 Experimental results

Leaching tests were undertaken on six treated sediment samples. Treatments were lagunation and mechanical dewatering with either lime or polyelectrolyte. For each treatment, a low and a high organotin containing sediment was used in the experiments. The leaching test was a two stage batch leaching test at L/S=2 and L/S=8 (L/S = Liquid to Solid Ratio). The leachates at L/S=2 were used in the ecotoxicity tests. Following table shows the results of the leaching test at L/S=2. In the experiments less than 1 % of the organotin present in the sediments was leached out. The sorption coefficient can then be calculated as the ratio between concentration in sediment and concentration in leachate and does not need to be corrected for the L/S ratio.

Results of the leaching test on six sediment samples (results of L/S=2)

sample		**Sediment (µg/kg dm)**	**Leachate (µg/kg dm)**	**K_D* (l/kg)**
lagun. - low	MBT	129	0.044	5864
	DBT	246	0.531	928
	TBT	1020	3.0	680
lagun. - high	MBT	884	0.306	5778
	DBT	2271	2.403	1893
	TBT	27554	40	1378
lime - high	MBT	3492	0.611	11449
	DBT	1418	3.004	945
	TBT	31100	48	1296
lime - low	MBT	374	0.091	8500
	DBT	127	0.681	384
	TBT	1445	10.1	295
PE - high	MBT	1469	0.356	8347
	DBT	3521	2.425	2934
	TBT	52777	34	3105
PE - low	MBT	101	0.088	2295
	DBT	350	0.614	1140
	TBT	2554	3.4	1502

*: $K_D = C_{sediment}/C_{leachate}$

Two ecotoxicological tests, which are designed to detect the toxicity of organotins on the basis of their possible working mechanism, were applied first (Yeast Androgen Receptor or YAR assay, and aromatase inhibition assay on human JEG-3 cells). In both tests, an organotin-specific dose-response could not be measured. Therefore the early embryo development test in zebrafish was used as an alternative. This is not an organotin specific test. From the spiking experiments on both fish water and leachate from the lagunated sediment, a NOEC of 1 µg/l could be derived for TBT. However, this NOEC did not give any indication that a higher value than the PNECs published in the literature could be used. For this reason, preference was given to a PNEC published in the literature and based on the extensive database of aquatic toxicity data. The value derived by the German UmweltbundesAmt for aquatic ecosystems (0.07 ng/l) was chosen to serve as and endpoint in surface water. For comparison, an Environmental Assessment Criterion of 0.1 ng/l is proposed within OSPAR for the marine environment.

0.3 Calculation of quality criteria

0.3.1 Upper limits

The upper limits for free re-use and for restricted re-use were set equal to the soil remediation values for residential land-use (free re-use) and industrial land-use (restricted re-use). The choice of the SRV(III) as an upper limit (SedUL) for free re-use is in accordance with the present regulations. In case of restricted re-use, direct contact of humans with the sediment is not present due the the coverage layer. As such a higher total concentration limit can be chosen. SRV(V) was chosen as the upper limit for restricted re-use.

Soil remediation values for residential and industrial land-use are mainly based on human-health criteria and are then calculated with the model Vlier-humaan. This model accounts for transfer of contaminants from soil to various environmental compartments (air, drinking water, vegetation, cattle, ..), calculates human exposure from defined exposure pathways and calculates a risk index as the ratio between dose and a toxicological criterion (Tolerable Daily Intake or TDI for non-carcinogens). The soil remediation value equals the level at which following criteria are met: risk index ≤ 1; predicted concentration in outdoor/indoor air ≤ Tolerable Concentration in Air; predicted concentration in drinking water ≤ guideline or legal value for drinking water; predicted concentration in animal or vegetable food/feed ≤ legal values for food/feed.
If ecotoxicological values are available, an ad-hoc estimate of the necessity to lower the proposed soil remediation value is given. However, a draft method for calculation of ecotoxicology based soil remediation values exists and is applied here. The method is based on the Canadian approach for Soil Quality Guidelines.

Input parameters of the butyltin compounds for the Vlier-humaan model are given in the following table. A soil remediation value was not calculated for monobutyltin as toxicity data were lacking. Physicochemical properties are also very uncertain for the latter compound.

Input parameters for the Vlier-humaan model, specific for butyltin compounds

	TBTCl	DBTCl
M	325.59 (TBTCl) 290.03 (TBT)	303.85 (DBTCl) 268.39 (DBT)
S (mg/l)	$1^{(as\ Sn)}$ (20 °C)	47.5 (20°C)
P (Pa)	1.2 (25 °C)	10.3 (25°C)
H ($Pa.m^3/mol$)	142 (25°C)	66 (25 °C)
log Kow	3.6	0.58
Koc (l/kg)	$10^{\wedge(4.71)}$	$10^{\wedge(4.73)}$
BCF root (-)	25 (Lespes) 1.1 (Brandsch) f (Kow)	0.6 (Lespes) 8.3 (Brandsch) f (Kow)
BCF stem (-)	12 (Lespes) 1.1 (Brandsch) f (Kow)	1.5 (Lespes) 8.3 (Brandsch) f (Kow)
Dpe (m^2/d)	5E-7	5E-7
TDI (mg/kg.d)	2.5E-4	2.5E-4
TCA (g/m^3)	5.75E-7	5.75E-7
limit water (µg/l)	0.75	0.75
background exposure (mg/kg.d)	8.9E-6	6.3E-6

The vapour pressure found in the literature for dibutyltin deviated largely from the expected increase of vapour pressure from tributyltin to monobutyltin. Vapour pressures were calculated with the Epiwin software and corresponded well with experimental data for tributyltin and monobutyltin. Epiwin predicted values were taken for the calculations. Solubility was taken at the lower range of the literature data to provide a conservative estimate of Henry's law coefficient (H = vapour pressure/solubility). K_{oc} was calculated as the geometric mean of the values found in this project; the value corresponded well with the geometric mean of literature values. D_{pe} (diffusion through polyethylene) was taken from the RIVM report. Plant uptake values (BCF) were taken as the highest values from field experiments to provide a conservative estimate. The Tolerable Daily Intake (TDI) was taken from WHO and EFSA and should be used for both TBT and DBT. Additivity of both compounds should be assumed. The Tolerable Concentration in Air (TCA) was extrapolated from the TDI; the limit in drinking water was calculated from the TDI using the WHO approach for deriving drinking water guideline values. Background exposure in food is calculated from mean concentrations given in the EFSA report and average food and seafish consumption in Belgium.

The calculated SRV values were:

SRV(III)	0.51 mg/kg dm for TBT and 0.07 mg/kg dm for DBT
SRV(V)	196 mg/kg dm for TBT and 204 mg/kg dm for DBT

An ecosystem based soil remediation value was calculated for TBT from the data of Hund-Rinke. The lowest EC_{50} of 1.5 mg/kg dm (*Eisenia fetida*) was divided by a safety factor of 5 (according to the methodology) to provide an $SRV(III)_{eco}$ of 0.3 mg/kg dm. No ecotoxicology based value could be calculated for industrial land-use.
Because the human-health based and the ecotoxicoloy-based value are in line with each other, the human-health based value is restrained as upper limit (SedUL).

0.3.2 Leaching values

The leaching values are back calculated from the limit in groundwater by means of a leaching model and a default scenario. The limit in groundwater is set at 10 % of the calculated drinking water limit and equals 0.075 µg/l.

The scenario for free re-use of treated sediment as granular building material corresponds with the framework under development for OVAM for organic contaminants present in secondary raw materials. The reference scenario assumes the presence of a sediment layer of 150 m long and 0.7 m high on top of a soil layer of 1 m depth. Groundwater velocity is 20 m/y and the thickness of the phreatic layer is 5 m. Rainwater infiltration rate is 300 mm/y. Groundwater concentrations are calculated at a distance of 20 m in the direction of groundwater flow. The K_D for soil was taken as the geometric mean of literature values (1863 l/kg for TBT and 3419 l/kg for DBT). The K_D of the phreatic layer was assumed to be 10 times lower. Results are given in the following table for a range of K_D values in the sediment. The SedUL shows an almost linear dependence on K_D and can be calculated from the measured K_D with the relationship given.

Leaching criteria for "free re-use"

K_D of sediment (l/kg)	TBT (mg/kg dm)	DBT (mg/kg dm)
100	0.34	0.60
500	0.36	0.64
1000	0.41	0.67
1500	0.46	0.72
2000	0.52	0.77
2500	0.57	0.82
3000	0.62	0.88
4000	0.73	0.98
5000	0.84	1.09
6000	0.96	1.19
7000	1.07	1.30
8000	1.18	1.42
9000	1.29	1.53
10000	1.41	1.63

TBT: $\text{SedLV} = 0.0001K_D + 0.3019$
DBT: $\text{SedLV} = 0.0001K_D + 0.5679$

The scenario for restricted re-use with a coverage and above groundwater level deviates from the reference scenario in that it is assumed that a reduced infiltration rate of 6 mm/y applies. This value is taken from the Dutch Bouwstoffenbesluit. The coverage material should meet this preset infiltration rate. The results are given in the following table.

Leaching criteria for "restricted re-use" with coverage and above groundwater level

K_D of sediment (l/kg)	TBT (mg/kg dm)	DBT (mg/kg dm)
100	6.9	12.0
500	7.3	12.9
1000	8.3	13.5
1500	9.3	14.4
2000	10.6	15.4
2500	11.5	16.5
3000	12.7	17.6
4000	14.9	20.2
5000	17.2	23.3
6000	19.6	24.5
7000	22.0	26.7
8000	24.3	28.9
9000	26.6	31.1
10000	29.0	33.3

TBT: $\text{SedLV} = 0.0023K_D + 6.0545$
DBT: $\text{SedLV} = 0.0022K_D + 11.401$

The scenario for restricted re-use below groundwater level assumes an application of 150 m of length in the direction of groundwater flow with an evaluation of groundwater concentration at 20 m distance. Since the calculated concentration limits do no depend on the K_D value of the soil, the curves of the concentration limit in function of the K_D value of the sediment are the same for TBT and DBT. The values are given in the following table.

Leaching criteria for restricted re-use, application below groundwater level.

K_D of sediment (l/kg)	TBT/DBT (mg/kg dm)
100	0.007
500	0.038
1000	0.077
1500	0.115
2000	0.154
2500	0.192
3000	0.231
4000	0.308
5000	0.385
6000	0.463
7000	0.540
8000	0.617
9000	0.694
10000	0.772

TBT/DBT: SedLV = 8E-05K_D – 0.0007

Finally, exploratory calculations were made for a scenario in which surface water is the receptor and the organotin compounds reach the surface water by leaching from the sediment into the groundwater and subsequent discharge of the groundwater into the surface water. As such, an additional mixing factor for dilution of groundwater in surface water has to be taken into account. The ecotoxicological surface water criterion of 0.07 ng/l was back calculated towards a groundwater criterion by multiplying with the mixing factor (ratio between the sum of groundwater and surface water flow and groundwater flow) assuming an application of 150 m length along the river. This was done illustratively for three Flemish rivers. The resulting groundwater criterion could then be back calculated towards a SedLV using the same models as for free re-use and restricted re-use. The results are given in the following table.

Leaching criteria based on an ecotoxicological endpoint in surface water.

Stream	MF	GW criterion (µg/l)	Leaching criteria “free re-use” (mg/kg dm)	Leaching criteria “restricted re-use” (mg/kg dm)
- [N(eco)^{2}]	2.4	0.000168	0.0009	0.018
Bosbeek	211	0.0148	0.08	1.6
Mangelbeek	2066	0.145	0.78	16.1
Schelde	960742	67.3	364	7500

From the results it can be concluded that the impact on surface water is highly dependent on the local circumstances. In situations where the surface water has a moderate discharge rate, the impact of the re-use of organotin containing sediment could be critical.

0.4 Integration and conclusions

The quality criteria calculated were integrated into a framework for re-use of treated organotin containing sediment on land as granular building material. Quality criteria are given for three re-use options; for each option both upper limits (SedUL) and leaching values (SedLV) are given. The SedUL is a total concentration in the sediment that may not be exceeded. The SedLV is a total concentration in the sediment that is calculated from a measured K_D value (leaching test at L/S = 2). The lowest of SedUL and SedLV is taken to evaluate the re-use options of the sediment. The quality criteria apply to treated sediment that is geotechnically fit for re-use as granular building material. The criteria do not apply to in-situ of freshly dredged sediment.

Quality criteria for free re-use of organotin containing sediment

	TBT (mg/kg dm)*	DBT (mg/kg dm)*
SedUL (free re-use)	0.5	0.07
K_D of sediment (l/kg)**	SedLV(free re-use)	
100	0.34	n.l.
500	0.36	n.l.
1000	0.41	n.l.
1500	0.46	n.l.
2000	n.l.	n.l.
2500	n.l.	n.l.
3000	n.l.	n.l.
4000	n.l.	n.l.
5000	n.l.	n.l.
6000	n.l.	n.l.
7000	n.l.	n.l.
8000	n.l.	n.l.
9000	n.l.	n.l.
10000	n.l.	n.l.

n.l.: not limiting; the SedLV is higher than the SedUL

*: the decision on the re-use will be taken based on the following sum of ratios:

$$\frac{C(TBT)}{SedUL(TBT)}+\frac{C(DBT)}{SedUL(DBT)} \text{ and } \frac{C(TBT)}{SedLV(TBT)}+\frac{C(DBT)}{SedLV(DBT)},$$

if one of these sum of ratios exceeds the value of 1, no free re-use as granular building material

**: the SedLV for TBT can be calculated from the experimental K_D with the following equation:

$$SedLV^{free}(TBT) = 0.30 + 0.0001K_D$$

Quality criteria for re-use of organotin containing sediment under coverage (infiltration rate 6 mm/y) and above groundwater level

	TBT (mg/kg dm)*	DBT (mg/kg dm)*
SedUL(restricted re-use)	195	205
K_D of sediment (l/kg)**	SedLV(coverage, above GWL)	
100	6.9	12.0
500	7.3	12.9
1000	8.3	13.5
1500	9.3	14.4
2000	10.6	15.4
2500	11.5	16.5
3000	12.7	17.6
4000	14.9	20.2
5000	17.2	23.3
6000	19.6	24.5
7000	22.0	26.7
8000	24.3	28.9
9000	26.6	31.1
10000	29.0	33.3

*: the decision on the re-use will be taken based on the following sum of ratios:

$$\frac{C(TBT)}{SedUL(TBT)}+\frac{C(DBT)}{SedUL(DBT)} \text{ and } \frac{C(TBT)}{SedLV(TBT)}+\frac{C(DBT)}{SedLV(DBT)}$$

if one of these sum of ratios exceeds the value of 1, no re-use as granular building material under coverage and above groundwater level is allowed

**: the SedLV can be calculated from the experimental K_D with the following equation:

$$SedLV^{\mathrm{cov},above\ GWL}(TBT) = 6.1 + 0.0023K_D$$

$$SedLV^{\mathrm{cov},above\ GWL}(DBT) = 11.4 + 0.0022K_D$$

Quality criteria for re-use of organotin containing sediment under groundwater level

	TBT (mg/kg dm)*	DBT (mg/kg dm)*
SedUL(restricted re-use)	195	205
K_D of sediment (l/kg)**	SedLV(coverage, under GWL)	
100	0.007	0.007
500	0.038	0.038
1000	0.077	0.077
1500	0.12	0.12
2000	0.15	0.15
2500	0.19	0.19
3000	0.23	0.23
4000	0.31	0.31
5000	0.39	0.39
6000	0.46	0.46
7000	0.54	0.54
8000	0.62	0.62
9000	0.69	0.69
10000	0.77	0.77

*: the decision on the re-use will be taken based on the following sum of ratios:

$$\frac{C(TBT)}{SedUL(TBT)}+\frac{C(DBT)}{SedUL(DBT)} \text{ and } \frac{C(TBT)}{SedLV(TBT)}+\frac{C(DBT)}{SedLV(DBT)}$$

if one of these sum of ratios exceeds the value of 1, no re-use as granular building material below groundwater level is allowed

**: the SedLV can be calculated from the experimental K_D with the following equation:

$$SedLV^{under\ GWL}(TBT/DBT) = -0.0007 + 8*10^{-5}K_D$$

In addition to the values given above where groundwater is considered the receptor with a human-health based criterion (0.75 µg/l), attention should be paid to leaching of organotin compounds from sediment towards surface water. In surface water, an ecotoxicological based criterion applies (0.07 ng/l as preliminary value for TBT). Considering the significant impact of the ratio of groundwater flux to surface water flux on the dilution factor and thus on the quality criterion, the choice is made not to give sediment quality criteria with regard to surface water as a receptor. It is expected that re-use of the treated sediment in areas with groundwater drainage to large rivers as the Schelde, will not pose problems for the surface water if the dimensions of the application do not exceed the standard dimensions (0.7 m high and 150 m long in the direction of the groundwater flow) too strongly . If drainage to smaller rivers would occur, this pathway can be critical.

The calculated quality criteria depend on the choice of the parameter values and on the model scenarios. Uncertainty and variation in parameter values is discussed in the derivation of the criteria. Main uncertainties and variations are found in the plant uptake factors, K_D values and Henry's law coefficient. The choice of the plant uptake factor significantly influences the SedUL for free re-use; the choice of K_D and Henry's law coefficient influences the SedUL for restricted re-use. The plant uptake factor is the upper limit of the ranges of the field data; also Henry's law coefficient is taken as a conservative value. K_D is the geometric mean and should represent average conditions. K_D also influences SedLV because the geometric mean of literature values is taken for the soil layer under the sediment and as a basis for the sorption coefficient in the aquifer. The variation in K_D in the sediment, however, is taken into account by using K_D factors measured on the real sediment. SedLVs also depend on the default scenario chosen. When the application deviates significantly from the default scenario, site-specific SedLVs should be calculated. This is especially the case for soils with very low organic matter content (and low K_D) and for applications with a height and length that strongly exceeds the standard values.

1 INTRODUCTION

TBT CLEAN is a research project funded by the European Commission within the Life-Environment program (LIFE02 ENV/B/000341). Main objective is the development of an integrated approach for the removal of tributyltin from waterways and ports. The TBT CLEAN project has four main goals:

1. to briefly assess the environmental impact of already available alternatives for TBT;
2. to determine the release of TBT from sediments into the aquatic environment during dredging operations;
3. to test several treatment technologies for TBT contaminated sediments;
4. to check re-use possibilities for cleaned sediments.

The current report presents quality criteria for the re-use of treated port sediment containing organotin compounds. The quality criteria were developed within a framework for re-use of the treated sediment as granular building material on land. The initial framework is schematized in Figure 1.

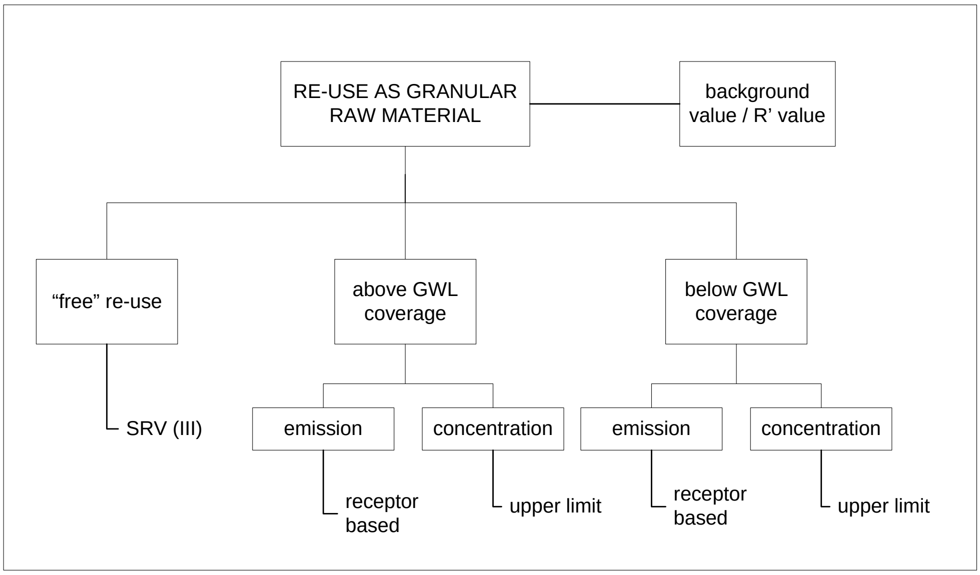

Figure 1: Initial framework for quality criteria for re-use of organotin containing sediment as granular building material (application on land); SRV(III): soil clean-up value for residential land-use; GWL: groundwater level; R': value for free re-use of waste material as soil

Three re-use options were to be considered:

1. "free" re-use: this re-use will be subject to the conditions specified in the Flemish Regulation on the Management and Prevention of Waste (Vlarea); in case of organic contaminants, Vlarea specifies an upper limit equal to the soil clean-up value for residential areas (SRV(III));
2. re-use with coverage above groundwater level;
3. re-use with coverage below groundwater level;

Under the latter two options criteria for both total concentration as well as concentration in the leachate would apply. The maximum concentration in the leachate would be receptor-based. Human health criteria and/or experimentally determined ecotoxicological safe levels should be accounted for.

In order to reach the project goals, following phases were distinguished:

- literature review on environmental fate; effects on human health; background exposure of the population and terrestrial ecotoxicity;
- experiments consisting of leaching tests on treated sediment samples; development of an adequate aquatic ecotoxicity test and application of the ecotoxicity test on the leachates;
- derivation of the quality criteria.

The project addresses butyltin compounds. Although phenyltin compounds are also found in port sediment, no quality criteria were derived for the latter compounds.

The report is structured according to the outline given hereafter. Chapter 2 provides a description of the legal framework that applies to the current project, the ongoing developments in this area and the framework developed within the project. The final framework is a modification of the initial framework as a consequence of constraints given by the model concept used and the results of the ecotoxicological tests. Chapters 3, 4, 5, 6 and 7 give the results of the literature review on environmental fate, plant uptake, human toxicity, dietary exposure and terrestrial toxicity. Chapter 8 presents the available soil quality values for organotin compounds found in legislations outside Flanders and the requisites from hazardous materials legislation. In chapter 9 the experimental design, the results of the leaching tests and of the ecotoxicity tests are described. Chapter 10 deals with the calculation of the quality criteria. Chapter 11 integrates the quality criteria and provides the framework and the values to be used when evaluating the re-use on land of treated butyltin containing sediment as granular building material.

2 FRAMEWORK DEVELOPMENT

2.1 Legal framework

2.1.1 Flemish Regulation on Prevention and Management of Waste

The re-use of treated harbour sediment is regulated by Vlarea, the Flemish Regulation on Prevention and Management of Waste (Fl. Gov., 2003 and amendments). Two re-use possibilities are open: either re-use as secondary material in or as granular building material or re-use as soil.

The re-use as *secondary material* is further regulated by Vlarea. Limits for total concentration and for emission are given in case of inorganic contaminants. The total concentration limits are indicative, whereas the emission criteria are binding. The emission criteria are derived from the condition of marginal soil load (or marginal groundwater load). This corresponds with a maximum enrichment in the top soil layer (thickness 1m) of 1% of the normal background over a period of 100 years. The leaching properties are determined in a standardized leaching test. The emission criteria are valid for a "standard" application with a height of 0.7 m, a density of 1550 kg/m^3 and an effective infiltration of 300 mm/y. If deviating leachability, application height or density occur, immission limits for soil should be used (and measured emission is converted to immission by standardized algorithms).
A total concentration limit is given for organic contaminants. This total concentration limit is binding and equals the soil remediation value for land-use category III (residential areas). No limits with regard to emission are available for organic contaminants.

For the *re-use as soil*, Vlarea provides a link with Vlarebo, the Flemish Regulation on Soil Remediation (Fl. Gov., 1995 and amendments). In this case, the conditions for re-use of excavated soil as soil apply.
In addition to this, Vlarea specifies limits for the levels of organochlorine pesticides and PCBs in dredged sediments in view of re-use as soil. The concentration limits for organochlorine pesticides and PCBs are dependent on the use of the area where re-use will take place. For re-use within land-use class I (nature reserves, groundwater protection areas), the analytical detection limits apply, which for the organochlorine pesticides are fixed at 0.1 mg/kg dry matter and for the PCBs at 0.002 mg/kg dry matter. For applications in land-use class II to V the limits are set to 2x the detection limit.
None of the regulations mentioned provides numbers for organotin compounds.

2.1.2 Flemish Regulation on Soil Remediation

Vlarebo provides limits for the evaluation of contamination present in the soil (background values and remediation values) and for the evaluation of excavated soil in view of its re-use as soil (R values and R' values). If excavated soil is to be re-used as secondary material, the conditions of Vlarea apply.

Background values correspond to the concentrations found in soils, that are not influenced by human activities. For natural substances (such as heavy metals) the concentrations correspond to the 90-percentile of the natural levels. For anthropogenic compounds, the concentrations correspond to the level of detection of the prescribed analytical method.

Soil remediation values represent the level above which harmful effects can arise for man or environment, taking into account the characteristics of the soil and its function. Soil remediation values for the solid phase of the soil are given for five land-use classes: I (nature), II (agriculture), III (residences), IV (recreation), and V (industry). The values for the land-use classes II to V are mainly (but not uniquely) based on human health criteria. The human health based values are calculated with the model Vlier-humaan, a soil-oriented multimedia model allowing for the calculation of a) fate and transfer in and from soil, b) human exposure and c) human health risk. Transfer pathways included are:

- evaporation from soil to outdoor and indoor air;
- air dispersion of soil particles;
- leaching from soil to groundwater;
- diffusion through synthetic drinking water pipes;
- uptake by plants;
- exposure of cattle.

The exposure pathways depend on the land-use class chosen and include:

- ingestion of soil/dust particles (II, III, IV, V);
- inhalation of soil/dust particles (II, III, IV, V);
- inhalation of volatile contaminants in air (II, III, IV, V);
- dermal absorption from soil (II, III, IV, V);
- ingestion of drinking water (III, IV, V) or groundwater (II);
- dermal uptake from drinking water (III, IV) or groundwater (II) during bathing or showering;
- vegetable intake (II, III);
- meat and dairy products intake (II).

Parameter values and exposed groups depend on land-use class and corresponding scenarios.

The human health criterion used is either a TDI[1] value or the dose corresponding with an excess lifetime cancer risk of 1 in 100,000 exposed individuals[2]. The soil remediation value corresponds to the level in soil at which the calculated dose is equal to the human health criterion or to the level in soil at which the calculated concentration in the critical contact medium[3] is equal to the human health based (or legally binding) maximum concentration.

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[1] TDI or Tolerable Daily Intake corresponds to the dose that can be taken in by the general population during a lifetime without harmful effects. This principle applies to noncarcinogens or to carcinogens where a threshold for effects is found.

[2] For carcinogens without a threshold for effects, the dose-response is expressed as a unit risk or slope factor, reflecting the excess cancer risk per unit dose or concentration. This can be transformed into a dose by taking the ratio of excess lifetime cancer risk and unit risk

[3] It is possible that, even if the TDI is not exceeded, calculated concentrations in air, vegetation, drinking water or animal products exceed either legal or human health based values. In this case, the remediation value is lowered until none of these values (if available) is exceeded.

An additional check is made with regard to ecotoxicological effects. If data on ecotoxicological effects are available, it is checked whether the human health based values are in discrepancy with the ecotoxicological effect levels. Lowering of the values is decided on an ad-hoc basis. However, a more systematic approach, based on the Canadian system for environmental soil quality guidelines (CCME, 1996) is available in draft version.

Remedation values for groundwater are based on the principle that groundwater should be suitable for drinking water consumption; their derivation follows the method used by the World Health Organization. Only the toxicological criterion is taken, taste and odour thresholds are usually not considered (whereas the WHO provides values for the latter endpoints).

Free re-use of excavated soil as soil is subject to a concentration limit, which depends on the use of the area where the soil will be applied. For re-use within land-use class I (nature), the R' values apply. These values are either equal to the background values in case of natural compounds or they correspond to the level of quantification in case of anthropogenic compounds. For re-use in the other land-use classes, the R values apply. They equal the average of the background value and the soil remediation value for land-use class II, with a maximum of 60% of the latter remediation value. Deviations from these values are possible under given conditions. In that case, a study has to be undertaken to show that the contaminants present do not pose an additional risk to man or environment. The technical guidance specifies that impact on groundwater should be evaluated; a method and software is available.

2.2 Ongoing developments

Accounting for recent developments on the European level and the lack of an adequate method for organic contaminants, work is currently undertaken in view of a modification of the Vlarea framework.

First, the technical background document of the European Landfill Directive (TAC, 2002) provides a method for calculation of leaching criteria. An exercise is undertaken to apply this methodology to the re-use of waste as secondary material as an additional criterion to marginal soil load.

Secondly, there is no method comparable with the approach for inorganic contaminants, for assessing the impact of organic contaminants leaching from secondary material. This is caused by two problems:

1. there is at present no standardized column leaching test to test leaching of organic compounds from waste materials; as such a framework based on emission/immission is not possible;
2. the principle of marginal soil load is rather difficult to apply for compounds with no natural background as the value will be very dependent on the analytical method and corresponding analytical specifications (limit of detection, limit of quantification).

To assess the impact on groundwater of the re-use of waste as secondary material, a groundwater criterion is back calculated to a maximum admissable concentration in the secondary material using a mathematical transport model. This approach is currently under development for both inorganic and organic compounds (Seuntjens et al., 2004).

A reference scenario is laid out defining the path of the contaminant from source to receptor and the dimensions of a typical application. The scenario is taken from the calculations at the base of the European Landfill Directive criteria (TAC, 2002) and only slightly modified for the application as granular building material (application height) and for Flemish conditions. The reference scenario in the draft framework consists of a layer of secondary material of 0.4 metres height and 150 metres length on top of a soil layer of 1 metre depth. Groundwater concentrations are considered in a point of compliance (POC) at 20 metres distance from the application. The groundwater criterion now under discussion for organic compounds is 10% of the soil remediation value for groundwater.

In the model calculations, the following processes are taken into account:

- leaching from the layer of granular building material;
- transport through soil and dispersion in soil;
- adsorption/desorption to soil;
- dilution of infiltrating water in groundwater;
- transport in groundwater and dispersion in aquifer;
- adsorption/desorption to aquifer material.

The framework currently under development for the use of secondary material as granular building material considers the impact of the application of the material on soil as well as on groundwater. The same mathematical model is used to calculate concentrations in soil at certain depths and times. However, currently there is not yet a clear direction as to how to evaluate these soil concentrations and therefore, the impact on soil is not considered in this report.

Although a framework for assessing the quality is under development, there is still no official leaching test for organic contaminants. A draft method is used in the project; details are given in the applicable section.

2.3 Framework development

As given in the introduction, the project aims at providing quality criteria for the re-use of treated organotin containing harbour sediment as secondary material. Quality criteria will be given for “free re-use” according to the principles in the legal framework, and for “restricted re-use”. Further more, the framework will be as close as possible to ongoing policy and technical developments in the field.

Taking this into account the quality criteria are calculated as follows:

- *limits of detection and of quantification* are given for information: as an official analytical method is lacking, no final value can be given here;

- *endpoints for leaching*:
    - a human health based criterion taken as the endpoint in groundwater;
    - an ecotoxicologically based criterion taken as the endpoint in surface water: seen the complexity of this approach, calculations are exploratory;
- *free re-use as granular secondary material*:
    - soil remediation value for land-use class III: this value is calculated with the Vlier-humaan model (human health) and also accounts for ecotoxicological criteria using the draft method. Its use is as the upper limit for “free” re-use as secondary granular building material, corresponding to the present legal condition for re-use of waste as secondary building material;
    - concentration limit based on leaching: in view of the recent developments, a concentration limit is calculated with the method outlined above under default conditions for infiltration and application height specified in Vlarea (0.7 m is still the official value and is more conservative than 0.4 m, which provides a safe estimate in case the change will take place);
- *re-use under restricted conditions:*
    - soil remediation value for land-use class V: this value is calculated with the Vlier-humaan model. The value is used as an upper limit for total concentrations in case of “restricted” re-use;
    - concentration limit for re-use under restricted conditions based on leaching: a concentration limit is calculated with the method outlined above under condition of reduced infiltration (re-use above groundwater level), and under condition of re-use in groundwater;
- *ecotoxicology based endpoint*: the ecotoxicology based endpoint is used in surface water; backcalculation requires assumptions of way of application, aquifer properties and surface water properties; seen the complexity of this approach, a range of possible concentration limits in case of re-use as raw secondary material is given.

The approach followed differs from the anticipated approach on two aspects:

- The criterion for free re-use is not only based on the SRV(III), but also accounts for leaching. This modification is justified by the recent developments and with a view to avoid conflicts and inconsistencies in the proposed framework and quality criteria;
- The ecotoxicologically based criterion is used for surface water and no firm criteria are derived. This change is justified by the fact that an ecotoxicogical criterion is more relevant for surface water than for groundwater and by the fact that the method is more in favour of a site-specific approach.

3 ENVIRONMENTAL FATE

3.1 Organotin in the environment

Organotin compounds are characterized by a Sn atom covalently bound to one or more organic substituents (e.g. butyl, ethyl). Chemically they are represented by formulas of the type $RSnX_3$, R_2SnX_2, R_3SnX, R_4Sn, in which R is an alkyl or aryl group and X is an anionic species, e.g. chloride or hydroxide. The Sn-C bonds are stable in the presence of water, atmospheric O_2 and heat and are reported to be stable at temperatures up to 200°C. The number of Sn-C bonds and the length of the alkyl chains have a profound effect on the chemical and physical properties of the organotins. In general, the solubility of organotin compounds in water decreases with increasing number and length of the organic substitutes but it also depends on X.

When introduced into water, organotin compounds undergo pH-dependent hydrolysis. Cations are formed in water at $pH < pKa$, and these monovalent organometallic cations behave as weak acids. For the hydroxocomplex TBTOH, a stability constant pKa of 6.51 was reported (Shoukry, 1993 in Fent, 1996). This means that at $pH < pKa$ (6.51), the dominant species is the cation TBT^+, whereas at $pH > 6.51$, TBT is present as neutral TBTOH. At pH 8 (normal for seawater), the major TBT species are tributyltin hydroxide and tributyltin carbonate (Champ and Seligman, 1996). This pH-dependent speciation of TBT has consequences for the partitioning between aqueous and organic phases and affects its bioavailability, bioaccumulation and toxicity.

Organotins have known various industrial applications as stabilizers in PVC, as pesticides, in timber preservatives and in antifouling paint for ships and have entered the environment through various pathways. The most relevant source for organotins in harbour sediments is from antifouling paint and the main compounds arising from that source are TBT and its degradation products DBT and MBT. Phenyltin compounds have also been detected, presumably from its use as cotoxicant to TBT in antifouling paints. Fent (1996) reports TBT-levels in sediments from 13 estuaries and harbours between 0.1 and 9.7 mg TBT/kg dry weight. TBT, DBT and MBT (in this order of concentrations) have been found in freshwater harbour water as well. Weidenhaupt et al. (1997) indicate a range of TBT-concentrations from 0.001 to 10 mg TBT/kg found in harbour sediments.

3.2 Physicochemical properties

Physicochemical properties necessary to calculate quality criteria are listed in Table 1 for the most relevant butyltin compounds for harbour sediments. Details are given in Appendix I.

Aqueous solubilities of TBT compounds are reported in a wide range and depend on pH as well as on temperature and ionic conditions. Inaba et al. (1995) studied the solubility of organotin compounds under changing conditions of salinity and pH. Expressed as Sn, the minimum solubility of TBT was 1 mg/l in seawater and 15 mg/l in distilled water at 25 °C; the minimum solubility was found at pH 6-8. Solubility at 10 °C was half that at 25 °C. It is not clear how the data in Appendix I are expressed; as the molecule itself, as the TBT ion or as Sn. Correction between the molecule and the ion is small; correction between the molecule (chloride) or the ion to Sn is a factor of 2.44 – 2.74.

Vapour pressures were also calculated with the EPIwin v3.10 software (modified Grain method). The calculated values were in line with the values reported in the databases consulted, with the exception of the value for dibutyltin chloride. Seen the consistency for the other butyltins, the calculated value is used for dibutyltin chloride in the derivation of quality criteria.

A value for Henry's coefficient is available for tributyltin chloride. This value is, however, not in correspondence with the value calculated from the ratio of vapour pressure to solubility.

Distribution coefficients describing phase partitioning between aqueous and particulate phase are discussed in more detail in the next section.

Table 1: Physicochemical properties of some organotin compounds.

Parameter	$((Bu)_3Sn)_2O$	$(Bu)_3SnCl$	$(Bu)_3SnOH$	$(Bu)_2SnCl_2$	$BuSnCl_3$
Name	bis(tributyltin) oxide	Tri-n-butyltin chloride	Tri-n-butyltin hydroxide	di-n-butyltin dichloride	mono-n-butyltin trichloride
Synonyms	oxybis(tributyltin);Tributyltin oxide; bis(tri-n-butyltin)oxide; TBTO; Tributyltin trioxide; tri-n-butylstannane oxide; bis(tributylstannyl) oxide	Chlorotributyltin; Chlorotri-n-butylstannane; tributylchlorostannane; Tributyltin chloride; Tri-n-butylchlorotin; tributylchlorostannane		Dibutyl dichloro tin; dibutyldichlorostannane; Dibutyltin dichloride; Di-n-Butyldichlorotin; Di-n-butyl Tin(IV) Dichloride	Butyl trichloro tin
Molecular formula	C24-H54-O-Sn2	C12-H27-Cl-Sn		C8-H18-Cl2-Sn	C4-H9-Cl3-Sn
CAS-number	56-35-9	1461-22-9		683-18-1	1118-46-3
Molecular weight (g mol^{-1})	596.11	325.49		303.85	282.17
Solubility (mg l^{-1})	4 (20°C; pH 7)	5-17 (20°C)		47.5-92 (20°C)	
Vapour pressure (Pa)	$8.5.10^{-5}$-$1.6.10^{-2}$ (20°C) $0.001^{(calc.)}$	1.236 (25°C) $1.2^{(calc.)}$		0.16 (25°C) $10.3^{(calc.)}$	173.3 (25°C) $166^{(calc)}$
Henry-coefficient (Pa m^3 mol^{-1})	0.01317 (25°C)	7721 (25°C) $142^{(calc.)}$*		$33 – 66^{(calc.)}$	
logK_{ow}	2.3-4.05	3.2-4.76	4.09	0.05-1.56	0.41
pKa		6.25	6.51		

(calc.): calculated

*: the value was calculated with the minimum solubility in seawater from the publication of Inaba (1995) (1 mg Sn/l), which gives conservative results; the minimum solubility in distilled water was 15 mg Sn/l

3.3 Organotin transport and mobility

The fate of organotins in the terrestrial environment is governed mainly by two processes: sorption and degradation, while volatilization is of minor importance. It is well known that triorganotins are strongly adsorbed onto soil particles. However, little is known about the degradation rates and desorption processes of these compounds under soil conditions (Hoch, 2001).

3.3.1 Sorption

Organotin compounds adsorb strongly to suspended particles in two ways: due to electrostatic interactions and/or hydrophobic forces. At low pH (pH<pKa), the organotin compound is present predominantly as cation and the main adsorption process is assumed to be a cationic exchange mechanism. At pH>pKa, the neutral organotin species are dominant and adsorption is mainly controlled by hydrophobic interactions. However, the adsorption material is also affected by pH. Clay minerals exhibit a permanent (pH independent) negative charge as well as a variable (pH dependent) charge. At low pH levels, this variable charge is positive due to protonation of exposed hydroxyl groups, while with increasing pH the variable charge becomes more and more negative. In general, the highest adsorption of TBT is observed between pH 6 and 7, which reflects the area of maximum overlap between the total negative surface charge and the concentration of TBT cations in solution (Fent, 1996; Weidenhaupt, 1997; Hoch, 2001; Hoch, 2004).

Under estuarine conditions or in seawater (pH~7-8), sorption is governed to a large extent by hydrophobic interactions, and a further rise in pH will not have a strong effect. Sorption can be described with the organic carbon-water distribution coefficient K_{oc} (l/kg), which is the sediment-water distribution coefficient normalized to organic carbon content:

$$K_{oc} = \frac{C_{sed} / f_{oc}}{C_{water}}$$

with f_{oc} the fraction of organic carbon in the sediment (-), C_{sed} the organotin concentration in the sediment (mg/kg) and C_{water} the organotin concentration in water (mg/l). Langston and Pope (1995) report sediment-water distribution coefficients in natural sediments between 248 and 24677 l/kg, with a (smaller) range of 188 to 2814 l/kg in K_{oc}. However, when sediments are disposed on land, marked changes occur in the chemical properties of sediment. Oxidation of anoxic sediment leads to increases in microbial activity and a decrease in sediment pH (mainly due to oxidation of sulphide). The extent of pH reduction depends on the amount of sulphide in the sediment and how much is oxidised (Eggleton and Thomas, 2004). This means that the sorption behaviour of organotins under different pH’s has to be taken into account and at a lower pH, when the principal sorption mechanism is assumed to be cation exchange, the use of a K_{oc} may not be more suitable than the use of the sediment-water distribution coefficient K_D.

Next to pH, clay content and organic matter content, there is also a strong influence of salinity on the sorption of TBT. Many studies demonstrate the effect of salinity on TBT-adsorption but the results are somewhat conflicting. Unger et al. (1988) reported a decline of TBT adsorption with increasing salinity while Randall and Weber (1986) and Harris and Cleary (1987) found an opposite trend (highest adsorption for high salinities). Hoch (2004) demonstrated highest TBT adsorption onto montmorillonite and kaolinite at a salinity value of 0 □ and decreasing adsorption with increasing salinity and proposed that the influence of salinity arises from competition with metal cations to the surface sites. Eggleton and Thomas (2004) describe highest desorption at intermediate salinities (≈30 □). It is difficult to isolate the effect of salinity from the other parameters (pH, TBT concentration, solid:solution ratio) in the different studies, but there appears to be a decreasing adsorption with increasing salinity when the dominant mechanism is cation exchange due to higher competition for adsorption sites. The effect on hydrophobic interactions is less clear, at high salinities a higher adsorption can be expected because of ‘salting-out’ but this effect is not always demonstrated.

Since the sorption of organotins is influenced by so many environmental factors, it is no surprise that there is a wide range of values for partition coefficients reported in literature. An overview is given in Table 2. The conditions under which the value is determined are given, as far as they are known.

Table 2: Literature values for K_D and K_{oc} for butyltin species

Organotin	K_D (l/kg)	K_{oc} (l/kg)	Conditions	Source
TBT	51-89		lab, pure clay, pH 6, salinity 0 ‰	Hoch, 2004
TBT	21900-24500	489800-537000	natural lake sediment, in situ values for sediment-pore water partitioning, 4% oc, pH 7, 12.5% clay	Berg et al., 2001
DBT	12900-27500	295000-603000		
MBT	1820-3800	40700-83200		
TBT	5-110		pure clay/(hydr)oxides, batch tests, pH4, I=0.01-10 mM KCl	Weidenhaupt et al., 1997
TBT	100-8000		natural sediment, batch test, estuarine conditions	Unger et al., 1987
TBT	8862		natural sediment, microcosm, pH 7.9, sal 15 ‰, oc 0.85%	Ma et al., 2000
TBT	4725-13128 (31‰)		field value for sediment/water partitioning; pH 8	
TBT	16660-18245 (16‰)			
DBT	9634-12987 (16‰)			
TBT	3906 (31‰)		field value for sediment/pore water partitioning; pH 8	
TBT	12634-14254 (16‰)			
DBT	11533 (16‰)			
TBT	7400		natural sediment from marina, field value for sediment-water partitioning	Sarradin et al., 1995
DBT	5500			
MBT	3400			
TBT	248-24677	32393-485137	field values, natural sediments from estuaries	Langston and Pope, 1995
TBT		4.5	natural sediments, estuarine conditions	Meador, 2000
TBT	18000		batch tests, natural sediments	Brandsch, 2001
DBT	3800			
MBT	1400			
TBT	2900		batch tests, natural soils	
DBT	560			
MBT	190			
TBT	88-17500		batch tests, different soil horizons (mineral and organic)	Huang and Matzner, 2004
DBT	896-22300			
MBT	9470-35800			
TBT	576		experiments on natural river sediments	Dai et al., 2003
DBT	1520			
MBT	2790			

3.3.2 Degradation

The degradation of organotins in the environment may be defined as a progressive loss of organic groups from the Sn cation:

$$R_4\mathrm{Sn} \rightarrow R_3\mathrm{Sn}X \rightarrow R_2\mathrm{Sn}X_2 \rightarrow R\mathrm{Sn}X_3 \rightarrow \mathrm{Sn}X_4$$

The removal of organic groups can be caused by various processes such as ultraviolet (UV) irradiation, biological cleavage or chemical cleavage. Photolysis by sunlight appears to be the fastest route of degradation in water, but is probably not important at greater depths in water nor in sediments or soils. Some bacteria and microalgae have been demonstrated to degrade organotin compounds. Chemical cleavage by nucleophile and electrophile reagents is possible but not relevant under environmentally relevant conditions.

Estimations for half-lives of these reactions under natural conditions are rather few. In soil, biodegradation of TBTO and the formation of DBO by aerobic microorganisms was demonstrated and half of the compound disappeared after 15 to 20 weeks (Barug, 1981 in Fent, 1996). In sediments, only slow degradation occurs under anaerobic conditions, with half-lives on the order of years (Fent, 1996). Sarradin et al. (1995) reports butyltin half-lives in sediments as 1.9-2.3 years for TBT, 1.4-2.4 years for DBT and 0.6-1.6 years for MBT. Other studies report half-lives for TBT in sediments between 1 and 5 years (Hoch, 2001). De Mora (1989) found a TBT half-life of 1.85 years while Dowson et al (1993) found half-lives of 0.9-5.2 years for TBT, 1.5-3 years for DBT and 1.8-3.7 years for MBT.

Brandsch et al. (2001) describe biological degradation in sediments after land disposal under aerobic and anaerobic conditions. Half-lives for TBT under aerobic conditions and at 15°C were 9-10 months. Under anaerobic conditions, degradation rates were dramatically lower and no half-lives could be calculated after 12 months. From a field study, it appeared that the TBT-content of sediment without any treatment decreased 10% per year, while sediment which was restacked regularly showed a 30% decrease in TBT-concentration.

4 PLANT UPTAKE

Table 3 gives an overview of available bioconcentration factors[4] for plants. A discussion of the experiments with terrestrial plants is given hereafter.

Kannan et al. (1996) calculated BCFs based on the analysis of triphenyltin in soils of pecan tree orchards and in leaves of the pecan tree. The orchard has been sprayed for 10 – 12 years with a commercial TPT fungicide. Samples were taken in the orchard during the same period after spraying, but not at the same moment (august for the leaves, june for the soils). BCF values were calculated from measured concentrations. A distinction between bioaccumulation or adsorption of TPT on the leaves could not be made.

Lespes et al. (2003) studied the uptake capacity of potatoes and french beans for TBT and TPT. Sandy soil (94 % sand, 3.3 % clay) was either spiked with 20 µg Sn/kg dm (both for TBT and TPT) or mixed with 1 % of sewage sludge. Organotin concentrations were determined in the sludge. In each pot (double) 25 french bean plants or 2 potatoe tubers were planted. Primary leaves and stems were harvested after 15 days, secondary leaves and stems were harvested after 30 days, whereas the beans were harvested after 60 days. Potatoes were harvested after 3 months. No actual concentrations were measured in the soil after spiking or mixing or during the pot experiments. Plant samples were washed with distilled water prior to further sample preparation. The BCF values in Table 3 were calculated from the measured concentration in the plant parts and the spiked or calculated concentration.

The study of Lespes et al. (2003) is the only study known to provide a quantitative estimate of uptake of organotin compounds in plants under controlled conditions. Limitations of the study are however that no organotin measurements in soil are available and that only one concentration was tested. A comparison of the BCF values calculated for TBT in french bean parts is given in Figure 2. Contamination of cultures can not be excluded, as in experiments with spiked TPT no TPT was detected in above-ground bean parts, but TBT was detected instead. From the experiments, in-plant metabolisation of butyltins could not be evaluated. Transformation of TBT to MBT took place in the TBT spiked experiments, where significant amounts of MBT were detected in potatoe plants. Distinction between transformation in soil or in plants could not be made.

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[4] BCF or bioconcentration factor is the ratio between the concentration in the plant and the concentration in soil or solution

Table 3: Overview of bioconcentration factor for organotin compounds in plants

		OT[1]	BCF	unit	time	OT source	reference	o[2]/b[3]
marine organisms								
seagrass[4]	Zostera marina	TBT	12000	nv[5]		water	Jensen et al., 2004	o
seagrass[4]	Thalassia testudinum	TBT	12000	nv		water	Jensen et al., 2004	o
fresh water organismen								
green alga	Ankistrodesmus falcatus	TBTO	300	µg/l	7 d	water	EPA, 2003	o
green alga	Ankistrodesmus falcatus	TBTO	253	µg/l	14 d	water	EPA, 2003	o
green alga	Ankistrodesmus falcatus	TBTO	448	µg/l	21 d	water	EPA, 2003	o
green alga	Ankistrodesmus falcatus	TBTO	467	µg/l	28 d	water	EPA, 2003	o
algae from effluent municipal waste water treatment plant		TBT	2903	(µg Sn/kg) / (µg Sn/l)		spiked food solution	Simon et al., 2002	b
algae from effluent municipal waste water treatment plant		DBT	2040	(µg Sn/kg) / (µg Sn/l)		spiked food solution	Simon et al., 2002	b
algae from effluent municipal waste water treatment plant		MBT	2000	(µg Sn/kg) / (µg Sn/l)		spiked food solution	Simon et al., 2002	b
green algae	Ankistrodesmus falcatus	TBT	30 000	nv		water	Waite et al., 1989	o
terrestrial organisms								
leaves of pecan tree		MPT	2.35	(µg Sn/g dm) / (µg Sn/g dm)	0.5 d	spraying solution	Kannan et al., 1996	b
leaves of pecan tree		DPT	4.47	(µg Sn/g dm) / (µg Sn/g dm)	0.5 d	spraying solution	Kannan et al., 1996	b
leaves of the pecan tree		TFT	20.63	(µg Sn/g dm) / (µg Sn/g dm)	0.5 d	spraying solution	Kannan et al., 1996	b
french beans	primary leaves	TBT	3.65	(µg Sn/kg dm) / (µg Sn/kg dm)	15 d	TBT spiked soil	Lespes et al., 2003	b
french beans	primary stem	TBT	0.65	(µg Sn/kg dm) / (µg Sn/kg dm)	15 d	TBT spiked soil	Lespes et al., 2003	b
french beans	secondary stem	TBT	0.7	(µg Sn/kg dm) / (µg Sn/kg dm)	30 d	TBT spiked soil	Lespes et al., 2003	b
french beans	beans	TBT	0.65	(µg Sn/kg dm) / (µg Sn/kg dm)	60 d	TBT spiked soil	Lespes et al., 2003	b

Table 3: Overview of bioconcentration factor for organotin compounds in plants (continued)

		OT[1]	BCF	unit	time	OT source	reference	o[2]/b[3]
potatoe	tubers	TBT	24	(µg Sn/kg dm) / (µg Sn/kg dm)	90 d	TBT spiked soil	Lespes et al., 2003	b
potatoe	tubers	MBT	110	(µg Sn/kg dm) / (µg Sn/kg dm)	90 d	TBT spiked soil	Lespes et al., 2003	b
french beans	primary leaves	TPT	0.8	(µg Sn/kg dm) / (µg Sn/kg dm)	15 d	TPT spiked soil	Lespes et al., 2003	b
potatoe	tubers	MPT	9.25	(µg Sn/kg dm) / (µg Sn/kg dm)	90 d	TPT spiked soil	Lespes et al., 2003	b
potatoe	tubers	DPT	3	(µg Sn/kg dm) / (µg Sn/kg dm)	90 d	TPT spiked soil	Lespes et al., 2003	b
potatoe	tubers	TPT	13	(µg Sn/kg dm) / (µg Sn/kg dm)	90 d	TPT spiked soil	Lespes et al., 2003	b
french beans	primary leaves	TBT	0.9	(µg Sn/kg dm) / (µg Sn/kg dm)	15 d	soil mixed with sludge	Lespes et al., 2003	o
french beans	secondary leaves	TBT	11.9	(µg Sn/kg dm) / (µg Sn/kg dm)	30 d	soil mixed with sludge	Lespes et al., 2003	o
french beans	secondary leaves	MBT	24	(µg Sn/kg dm) / (µg Sn/kg dm)	30 d	soil mixed with sludge	Lespes et al., 2003	o
french beans	secondary leaves	DBT	1.5	(µg Sn/kg dm) / (µg Sn/kg dm)	30 d	soil mixed with sludge	Lespes et al., 2003	o
french beans	secondary leaves	MPT	70	(µg Sn/kg dm) / (µg Sn/kg dm)	30 d	soil mixed with sludge	Lespes et al., 2003	o
french beans	primary leaves	TBT	9.30 – 16.76	(µg Sn/kg dm) / (µg Sn/l)	15 d	spiked food solution	Simon et al., 2002	b
french beans	primary leaves	TPT	2.30 – 3.70	(µg Sn/kg dm) / (µg Sn/l)	15 d	spiked food solution	Simon et al., 2002	b
willow treas	roots	TBT	1.79 – 27.4	(mg TBT/kg fw) / (mg TBT/l)	14 d	spiked food solution	Ciucani et al., 2004	b
willow treas	lower stem	TBT	0.18 – 15	(mg TBT/kg fw) / (mg TBT/l)	14 d	spiked food solution	Ciucani et al., 2004	b
willow treas	upper stem	TBT	< dl – 0.016	(mg TBT/kg fw) / (mg TBT/l)	14 d	spiked food solution	Ciucani et al., 2004	b
willow treas	leaves	TBT	< dl	(mg TBT/kg fw) / (mg TBT/l)	14 d	spiked food solution	Ciucani et al., 2004	b

[1]: organotin compound

[2]: o = taken from publication

[3]: b = calculated

[4]: important food source, potential risk for biomagnification

[5]: not given

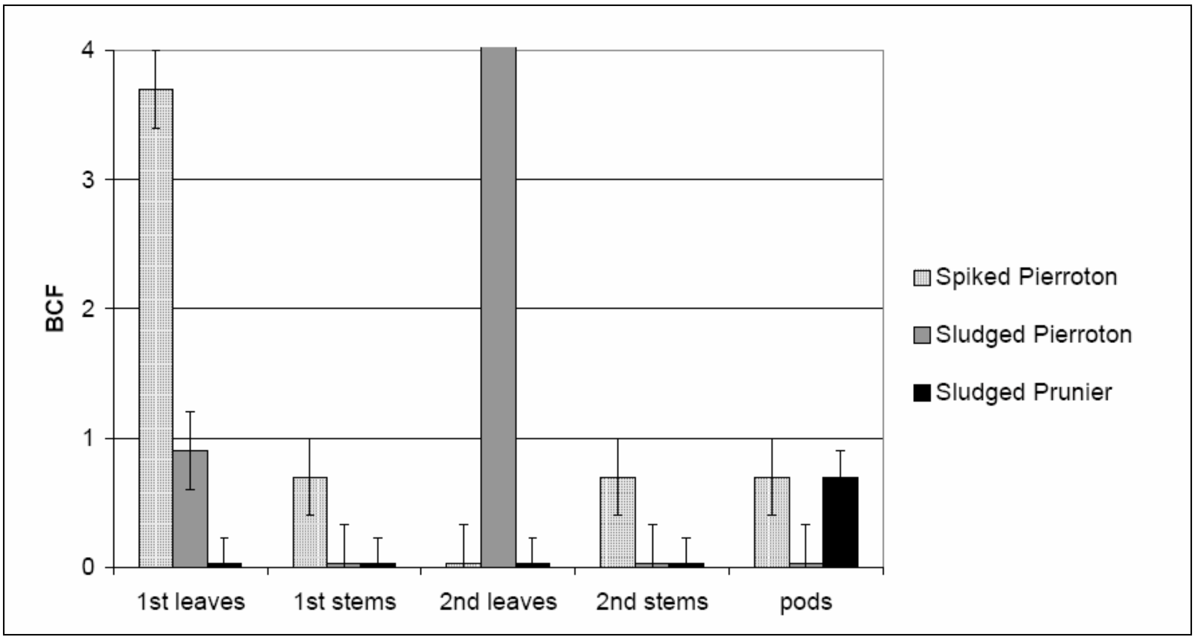

Figure 2: Bioconcentration factor (dry weight basis) of TBT for the different parts of french beans (taken from Lespes et al., 2003)

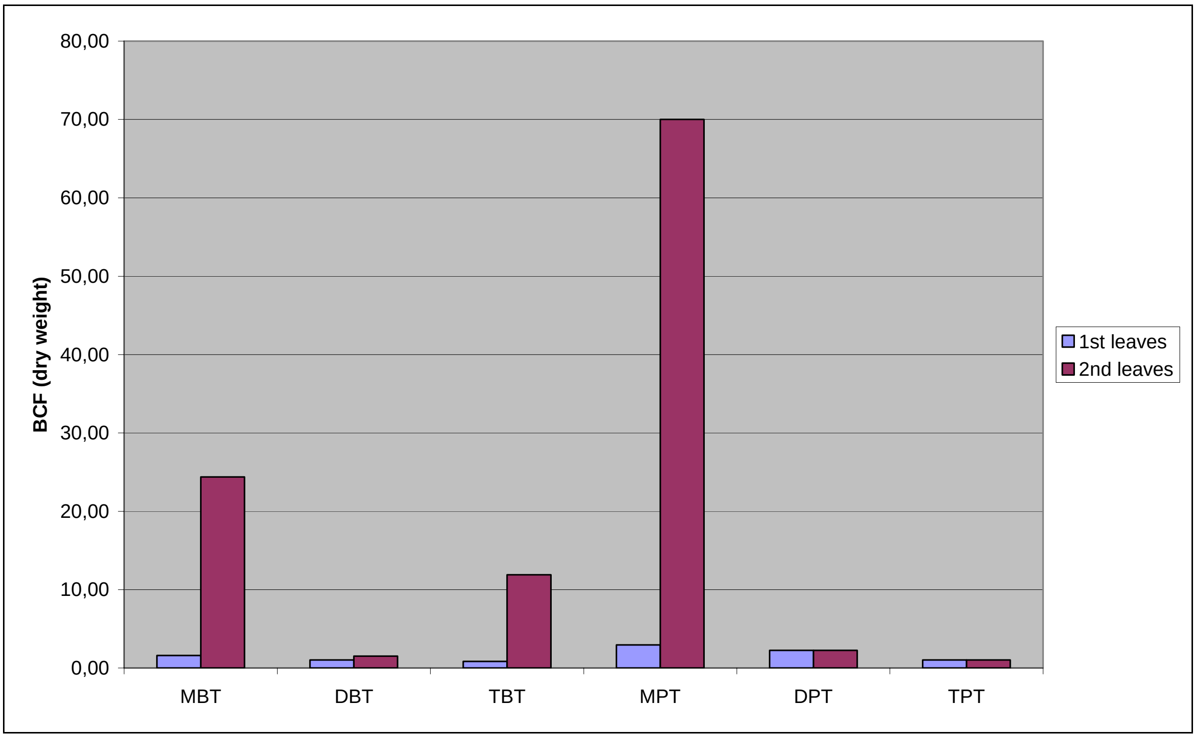

Figure 3: Bioconcentration factors for organotin species in french beans on sludge amended soil (calculated from Lespes et al., 2003)

From the data on spiked soil, it can be seen that the monoalkylated organotins were taken up to a higher extent than the dialkylated an trialkylated organotins (Figure 3). Uptake of organotins in potatoe tubers was higher than in aboveground plant parts (Figure 4).

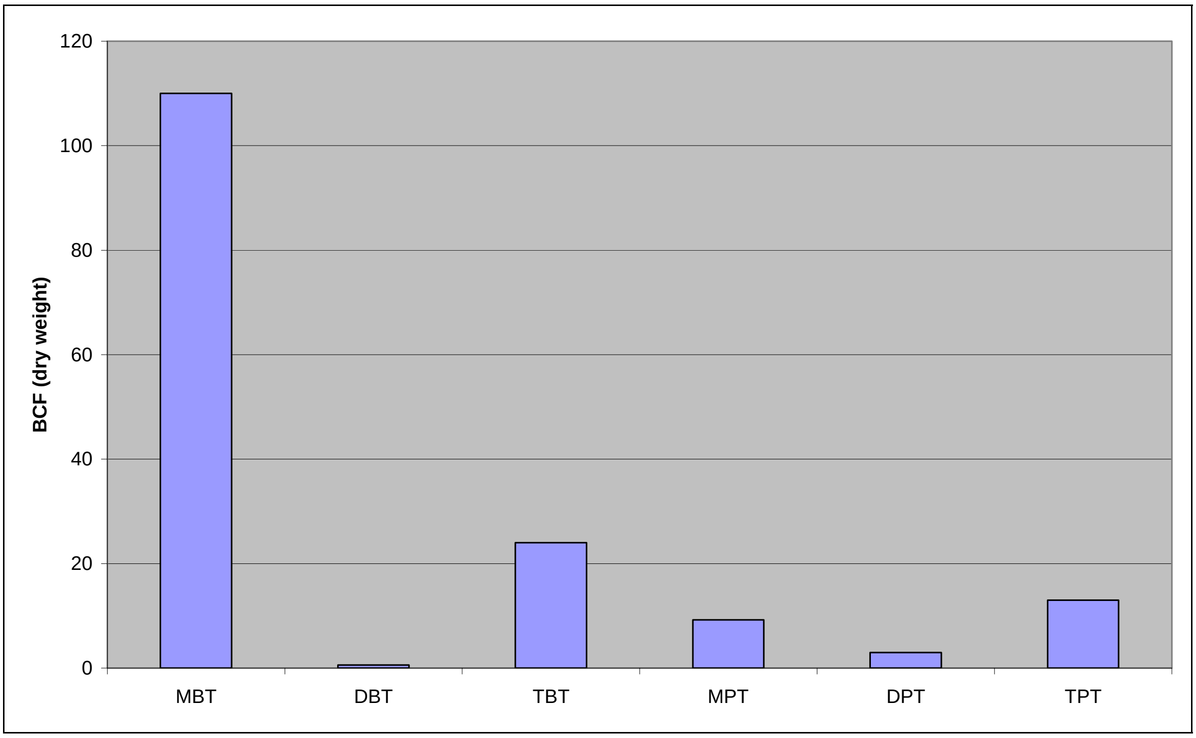

Figure 4: Bioconcentration factors for organotin species in potatoe tubers on spiked soil (calculated from Lespes et al., 2003)

Brandsch (2001) measured the concentration of organotin compounds in plants growing naturally on an area filled with harbour sediment and in some plants cultivated on the same location (sunflower, Juncus, potatoe, Typha, Elymus and Scirpus). Measurements in naturally growing plants were done in the first and second vegetation year. In the latter period, some additional plants were grown. The results are given in Table 4. Ranges of BCF values were calculated by the ratio of highest concentration in plant and lowest concentration in sediment and by the ratio of lowest concentration in plant and highest concentration in sediment. Values lower than detection limit were taken as half of the detection limit. Comparing the results of the second year, potatoes seem to accumulate more than the other plants in the above-ground parts (highest concentrations in the table for test plants). Bioconcentration factor are lower than those reported by Lespes et al., 2003 (except for DBT); concentrations in natural vegetation were lower in the 2nd year compared to the 1st year of vegetation.

Table 4: Concentration of organotin compounds in plants growing on harbour sediment (concentrations in µg/kg dm) (concentrations from Brandsch, 2001)

	sediment (1999-2000)	natural vegetation (1st year)	natural vegetation (2nd year)	test plants	BCF (dry weight)
MBT	2 - 9	5 - 37	< 2 - 7	< 2 - 7	0.11 – 3.5
DBT	3 – 20	< 5 – 25	< 2	< 2 - 2	0.05 – 8.3
TBT	14 – 78	< 5 - 15	< 2 - 8	< 2 -12	0.01 – 1.1

Hartmann et al. (2004) investigated the behaviour of organotin compounds in sewage sludge in view of agricultural application. Sewage sludge was applied and worked into the soil on two locations (5 t/ha dw), one was a sandy soil, the other location was a loamy soil. Carrots were sown on all locations. The results of the analysis of Oberndorf (carrots had growth problems on the heavier soil) show that almost no butyltin was taken up by the plants. Concentrations were not detected in carrots, however some butyltin was present in vegetation naturally growing on both the plot without and with sludge application.

Table 5: Concentrations of organotin in plants grown on soil mixed with sludge

	Oberndorf (0-30 cm)			
% C	1.8			
% loam	65			
% clay	31			
pH(CaCl$_2$ 0.01 M)	7.3			
density (kg/m^3)	1380			
sludge				
TBT (µg/kg dm)	2000			
DBT (µg/kg dm)	1300			
MBT (µg/kg dm)	1200			
soil (estimated)*				
TBT (µg/kg dm)	2.4			
DBT (µg/kg dm)	1.6			
MBT (µg/kg dm)	1.4			
plants	carrots ref	carrots	veget. ref	vegetation
TBT (µg/kg dm)	< 1	< 1	1.9	3.7
DBT (µg/kg dm)	< 1	< 1	1.8	1.2
MBT (µg/kg dm)	< 1	< 1	2.1	< 1

*: concentrations in soil after mixing with sewage sludge could not be detected; an estimate was made by assuming that 5 t/ha was mixed in the upper 30 cm of the soil (organotins were detected in leachates)

Trapp et al. (2004) investigated the possibility for phytoremediation of organotin contaminated harbour sludge within the TBT Clean project. Fresh and lagooned harbour sludge with high and moderate contamination was tested in a field trial. A range of plant species was sown in 4 field plots of lagooned sludge[5] (high and moderate contamination, sludge turned and not turned). Several species grew as good in the lagooned sludge as in normal garden soil. Also some wild plants developed in the plots. Plants were sown in May 2004 and harvested in August 2004. Organotin analyses were performed on corns of barley,

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[5] Fresh harbour sludge seemed to be an unsuitable substrate for plant growth

reed and clover/grass mix. The calculated BCF values, based on concentration in plants versus average concentration in the soil (5-15 cm of depth) are given in Table 6. More details on concentrations can be found in the report of Trapp et al. (2004). Relative uptake in plants seemed to be higher at low organotin concentrations than at high organotin concentrations (low concentrations for TBT were between 1221 and 1861 µg/kg dw; high concentrations were between 7802 and 13669 µg/kg dw; both in the field trials). The results of Trapp et al. (2004) are in line with the results of Brandsch (2001) and confirm that the uptake of organotin compounds in the field is lower than what is measured by Lespes et al. (2003).

Table 6: BCF ((µg/kg)/(µg/kg dw)) values for some plants grown on TBT Clean lagooned sludge (from: Trapp et al., 2004)

	TBT	DBT	MBT
high OT sludge			
barley corn	0.0[1]	0.0	0.0
reed	0.0	0.0	0.0084
clover/grass	0.0	0.0	0.00168
moderate OT sludge			
barley corn	0.0	0.0	0.0
reed	0.086	0.069	0.38
clover/grass	0.027	0.029	0.042

[1]: The limit of detection for concentrations in plants was 5 µg/kg

5 HUMAN TOXICITY OF ORGANOTIN COMPOUNDS

Discussion of the human toxicity of organotin compounds is based mainly on tributyltin and dibutyltin.

5.1 Absorption, distribution and metabolism

Organotin compounds are partly transformed to organotin chloride after oral intake. Organotin chloride is easily taken up in the gut. The lipophilic properties of organotin compounds allow accumulation in fat; binding to proteins and glutathione is possible because of their ionic properties.

Tributyltin is absorbed slowly and partly (20 – 55 %) in the intestinal system. Distribution within the body is fast, with accumulation in liver and kidneys, both after single and after chronic administration in rats. Tributyltinoxide (TBTO) is able to pass through the placenta. It is estimated that equilibrium is reached after 3 – 4 weeks of daily oral administration, with a maximum accumulation factor of 10. Also the testis show elevated concentrations, the blood shows very low levels (Humpel, 1986; Evans, 1979).
Metabolization mainly takes place in the liver, where highest metabolite concentrations are found. Tributyltin compounds are substrates for mixed function oxidases. Cyt P450 dependent hydroxylation and dealkylation results in the formation of dibutyltin, monobutyltin, 1-butanol, butene and inorganic tin (Casida, 1971; Kimmel; 1971). The transformation of tributyltin is a relatively slow process.
Excretion mainly takes place by the faeces. Fifteen days after cessation of the administration of TBTO in the mouse, the concentration in liver, kidneys and fat tissue decreased with 97 %, 73 % and 30 % respectively (Evans, 1979). The biological half life in the mouse is estimated to be 30 days (Brown, 1977).

Dibutyltin is a metabolite of tributyltin with a similar action profile and potency as tributyltin. It also binds to tissue and can be converted to monobutyltin.

5.2 Toxicity in animals

5.2.1 Acute toxicity

tributyltin	LD_{50} (mouse): 44 – 230 mg/kg bw (WHO, 1999)
dibutyltin	LD_{50} (rat): 100 mg/kg bw (chloride); 500 mg/kg bw (oxide)
	LD_{50} (mouse): 25 mg/kg bw (chloride); 24 mg/kg bw (oxide) (WHO, 1980)

5.2.2 Chronic toxicity / immunotoxicity

Subchronic and chronic studies, mainly in rodents, indicated that the immunological system is the most sensitive target for TBT.
At higher doses of *TBT*, reduced weight gain was also seen, histopathological changes in the liver, changes in serum enzymes and in the composition of blood cell populations were

noted as well. A 2-year chronic rat study revealed changes in the endocrine system, immunoglobulines and blood parameters as most sensitive endpoints (NOAEL 0.025 mg/kg bw) (Wester, 1988, 1990). The immunological system also shows functional damage (reduced resistance against infections) (Vos, 1990). From these data, a LOAEL and a NOAEL of 0.25 and 0.025 mg/kg bw respectively, were derived. US-EPA calculated the 10 % bench mark response with a 95 % confidence interval as 0.03 mg/kg bw (US-EPA, 1997). Young animals seem to be more sensitive than older animals. A recent study, in which rats were chronically exposed to TBTchloride *in utero* (day 8 of pregnancy) until the age of 30, 60 or 90 days, showed changes in immunological parameters that are linked to the humoral (immunoglobulines) and cellular immunity (NK cells), with altered resistance to infections and delayed allergic response. The effects were more pronounced in the longer treatments and in the higher dose groups, but some changes were also seen in the lowest dose (0.025 mg/kg.d) group (Tryphonas, 2004).
Cynomolgus monkeys that were treated for a period of 22 weeks (6d/week with 0.16 mg TBToxide/kg) showed a temporal reduction in leucocytes (Karrer, 1992).

DBT shows a similar type of response as TBT. In a comparison study, atrophy of the thymus and liver toxicity of TBT are caused by the metabolite DBT. DBT seems to be 40 % more potent than TBT with regard to the induction of thymus atrophy (EC_{50} DBTchloride: 18 mg/kg bw.d, EC_{50} TBTchloride: 29 mg/kg bw.d) (Snoeij, 1988).

5.2.3 Genotoxicity

TBTO was tested extensively, both *in vitro* and *in vivo*. *In vitro* results do not show a genotoxic potency, except in some tests with high cytotoxic concentrations.

Tributyltinoxide compounds enhance the effects of other genotoxic substances (e.g. chromosome aberrations in CHO cells and micronuclei in peripheric mouse reticulocytes after mitomycine C stimulation) (Sasaki, 1993, Yamada, 1993).

5.2.4 Cancer

US-EPA (1997) concluded that tributyltin could not be classified with regard to its carcinogenicity. TBT has not been evaluated by IARC.
Two carcinogenicity studies on TBTO are available (rats, mice). The rat study showed tumors at the hypophysis and parathyroid without a clear dose-response. Interpretation was inconclusive (Wester, 1988). In mice no effect on cancer incidence was noted (Dalu, 1992).

5.2.5 Reproductive toxicity

Tributyltin and dibutyltin are teratogenic for rodents: reduction in body weight and skeletal deformations were seen if TBTO was administered during pregnancy (Schroeder, 1981; Davis, 1987; Crofton, 1989; Noda, 2001). TBTchloride, administered during the first days of pregnancy prevented successfull implantation of the embryo and caused loss of the foetus (Harazono, 1998; Ema, 1999). The effects were seen at doses that were also toxic for the mother animal.

Two-generation studies were done for TBT and DBT. Reproduction toxicity was noted. TBTchloride induced dosis-dependent reductions in the weight of testes, and increase in the anogenital distance in female mice, both in the F1-generation. The effect was seen at all dose levels, a LOEL of 0.25 mg/kg bw was derived. A number of other endpoints were also influenced: number of sperm cells, weight of the prostate, decrease in serum ß-oestradiol, increase of testosteron (males), abnormal oestrus cycle, decreas of ovarian weight and increase in uterus weight (females) (Ogata, 2001; Omura, 2001). These symptoms are indicative of endocrine disruption, probably by the activation of the androgen receptor and inhibition of the aromatase that is responsible for the estrogen synthesis.

Inhibition of aromatase (Cyp19) activity
TBT is an inhibitor of the human placental aromatase activity *in vitro*, DBT is less potent; TeBT and MBT had no effect (Heidrich, 2001). TBT and DBT prevent the affinity of aromatase for androstendione. TBTchloride and DBTchloride inhibited 5-α-reductase type 1 activity (present in the brains), whereas 5-α-reductase type 2 activity, being present in the prostate, was only inhibited by TBTchloride. Both isoenzymes were not influenced by TeBT and MBT (Doering, 2002). α-Reductase transforms androstenedione and testosterone to androstanedione and dihydrotestosterone.

Interaction with the androgen receptor
In vitro studies showed that TBT activates the human androgen receptor and the androgen receptor target genes, such as the prostate specific antigen. This probably does not happen by direct interaction with the androgen binding site of the receptor, as androgen antagonists do not inhibit activation.

5.2.6 Neurotoxicity

Trimethyltin (TMT) and triethyltin (TET) are neurotoxic in test animals. TET affects myeline, TMT affects the neurones. The *in vivo* results are less univocal for the other compounds. However, transfer through the blood brain barrier was shown for compounds such als TBT and DBT (Iwai, 1989; Lehotzky, 1982). Neurotoxicity was only reported at lethal doses (TBT). One study showed behavioural and cognitive changes after administration of TBT during pregnancy in rats; the effects were not correlated with biochemical or morphological changes (Gardlund, 1991). However, *in vitro* studies show that most organotin compounds are toxic for the mitochondria, that generate chemical energy needed for the maintenance of the membrane potention of the neurones (Boyer, 1989). Some compounds induce apoptosis in neural cells in *in vitro* experiments. The *in vivo* relevance of these observations is not clear yet.

5.2.7 Observations in humans

No studies are available in humans about the effects of long term exposure, descriptions after incidences of inhalation or dermal exposure are available. Inhalation of TBT results in symptoms such as dizziness, vomiting, headaches, fatigue and respiratory irritation. TPT exposure results mainly in dizziness and photophobicness. TBT and TPT are, respectively, a strong and moderate skin irritant (Boyer, 1989; Lisi, 1987).

5.3 Risk characterization

Data are inadequate to derive a protection level for exposure by skin or inhalation. Organotin compounds are, however, absorbed by these routes.

Food is considered the dominant pathway in case of environmental pollution. The compounds are not considered carcinogenic at low doses. TBT is an endocrine discruptor and effects on reproduction are described. Based on the observations, immunological effects can be considered the most sensitive endpoint after exposure to organotin compounds. The derivation of a protection level is based on the latter effects (Penninks, 1993; WHO, 1999; EPA, 1997). A Tolerable Daily Intake (TDI) was derived by WHO and EFSA (0.25 µg/kg.d) and US-EPA (0.34 µg/kg.d). These values are based on the same data set. WHO used a NOAEL of 0.025 mg/kg as basis, whereas US-EPA used the 10 % benchmark response. A safety factor of 100 was used in both derivations (10 for extrapolation from animal to human; 10 for protection of sensitive individuals). Recent data indicate that some changes in immunological parameters can be seen at the NOAEL (Tryphonas, 2004), which could lead to a future re-evaluation of the protection level. As the common endpoint of thymus atrophy is affected at similar dietary level of the trialkyl tin compounds, EFSA (EFSA, 2004) considered it appropriate to establish a **group TDI of 0.25 µg/kg.d for TBT, DBT, TPT and DOT**. Based on TBTO molecular mass, this group TDI is 0.1 µg/kg.d when expressed as Sn content or 0.27 µg/kg.d when expressed as chloride (TBT-Cl).

6 DIETARY EXPOSURE OF THE GENERAL POPULATION TO ORGANOTINS

Organotin compounds reach humans primarily through the diet, mainly by fish and fish products. Other exposure routes could contribute to exposure of the general population. In this report, only food exposure was addressed as it can be considered most important for TBT exposure.

Within the frame of the SCOOP (Scientific Cooperation) projects an assessment of the dietary exposure to organotin compounds was undertaken and reported in 2003 (DG HCP, 2003). Participating countries were Belgium, Denmark, France, Germany, Greece, Italy, the Netherlands and Norway.

For Belgium data were given for samples in a marine harbour for the species fish (sole and cod), scallops, gasteropods and mussels. An overview of the results is given in Table 7. However, these data should not be considered to be representative for Belgium.

Table 7: Occurrence of organotin compounds in aquatic food in Belgium (from: DG HCP, 2003, sampled 2001).

food name	OTC	min (µg/kg fw)	max (µg/kg fw)
sole	DBT	< 20	
scallops	DBT	< 20	
cod	DBT	< 20	
gasteropods	DBT	< 20	
sole	TBT	< 20	
scallops	TBT	< 20	22
cod	TBT	< 20	20
gasteropods	TBT	< 20	
mussels	TBT	1.5	3

An overview of the range of concentrations for six European countries (excluding Belgium and France) is given in Table 8

Table 8: Range of concentrations of organotin compounds in aquatic food (µg/kg fresh weight, based on: DG HCP, 2003)

food	TBT	DBT	MBT
fresh molluscs	2-108.9	2.5-70.3	0.6-66.8
fresh crustaceans	2.97-145.4	0.87-28.4	0.87-12
fresh fish marine	1-96.5	0.1-216.7	0.1-14.37
fresh fish, fresh water (lake, farm)	11-22.34	0.5-5.13	4.78
fresh fish fresh water (inland, brackish)	7.8-198	0.5-38.9	0.2-17.3
fully preserved + semi-preserved	2*-7.44	2.75-5*	3*-13.55

*: value equals Limit of Detection/2

Table 9 presents the mean intake of organotin compounds expressed as a range for all data and followed by the data for the Netherlands on the next line. The data are presented on a population basis; higher values are calculated on a consumer basis. In the latter case, the range is more narrow, but less data are available. Total organotin intake for the Netherlands is given in Table 10, both for the mean and the high intake range.

Table 9: Range of dietary intake of organotin compounds (ng/kg day, based on: DG HCP, 2003), mean values by population (range and mean values for the Netherlands)

food	TBT	DBT	MBT
fresh molluscs	0.008-2.5	0.0021-1.5	0.0008-2.4
	0.13	0.05	0.014
fresh crustaceans	0.02-2.8	0.01-0.69	0.01-0.34
	0.10	0.012	0.012
fresh fish marine	0.002-5.7	0.004-1.36	0.0001-1.3
	0.56	0.085	0.0693
fresh fish, fresh water (lake, farm)	0.40-6.7	0.09-0.69	0.09-0.017
	-	-	-
fresh fish fresh water (inland, brackish)	0-0.03	0-0.004	0-0.002
	0.03	0.004	0.002
fully preserved + semi-preserved	0.04*-0.6	0.11*-0.22	0.06*-1.08
	-	-	-

*: never detected

Table 10: Estimated dietary intake of organotin compounds for the Netherlands (ng/kg day, based on: DG HCP, 2003), mean and high intake values by population

	TBT	DBT	MBT
mean	0.82	0.151	0.097
high	1.48	0.276	0.163

The OT-Safe project estimates TBT intake from Dutch fish and seafood to be about 4.5 ng/kg.d or (about 120 µg/cap.y, value taken from the report). This higher estimate is caused by the higher TBT concentrations measured.

No recent dataset on fish and seafood consumption is available for Belgium. In the SCOOP report, data for Belgium on mussels and fish are provided on a by consumer basis. The DAFNE database provides more detailed data based on household budget surveys (most recent data from 1999). In the OT-Safe project, an estimate of fish and seafood consumption was made from import and export data. In the latter study, data for mussels were corrected for shell and meat ratios assuming that 30% of the mussel weight is edible. The data are given in Table 11, grouped according to the SCOOP grouping.

Table 11: Estimated mean fish and seafood consumption in Belgium (g/day) according to different sources and mean fish and seafood consumption in the Netherlands; by population

		Belgium		the Netherlands
food	SCOOP[1]	Dafne	OT-SAFE[4]	SCOOP[5]
fresh molluscs	0.66 (high: -)	5.1 (1.53)[2]	3.22	0.41 (high: 0.6)
fresh crustaceans		0.74	1.05	0.5 (high: 0.57)
fresh fish marine		5.9[3]	8.39	
fresh fish, fresh water (lake, farm)	13.37 (high: 47.7)			
fresh fish fresh water (inland, brackish)		2.37[3]	4.44	
fully preserved + semi-preserved		6.48		
total fish (not molluscs or crust.)	13.37	14.75	12.83	16.1

[1]: by consumer
[2]: 1.53 g/day taking the assumption of 30% edible meat
[3]: including frozen fish
[4]: no distinction was made between fresh and processed
[5]: based on mussels, shrimps and eel, herring, cod, mackerel and plaice

Recently, EFSA (EFSA, 2004) reconsidered the OT concentration data from the SCOOP report. Concentrations were calculated by means of statistical techniques. The statistical descriptors for TBT, DBT and MBT in fish and fishery products, and in seafood other than fish are given in Table 12. Distributions are highly skewed towards the high concentrations.

Table 12: Statistical descriptors of organotin concentrations in seafood in Europe (from EFSA, 2004) (concentrations in µg/kg)

	mean	median	95 %
fish and fishery products			
TBT	28.4	7.00	107
DBT	16.8	2.50	34.8
MBT	10.1	2.50	25.0
seafood other than fish			
TBT	60.3	14.0	210
DBT	52.4	4.00	370
MBT	34.4	4.00	215

EFSA then uses the high average fish and seafood consumption data of Norway to calculate a conservative estimate of average European organotin exposure from food. Table 13 provides the EFSA estimate for Europe as well as a calculation for Belgium based on the EFSA concentration data and the OT-SAFE fish and seafood intake data for Belgium.

Table 13: Estimate of organotin intake (ng/kg.d) from fish and seafood in Europe (EFSA, 2004) and an estimate based on Belgian fish and seafood consumption

	median based			mean based		
	TBT	DBT	MBT	TBT	DBT	MBT
Europe						
	9.3	3.3	5.3	37.9	22.4	22.7
total		18.0			83.0	
% TDI		7.2%			33.2%	
Belgium						
	2.1	0.7	0.7	8.9	6.3	4.0
total		3.5			19.0	
% TDI		1.4%			7.6%	

The dietary intake values based on the mean scenario for Belgium are taken as an estimate of average organotin intake.

In the OT-Safe project the influence of preparation of butyltin content of mussels was investigated. Home-cooking or industrial cooking resulted in slight reduction of butyltin content, with percentages below 30 %. Only in case of frying pan cooking, the concentration in mussels dropped to less than 40 % of the initial concentration.
The estimate based on concentrations in food products is not modified based on the results of preparation.

7 TERRESTRIAL ECOTOXICITY

Organotin compounds are highly toxic pollutants but have been investigated mostly in aquatic systems and sediments. Potential reproductive impairment has been reported at a concentration of TBT in water as low as 0.1 ng/l (McAllisterand Kime, 2003). The lowest acute value compiled in the Vito data base is a 48h-LC_{50} of 1.2 µg/l for the crustacean Caprella sp. (Ohji et al., 2004). An extensive review on the ecotoxicoty of organotin compounds was published by Fent (1996) and numerous papers thereafter (Fent 1998, Fent, 2003).

Within the context of this study an additional literature survey was performed with the focus on terrestrial ecosystems. Although very few data are available on terrestrial organisms, three relevant papers were retrieved. Two of them pertain to the use of organotin compounds as pesticides.

Trapp et al. (2004) report reduced transpiration in willow trees at a concentration of 0.1 mg/l TBTCl and 1 mg/l TBTH/l in the nutrient solution (pH 4). However at 0.1 mg/l recovery in time took place, and the trees survived concentrations up to 10 mg/l. With 1 mg/l TBTCl or TBTH in pH 7 nutrient solution, willows reduced transpiration to below 50%. Recovery was very slow.

In a comparative study Kuthubutheen et al. (1989a) compare the effects of Thiram and six triorganotin(IV) compounds on the nitrification and ammonification in soils. The triorganotin(IV) compounds investigated include diphenylbutyltin bromide, p-tolyldiphenyltin acetate, triphenyltin acetate, triphenyltin chloride.triphenylphosphine oxide, triphenyltin indole-3-acetate and 2-ethylamino-4-triphenylstannoxy-5-n-butyl-6-methylpyrimidine. They report complete inhibition of ammonification in soil at a concentration of 50 mg/kg Thiram 21-28 days after application. For the six triorganotin(IV) compounds, with the exception of diphenylbutyltin at concentrations of 10-50 mg/kg, ammonification persisted at all concentrations 28 days after application. At concentrations of 100 mg/kg all triorganotin (IV) compounds, with the exception of triphenyltin indole-3-acetate and 2-ethylamino-4-triphenylstannoxy-5-n-butyl-6-methylpyrimidine, inhibited nitrification.

From a parallel study on the effect of two triorganotin(IV) compounds (diphenylbutyltin bromide and triphenyltin chloride.triphenylphosphine oxide) on fungal and bacterial populations in soil Kuthubutheen et al. (1989b) conclude that although the treatment of soil with triorganotin(IV) compounds reduced its fungal population, the spectrum of fungal species in soil was not greatly altered to affect adversely the soil fertility. They suggest both organotin compounds can be used for the control of plant pathogenic fungi at concentrations of 50-250 mg/kg without adversely affecting the non-target soil micro-organisms which help to maintain soil fertility.

As terrestrial ecotoxicology is an emerging field of research also some data exist in grey literature (e.g. poster presentations, abstracts, etc). Two of these sources were of particular interest to this study. The first paper entitled "Terrestrial ecotoxicity – can aquatic ecotoxicity data give a clue?" was published at the SETAC Europe conference, Hamburg, 2003 (Hund-Rinke et al., 2003). Contact was sought with the author in order to obtain more detailed information on the results presented. The results from this enquiry are described below.

Experiments performed by Hund-Rinke (Details provided by the author)

Soils

Four soils - two sandy soils, one silty soil and a loamy soil - were applied. The physico-chemical parameters are described in Table 14.

Table 14: Physico-chemical properties of the test soils

	sandy soil (I)	sandy soil (II)[a]	silty soil	loamy soil
particle size distribution (%)				
sand (63-2000 µm)	70.8	73.2	3.0	21.7
silt (2-63 µm)	25.6	18.5	82.4	46.8
clay (< 2 µm)	3.6	8.2	14.6	31.5
org C (%)	1.0	2.3	1.7	3.3
pH ($CaCl_2$)	5.5	5.8	6.1	5.4
WHCmax[b]	269	510	567	653

[a]: sandy soil (II) only applied for the plant test
[b]: WHC = water holding capacity

The soils were sieved (≤ 2 mm) and adjusted to 50 – 60 % of WHCmax.
TBT was applied in acetone. Five concentrations with a spacing factor between 3 and 4 were tested. For the application in organic solvents the same amount of solvent was applied to the control. 10 ml of solvent was used per kg of soil, dry matter. Before the chemicals were applied the soil was spread to form a thin layer. The solvent was allowed to evaporate for 3 hours. Losses of water were determined gravimetrically, and the water content was adjusted. The soil was used after a 14 days aging period at 4 °C.

Terrestrial ecotoxicological tests and calculations

The following ecotoxicity tests were performed according to guidelines: microbial basal respiration and substrate induced respiration (SIR) according to ISO 17155, potential ammonium oxidation (ISO/DIS 15685), reproduction tests with earthworms (Eisenia fetida; ISO 11268-2) and with collembolans (Folsomia candida; ISO 11267) as well as growth tests with plants (ISO 11269-2). The plants Avena sativa and Brassica rapa were used. The tests were performed with the soils described above. For the plant test the sandy soil (II) was applied.

EC50-values and the confidence interval were calculated using probit analysis (calculation program "ToxRat"). If one of two adjacent test concentrations yielded no effect, whereas the other concentration caused a 100 % effect, an EC50 could not be determined. In this case the range of both concentrations is reported as EC50.

The concentrations of selected compounds were verified by chemical analyses at the beginning and at the end of the test except for the potential ammonium oxidation, for which only one determination was performed due to the short test duration of 6 hours. For some substances chemical analyses indicated biodegradation during aging and test performance. Therefore, the EC50-values were recalculated on the basis of modified concentrations assuming a first order kinetic for biodegradation; the concentration calculated after the first half of the test period was used for recalculation.

Chemical analyses

All methods are internal methods of the Fraunhofer Institute, developed for the determination of the below given analytes in the ppm range. In all cases the moistened soil was used without drying.

Tributyltinchloride (TBT):
Soil extraction with ethanol/diethyldithiocarbamate; ethylborate derivatization; silica gel cleanup; quantification by GC-AED: Basis: DIN 38407-13 and EDANA method "Determination of organotin species in absorbent hygiene products and materials" (360.0-01).

Results and discussion

The results as provided by Hund-Rinke, which were expressed as concentrations on the soil as tested, were transformed to concentrations on a dry matter basis (by assuming that the soil was at 50 % of the WHC). They are given in Table 15. The analysed TBT concentrations were comparable to nominal concentrations (deviations of less than 25 %). Therefore, the calculated toxicity values were not corrected

Table 15: EC_{50} values for TBT (mg/kg dm), nominal concentrations

	sandy soil	silty soil	loamy soil
microorganisms, basal respiration	> 1135	> 1284	> 1327
microorganisms, SIR	> 1135	> 1284	> 1327
microorganisms, NH_4-oxidation	12.5	82	207
Folsomia candida	25	14	88
Eisenia fetida	1.5	3.9	3.6
Brassica rapa	28	21	45
Avena sativa	513	710	911

In the second publication from grey literature entitled "Contaminants in arable soils fertilised with sewage sludge" which was presented at the Int. Workshop SOWA, Prague, 28-29th June 2004 (Dreher, 2004) a Predicted No Effect Concentration (PNEC) of 8 µg/kg dm for soil was derived. The PNEC value represents the environmental concentration of a compound which does not induce adverse effects in organisms after life-long exposure. Contact was sought with the author to ask how this value was derived. At the time of finalization of this report, no further information was obtained.

In comparison, van den Berg et al. (1994) calculated serious Soil Contamination Concentrations (SCC) for triphenyltin and tributyltin oxide in the Netherlands. The SCC values are derived from HC_{50} values, i.e. Hazardous Concentrations for 50% of species in the environmental compartment under consideration. These HC_{50} values are based on existing effect values that are assumed to have consequences at population level for species under chronic exposure (NOEC, LC_{50}, EC_{50} for reproduction and growth). Preferably terrestrial effect data are used (e.g. triphenyltin). When insufficient effect values are available on terrestrial organisms the HC_{50} value is derived from aquatic data using the "equilibrium-partitioning" method. In order to take the influence of soil characteristics on the bioavailability of compounds into consideration, the ecotoxicological data had first been corrected for organic matter and clay content. For organic compounds correction for the organic matter content was made. In the derivation of SCC values only the risk for organisms directly in contact with the soil was considered, but not the risk of secondary poisoning by magnification. The results for triphenyltin and tributyltin oxide are shown in Table 16.

Table 16: Eco-SCC values for standard soil (10% organic matter; 25% lutum) based on terrestrial and aquatic (re-calculated for partitioning) ecotoxicological data

Compound	Terr. Ecotox. HC_{50} value (mg/kg)	Aquatic Eq. part. Ecotox. HC_{50} value (mg/kg)	Recommended eco-SCC (mg/kg)
Triphenyl compounds	3.2	8.2	5.1
Tributyltin oxide	-	0.48	0.48

In conclusion, only limited data on organotin compounds are available from terrestrial ecotoxicity tests. All data suggest that terrestrial organisms are only affected at much higher organotin concentrations compared to aquatic organisms. Microorganisms seem to be the least sensitive trophic level. Invertabrates on the other hand seem to be the most sensitive organisms.

8 AVAILABLE STANDARDS FOR ORGANOTINS

8.1 Soil and groundwater

In the Netherlands a target value of 0.001 mg/kg dm and an intervention value[6] of 2.5 mg/kg dm is given for total organotin compounds. For groundwater a target value of 0.05-16 ng/l and an intervention value of 0.7 µg/l is given.
The background information on the proposal for intervention values is given in van den Berg, et al. (1994) and is summarized in Table 17..

Table 17: Background information on the Dutch intervention values for organotin compounds

	ecotox soil (mg/kg dm)	human tox (mg/kg dm)	proposed intervention value soil (mg/kg dm)	official interventio n value soil (mg/kg dm)	proposed intervention value groundwater (µg/l)	offical intervention value groundwater (µg/l)
tributyltin oxide	0.48	21.5	5		0.7	
triphenyltin compounds	5.1	110	5		0.4	
total organotin			5	2.5	-	0.7

The background for the ecotoxicological values is given in chapter 7- Terrestrial ecotoxicity. For the human toxicological values the Dutch C-Soil model was used. This model is comparable with the Vlier-humaan model for the residential scenario. Differences are found in the parameter values, the averaging of child and adult exposure (which is not done in Vlier-humaan for noncarcinogens), and the fact that background exposure is not accounted for. For TBT the following values were used:

- M = 290.04 g/mol (which is the value for TBT as ion);
- solubility = 0.75 mg/l;
- log Kow = 3.64 (as the average of literature data);
- log Koc = 4.10 (as the average of literature data);
- vapour pressure = $8.53.10^{-5}$ Pa;
- Henry's coefficient = 0.035 Pa.m^3/mol (calculated from P and S)

Plant uptake was calculated with the C-Soil algorithm (where the BCF is estimated from the log Kow). The intervention value is calculated for a soil with an organic matter content of 10 %. The standard Flemish soil has a 2 % organic matter content. The Dutch values should be divided by a factor of 5 to be comparable with Flemish values.

The intervention value for groundwater is calculated from the intervention value in soil, using the equilibrium approach - where the concentration in soil pore water is calculated from the total concentration and the K_D value – and a groundwater dilution factor of 10.

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[6] The intervention level is the concentration above which a need for remediation exists.

Preliminary Remediation Goals (PRG) for tributyltin (TBTO) are available from US-EPA (http://www.epa.gov/region09/waste/sfund/prg/index.htm). For residential soil a value of 18 mg/kg dm is given; for industrial soil the value is 180 mg/kg dm. The PRG for tap water equals 11 µg/l (corresponding with a 100 % intake of the TDI by tap water; TDI = 0.3 µg/kg.d).

8.2 Regulations on hazardous materials

The Flemish Regulation on Waste Prevention and Management (Vlarea) (OVAM, 2004) provides a classification of waste materials. Waste is considered hazardous if it meets specified properties or classifications. Table 18 gives the classification of relevant organotin compounds according to the European directive on classification and labelling of hazardous substances (appendix I) and the concentration limits for hazardous waste according to Vlarea.

Table 19 gives the concentration limits and corresponding classifications for relevant organotin compounds according to the European directive on classification and labelling of preparations.

Table 18: Classification of organotin compounds according to the hazardous substances directive and concentration limits according to Vlarea

name	EEGn°	CAS	classification1	classificiation2	classification3	classification4	classificiation5	classification6	symbol	concentr. limit (mg/kg dm)
fentin hydroxide (ISO); triphenyltin hydroxid	200-990-6	76-87-9	Carc. Cat. 3; R40	Repr. Cat. 3; R63	T+; R26	T; R24/25-48/23	Xi; R37/38-41	N; R50-53	T+;N	10 000 (carc3) 1 000 (T^+)
trimethyltin compounds except those specified by name	#	#	T+; R26/27/28	N; R50-53					T+;N	1 000 (T^+)
triethyltin compounds except those specified by name	#	#	T+; R26/27/28	N; R50-53					T+;N	1 000 (T^+)
tripropyltin compounds except those specified by name	#	#	T; R23/24/25	N; R50-53					T;N	30 000 (T)
tributyltin compounds except those specified by name	#	#	T; R25-48/23/25	Xn; R21	Xi; R36/38	N; R50-53			T;N	30 000 (T)
trifenyltin compounds except those specified by name	#	#	T; R23/24/25	N; R50-53					T;N	30 000 (T)
trioctyltin compounds except those specified by name	#	#	Xi; R36/37/38	R53					Xi;	-

Table 19: Concentration limits according to the European directive on preparations

name	EEGn°	CAS	classification1	classificiation2	classification3	classification4	classificiation5	classfication6
fentin hydroxide (ISO); triphenyltin hydroxid	200-990-6	76-87-9						
trimethyltin compounds except those specified by name	#	#	T+, N; R26/27/28-53/55 (C≥25 %)	T+, N; R26/27/28-51/53 (2.5% ≤C<25 %)	T+; R26/27/28-52/53 (0.5 %≤C<2.5 %)	T; R23/24/25-52/53 (0.25 %≤C<0.5 %)	T; R23/24/25 (0.1 %≤C<0.25 %)	Xn; R20/21/22 (0.05 %≤C<0.1 %)
triethyltin compounds except those specified by name	#	#	T+, N; R26/27/28-50/53 (C≥25 %)	T+, N; R26/27/28-51/53 (2.5% ≤C<25 %)	T+; R26/27/28-52/53 (0.5 %≤C<2.5 %)	T; R23/24/25-52/53 (0.25 %≤C<0.5 %)	T; R23/24/25 (0.1 %≤C<0.25 %)	Xn; R20/21/22 (0.05 %≤C<0.1 %)
tripropyltin compounds except those specified by name	#	#	T, N; R23/24/25-50/53 (C≥25 %)	T, N; R23/24/25-51/53 (2.5% ≤C<25 %)	T; R23/24/25-52/53 (0.5 %≤C<2.5 %)	Xn; R20/21/22-52/53 (0.25 %≤C<0.5 %)	Xn; R20/21/22 (0.1 %≤C<0.25 %)	
tributyltin compounds except those specified by name	#	#	T,N; R21-25-36/38-48/23/25-50/53 (C≥25 %)	T,N; R21-25-36/38-48/23/25-51/53 (2.5% ≤C<25 %)	T; R21-25-36/38-48/23/25-52/53 (1 %≤C<2.5 %)	Xn; R22-48/20/22-52/53 (0.25 %≤C<1 %)		
triphenyltin compounds except those specified by name	#	#	T, N; R23/24/25-50/53 (C≥25 %)	T, N; R23/24/25-51/53 (2.5% ≤C<25 %)	T, R23/24/25-52/53 (1 %≤C<2.5 %)	Xn; R20/21/22-52/53 (0.25 %≤C<1 %)		
trioctyltin compounds except those specified by name	#	#	Xi; R36/37/38-53 (C≥25 %)	Xi; R36/37/38 (1% ≤C<25 %)				

9 EXPERIMENTS

9.1 Introduction

Leaching experiments and ecotoxicity tests were done on six organotin containing treated sediment samples. Treatments were lagunation, mechanical dewatering with lime as an additive and mechanical dewatering with polyelectrolyte (PE) as an additive. For each of the treatments a sediment with a low and a high concentration was used in the tests.

The tests were undertaken with the following objective:

- provide leachate for the ecotoxicity tests, where organotin specific tests would be used to derive a quality criterion for the leachate;
- evaluate the use of the draft leaching test for organic compounds;
- evaluate measured K_D (or Koc) values in view of literature data.

The lagunated sediments were sampled at the lagunation fields of DEC near Ruisbroek on 14/05/2004. The sediments contained lumps of black, not fully oxidised material. The mechanically dewatered samples were delivered in glass containers by ENVISAN on 26/05/2004. A short description of the six samples is given in Table 20.

Table 20: Description of the samples selected for leaching experiments

Sample ID	sample	description
ASG/04041	lagun. - low	Dredgings from zone 1 after lagunation (low TBT content)
ASG/04042	lagun. - high	Dredgings from zone 6 after lagunation (high TBT content)
ASG/04043	lime - high	Mechanically dewatered dredgings with lime additive (high TBT content)
ASG/04044	lime - low	Mechanically dewatered dredgings with lime additive (low TBT content)
ASG/04045	PE - high	Mechanically dewatered dredgings with polymer (PE) additive (high TBT content)
ASG/04046	PE - low	Mechanically dewatered dredgings with polymer (PE) additive (low TBT content)

9.2 Concentrations of TBT, Fe, Mn, TOC and AVS-SEM of the dredgings

The dredgings were analysed for Fe and Mn content, TOC and TBT-content at ERC and for AVS-SEM content at VITO. The results are given in Table 21, Table 22 and Table 23.

The AVS-content (Acid Volatile Sulfide) of sediment samples is a measure of the S-pool present which has a high binding capacity for metals. In the pH range of the sediment samples investigated (pH>7.35), it is unlikely TBT will behave as a cation so binding of TBT to sulfide will not be important in this case. When sediments are brought on land, the oxidation of sulfide can result in a release of metals and in a lowering of pH. This could also alter the behaviour of TBT since the speciation is pH-dependent. However, the investigated sediment samples contain very low amounts of AVS (see Table 22 and Table 23) so the sediment can be considered fully ripened and no further pH-shift is expected. The high SEM/AVS fraction of the samples (SEM= Simultaneously Extracted Metals) indicate a high availability of the metals present to plant and soil organisms.

Table 21: Fe, Mn, TOC and TBT content of the dredgings

sample	**TOC (%)**	**Fe (mg/kg dm)**	**Mn (mg/kg dm)**	**TBT (µg/kg dm)**
lagun. - low	1.06	11089	123	1020
lagun. - high	1.35	12247	244	27554
lime - high	2.5	16394	309	31100
lime - low	2.72	14197	132	1445
PE - high	3.14	16748	323	52777
PE - low	2.84	8069	86	2554

Table 22: AVS-SEM contents in mg/kg dm

Sample	lagun. - low	lagun. - high	lime - high	lime - low	PE - high	PE - low
Cd	2.26	3.46	5.08	4.89	5.53	4.52
Cu	38.87	118.67	214.28	83.87	205.00	66.25
Pb	86.88	116.20	160.71	144.44	172.46	153.57
Ni	6.86	6.43	8.18	8.39	8.79	8.43
Zn	251.48	296.68	535.70	326.17	488.09	331.23
AVS	< 1.9	< 2.0	< 2.3	< 1.9	< 2.7	< 2.5
Fe	9762	12040	19595	16728	19231	16050

Table 23: AVS-SEM analysis of the dredgings (contents in mmol/kg dm)

Sample	lagun. - low	lagun. - high	lime - high	lime - low	PE - high	PE - low
SEM	5.0	7.1	13	7.2	12	7.0
AVS	< 0.06	< 0.06	< 0.07	< 0.06	< 0.08	< 0.08
SEM/AVS	> 83.6	> 118	> 179	> 120	> 146	> 88

9.3 Leaching experiments

The performed leaching tests are based on the European draft organic compliance test SMT4-CT97-2160, Version 1.0 for the leaching of non-volatile organic components from granular waste materials and sludges and the - for regulatory purposes - frequently used European inorganic compliance test EN 12457 part 3. Both leaching tests are based on the assumption that equilibrium or near-equilibrium is achieved between the liquid and solid phases during the test period.

Short description of test conditions:

- The moisture contents of the samples was determined on separate sub-samples by drying the sample overnight at a temperature of 105°C;
- A fresh sample for analysis corresponding to a dry matter content of 87.5 ± 0,3 g was transferred to a glass bottle with a volume of 1000 ml, having a cap of inert material. No size reduction was applied to the samples, because 95% of the material had a grain size of less than 4 mm;
- A volume of leaching liquid consisting of demineralized water was added to the glass bottle to make up a liquid to solid (L/S) ratio equal to 2;
- The glass bottle was placed in an end-over-end tumbler at 7 rpm and agitated for 6 hours;
- Liquid/solid separation: After removing the bottle from the agitation device suspended solids were allowed to settle for 15 minutes. The liquid was decanted in a centrifuge tube and centrifuged at a g-force of > 1100 g for 15 minutes. Following this pre-centrifugation step the liquid was decanted into a new centrifuge tube and centrifuged for another hour. Because some matter was still floating on top of the liquid after centrifugation, a 50 ml liquid aliquot was removed from the centrifuge tube by the use of a pipette.
- Solids remaining in the centrifugation tubes were transferred back to the 1000 ml glass bottles. Demineralized water was added to the bottle to obtain a L/S equal to 8. The bottles were then placed back in the end-over-end tumblers (7 rpm) and agitated for another 18 hours. Afterwards the same liquid/solid separation procedure was followed as for the first step of the leaching test.
- Finally 10% ethanol was added to the eluates for preservation, before they were shipped to ERC for analyses.

The above described leaching test only deviates from the frequently used EN 12457 part 3 inorganic compliance leaching test in the way the liquids are separated from the solids.
In the EN 12457 leaching test the solids are separated by filtration with membrane filters (0.45 μm) consisting of regenerated cellulose. Filtration of spiked TBT solutions in the concentration range of 20 to 100 μg/l, however, showed that the recovery of TBT using this technique could be as low as 50% (depending on the TBT concentrations in solution), due to adsorption of TBT on the cellulose of the filtration paper.
In the European draft organic compliance test SMT4-CT97-2160 the solids are separated by centrifugation. Tests with spiked solutions in the same concentration range, i.e. between 20 and 100 μg/l, showed that the recovery of TBT with the centrifugation method was always in excess of 85 %.
The two tests differ furthermore in the contact time between solid and leaching liquid. In the EN 12457 (part 3) two-step batch test the contact time in the first step (L/S=2) is 6 hours and 18 hours in the second step at L/S = 8. In the organic leaching test the contact time in both steps is 24 hours.
Results of the leaching experiments are given in Table 24.

Table 24: TBT-concentrations in sediment and the eluates at L/S = 2 and L/S = 10 (calculatation based on emission at L/S = 2 and L/S = 8). Concentrations are given in μg/kg dry matter.

sample		**Leachate (L/S = 2)**	**Leachate (L/S = 10)**	**Sediment**
lagun. - low	MBT	0.044	0.215	129
	DBT	0.531	0.639	246
	TBT	3.0	3.2	1020
lagun. - high	MBT	0.306	0.795	884
	DBT	2.403	5.105	2271
	TBT	40	61	27554
lime - high	MBT	0.611	1.683	3492
	DBT	3.004	12.626	1418
	TBT	48	140	31100
lime - low	MBT	0.091	0.245	374
	DBT	0.681	0.869	127
	TBT	10.1	10.0	1445
PE - high	MBT	0.356	0.257 - 0.417	1469
	DBT	2.425	1.754 - 1.914	3521
	TBT	34	24.8 - 25.0	52777
PE - low	MBT	0.088	0.067 - 0.228	101
	DBT	0.614	0.469 - 0.630	350
	TBT	3.4	2.6 - 2.8	2554

In Table 25 the relative emissions of MBT, DBT and TBT compared to the total MBT, DBT and TBT content of the dredgings, have been calculated. The sorption coefficient K_D was calculated from the ratio between concentration in sediment and concentration in leachate, whereas the sorption coefficient K_{oc} equals the K_D divided by the fraction organic matter in the sediment.

Table 25: relative emission of MBT, DBT and TBT from the dredgings

sample		L/S = 2	L/S = 10	K_D (l/kg) at L/S=2	K_{oc} (l/kg) at L/S=2
lagun. - low	MBT	0.03 %	0.17 %	5864	553173
	DBT	0.22 %	0.26 %	928	87576
	TBT	0.29 %	0.31 %	680	64151
lagun. - high	MBT	0.03 %	0.09 %	5778	427984
	DBT	0.11 %	0.22 %	1893	140185
	TBT	0.15 %	0.22 %	1378	102085
lime - high	MBT	0.02 %	0.05 %	11449	457967
	DBT	0.21 %	0.89 %	945	37813
	TBT	0.15 %	0.45 %	1296	51833
lime - low	MBT	0.02 %	0.07 %	8500	312500
	DBT	0.54 %	0.68 %	384	14106
	TBT	0.70 %	0.69 %	295	10842
PE - high	MBT	0.02 %	0.03 %	8347	265815
	DBT	0.07 %	0.05 %	2934	93445
	TBT	0.06 %	0.05 %	3105	98870
PE - low	MBT	0.09 %	0.23 %	2295	80826
	DBT	0.18 %	0.18 %	1140	40143
	TBT	0.13 %	0.11 %	1502	52900

Discussion:

Only a very small part of the TBT present is effectively leached from the dredgings. The concentrations in the eluates of the second leaching step at L/S = 8 are significantly lower than in the first leaching step at L/S = 2. The leached concentrations (i.e. in µg/kg dry matter) are in the same order of magnitude in both steps.

The use of PE as additive in the mechanically dewatered sediments apparently reduces the leaching of TBT from these sediments. In both the high TBT and low TBT containing sediments the concentrations of TBT in the second eluate were below the detection limit. Concentrations in the first step were also lower compared to sediments with similar or higher contents treated in a different way.

9.4 Ecotoxicity tests

9.4.1 Introduction

The primary aim of ecotoxicity testing as part of the current study was a targeted screening for organotin compounds in eluates from sediment that might contain different co-contaminants such as heavy metals, PCBs, PAHs, etc. These co-contaminants could also exert toxicity to organisms exposed to the eluates. Since organotin compounds are described as very potent pseudo-androgens, screening with bioassays for this mode of action was suggested to screen the eluates for the presence of organotin compounds. However, only limited information concerning the exact mechanisms underlying this mode of action is available. Increases in testosterone titres or inbalance in the androgens/estrogens ratio have been described for several gastropod species after exposure to TBT and these findings have been associated with the phenomenon of imposex, the imposition of male characteristics in females (Fent, 1998; 2003). Two different mechanisms might be involved: direct inhibition of the androgen receptor and indirect interference with aromatase activity. In the current study both potential mechanisms were investigated in order to be able to specifically detect TBT in eluates, in order to distinguish between the effects induced by TBT and other pollutants (e.g; heavy metals, PCB's, etc.) that might coexist in these eluates. Two cost-effective tests using *in vitro* cellular systems were selected for rapid screening. Direct interference of TBT with the androgen receptor was studied using the Yeast Androgen Receptor (YAR) assay. Indirect interference of TBT was studied using an aromatase inhibition assay on human JEG-3 cells.

Yeast Androgen Receptor (YAR) assay.

Recently, a cellular *in vitro* assay was developed for the detection of the direct interference of pseudo-androgens with the androgen receptor. To this end yeast cells were stably transformed with the human androgen receptor (AR) cDNA, together with a reporter plasmid containing a β-galactosidase gene under the transcriptional control of an androgen (ARE) reporter element. The bioassay end-point was β-galactosidase activity in yeast cell lysates. In this study the YAR-assay was performed in parallel with a cytotoxicity assay (turbidity measurement) in order to be able to account for toxic effects of TBT on yeast cells.

For TBT no results in the YAR-assay have been reported in literature. However, using a (a-cellular) competitive binding assay for the androgen receptor Satoh et al. (2001) report the highest binding affinity for the androgen receptor (IC_{50} of 7.6×10^{-6} M) for TBT among all tested chemicals, including phenolic compounds (bisphenol A, 4-octylphenol), phtalates (di-n-butylphtalate, dicyclohexyl phthalate and di(2-ethylhexyl) phthalate) and sterene oligomers. TBT showed no affinity for the estrogen receptor.

Aromatase inhibition assay on human JEG-3 cells.

Also aromatase, an enzyme of the cytochrome P450 system, responsible for the conversion of androgens to estrogens, has been anticipated as causal mechanism (Matthiesen and Gibbs, 1998). Nevertheless, virtually nothing is known about the potential interaction of organotin compounds with the cytochrome P450 system; this system plays a key role in the metabolism of xenobiotic compounds but also in the conversion of cholesterol into a variety of hormones. Thus, inhibition or stimulation of cytochrome P450 isozymes by TBT can result in changes in hormone production or clearance, and subsequent sexual characteristics. Heindrich et al. (2001) looked into the concentration-dependent effects of butyltins on the human cytochrome P450 aromatase activity *in vivo*. TBT was found to be a partial competitive inhibitor of aromatase activity with an IC_{50} value of 6.2 μM with 0.1 μM androstenedione as substrate. Also DBT acted as a partial but less potent inhibitor of human aromatase activity (65% residual activity), whereas TBT and MBT had no effect. Only few *in vivo* studies are available to confirm this potential mode of action (Morcillo and Porte, 1998; Morcillo et al., 1998; McAllister and Kime, 2003). Oberdörster et al (2002) conclude that although aromatase inhibition may play a role in the maintenance of imposex, it clearly is not the primary mechanism.

In the current study placental JEG-3 cells were used to detect the inhibitory potential of TBT. Interference of TBT (or any other aromatase inhibiting substance) with the catalytic activity of aromatase results in a decline in estrogen production. An enzyme linked immunosorbed assay (ELISA) for the detection of estrone is subsequently applied to quantify the effects induced. In this study the aromatase inhibition assay was performed in parallel with a cytotoxicity assays (neutral red assay) in order to be able to account for toxic effects of TBT on JEG-3 cells.

9.4.2 Results

Yeast Androgen Receptor (YAR) assay.

Detailed description of methods and materials used in the YAR-assay are available at Vito. At the onset of the project the YAR assay was optimized using 5α-androstan as a positive control and typical test conditions were set at an exposure time of 5 days during which temperature was gradually decreased from 32°C (18 h), over 28°C (7 hrs) to room temperature (RT) for the remaining period, as these conditions were most favourable for the yeast cells. Photospectrometric measurements were performed at 540 nm to detect the amount of β-galactosidase produced. Turbidity measurements at 620 nm were performed at the end of the assay in order to account for cytotoxicity.

In order to detect the interference of TBT with the androgen receptor in yeast cells, in a first experiment the cells were exposed to a concentration range of TBTCl (dissolved in DMSO to a final concentration in the culture medium of 0.1%) which was directly added to the yeast cultures. The applied TBT concentrations ranged from 6.25×10^{-8} to 4.0×10^{-6} M (Figure 5). As illustrated significant cytotoxicity was observed at a concentration TBT of 1 μM (325.5 μg/L). At this concentration an equal decline in the androgen response was noticeable. No effects of TBT, both on the viability of the yeast cells and on the androgen response, were seen in the range below 325.5 μg/L. Because this concentration is well above the environmental concentrations of TBT we might expect in the eluates of dredged material the YAR assay was excluded for further screening as it is sensitive to general cell death. Scrutiny of the international literature (Satoh et al. (2001)) seems to confirm that the affinity of TBT for the androgen receptor (IC_{50} of 7.6×10^{-6} M) might be too low to use this interaction in a short term screening assay.

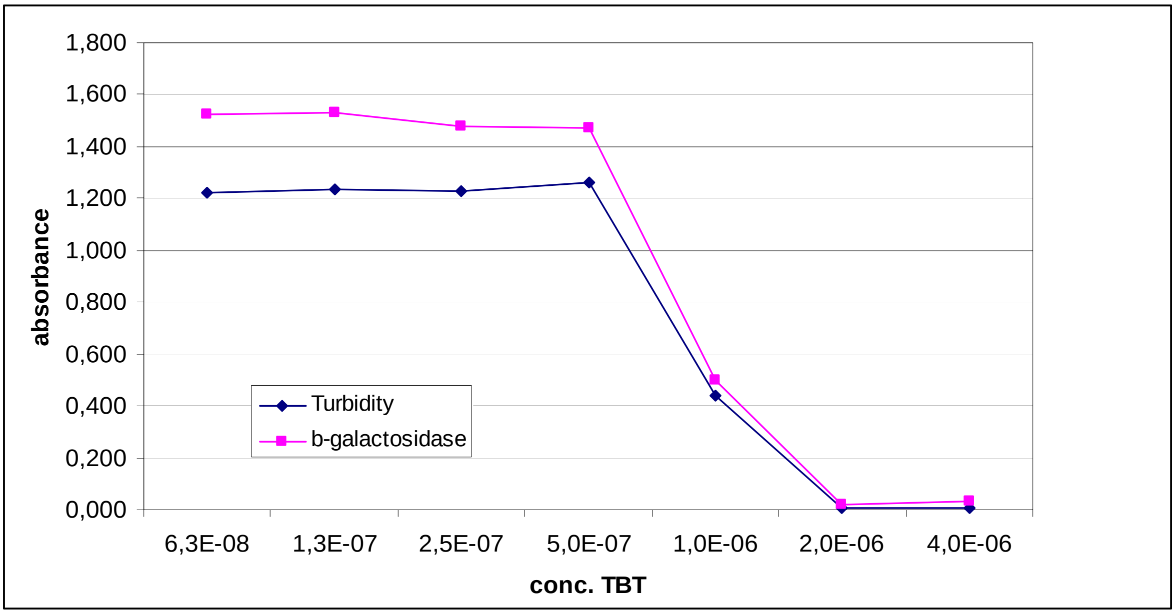

Figure 5: Cytotoxicity and β-galactosidase production in yeast cells exposed to TBT (M)

Aromatase inhibition assay on human JEG-3 cells.

Detailed description of methods and materials used in the aromatase inhibition-assay are available at Vito. Typically, JEG-3 cells (70-80% confluence) are exposed to a test range of the suspect pseudo-androgen for 24 hrs. In the current experiments TBT was applied in the concentration range 0.1, 1, 10, 100 and 200 nM (dissolved in DMSO to a final concentration in the culture medium of 0.1%). Atrazine, a potent androgen inducer, was used as a positive control. At the end of the experiments viability of the JEG-3 cells was tested using the neutral red retention assay (fluorometric measurement at 530-620 nm). The estrone titre was determined using a commercial ELISA kit. Photometric measurements are performed at 450 nm.

Atrazine, used as a positive control induced the aromatase activity from a concentration of 10 µM onwards, while the neutral red assay did not show cellular toxicity (Figure 6). The results of a typical response to TBT in the aromatase assay is shown in Figure 7. At a concentration of 200 nM TBT (± 65 µg/L) a significant inhibition of the aromatase activity is observed. However, the decline in aromatase activity co-incided with a significant reduction in cell viability as seen from the neutral red assay. Again no significant effects are seen in the range of environmentally relevant TBT concentrations in eluates from sediment. Based on these results and a reported IC_{50} value for aromatase inhibition of 6.2 µM (Heindrich et al., 2001) a similar conclusion was drawn as for the YAR assay, i.e. the aromatase inhibition-assay as it stands does not meet the requirements for the screening of TBT at environmentally relevant concentrations due to its sensitivity to general cellular toxicity.

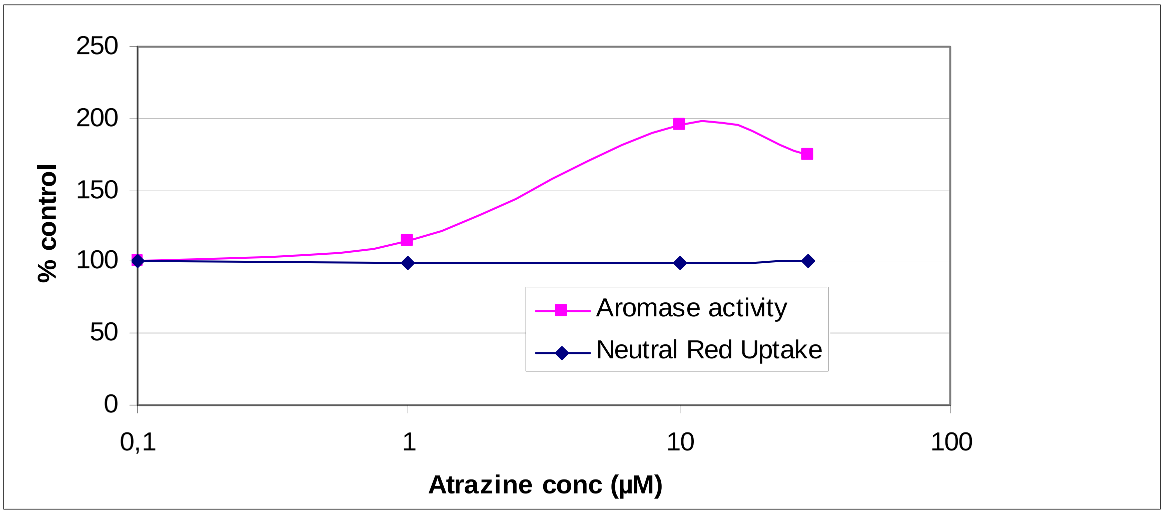

Figure 6: Aromatase activity and cell viability in JEG-3 cells following exposure to atrazine (positive control)

In conclusion, two different assays which are based on two potential mechanisms through which androgen mimicking substances exert their effect have been performed. In both assays a significant reduction in the viability of the cells was observed, covering up potential interference of TBT with the androgen metabolism. As such these assays were not withheld for further screening of TBT contaminated eluates from sediments. One explanation might be that the very short exposure time of the assays may render them less suitable to reveal the effects of androgen mimicking substances at low environmental concentrations.

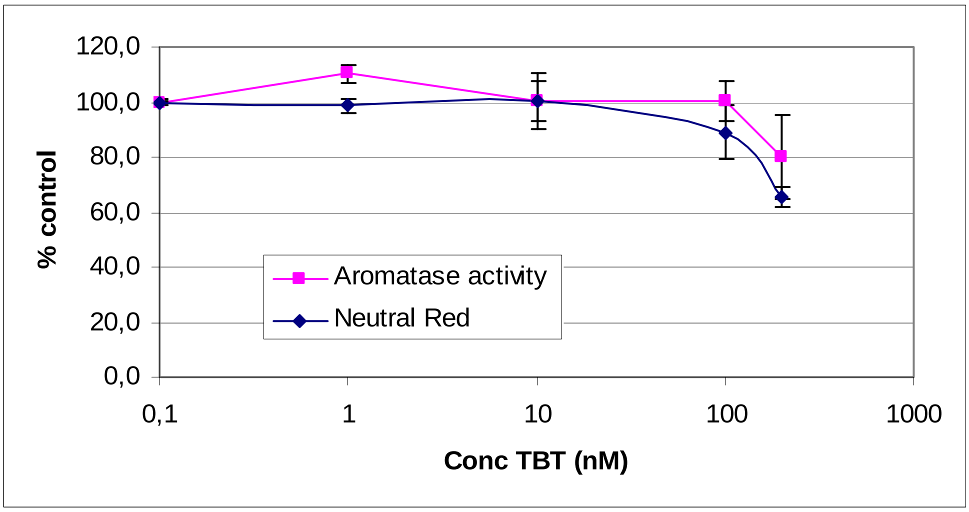

Figure 7: Aromatase activity and cell viability in JEG-3 cells following exposure to TBT

9.4.3 Alternative approach

Early embryo development in zebrafish (Danio rerio)

Previous section described assays that specifically target mechanisms that may be involved in the androgen mimicking features of TBT. As both these assays showed a similar sensitivity to TBT as to general cytotoxicity endpoints, they were not selected for further screening of TBT contaminated eluates from sediment. As such, an alternative test had to be selected. From literature it is obvious that TBT derives its extreme toxicity through interference with the early life stages of the developing embryo. Therefore a 10 day early embryo development test on zebrafish (*Danio rerio*) was chosen because it allowed us to look into a semi-chronic exposure scenario which could fit into the strict planning of this study[7]. Applying semi-chronic exposure conditions allowed us to adhere to the requirement of the precautionary principle. A drawback of the test is that it will respond to all contaminants that may be present in the eluates.

The embryo development test is a semi-chronic toxicity test on fish embryo and sac-fry stages in which the life stages from the newly fertilized egg to the end of the sac-fry stage are exposed. No feeding is provided in the embryo and sac-fry test, and the test should be terminated while the sac-fry are still nourished from the yolk-sac. Through the administration of a test substance in water, this test intends to define lethal, and to a limited extent, sub-lethal effects of the test substance on the specific life stages of the tested species. Zebrafish eggs are exposed as soon as possible after fertilisation (within 2-4 hours after spawning, at least before gastrula stage) to test media containing different concentrations of the test substance. The developmental stage of the embryos at the onset of exposure is evaluated (and documented) through consultation of available literature with the description and illustration of embryonic stages ("The zebrafish book: a guide for the laboratory use of zebrafish Brachy*danio rerio*"). As larvae are not fed during the exposure period, the test will be terminated just before the yolk sac of any larvae in any of the test chambers has been completely absorbed or before mortalities by starvation occur in control group. For zebrafish the total test duration is approximately 8-10 days, or 3-5 days in the embryo stage and up to 5 days post-hatch. In control conditions (no test substance present) hatching success should be at least 80% and the survival of post-hatch larvae should be 90% within the full duration of the test.

During the course of the test several observations are made:

- After a first rough distribution of eggs between test solutions, the eggs which have been collected in breeding tanks will be checked for successful fertilization. Non-fertilized eggs (opaque appearance) will be removed. Moreover, for a representative sample of eggs, a detailed microscopic evaluation will be conducted in order to describe the stage of embryonic development at the start of exposure.
- Hatching and survival: at least once a day and numbers are recorded on specific data sheets. More frequent observations will be made at the beginning of the test. As soon as observed, dead embryos and larvae will be removed. Extreme care should be taken when removing dead individuals not to physically damage the very sensitive adjacent young organisms. Criteria for death are defined as follows for each of life stages:
    - Eggs: particularly in early stages, a marked loss of translucency and change in colouration caused by coagulation and/or precipitation of protein leading to a white opaque appearance

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[7] A typical early life stage test on zebrafish may last from 30 up to 70 days.

    - Embryos: absence of body movement and/or absence of heart-beat and/or opaque discolouration
    - Larvae: immobility and/or absence of heart-beat and/or white opaque colouration of central nervous system and/or lack of swimming response after gentle mechanical stimulation (external to glass vial).
- Abnormal appearance: observations for abnormal appearance (body form, pigmentation) and for the stage of yolk-sac absorption will be recorded at adequate intervals. This will be at least at the end of the test, and at one point in between fully hatched eggs (90% of control) and the end of the test, likely at the 6th or 7th day of exposure. Abnormalities will be scored, but surviving organisms with abnormal appearance will remain in the test vessels.
- Abnormal behaviour: observations for abnormal behaviour, such as hyperventilation, uncoordinated swimming and atypical quiescence will be recorded at adequate intervals. This will be at least at the end of the test, and at one point in between fully hatched eggs (90% of control) and the end of the test, likely at the 6th or 7th day of exposure. These abnormalities will be scored, but surviving organisms with abnormal appearance will remain in the test vessels.
- The above mentioned observations will provide the following data for statistical evaluation:
    - Cumulative mortality
    - Number of healthy larvae at the end of the test
    - Numbers of larvae hatching each day
    - Numbers of larvae with abnormal appearance or abnormal behaviour at end of test

The results of the embryo development test performed on the eluates obtained from Envisan and subsequently diluted with fish water (2 – 2.5x) are summarized in Figure 8. Dilutions were necessary in order to avoid indirect toxic matrix effects on *Brachydanio rerio,* i.e. pH, NH_4^+ and conductivity values incompatible with the normal development of the fishes (Postma et al., 2002). The concentrations TBT shown in Figure 8 were recalculated taking into account the dilution factor applied. The eluates obtained from mechanically dewatered sediment with lime addition induce a significantly higher mortality rate than eluates from mechanically dewatered sediment with polymer addition and from lagunated sediment. No correlation is found between the TBT concentration in eluate and effects observed. On the contrary, the highest effects are consistantly found in those eluates with the lowest concentrations of TBT. One possible explanation might be the presence of different (undetermined) co-contaminants in the different eluates. Also, different physico-chemical conditions in the different eluates may underly this inconsistency. The parameters that have been measured in the eluates are listed in Table 26.

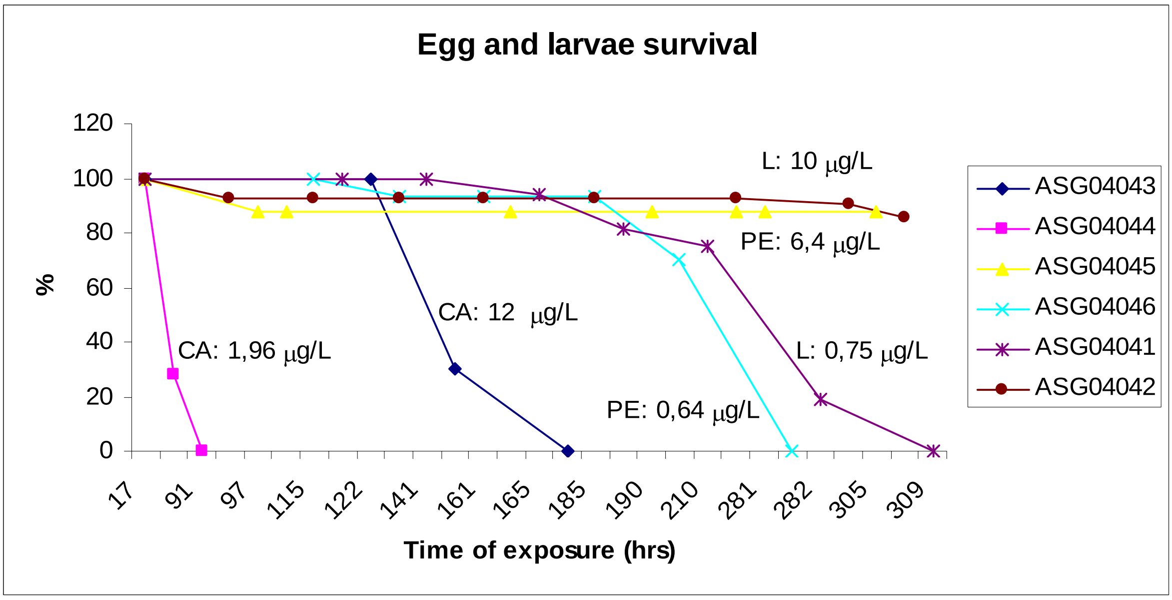

Figure 8: Results from the embryo development test on Brachydanio rerio exposed to eluates obtained from lagunated (L) and mechanically dewatered sediment with lime addition (CA) or polimer(PE) additive

Table 26: Physico-chemical parameters measured in the different eluates.

Code	pH	O_2 %	conductivity mS/cm	N* mg/l
ASG/04041	7.35	66	4.32	<0.1
ASG/04042	7.79	66	4.30	<0.1
ASG/04043	8.63	86	4.19	2.05
ASG/04044	8.65	90	5.40	3.03
ASG/04045	8.64	83	4.18	0.13
ASG/04046	7.8	73	4.51	<0.1

*: measured on the test solution (dilution 2 – 2.5 of the eluate)

In addition to the tests performed on the original eluates, also spiking experiments were performed using TBTCl. The results of a broad dose-range finding experiment (concentrations TBTCl between 5 ng/L and 50 µg/L) in fish water are shown in Figure 9. Significant mortality only occurred from a concentration of 5 µg/L onwards. In order to be able to derive a more accurate value to set a safe concentration TBT in eluates, subsequently a refined dose-range finding test was performed in fish water in the concertration range 0.5 and 10 µg/L (Figure 10). Again, 5 µg/L TBTCl induced significant mortality in fish. At a concentration of 2.5 µg/L no significant effects were observed. In comparison, the results of a refined dose-range finding spiking test in ASG/04042[8] are given in Figure 11. In this test significant mortality occurred from 2.5 µg/L onwards.

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[8] ASG/04042 is the only eluate in which the fishes survive in the non-spiked eluate and for which refined dose-range finding data are available.

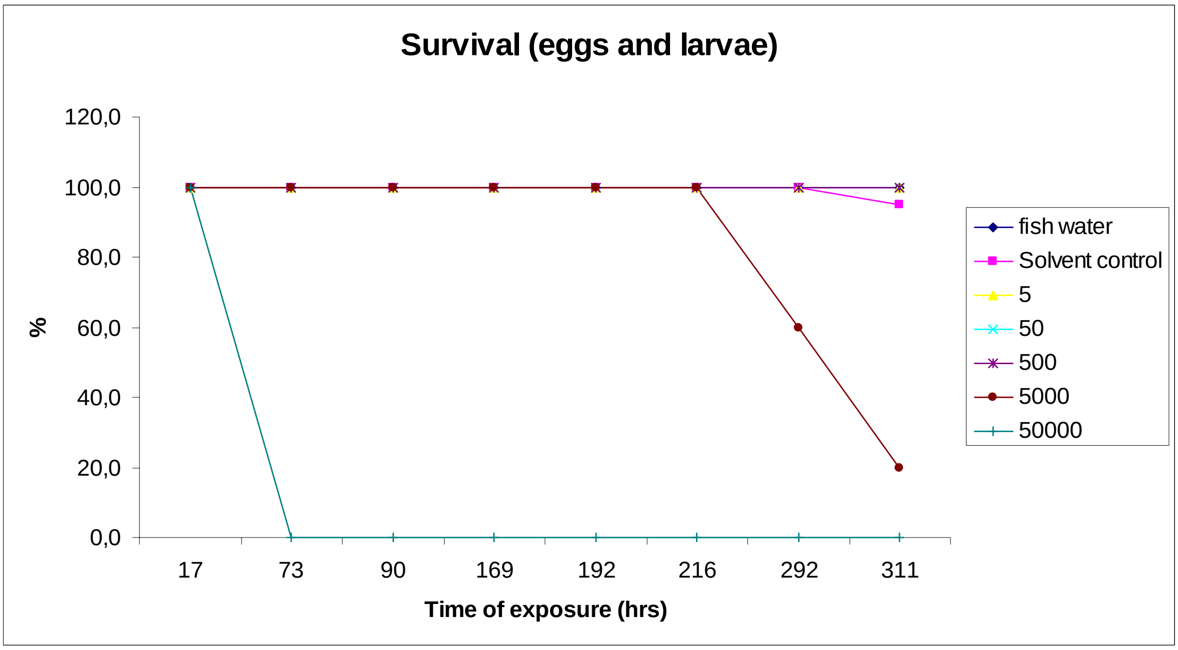

Figure 9: Broad dose-range finding test in fish water spiked with TBTCl (ng/l)

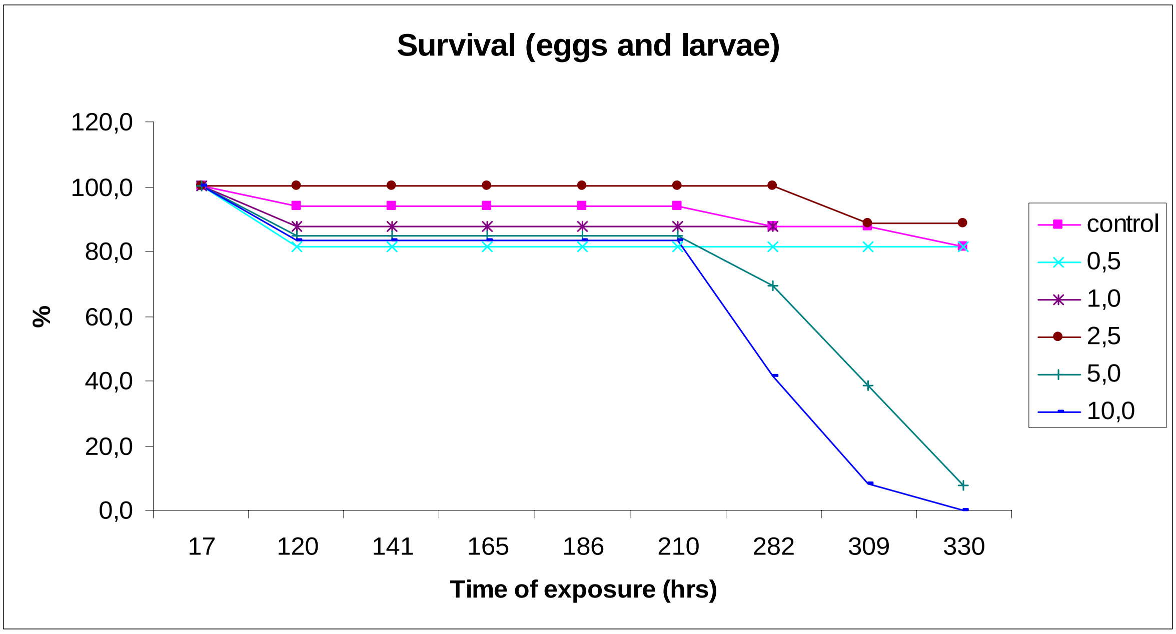

Figure 10: Refined dose-range finding test in fish water spiked with TBTCl (µg/l)

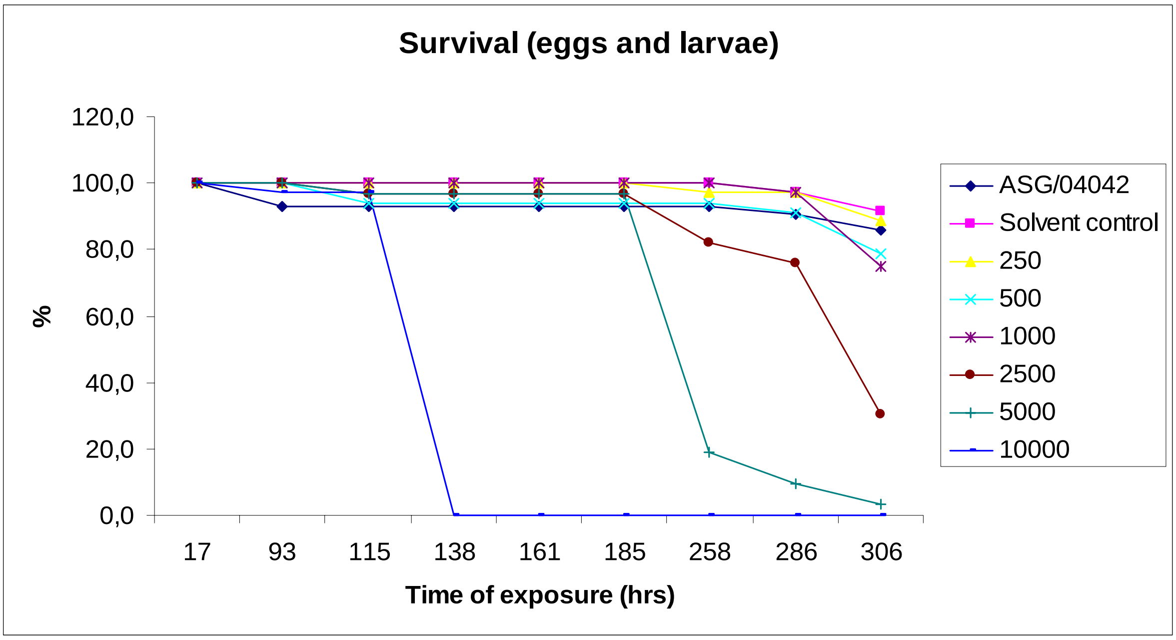

Figure 11: Refined dose-range finding test on ASG/04042 eluate spiked with TBTCl

In conclusion, eluates obtained from sediment may induce significant effects on the development and survival of *Brachydanio rerio*. Eluates obtained from differently treated sediment resulted in considerable differences in the effects that are induced. Eluates derived from mechanically dewatered sediment with lime addition induce significant mortality within the first week of exposure. Over a longer time frame also eluates from lagunated sediment and mechanically dewatered sediment with PE addition may induce significant mortality. However, the test set-up used in this study does not allow to assign the effects that are observed exclusively to TBT. Inconsistency between the TBT concentrations measured in the eluates and the percentage mortality that are observed in the tests may be indicative of the occurence of co-contaminants and/or matrix effects.

The Lowest Observed Effect Concentration (LOEC) derived from spiking experiments in fishwater using TBTCl is 5 µg/L. In ASG/04042, an eluate that in itself did not induce significant mortality in fish, addition of 2.5 µg/L TBTCl resulted in significant reduction in surviving larvae. The No Effect Concentration (NOEC) in this test corresponded with 1 µg/L.

9.4.4 Ecotoxicological quality criteria

The results of the two test systems that are based on the potential mechanisms through which androgen mimicking substances - such as organotin compounds - exert their effect, do not allow to derive a limit value.

The early embryo development test in zebrafish allowed to calculate a LOEC from the spiked solution and from the eluate of the lagunated sediment; the NOEC in the lagunated sediment eluate corresponds to a value of 1 µg/l.

In order to derive an ecological limit value based on these results, the Technical Guidance document (TGD; EU, 2003) of the EU stipulates that when only 1 NOEC is available from an acute test[9], a safety factor of 1000 should be applied in order to obtain a PNEC value (Predicted No Effect Concentration), i.e. an environmental concentration that is considered to induce no deleterious effects to biota after a life time exposure. As a result a PNEC for surface waters of 1 ng/l is obtained. Although this value is higher than a PNEC value based on aquatic ecotoxicity data from literature (between 0.1 and 0.01 ng/L[10]), it does not provide sufficient evidence to reconsider the extreme ecotoxicity of TBT. For this reason, preference is given to the PNEC values derived from the extensive database of aquatic toxicity data.

Within the Water Framework Directive, environmental quality standards for surface water are derived. A draft document was published (Fraunhofer, 2003) and has been reviewed by the CSTEE (CSTEE, 2004). The CSTEE recommended a reappraisal of the proposed quality standard for TBT. At the OSPAR/ICES workshop of February 2004 (OSPAR, 2004) however, the substance datasheet of Fraunhofer was accepted as a more extended effect assessment. For the marine environment an Environmental Assessment Criterion (EAC) of 0.1 ng/l in water is proposed; the current EAC equals 0.1 – 0.01 ng/l. In Germany, a PNEC of 0.07 ng/l was derived for aquatic ecosystems (BUA, 2003). The background of this value is the lowest effective value of 0.7 ng/l as an EC_{10} in *Acartia tonsa* (copepod). Seen the extensive database, an assessment factor of 10 was used to calculate the PNEC. The latter value is retained as the PNEC for surface water in this project.

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[9] The egg development test lasts 14 days and is considered to be a sub-chronic test. In the derivation of the PNEC value the safety factor for acute tests has been applied.

[10] Depending on the fact whether a safety factor 10 is applied or not.

10 CALCULATION OF QUALITY CRITERIA

10.1 Background value and R' value

For compounds which are considered to be of anthropogenic origin, the background value according to Vlarebo corresponds to the limit of detection. The R' value, the quality criterion to be used when soil or waste is to be re-used as soil in land use category I, equals the limit of quantification. In current practice at the Vito laboratory, the limit of quantification is twice the limit of detection.

Limits of detection are provided by Vito and ERC and are given in Table 27.

Table 27: Limits of detection (LoD) and quantification (LoQ) for butyltin compounds (µg/kg dm)

	Vito LoD / LoQ	ERC LoD
TBT	3.75 / 7.5	0.4
DBT	2.35 / 4.7	0.3
MBT	-	0.3

A LoQ can not be given for the MBT analysis at the Vito laboratory because of interference on the measurements.

10.2 Remediation values

A remediation value for groundwater is calculated in view of its use as a receptor-based endpoint in groundwater. Two soil remediation values are calculated: a soil remediation value for residential land-use (SRV(III)) as the condition for free re-use of waste as secondary material (organic compounds) according to Vlarea, and a soil remediation value for industrial land-use (SRV (V)) as a possible upper concentration limit for re-use of the sediment under restricted conditions.

10.2.1 Remediation value for groundwater

The remediation value for groundwater is calculated according to the method used by the WHO for derivation of human-health based drinking water guideline values. The equation for noncarcinogens is as follows:

$$SRV_{groundwater}(\mu g/l) = \frac{TDI(\mu g/kg.d) * RF * BW}{Q(l/d)}$$

In the equation RF stands for the reduction factor on the TDI. This reduction factor represents the fraction of the exposure of the general population that results from the use of drinking water. The default value of 0.1 is used here. BW is the body weight, which for an adult is given as 60 kg; Q is the daily drinking water rate (2 l/d for an adult). Using these values a soil remediation value for groundwater of 0.75 µg/l is calculated. This value applies to TBT and DBT. The sum of measured TBT and DBT should be compared to the value of 0.75 µg/l. No value is calculated for MBT as no adequate toxicity data are available.

10.2.2 Input parameters for the human health based remediation values

Soil remediation values are calculated for tributyltin chloride and dibutyltin chloride. Values for tributyltin oxide are not calculated as it is assumed that the chloride is more representative for the butyltin salt present in soils than is the oxide (however, it is expected that the hydroxide, for which almost no data exist, could be dominant in a soil environment). Insufficient data are available for monobutyltin.
Physicochemical properties show a broad range of values, depending on the test conditions under which they are measured. The values used in the calculations are given in Table 28.

Table 28: Parameter values for calculation of soil remediation values for human health

	TBTCl	DBTCl
M	325.59 (TBTCl) 290.03 (TBT)	303.85 (DBTCl) 268.39 (DBT)
S (mg/l)	$1^{(as\ Sn)}$ (20 °C)	47.5 (20°C)
P (Pa)	1.2 (25 °C)	10.3 (25°C)
H (Pa.m^3/mol)	142 (25°C)	66 (25 °C)
log Kow	3.6	0.58
Koc (l/kg)	$10^{\wedge(4.71)}$	$10^{\wedge(4.73)}$
BCF root (-)	25 (Lespes) 1.1 (Brandsch) f (Kow)	0.6 (Lespes) 8.3 (Brandsch) f (Kow)
BCF stem (-)	12 (Lespes) 1.1 (Brandsch) f (Kow)	1.5 (Lespes) 8.3 (Brandsch) f (Kow)
Dpe (m^2/d)	5E-7	5E-7
TDI (mg/kg.d)	2.5E-4	2.5E-4
TCA (g/m^3)	5.75E-7	5.75E-7
limit water (µg/l)	0.75	0.75
background exposure (mg/kg.d)	8.9E-6	6.3E-6

Log Kow is the geometric mean of the values reported in Appendix I. As the differences in Koc values within treatments is as great as the differences between treatments, the geometric mean of all Koc values is used for the calculations (this value corresponds well with the value used in the Dutch intervention values, which is based on the geometric mean of literature values). Dpe (diffusion through polyethylene) is taken from the RIVM report (value for pesticides).

For plant uptake, there seems to be a broad range between the extremes of the values; the study of Lespes provides the highest values. Higher concentrations are expected because the plant roots are contained within a limited volume of soil. Also, (cross)-contamination can not be excluded. Preference is given to the results of the field experiments, where the studies show more consistency. When listing the results separately, the majority of the values is more in favour of a BCF value of 1 or less. For this reason, but accounting for uncertainty in the data, the highest values calculated from the study of Brandsch were selected. With the aim to evaluate the influence of the BCF value on the calculation of soil remediation values, three options are taken for plant uptake: the highest values of Lespes, the highest values of the field results of Brandsch and the default calculations from log Kow in Vlier-humaan. The plant uptake route is considered to be subject to rather large uncertainties because of the following reasons:

- the literature provides a large range of uptake values;
- plant uptake results are given for experimental conditions where the organotin concentrations were lower than the concentrations found in the sediments of the TBT Life project;
- plant uptake of organotin compounds is expected to be more correlated with concentrations in soil water than with total concentration, a dependency on soil organic matter or soil type can be expected (with lower uptake in soils with a higher organic matter content).

The tolerable concentration in air is extrapolated from the oral TDI, taking a breathing rate of 20 m^3/d and a body weight of 70 kg (default values). The limit in drinking water is calculated from 10 % of the TDI, a body weight of 60 kg and a drinking water consumption of 2 l/d (according to the method of the WHO, see remediation value in groundwater). As values for background exposure by food, the mean exposure, calculated from mean European concentrations and average fish and seafood consumption for Belgium, was taken.

10.2.3 Human health based remediation values

Soil remediation values are calculated with the Excel version of the Vlier-humaan model. The use of the Excel version allows for more flexibility in input and in the calculation of remediation values. The results for residential land-use (SRV(III)) are given in Table 29. All values were calculated as the ion. The values, which are selected, are marked bold in the table.

Table 29: Calculated SRV(III) values (mg/kg dm)

	Lespes	Brandsch	Kow
TBTCl (as TBT)	0.027	**0.51**	3.8
DBTCl (as DBT)	0.67	**0.07**	27

bold: values selected as SRV(III)

Appendix II shows the detailed results of the calculations, with concentrations in contact media and doses by exposure pathway.

The calculations for SRV(V) are shown in Table 30. Two scenarios are used: light industry where activities mainly take place indoors and heavy industry with more time spent outdoors and higher soil/dust intake. First, calculations were based on exceedance of the

TDI, then a check was done for possible exceedance of TCA (Tolerable Concentration in Air) or drinking water limits (caused by permeation through drinking water pipes). The latter values are given in the table under “additional check”. The values selected are given in bold. Detailed calculations are given in appendix II (for the selected values).

Table 30: Calculated SRV(V) values (mg/kg dm)

SRV(V)	TDI	additional check
light		
TBTCl (as TBT)	725	**196**^{d}
DBT (as DBT)	832	**204**^{d}
heavy		
TBTCl (as TBT)	300	196^d
DBT (as DBT)	309	204^d

additional check: reduction of the SRV because of exceedance of drinking water limit (d)
bold: values selected as SRV(V)

Soil remediation values can depend on soil organic matter content, because of the dependence of sorption on organic matter content (use of a Koc value). Consequently pore water concentration and (soil) air concentration can vary with varying organic matter content. Using a BCF on total soil concentration, no variation of plant uptake with organic matter is calculated. The dependence of the SRV to soil organic matter is calculated by varying the organic matter content in the Vlier-humaan model and calculating the corresponding SRV. The SRV(III) values for TBT and DBT are almost independent of the organic matter content, because the dominant pathway is vegetable intake and fixed bioconcentration factors are used there.

Figure 12 shows the relationship between SRV(V) and soil organic matter for TBT. The relation is purely linear and follows the default relationship where SRV(x %) = SRV(2%)*x/2. The same relationship is valid for the SRV(V) of DBT.

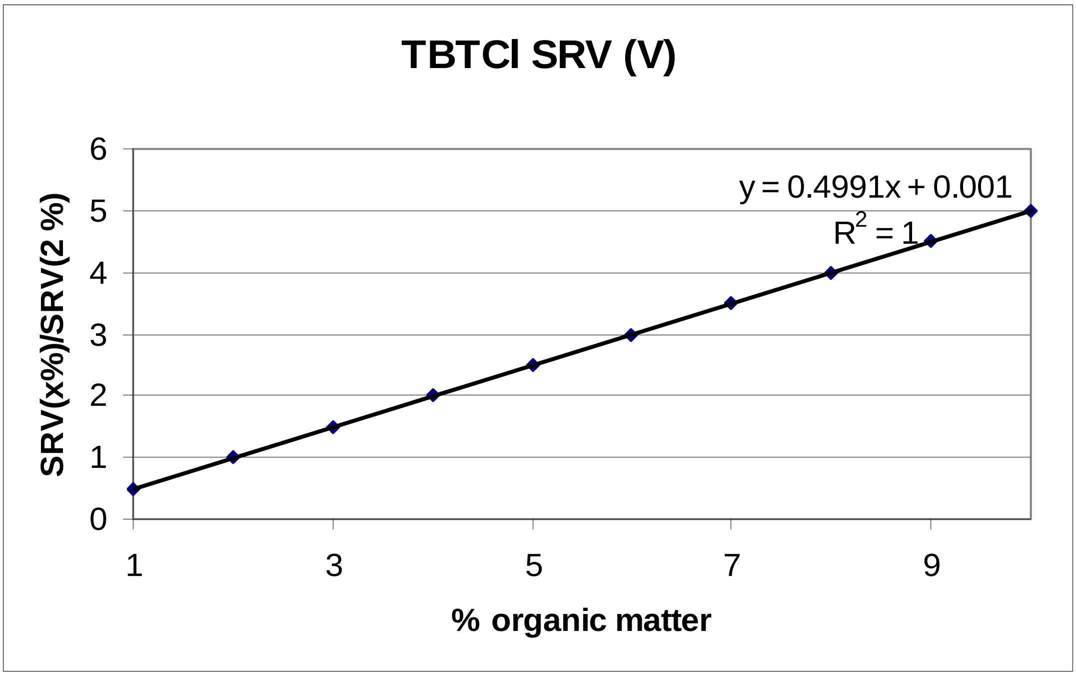

Figure 12: Dependence of SRV(V) on soil organic matter

The correction of soil remediation value for organic matter content of the soil is the standard approach in Vlarebo. However, when SRV(III) values are used in VLAREA, they are *not* corrected for organic matter content.

10.2.4 Ecosystem based remediation values

Based on the data from the study of Hund-Rinke a remediation value can be calculated, looking at protection of the ecosystem. At present, the soil remediation values in Vlarebo are checked for ecotoxicological effects on the basis of expert judgment. However, a draft method is available. This draft method is largely based on the Canadian method for derivation of soil quality guidelines.

If sufficient NOEC and LOEC data are available, a statistical approach is followed. As only EC_{50} values are available for TBT, the Median Effect Method should be applied. The lowest EC_{50} is divided by an uncertainty factor of 5. The lowest EC_{50} equals 1.5 mg/kg dm, resulting in an $SRV(III)_{eco}$ of 0.3 mg/kg dm. An additional uncertainty factor is not needed as the minimal requirements with regard to the dataset are met. Results for microbial effects give much higher levels and are for this reason not taken into account (according to the method). Insufficient data are available to calculate a value for industrial land-use. The human health and ecotoxicological remediation value for TBT are in line with each other, no ecotoxicological values can be derived for MBT because of lack of data.

10.3 Conditions with regard to leaching

10.3.1 Introduction

Conditions with regard to leaching are calculated for the following scenarios:

- leaching criteria with groundwater as receptor – the receptor-based criterion equals 0.1 times the groundwater remediation value:
  - application above groundwater level: this scenario is – with the exception of the application height – equal to the draft method for assessing leaching of secondary material to groundwater;
  - application above groundwater level – reduced infiltration rate because of the presence of a coverage;
  - application below groundwater level;
- leaching criteria with surface water as receptor – the receptor-based criterion equals the PNEC for surface water:
  - application above groundwater level under normal infiltration and under reduced infiltration;
  - exploratory calculations.

At the beginning of the project, it was foreseen that for free re-use of treated sediment as granular secondary material, only the SRV(III) would be used. However, in the light of recent developments for the Vlarea framework, it is considered necessary to include a leaching criterion for free re-use as well. The latter is an option taking now as exploratory for a possible revision of the Vlarea framework and should be accounted for here as well. Additionally, not accounting for leaching in the free re-use scenario could lead to inconsistencies or conflicts in the application of the framework.

Another change to the project lay-out, is that the leaching criteria are not given as concentrations in the leachate, but as concentrations in the sediment itself. The reason for this is the fact that the leaching test used (2-stage batch test) does not allow to give criteria in the leachate (this is in contrast to the column test). However, this does not lead to more complexity in the system, as will be demonstrated in the next chapters.

10.3.2 Leaching criteria for application above GWL – groundwater as receptor

- Criteria for “free re-use”

Concentration limits for the sediment as granular building material are calculated according to the framework for organic compounds under development for OVAM that is discussed in chapter 2.3 - Framework development. The reference scenario is a layer of secondary raw material of 150 m length on top of a soil layer of 1 m depth. Groundwater concentrations are calculated at a distance of 20 m in the direction of groundwater flow. The application height is the standard height used in Vlarea and equals 0.7 m. Groundwater velocity is 20 m/y and the thickness of the phreatic layer is 5 m. For the soil, a K_D value was obtained by taking the geometric mean of literature values and this value was 1863 l kg^{-1} for TBT and 3419 l kg^{-1} for DBT. The K_D of the phreatic layer is assumed to be 10 times lower. Calculations are carried out for the range of K_D values that can be expected to occur in the treated sediment. The groundwater criterion for both TBT and DBT was set to 0.075 µg l^{-1} (10% of groundwater remediation value). Infiltration rate in this case (no coverage) is set to 300 mm y^{-1} (standard value in Vlarea). Results are given in Table 31.

Table 31: Leaching criteria for "free re-use"

K_D of sediment (l/kg)	TBT (mg/kg dm)	DBT (mg/kg dm)
100	0.34	0.60
500	0.36	0.64
1000	0.41	0.67
1500	0.46	0.72
2000	0.52	0.77
2500	0.57	0.82
3000	0.62	0.88
4000	0.73	0.98
5000	0.84	1.09
6000	0.96	1.19
7000	1.07	1.30
8000	1.18	1.42
9000	1.29	1.53
10000	1.41	1.63

Under this scenario, the upper limit (SRV(III)) is lower than the leaching criterion for DBT. For TBT the upper limit will be critical for K_D values of 1980 l/kg or more. The relation between leaching criterion and K_D is almost linear; the relationship for TBT and DBT is given in Figure 13.

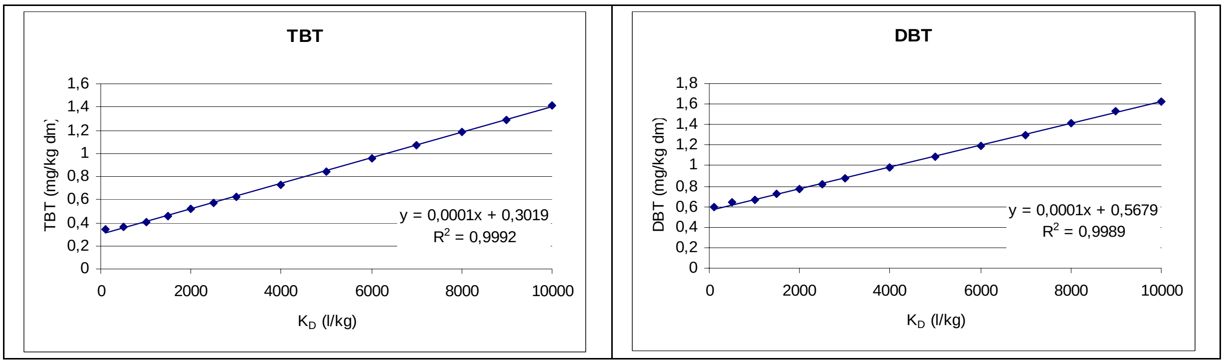

Figure 13: Leaching criteria for TBT and DBT for "free re-use" (SLV(TBT) = $0.0001K_D+0.3019$; SLV(DBT) = $0.0001K_D+0.5679$)

- Criteria for "restricted re-use"

For re-use with coverage, leaching criteria are calculated following the same approach, only with a different infiltration rate. Infiltration was set to 6 mm y^{-1}, as is done in the Dutch Bouwstoffenbesluit for infiltration below coverage. This assumption requires, of course, the use of coverage material which meets the preset infiltration rate. Calculations are done for a receptor in the groundwater at 20 m distance from the application. Results are given in Table 32.

Table 32: Leaching criteria for "restricted re-use" with a coverage (infiltration rate of 6 mm/y) and above groundwater level

K_D of sediment (l/kg)	TBT (mg/kg dm)	DBT (mg/kg dm)
100	6.9	12.0
500	7.3	12.9
1000	8.3	13.5
1500	9.3	14.4
2000	10.6	15.4
2500	11.5	16.5
3000	12.7	17.6
4000	14.9	20.2
5000	17.2	23.3
6000	19.6	24.5
7000	22.0	26.7
8000	24.3	28.9
9000	26.6	31.1
10000	29.0	33.3

For this scenario, the upper limit (SRV(V)) will not be critical at K_D values within a realistic range. The almost linear relationship between leaching criterion and K_D is given in Figure 14.

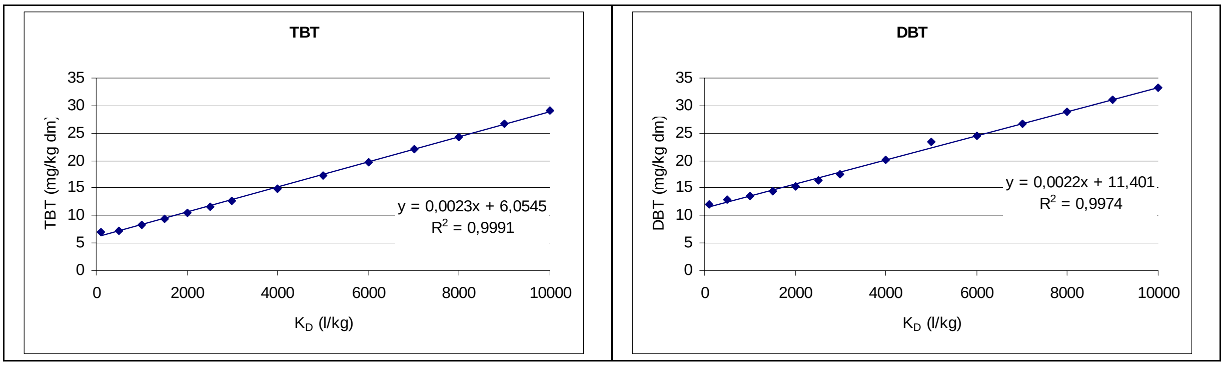

Figure 14: Leaching criteria for "restricted re-use" with coverage (infiltration rate 6 mm/y) and above groundwater level (SLV(TBT) = $0.0023K_D+6.0545$; SLV(DBT) = $0.0022K_D+11.401$)

Concentrations limits are considerably higher than in the previous cases. This is mainly due to the high dilution factor in this scenario. With the reduced infiltration rate, a much smaller amount of soil water is mixed with a large amount of groundwater when entering the saturated zone, resulting in this case in a dilution factor of 34.

10.3.3 Leaching criteria for application below GWL – groundwater as receptor

Concentration limits are also calculated for the application of granular secondary material below groundwater level. The considered scenario is an application of 150 m length in the direction of the groundwater flow with an evaluation of groundwater concentration at 20 m distance. The groundwater criterion is 0.075 µg/l for both TBT and DBT as in the previous calculations. Since the calculated concentration limits do not depend on the K_D value of the soil, the curves of concentration limit in function of the K_D value of the sediment are the same for TBT and DBT. The values are given in Table 33.

Table 33: Leaching criteria for" restricted re-use", application below groundwater level.

K_D of sediment (l/kg)	TBT/DBT (mg/kg dm)
100	0.007
500	0.038
1000	0.077
1500	0.115
2000	0.154
2500	0.192
3000	0.231
4000	0.308
5000	0.385
6000	0.463
7000	0.540
8000	0.617
9000	0.694
10000	0.772

The linear relationship between leaching criterion and K_D value is given in Figure 15.

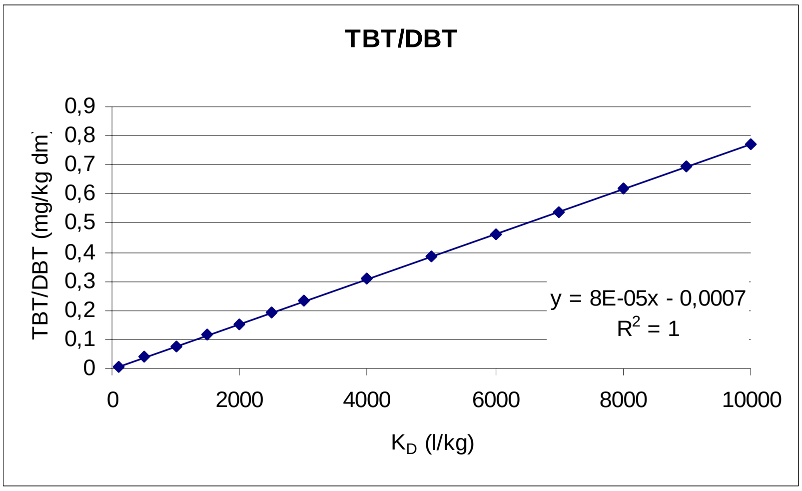

Figure 15: Leaching criteria for application below groundwater level (SLV(TBT/DBT) = $8.10^{-}5K_D$-0.0007)

10.3.4 Leaching criteria – surface water as receptor

To determine leaching criteria based on a surface water receptor, an additional mixing factor for dilution of groundwater in surface water has to be taken into account. The path from the application of the sediment to the receptor then includes leaching from the layer of secondary material, transport through soil, dilution of soil pore water in groundwater, transport in groundwater and dilution of groundwater in surface water.

The mixing factor *MF* indicating how much groundwater is diluted can be calculated as:

$$MF = \frac{Q_{gw} + Q_{sw}}{Q_{gw}}$$

with *MF* the mixing factor (-), Q_{gw} the groundwater flux ($m^3\ y^{-1}$) and Q_{sw} the surface water flux ($m^3\ y^{-1}$). The groundwater flux is the product of the length of the application along the river, the thickness of the mixing layer between soil water and groundwater, the saturated hydraulic conductivity and the hydraulic gradient of the phreatic layer. The value of Q_{gw} thus depends on the characteristics of the aquifer and the dimensions of the application of sediment.

The mixing factor *MF* is calculated illustratively for three Flemish rivers, using river discharge data and local aquifer characteristics and assuming an application length of 150 m along the river. For the lower reach of the river Schelde, a low-tide discharge of 432 $m^3\ s^{-1}$ and a yearly incoming groundwater flux of 14180 $m^3\ y^{-1}$ is used, resulting in a mixing factor of 960742. For the Mangelbeek (Lummen) and the Bosbeek (Opoeteren), a discharge flux of 1.04 $m^3\ s^{-1}$ and 0.3 $m^3\ s^{-1}$ and a calculated groundwater flux of 15878 $m^3\ y^{-1}$ and 44939 $m^3\ y^{-1}$ result in mixing factors of 2066 and 211 respectively. This indicates the wide range and the site dependence of mixing factors for dilution in surface water.

Alternatively, in the $N(eco)^2$ research project that looked into the leaching of nitrate from the root zone and transport to surface water, a 'process factor' or mixing factor of 2.4 was derived by comparing measurements of nitrate concentrations in groundwater and in surface water for different locations in Flanders (VLM, 2001). Since this value was based mainly on drainage and leaching from agricultural fields to nearby ditches, it can be considered to be representative for small streams and ditches.

To calculate leaching criteria in the layer of granular secondary material for a surface water endpoint, the (ecotoxicological) surface water criterion is multiplied by the mixing factor to derive a groundwater criterion. Then the calculation of leaching criteria for "free re-use" (infiltration of 300 mm y^{-1}) or "restricted re-use" (infiltration of 6 mm y^{-1}) can be carried out using the same model as before. Table 34 gives results for an ecotoxicological criterion of 0.07 ng l^{-1} and a K_D value for the sediment of 1000 l kg^{-1}.

Table 34: Leaching criteria based on an ecotoxicological endpoint in surface water.

Stream	MF	GW criterion (µg/l)	Leaching criteria “free re-use” (mg/kg dm)	Leaching criteria “restricted re-use” (mg/kg dm)
- [N(eco)^{2}]	2.4	0.000168	0.0009	0.018
Bosbeek	211	0.0148	0.08	1.6
Mangelbeek	2066	0.145	0.78	16.1
Schelde	960742	67.3	364	7500

The results indicate that:

- the impact of the re-use of granular secondary material on surface water quality, resulting from leaching to groundwater, is highly dependent on the local circumstances;
- for application of organotin containing sediment in a situation where the groundwater is drained towards the river Schelde (province of Antwerp), little impact on the surface water is expected (attention should be paid to the length and the height of the application);
- for application of organotin containing sediment in a situation where the surface water has a moderate discharge rate, the impact on surface water could be critical.

11 INTEGRATION AND CONCLUSIONS

11.1 Integration

This chapter provides the integration of the various quality criteria derived in the previous chapter in the (modified) framework.

Background values and R' values are given in Table 35. As they are not really part of the framework and no decision can be taken on the values themselves because of the lack of an official analytical method, they are not further discussed here.

For all re-use options, at least two criteria should be used to evaluate the possible application: a human-health based upper limit (SedUL: sediment upper limit) and a leaching based value (SedLV: sediment leaching value) with groundwater as a receptor. In addition, the impact on surface water should be evaluated on a case by case basis, using an ecotoxicology based criterion and site-specific information.

The SedUL is only based on human health criteria because in the case of residential land-use, the ecotoxicologically derived value was in line with the human health based value; in the case of industrial land-use no ecotoxicological value could be calculated. The SedUL for free re-use equals the SRV(III); the SedUL for restricted re-use equals the SRV(V). The limits for hazardous substances and hazardous waste are much higher than the SRV(V), for this reason the SRV(V) was chosen. It is anticipated that restricted re-use prohibits the direct contact of persons with the sediment. The SLVs for re-use above groundwater level are given for a reference scenario that is based on ongoing developments in the regulation of the application of granular building materials. For free re-use, a POC at 20 m (and a dilution factor of 2) is applied in the draft scenario. The SedLVs are calculated for a standard scenario; the values are rather sensitive to changes in application height, with lower SedLVs at higher application height. The SedLVs are given for a range of K_D values; a regression line is given for calculation of the SedLV from the experimentally determined K_D values. K_D values are calculated as the ratio of the concentration in the sediment to the concentration in the leachate at L/S = 2. Given the rather high K_D values, no correction for L/S is needed.

The quality criteria given hereafter apply to sediments that are geotechnically suitable for re-use as granular building material; i.e. the sediment has undergone the necessary treatments (such as dewatering). Concentrations and K_D values are measured on representative samples of the sediment; variation in results should be taken into account.

The conditions that apply to the **free re-use** of treated organotin containing sediment are given in Table 35. The SedLV can be calculated from the experimentally determined K_D value by means of the regressions given below the table.

Table 35: Quality criteria for free re-use of organotin containing sediment

	TBT (mg/kg dm)*	DBT (mg/kg dm)*
SedUL (free re-use)	0.5	0.07
K_D of sediment (l/kg)**	SedLV(free re-use)	
100	0.34	n.l.
500	0.36	n.l.
1000	0.41	n.l.
1500	0.46	n.l.
2000	n.l.	n.l.
2500	n.l.	n.l.
3000	n.l.	n.l.
4000	n.l.	n.l.
5000	n.l.	n.l.
6000	n.l.	n.l.
7000	n.l.	n.l.
8000	n.l.	n.l.
9000	n.l.	n.l.
10000	n.l.	n.l.

n.l.: not limiting; the SedLV is higher than the SedUL

*: the decision on the re-use will be taken based on the following sum of ratios:

$$\frac{C(TBT)}{SedUL(TBT)}+\frac{C(DBT)}{SedUL(DBT)} \text{ and } \frac{C(TBT)}{SedLV(TBT)}+\frac{C(DBT)}{SedLV(DBT)},$$

if one of these sum of ratios exceeds the value of 1, no free re-use as granular building material is allowed

**: the SedLV for TBT can be calculated from the experimental K_D with the following equation:

$$SedLV^{free}(TBT) = 0.30 + 0.0001K_D$$

The conditions that apply to the **re-use** of treated organotin containing sediment **under coverage and above groundwater level** are given in Table 36. The SedLV can be calculated from the experimentally determined K_D value by means of the regressions given below the table.

Table 36: Quality criteria for re-use of organotin containing sediment under coverage (infiltration rate 6 mm/y) and above groundwater level

	TBT (mg/kg dm)*	DBT (mg/kg dm)*
SedUL(restricted re-use)	195	205
K_D of sediment (l/kg)**	SedLV(coverage, above GWL)	
100	6.9	12.0
500	7.3	12.9
1000	8.3	13.5
1500	9.3	14.4
2000	10.6	15.4
2500	11.5	16.5
3000	12.7	17.6
4000	14.9	20.2
5000	17.2	23.3
6000	19.6	24.5
7000	22.0	26.7
8000	24.3	28.9
9000	26.6	31.1
10000	29.0	33.3

*: the decision on the re-use will be taken based on the following sum of ratios:

$$\frac{C(TBT)}{SedUL(TBT)}+\frac{C(DBT)}{SedUL(DBT)} \text{ and } \frac{C(TBT)}{SedLV(TBT)}+\frac{C(DBT)}{SedLV(DBT)}$$

if one of these sum of ratios exceeds a value of 1, no re-use as granular building material under coverage and above groundwater level is allowed

**: the SedLV can be calculated from the experimental K_D with the following equation:

$$SedLV^{\text{cov},above\ GWL}(TBT)=6.1+0.0023K_D$$

$$SedLV^{\text{cov},above\ GWL}(DBT)=11.4+0.0022K_D$$

The conditions that apply to the **re-use** of treated organotin containing sediment **under groundwater level** are given in Table 37. The SedLV can be calculated from the experimentally determined K_D value by means of the regression given below the table.

Table 37: Quality criteria for re-use of organotin containing sediment under groundwater level

	TBT (mg/kg dm)*	DBT (mg/kg dm)*
SedUL(restricted re-use)	195	205
K_D of sediment (l/kg)**	SedLV(coverage, under GWL)	
100	0.007	0.007
500	0.038	0.038
1000	0.077	0.077
1500	0.12	0.12
2000	0.15	0.15
2500	0.19	0.19
3000	0.23	0.23
4000	0.31	0.31
5000	0.39	0.39
6000	0.46	0.46
7000	0.54	0.54
8000	0.62	0.62
9000	0.69	0.69
10000	0.77	0.77

*: the decision on the re-use will be taken based on the following sum of ratios:

$$\frac{C(TBT)}{SedUL(TBT)} + \frac{C(DBT)}{SedUL(DBT)} \text{ and } \frac{C(TBT)}{SedLV(TBT)} + \frac{C(DBT)}{SedLV(DBT)}$$

if one of these sum of ratios exceeds the value of 1, no re-use as granular building material below groundwater level is allowed

**: the SedLV can be calculated from the experimental K_D with the following equation:

$$SedLV^{under\ GWL}(TBT / DBT) = -0.0007 + 8 * 10^{-5} K_D$$

In addition to the values given above where groundwater is considered the receptor with a human-health based criterion (0.75 µg/l), attention should be paid to leaching of organotin compounds from sediment towards surface water. In surface water, an ecotoxicological based criterion applies (0.07 ng/l as preliminary value for TBT). Considering the significant impact of the ratio of groundwater flux to surface water flux on the dilution factor and thus on the quality criterion, the choice is made not to give sediment quality criteria with regard to surface water as a receptor. It is expected that re-use of the treated sediment in areas with groundwater drainage to large rivers as the Schelde, will not pose problems for the surface water. If drainage to smaller rivers would occur, this pathway can be critical.

11.2 Conclusions and discussion

The project aimed to develop a framework and quality criteria for the re-use of treated organotin containing sediment on land as granular raw material. The project focussed at butyltin compounds. At the beginning of the project, a framework was anticipated with the following scenarios:

- free re-use: the SedUL equals SRV(III); this corresponds to the present approach for organic contaminants in Vlarea;
- re-use under coverage and above groundwater level; re-use under coverage and below groundwater level: an upper concentration limit (SedUL = SRV(V) or hazardous substances/hazardous waste regulations) would apply as well as a limit on the leachate (SedLV); the latter limit would be based on either human-health based criteria or ecotoxicologically based criteria.

The ecotoxicological criterion would be derived from ecotoxicity tests on the sediment eluate, using a test which is organotin-specific.

SRV(III) values and SRV(V) values were calculated according to the method used for calculating soil remediation values within the legal framework of soil remediation. Uncertainties on these values are caused by the limited information on plant uptake (critical for SRV(III)), where values show a broad range, and to a lesser extent on Henry's law coefficient (critical in SRV(V)). The dependency of plant uptake on sediment/soil texture or organic matter content could not be evaluated on the basis of the available studies. There are indications however, that organotin compounds are taken up to a lesser extent in heavier soils. A groundwater remediation value was calculated for use in the derivation of SedLVs with groundwater quality as an endpoint. No values could be calculated for MBT because of a lack of adequate human toxicity and physico-chemical data.

Leaching tests were undertaken on six treated sediment samples. Treatments were lagunation and mechanical dewatering with either lime or polyelectrolyte. For each treatment, a low and a high organotin containing sediment was used in the experiments. The leaching test was a two stage batch leaching test at L/S=2 and L/S=8. The leachates at L/S=2 were used in the ecotoxicity tests. Two tests, which are designed to detect the toxicity of organotins on the basis of their possible working mechanism, were applied first. In both tests, an organotin-specific dose-response could not be measured. Therefore the early embryo development test in zebrafish was used as an alternative. This is not an organotinspecific test. From the spiking experiments on both fish water and leachate from the lagunated sediment, a NOEC could be derived for TBT. However, this NOEC did not give any indication that a higher value than the PNECs published in the literature could be used. For this reason, a PNEC was taken from the literature for use in SedLV calculations with surface water quality as an endpoint.

Accounting for the ongoing developments in the framework for re-use of waste as granular building material, the design of the leaching test and the outcome of the experiments, the organotin framework was slightly modified:

- quality criteria based on leaching with groundwater quality as an endpoint were calculated for all scenarios including free re-use;
- quality criteria based on leaching are expressed as a concentration in the sediment and not as a concentration in the leachate: the reason for this is the design of the leaching test, which does not allow for calculation of an emission curve;
- the ecotoxicological criterion was taken as an endpoint in surface water; no final values could be calculated here because the range of dilution factors is very broad (5 orders of magnitude) and evaluation should be done on a site-specific basis.

The SedLV is back calculated from the human-health based groundwater criterion, using a mathematical transport model. The scenario used accounts for the ongoing developments at the policy level with regard to re-use of waste as granular building material, both for inorganic and organic contaminants. The default scenario starts from 10 % of the groundwater remediation value as the groundwater criterion. The application scenario considers an application height of 0.7 m and a length of 150 m on top of a soil layer of 1m thickness. Groundwater concentrations are considered in a point of compliance at 20 m distance from the application (accounting for dilution and dispersion). The results are sensitive to changes in application height. For free re-use an infiltration rate of 300 mm/y is used; for re-use under coverage an infiltration rate of 6 mm/y is used. Coverage needs to meet this infiltration condition.

Integrating all calculations, the following resulted:

- for free re-use both the SedUL and SedLV are needed for TBT; for DBT the SedUL is the limiting criterion; the SedLV depends on the experimentally determined K_D value;
- for re-use under coverage and above groundwater level both the SedLV is critical within the K_D range for which calculations were done; the SedLV depends on the experimentally determined K_D value;
- for re-use under groundwater level, the SedLV is critical; there is no influence of coverage on the values as the values are independent of infiltration rate; the SedLV depends on the experimentally determined K_D value;

Drainage of groundwater to surface water should be evaluated on a case-by-case basis. Applications where drainage to large rivers such as the Schelde occur, are not likely to cause unacceptable concentrations in surface water. In smaller rivers, drainage to surface water could be critical.

K_D values are calculated from the leaching test at L/S=2. The K_D is equal to the ratio of the concentration in the sediment (µg/kg dm) to the concentration in the leachate (µg/l).

The calculated quality criteria depend on the choice of the parameter values and on the model scenarios. Uncertainty and variation in parameter values is discussed in the derivation of the criteria. Main uncertainties and variations are found in the plant uptake factors, K_D values and Henry's law coefficient. The choice of the plant uptake factor significantly influences the SedUL for free re-use; the choice of K_D and Henry's law coefficient influences the SedUL for restricted re-use. The plant uptake factor is the upper limit of the ranges of the field data; also Henry's law coefficient is taken as a conservative value. K_D is the geometric mean and should represent average conditions. K_D also influences SedLV because the geometric mean of literature values is taken for the soil layer under the sediment and as a basis for the sorption coefficient in the aquifer. The variation in K_D in the sediment, however, is taken into account by using K_D factors measured on the real sediment. SedLVs also depend on the default scenario chosen. When the application deviates significantly from the default scenario, site-specific SedLVs should be calculated. This is especially the case for soils with very low organic matter content (and low K_D) and for applications with a height and length that strongly exceeds the standard values.

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APPENDIX I: PROPERTIES OF BUTYLTIN COMPOUNDS

Databases:

HSDB database via Toxnet (http://toxnet.nlm.nih.gov/)
Syracuse database (http://esc.syrres.com)
IUCLID database van European Bureau of Chemicals
Chemfinder (http://www.chemfinder.com)

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Substances:

Bu_3Sn
$(Bu_3Sn)_2O$
Bu_3SnCl
Bu_2SnCl_2
Ph_3SnOH
Ph_3SnCl
$BuSnCl_3$
dibutyltin dilaurate
$SnCl_4$

TRI-N-BUTYLTIN HYDRIDE

Parameter	**unit**	**value**	**reference**
chemical formula	C12-H28-Sn		HSDB(1)
name	TRI-N-BUTYLTIN HYDRIDE; tributylstannane; Tributyltin; Tri-n-butyltin; Tri-n-butyltin hydride; tri-n-Butyltin (TBT);		HSDB Chemfinder
IUPAC name	tri-n-butyltin hydride		
CAS number	688-73-3		HSDB
molecular weight	g/mol	291.09 291.0432	HSDB(1) chemfinder
solubility	mg/l		
vapour pressure	Pa		
Henry’s coefficient	Pa m^3/mol		
K_{ow}	g/g		
K_{oc}	(-) dm^3/kg		
KD	(-) dm^3/kg		
diffusion coefficient air	m^2/h		
diffusion coefficient water	m^2/h		

BIS(TRIBUTYLTIN) OXIDE

Parameter	unit	value	reference
chemical formula	$C_{24}H_{54}OSn_2$ (printed: C24-H54-O-Sn2)		HSDB
name	BIS(TRIBUTYLTIN) OXIDE; OXYBIS(TRIBUTYLTIN);Tributyltin oxide; BIS(TRI-N-BUTYLTIN) OXIDE AF-SeafloZ-100; AW 75-D; TBTO; Tributyltin oxide; Tributyltin oxide ; Tributyltin trioxide; tri-n-butylstannane oxide; Biomet; Biomet 75; biomet tbto; bis(tributyloxide) of tin; bis(tributylstannyl) oxide; Bis(tributyltin)oxide; Bis(tri-n-butyltin)oxide; Bis(tri-normal-butyltin) oxide; Bis(tri-n-tributyltin)oxide; BTO; butinox; C-SN-9; HBD; Hexabutlydistannoxane; hexabutyldistannoxane; hexabutylditin; Interlux Micron; Interswift BKA007; L.S. 3394; Navicote 2000; oxybis(tributyltin); Sigmaplane 7284; Super Sea Jacket; TBOT;		HSDB Syracuse Chemfinder
IUPAC name	BIS(TRIBUTYLTIN) OXIDE		
CAS number	56-35-9		HSDB
molecular weight	g/mol	596.11 596.08 596.07	HSDB(4) Syracuse chemfinder
solubility	mg/l	4 (20 °C; pH 7) from <1 to >100 mg/liter, depending on temperature and pH Less than 20 ppm (20°C) 19.5 <0.1 g/100 mL at 21.5 C 71.2 8-10 in sea water (22°C)	HSDB(2) HSDB(6) HSDB(7) Syracuse(16) chemfinder IUCLID Lintelmann et al(2003)
vapour pressure	Pa	0.00104 (at 25°C) 0.002167 0.0009999 (at 20°C) 0.000085-0.016 (at 20°C)	HSDB(3) HSDB(2) Syracuse(16) IUCLID
Henry's coefficient	Pa m^3/mol	0.01317 (25 °C) 0.0306 (25°C)	HSDB(2) VP/WSOL
K_{ow}	g/g	10^3.84 10^4.05 10^3.2-10^3.8 10^3.62 10^2.3 10^3.34 10^3.19 10^3.85	HSDB(5) Syracuse(26) IUCLID Lintelmann et al(2003) Fent (1996)
K_{oc}	(-) dm^3/kg	(geometrisch gem.)	
KD	(-) dm^3/kg		
diffusion coefficient air	m^2/h		
diffusion coefficient water	m^2/h		

TRIBUTYLCHLOROSTANNANE

Parameter	**unit**	**value**	**reference**
chemical formula	C12H27ClSn		Syracuse
name	TRIBUTYLCHLOROSTANNANE Chlorotributyltin; Chlorotri-n-butylstannane; tributylchlorostannane; Tributyltin chloride; Tri-n-butylchlorotin; Tri-n-butyltin chloride;		HSDB Chemfinder
IUPAC name	tributylchlorostannane		
CAS number	1461-22-9		HSDB
molecular weight	g/mol	325.49 325.4883	Syracuse Chemfinder
solubility	mg/l	Insoluble in cold water but hydrolyzes in hot water (20 °C) 17 (20°C) 5-17	HSDB(9) Syracuse(16) Hoch(2001)
vapour pressure	Pa	1.733 (25°C) 1.236 (25°C)	HSDB Syracuse(27)
Henry’s coefficient	Pa m³/mol	7721 (25 °C)	Syracuse(28)
K_{ow}	g/g	10^4.76 3.11 3.19 3.2-4.1	HSDB(8) Fent(1996)
K_{oc}	(-) dm³/kg	(geometrisch gem.)	
KD	(-) dm³/kg		
diffusion coefficient air	m²/h		
diffusion coefficient water	m²/h		

DI-N-BUTYLTIN DICHLORIDE

Parameter	unit	value	reference
chemical formula	C8-H18-Cl2-Sn		HSDB(10)
name	DI-N-BUTYLTIN DICHLORIDE Dibutyl dichloro tin dibutyldichlorostannane; Dibutyltin dichloride; Di-n-Butyldichlorotin; Di-n-butyltin dichloride; Di-n-butyl Tin(IV) Dichloride		HSDB Syracuse Chemfinder
IUPAC name			
CAS number	683-18-1		HSDB
molecular weight	g/mol	303.85 303.83 303.8262	HSDB(10) Syracuse Chemfinder
solubility	mg/l	Insoluble in cold water; hydrolyzed in hot water 92 (20°C) 47.5	HSDB(12) Syracuse(16) IUCLID
vapour pressure	Pa	266.6 (at 100°C) 0.16 (at 25°C)	HSDB IUCLID
Henry's coefficient	Pa m^3/mol	(25 °C)	
K_{ow}	g/g	10^0.97 10^1.56 10^0.05; 10^1.5; >10^6	HSDB(11) Syracuse(29) IUCLID
K_{oc}	(-) dm^3/kg	(geometrisch gem.)	
KD	(-) dm^3/kg		
diffusion coefficient air	m^2/h		
diffusion coefficient water	m^2/h		

MONO-N-BUTYLTIN TRICHLORIDE

Parameter	**unit**	**value**	**reference**
chemical formula	C4-H9-Cl3-Sn		HSDB(13)
name	MONO-N-BUTYLTIN TRICHLORIDE; Butyl trichloro tin		HSDB Syracuse
IUPAC name			
CAS number	1118-46-3		
molecular weight	g/mol	282.17	HSDB(13)
solubility	mg/l	(20 °C)	
vapour pressure	Pa	173.3 (25°C)	HSDB
Henry’s coefficient	Pa m^3/mol	(25 °C)	
K_{ow}	g/g	10^0.41	HSDB(5)
K_{oc}	(-) dm^3/kg	(geometrisch gem.)	
KD	(-) dm^3/kg		
diffusion coefficient air	m^2/h		
diffusion coefficient water	m^2/h		

DIBUTYLTIN DILAURATE

Parameter	unit	value	reference
chemical formula	C32-H64-O4-Sn		HSDB(14)
name	DIBUTYLTIN DILAURATE		
IUPAC name			
CAS number	77-58-7		
molecular weight	g/mol	631.57 631.55	HSDB(15) Syracuse
solubility	mg/l	3 ppm (25)	HSDB(16)
vapour pressure	Pa	6e-7 (at 25°C) 4e-8 (at 25°C)	HSDB CLAUSIUS-CLAPEYRON EQN
Henry's coefficient	Pa m³/mol	16310 (25 °C)	Syracuse(28)
K_{ow}	g/g	10^3.12	HSDB(11)
K_{oc}	(-) dm³/kg	(geometrisch gem.)	
KD	(-) dm³/kg		
diffusion coefficient air	m²/h		
diffusion coefficient water	m²/h		

TRIPHENYLTIN HYDROXIDE

Parameter	unit	value	reference
chemical formula	C18-H16-O-Sn		HSDB(17)
name	TRIPHENYLTIN HYDROXIDE		
IUPAC name	TRIPHENYLTIN HYDROXIDE; TRIPHENYLTIN(IV)HYDROXIDE		
CAS number	76-87-9		
molecular weight	g/mol	367.03 367.02	HSDB(18) Syracuse
solubility	mg/l	1.2 (20 °C) 0.4 (25°C) 0.4 in seawater (22°C)	HSDB(19) Syracuse Lintelmann et al(2003)
vapour pressure	Pa	0.00004706 (25°C) 0.00001333 (25°C)	HSDB(20) Hoch (2001)
Henry's coefficient	Pa m^3/mol	0.04316 (25 °C)	VP/WSOL
K_{ow}	g/g	10^3.53 10^3.5 3.1-3.6 2.02 2.8	HSDB(8) Weidenhaupt et al (1997) Fent(1996)
K_{oc}	(-) dm^3/kg		
KD	(-) dm^3/kg		
diffusion coefficient air	m^2/h		
diffusion coefficient water	m^2/h		
pKa		5.2	Syracuse(8)

TRIPHENYLTIN CHLORIDE

Parameter	unit	value	reference
chemical formula	C18-H15-Cl-Sn		HSDB(21)
name	TRIPHENYLTIN CHLORIDE		HSDB
IUPAC name			
CAS number	639-58-7		HSDB
molecular weight	g/mol	385.48 385.46	HSDB(4) Syracuse
solubility	mg/l	40 (20 °C) 1 (25°C)	HSDB(22) Syracuse(16)
vapour pressure	Pa	0.0007306 (25°C)	Syracuse(27)
Henry’s coefficient	Pa m^3/mol	6.313 (25 °C)	Syracuse(28)
K_{ow}	g/g	10^4.19	HSDB(8)
K_{oc}	(-) dm^3/kg		
KD	(-) dm^3/kg		
diffusion coefficient air	m^2/h		
diffusion coefficient water	m^2/h		

STANNIC CHLORIDE

Parameter	**unit**	**value**	**reference**
chemical formula	Cl_4-Sn		HSDB(23)
name	STANNIC CHLORIDE; tin tetrachloride		HSDB IUCLID
IUPAC name			
CAS number	7646-78-8		
molecular weight	g/mol	260.52	HSDB(24)
solubility	mg/l	60 (20 °C and pH 0.2)	IUCLID
vapour pressure	Pa	2400 (at 20°C) 3100 (at 20°C)	HSDB(25) IUCLID
Henry's coefficient	Pa m^3/mol	(25 °C)	
K_{ow}	g/g		
K_{oc}	(-) dm^3/kg		
KD	(-) dm^3/kg		
diffusion coefficient air	m^2/h		
diffusion coefficient water	m^2/h		

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APPENDIX II: RESULTS OF THE SRV CALCULATIONS

output sheet

versie 5.0

land-use: type III (residential) - BCF Lespes

substance: tributyltinchloride as TBT

soil concentration (mg/kg dm)	0.027	*0-0.25 m*
	0.027	*0.25-1.5 m*
	0.027	*1.5-2.5 m*

concentration outdoor air	*g/m³*	6.32E-12
concentration indoor air	*g/m³*	2.49E-10
concentration suspended outdoor	*g/m³*	1.23E-12
concentration suspended indoor	*g/m³*	1.58E-12
concentration drinking water	*g/m³*	1.03E-07
concentration root vegetable	*mg/kg fw*	1.35E-01
concentration leafy vegetable	*mg/kg fw*	3.77E-02
concentration vegetable deposition	*mg/kg fw*	3.39E-06
concentration vegetables	*mg/kg fw*	9.64E-02

	child		*adult*	
	mg/kg.d	*%*	*mg/kg.d*	*%*
ingestion soil particles	8.95E-08	0.0	7.76E-09	0.0
dermal contact soil particles	1.45E-08	0.0	6.73E-09	0.0
intake vegetables	2.41E-04	99.9	1.19E-04	99.9
dermal contact bathing	1.14E-08	0.0	0.00E+00	0.0
dermal contact showering	0.00E+00	0.0	3.51E-10	0.0
intake drinking water	6.28E-09	0.0	2.69E-09	0.0
total oral + dermal	2.41E-04	99.96	1.19E-04	99.95
oral background exposure	8.90E-06		8.90E-06	
inhalation soil particles	5.30E-10	0.0	2.99E-10	0.0
inhalation outdoor air	4.89E-10	0.0	1.80E-10	0.0
inhalation indoor air	9.65E-08	0.0	5.44E-08	0.0
inhalation showering	0.00E+00	0.0	1.50E-10	0.0
total inhalation	9.76E-08	0.04	5.51E-08	0.05
inhalation background exposure	0		0	

TDIor (mg/kg.d)	2.50E-04	*oral TDI*
TDIinh (mg/kg.d)	2.50E-04	*inhalation TDI*
TCA (g/m³)	8.75E-07	*limit value air*
GWdw (g/m³)	7.50E-04	*limit value drinking water*

RISK

	child	*adult*
oral + dermal intake (mg/kg.d)	2.41E-04	1.19E-04
oral background exposure (mg/kg.d)	8.90E-06	8.90E-06
inhalation intake (mg/kg.d)	9.76E-08	5.51E-08
inhalation background exposure (mg/kg.d)	0	0

carcinogen	N
risk index (RI) carcinogens (new 2000)	n.v.t.
risk index (RI) non-carcinogens child	**1.00E+00**
risk index (RI) non-carcinogens adult	5.11E-01
concentration outdoor air / TCA	8.63471E-06
concentration indoor air /TCA	0.000286884
concentration drinking water / GWdw	0.000137085

output sheet

versie 5.0

land-use:	type III (residential) - BCF Brandsch
substance:	tributyltin chloride as TBT

soil concentration (mg/kg dm)	0.513	*0-0.25 m*
	0.513	*0.25-1.5 m*
	0.513	*1.5-2.5 m*

concentration outdoor air	*g/m³*	1.21E-10
concentration indoor air	*g/m³*	4.77E-09
concentration suspended outdoor	*g/m³*	2.36E-11
concentration suspended indoor	*g/m³*	3.02E-11
concentration drinking water	*g/m³*	1.96E-06
concentration root vegetable	*mg/kg fw*	1.14E-01
concentration leafy vegetable	*mg/kg fw*	6.60E-02
concentration vegetable deposition	*mg/kg fw*	6.48E-05
concentration vegetables	*mg/kg fw*	9.48E-02

	child		*adult*	
	mg/kg.d	*%*	*mg/kg.d*	*%*
ingestion soil particles	1.71E-06	0.7	1.48E-07	0.1
dermal contact soil particles	2.77E-07	0.1	1.29E-07	0.1
intake vegetables	2.37E-04	98.3	1.17E-04	98.8
dermal contact bathing	2.17E-07	0.1	0.00E+00	0.0
dermal contact showering	0.00E+00	0.0	6.70E-09	0.0
intake drinking water	1.20E-07	0.0	5.15E-08	0.0
total oral + dermal	2.39E-04	99.23	1.17E-04	99.11
oral background exposure	8.90E-06		8.90E-06	
inhalation soil particles	1.01E-08	0.0	5.71E-09	0.0
inhalation outdoor air	9.35E-09	0.0	3.43E-09	0.0
inhalation indoor air	1.84E-06	0.8	1.04E-06	0.9
inhalation showering	0.00E+00	0.0	2.87E-09	0.0
total inhalation	1.86E-06	0.77	1.05E-06	0.89
inhalation background exposure	0		0	

TDIor (mg/kg.d)	2.50E-04	*oral TDI*
TDIinh (mg/kg.d)	2.50E-04	*inhalation TDI*
TCA (g/m³)	8.75E-07	*limit value air*
GWdw (g/m³)	7.50E-04	*limit value drinking water*

RISK

	child	*adult*
oral + dermal intake (mg/kg.d)	2.39E-04	1.17E-04
oral background exposure (mg/kg.d)	8.90E-06	8.90E-06
inhalation intake (mg/kg.d)	1.86E-06	1.05E-06
inhalation background exposure (mg/kg.d)	0	0

carcinogen	N
risk index (RI) carcinogens (new 2000)	n.v.t.
risk index (RI) non-carcinogens child	**1.00E+00**
risk index (RI) non-carcinogens adult	5.08E-01
concentration outdoor air / TCA	0.000165007
concentration indoor air /TCA	0.005482292
concentration drinking water / GWdw	0.00261966

output sheet
versie 5.0

land-use:	type III (residential) - BCF default
substance:	tributyltin chloride as TBT

soil concentration (mg/kg dm)	3.789	*0-0.25 m*
	3.789	*0.25-1.5 m*
	3.789	*1.5-2.5 m*

concentration outdoor air	*g/m³*	8.93E-10
concentration indoor air	*g/m³*	3.52E-08
concentration suspended outdoor	*g/m³*	1.74E-10
concentration suspended indoor	*g/m³*	2.23E-10
concentration drinking water	*g/m³*	1.45E-05
concentration root vegetable	*mg/kg fw*	1.19E-01
concentration leafy vegetable	*mg/kg fw*	3.12E-02
concentration vegetable deposition	*mg/kg fw*	4.79E-04
concentration vegetables	*mg/kg fw*	8.41E-02

	child		*adult*	
	mg/kg.d	*%*	*mg/kg.d*	*%*
ingestion soil particles	1.26E-05	5.2	1.10E-06	1.0
dermal contact soil particles	2.05E-06	0.8	9.51E-07	0.8
intake vegetables	2.10E-04	87.2	1.04E-04	91.0
dermal contact bathing	1.61E-06	0.7	0.00E+00	0.0
dermal contact showering	0.00E+00	0.0	4.95E-08	0.0
intake drinking water	8.87E-07	0.4	3.80E-07	0.3
total oral + dermal	2.27E-04	94.28	1.06E-04	93.17
oral background exposure	8.90E-06		8.90E-06	
inhalation soil particles	7.49E-08	0.0	4.22E-08	0.0
inhalation outdoor air	6.91E-08	0.0	2.54E-08	0.0
inhalation indoor air	1.36E-05	5.7	7.69E-06	6.8
inhalation showering	0.00E+00	0.0	2.12E-08	0.0
total inhalation	1.38E-05	5.72	7.78E-06	6.83
inhalation background exposure	0		0	

TDIor (mg/kg.d)	2.50E-04	*oral TDI*
TDIinh (mg/kg.d)	2.50E-04	*inhalation TDI*
TCA (g/m³)	8.75E-07	*limit value air*
GWdw (g/m³)	7.50E-04	*limit value drinking water*

RISK

	child	*adult*
oral + dermal intake (mg/kg.d)	2.27E-04	1.06E-04
oral background exposure (mg/kg.d)	8.90E-06	8.90E-06
inhalation intake (mg/kg.d)	1.38E-05	7.78E-06
inhalation background exposure (mg/kg.d)	0	0

carcinogen	N
risk index (RI) carcinogens (new 2000)	n.v.t.
risk index (RI) non-carcinogens child	**1.00E+00**
risk index (RI) non-carcinogens adult	4.91E-01
concentration outdoor air / TCA	0.001219582
concentration indoor air /TCA	0.040520085
concentration drinking water / GWdw	0.019362128

output sheet

versie 5.0

land-use: type III (residential) - BCF Lespes

substance: dibutyltin chloride as DBT

soil concentration (mg/kg dm)	0.671	*0-0.25 m*
	0.671	*0.25-1.5 m*
	0.671	*1.5-2.5 m*

concentration outdoor air	*g/m³*	8.22E-11
concentration indoor air	*g/m³*	3.24E-09
concentration suspended outdoor	*g/m³*	3.08E-11
concentration suspended indoor	*g/m³*	3.95E-11
concentration drinking water	*g/m³*	2.45E-06
concentration root vegetable	*mg/kg fw*	8.13E-02
concentration leafy vegetable	*mg/kg fw*	1.18E-01
concentration vegetable deposition	*mg/kg fw*	8.48E-05
concentration vegetables	*mg/kg fw*	9.59E-02

	child		*adult*	
	mg/kg.d	*%*	*mg/kg.d*	*%*
ingestion soil particles	2.24E-06	0.9	1.94E-07	0.2
dermal contact soil particles	3.62E-07	0.1	1.68E-07	0.1
intake vegetables	2.40E-04	98.3	1.18E-04	99.0
dermal contact bathing	4.38E-10	0.0	0.00E+00	0.0
dermal contact showering	0.00E+00	0.0	1.36E-11	0.0
intake drinking water	1.50E-07	0.1	6.43E-08	0.1
total oral + dermal	2.42E-04	99.48	1.19E-04	99.40
oral background exposure	6.30E-06		6.30E-06	
inhalation soil particles	1.33E-08	0.0	7.47E-09	0.0
inhalation outdoor air	6.36E-09	0.0	2.34E-09	0.0
inhalation indoor air	1.26E-06	0.5	7.08E-07	0.6
inhalation showering	0.00E+00	0.0	3.28E-09	0.0
total inhalation	1.27E-06	0.52	7.21E-07	0.60
inhalation background exposure	0		0	

TDIor (mg/kg.d)	2.50E-04	*oral TDI*
TDIinh (mg/kg.d)	2.50E-04	*inhalation TDI*
TCA (g/m³)	8.75E-07	*limit value air*
GWdw (g/m³)	7.50E-04	*limit value drinking water*

RISK

	child	*adult*
oral + dermal intake (mg/kg.d)	2.42E-04	1.19E-04
oral background exposure (mg/kg.d)	6.30E-06	6.30E-06
inhalation intake (mg/kg.d)	1.27E-06	7.21E-07
inhalation background exposure (mg/kg.d)	0	0

carcinogen	N
risk index (RI) carcinogens (new 2000)	n.v.t.
risk index (RI) non-carcinogens child	**1.00E+00**
risk index (RI) non-carcinogens adult	5.02E-01
concentration outdoor air / TCA	0.000129171
concentration indoor air /TCA	0.00375121
concentration drinking water / GWdw	0.003272385

output sheet

versie 5.0

land-use:	type III (residential) - BCF Brandsch	
substance:	dibutyltin chloride as DBT	

soil concentration (mg/kg dm)	0.070	*0-0.25 m*
	0.070	*0.25-1.5 m*
	0.070	*1.5-2.5 m*

concentration outdoor air	*g/m³*	8.55E-12
concentration indoor air	*g/m³*	3.37E-10
concentration suspended outdoor	*g/m³*	3.21E-12
concentration suspended indoor	*g/m³*	4.11E-12
concentration drinking water	*g/m³*	2.55E-07
concentration root vegetable	*mg/kg fw*	1.17E-01
concentration leafy vegetable	*mg/kg fw*	6.78E-02
concentration vegetable deposition	*mg/kg fw*	8.82E-06
concentration vegetables	*mg/kg fw*	9.73E-02

	child		*adult*	
	mg/kg.d	*%*	*mg/kg.d*	*%*
ingestion soil particles	2.33E-07	0.1	2.02E-08	0.0
dermal contact soil particles	3.77E-08	0.0	1.75E-08	0.0
intake vegetables	2.43E-04	99.8	1.20E-04	99.9
dermal contact bathing	4.56E-11	0.0	0.00E+00	0.0
dermal contact showering	0.00E+00	0.0	1.42E-12	0.0
intake drinking water	1.56E-08	0.0	6.69E-09	0.0
total oral + dermal	2.44E-04	99.95	1.20E-04	99.94
oral background exposure	6.30E-06		6.30E-06	
inhalation soil particles	1.38E-09	0.0	7.78E-10	0.0
inhalation outdoor air	6.62E-10	0.0	2.43E-10	0.0
inhalation indoor air	1.31E-07	0.1	7.37E-08	0.1
inhalation showering	0.00E+00	0.0	3.41E-10	0.0
total inhalation	1.33E-07	0.05	7.50E-08	0.06
inhalation background exposure	0		0	

TDIor (mg/kg.d)	2.50E-04	*oral TDI*
TDIinh (mg/kg.d)	2.50E-04	*inhalation TDI*
TCA (g/m³)	8.75E-07	*limit value air*
GWdw (g/m³)	7.50E-04	*limit value drinking water*

RISK

	child	*adult*
oral + dermal intake (mg/kg.d)	2.44E-04	1.20E-04
oral background exposure (mg/kg.d)	6.30E-06	6.30E-06
inhalation intake (mg/kg.d)	1.33E-07	7.50E-08
inhalation background exposure (mg/kg.d)	0	0

carcinogen	N		
risk index (RI) carcinogens (new 2000)	n.v.t.	*soil concentration SRV*	
risk index (RI) non-carcinogens child	**1.00E+00**	*0.069785449*	*mg/kg dm*
risk index (RI) non-carcinogens adult	5.05E-01		

concentration outdoor air / TCA	1.34429E-05
concentration indoor air /TCA	0.000390391
concentration drinking water / GWdw	0.00034056

output sheet
versie 5.0

land-use:	type III (residential) - BCF default
substance:	dibutyltin as DBT

soil concentration (mg/kg dm)	27.382	*0-0.25 m*
	27.382	*0.25-1.5 m*
	27.382	*1.5-2.5 m*

concentration outdoor air	*g/m³*	3.36E-09
concentration indoor air	*g/m³*	1.32E-07
concentration suspended outdoor	*g/m³*	1.26E-09
concentration suspended indoor	*g/m³*	1.61E-09
concentration drinking water	*g/m³*	1.00E-04
concentration root vegetable	*mg/kg fw*	3.97E-02
concentration leafy vegetable	*mg/kg fw*	1.63E-02
concentration vegetable deposition	*mg/kg fw*	3.46E-03
concentration vegetables	*mg/kg fw*	3.17E-02

	child		*adult*	
	mg/kg.d	*%*	*mg/kg.d*	*%*
ingestion soil particles	9.14E-05	37.5	7.92E-06	9.2
dermal contact soil particles	1.48E-05	6.1	6.87E-06	8.0
intake vegetables	7.94E-05	32.6	3.91E-05	45.5
dermal contact bathing	1.79E-08	0.0	0.00E+00	0.0
dermal contact showering	0.00E+00	0.0	5.57E-10	0.0
intake drinking water	6.12E-06	2.5	2.62E-06	3.1
total oral + dermal	1.92E-04	78.64	5.65E-05	65.76
oral background exposure	6.30E-06		6.30E-06	
inhalation soil particles	5.41E-07	0.2	3.05E-07	0.4
inhalation outdoor air	2.60E-07	0.1	9.54E-08	0.1
inhalation indoor air	5.13E-05	21.0	2.89E-05	33.6
inhalation showering	0.00E+00	0.0	1.34E-07	0.2
total inhalation	5.21E-05	21.36	2.94E-05	34.24
inhalation background exposure	0		0	

TDIor (mg/kg.d)	2.50E-04	*oral TDI*
TDIinh (mg/kg.d)	2.50E-04	*inhalation TDI*
TCA (g/m³)	8.75E-07	*limit value air*
GWdw (g/m³)	7.50E-04	*limit value drinking water*

RISK

	child	*adult*
oral + dermal intake (mg/kg.d)	1.92E-04	5.65E-05
oral background exposure (mg/kg.d)	6.30E-06	6.30E-06
inhalation intake (mg/kg.d)	5.21E-05	2.94E-05
inhalation background exposure (mg/kg.d)	0	0

carcinogen	N
risk index (RI) carcinogens (new 2000)	n.v.t.
risk index (RI) non-carcinogens child	**1.00E+00**
risk index (RI) non-carcinogens adult	3.69E-01
concentration outdoor air / TCA	0.005274688
concentration indoor air /TCA	0.153180743
concentration drinking water / GWdw	0.133627906

output sheet

versie 5.0

land-use: type V (industry light)

substance: tributyltinchloride as TBT

soil concentration (mg/kg dm)	195.694	*0-0.25 m*
	195.694	*0.25-1.5 m*
	195.694	*1.5-2.5 m*

concentration outdoor air	*g/m³*	4.31E-08
concentration indoor air	*g/m³*	2.52E-07
concentration suspended outdoor	*g/m³*	1.05E-08
concentration suspended indoor	*g/m³*	1.34E-08
concentration drinking water	*g/m³*	7.50E-04

	child		*adult*	
	mg/kg.d	*%*	*mg/kg.d*	*%*
ingestion soil particles	n.a.	n.a.	4.02E-05	59.9
dermal contact soil particles	n.a.	n.a.	4.40E-06	6.6
intake drinking water	n.a.	n.a.	7.02E-06	10.5
total oral + dermal	n.a.	n.a.	5.16E-05	76.87
oral background exposure	n.a.		2.76E-07	
inhalation soil particles	n.a.	n.a.	6.18E-07	0.9
inhalation outdoor air	n.a.	n.a.	1.68E-07	0.3
inhalation indoor air	n.a.	n.a.	1.47E-05	22.0
total inhalation	n.a.	n.a.	1.55E-05	23.13
inhalation background exposure	n.a.	n.a.	0	

TDIor (mg/kg.d)	2.50E-04	*oral TDI*
TDIinh (mg/kg.d)	2.50E-04	*inhalation TDI*
TCA (g/m³)	8.75E-07	*limit value air*
GWdw (g/m³)	7.50E-04	*limit value drinking water*

RISK

	child	*adult*
oral + dermal intake (mg/kg.d)	n.a.	5.16E-05
oral background exposure (mg/kg.d)	n.a.	2.76E-07
inhalation intake (mg/kg.d)	n.a.	1.55E-05
inhalation background exposure (mg/kg.d)	0	0

carcinogen	N
risk index (RI) carcinogens (new 2000)	n.v.t.
risk index (RI) non-carcinogens child	n.a.
risk index (RI) non-carcinogens adult	2.69E-01
concentration outdoor air / TCA	0.061264376
concentration indoor air /TCA	0.303246654
concentration drinking water / GWdw	**1**

output sheet
versie 5.0

land-use:	type V (lichte industrie)
substance:	dibutyltin chloride as DBT

soil concentration (mg/kg dm)	204.914	*0-0.25 m*
	204.914	*0.25-1.5 m*
	204.914	*1.5-2.5 m*

concentration outdoor air	*g/m³*	2.35E-08
concentration indoor air	*g/m³*	1.21E-07
concentration suspended outdoor	*g/m³*	1.10E-08
concentration suspended indoor	*g/m³*	1.40E-08
concentration drinking water	*g/m³*	7.50E-04

	child		*adult*	
	mg/kg.d	*%*	*mg/kg.d*	*%*
ingestion soil particles	n.a.	n.a.	4.20E-05	60.8
dermal contact soil particles	n.a.	n.a.	4.60E-06	6.7
intake drinking water	n.a.	n.a.	7.02E-06	10.1
total oral + dermal	n.a.	n.a.	5.37E-05	77.57
oral background exposure	n.a.		6.30E-06	
inhalation soil particles	n.a.	n.a.	6.18E-07	0.9
inhalation outdoor air	n.a.	n.a.	1.68E-07	0.2
inhalation indoor air	n.a.	n.a.	1.47E-05	21.3
total inhalation	n.a.	n.a.	1.55E-05	22.43
inhalation background exposure	n.a.	n.a.	0	

TDIor (mg/kg.d)	2.50E-04	*oral TDI*
TDIinh (mg/kg.d)	2.50E-04	*inhalation TDI*
TCA (g/m³)	5.75E-07	*limit value air*
GWdw (g/m³)	7.50E-04	*limit value drinking water*

RISK

	child	*adult*
oral + dermal intake (mg/kg.d)	n.a.	5.37E-05
oral background exposure (mg/kg.d)	n.a.	6.30E-06
inhalation intake (mg/kg.d)	n.a.	1.55E-05
inhalation background exposure (mg/kg.d)	0	0

carcinogen	N
risk index (RI) carcinogens (new 2000)	n.v.t.
risk index (RI) non-carcinogens child	n.a.
risk index (RI) non-carcinogens adult	3.02E-01
concentration outdoor air / TCA	0.059921769
concentration indoor air /TCA	0.235109203
concentration drinking water / GWdw	**1**