



COHIBA

CONTROL OF HAZARDOUS SUBSTANCES
IN THE BALTIC SEA REGION

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Summary report ESTONIA

Work package 4: Identification of sources and
estimation of inputs/impacts on the Baltic Sea

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1 Introduction

Pollution caused by hazardous substances poses risks to the Baltic Sea area. Loads and impacts of some hazardous substances have been reduced considerably during the past 20-30 years, but concentrations of some other substances have increased in the marine environment.

With HELCOM Baltic Sea Action Plan (BSAP) the Baltic Sea countries have committed themselves to achieve a “Baltic Sea with life undisturbed by hazardous substances”. The overall objective of COHIBA is to support the implementation of the BSAP with regard to hazardous substances (**Table 1**) by developing joint actions to reach the goal.

Table 1: The 11 substances/substance groups identified in the Baltic Sea Action Plan to be of special concern.

| |
|--|
| 1. Dioxins (PCDD), furans (PCDF) and dioxin-like polychlorinated biphenyls (PCBs) |
| 2. Tributyltin compounds (TBT), triphenyltin compounds (TPhT) |
| 3. Pentabromodiphenyl ether (pentaBDE), octabromodiphenyl ether (octaBDE), decabromodiphenyl ether (decaBDE) |
| 4. Perfluorooctane sulfonate (PFOS), Perfluorooctanoic acid (PFOA) |
| 5. Hexabromocyclododecane (HBCDD) |
| 6. Nonylphenols (NP), nonylphenol ethoxylates (NPE) |
| 7. Octylphenols (OP), octylphenol ethoxylates (OPE) |
| 8. Short-chain chlorinated paraffins (SCCP), medium-chain chlorinated paraffins (MCCP) |
| 9. Endosulfan |
| 10. Mercury |
| 11. Cadmium |

1.1 The COHIBA project

The aim of the COHIBA (**C**ontrol of **H**azardous substances **I**n the **B**altic Sea region) project is to:

- Identify the most important sources of 11 hazardous substances of special concern
- Quantify inputs of the selected substances to the Baltic Sea
- Analyse the pathways of the selected substances from production, processes and uses to the marine environment
- Create cost-effective management options to reduce discharges
- Contribute to the development of national implementation programmes

The project consists of six work packages (WP), presented in **Table 2**.

Table 2: The work packages (WP) in the COHIBA project. The present WP is highlighted in bold.

| WP no. | Name |
|---------------|--|
| 1 | Project management and administration (lead by Finnish Environment Institute) |
| 2 | Communication and Information (lead by HELCOM Secretariat) |
| 3 | Innovative approaches to chemical controls of hazardous substances (lead by Finnish Environment Institute) |
| 4 | Identification of sources and estimation of inputs/impacts on the Baltic Sea (lead by IVL Swedish Environmental Research Institute) |
| 5 | Cost effective management options to reduce discharges, emissions and losses of hazardous substances (lead by Federal Environment Agency of Germany) |
| 6 | Capacity building and knowledge transfer (lead by Baltic Environmental Forum) |

1.2 Work package 4 (WP4)

The objective of Work package 4 (WP4) in the COHIBA project is to assess the release patterns and pathways to the Baltic Sea marine environment of the substances of concern. The aim is also to quantify the inputs of the selected hazardous substances to the Baltic Sea by assessing and using models. In the long term this will facilitate the understanding of the link between the sources and releases of the selected substances to the effects in the marine environment enhancing the ecosystem approach to the management of human activities also with regard to hazardous substances. The results of this work package also provides crucial input to the assessment of management options to reduce discharges, emissions and losses of hazardous substances, which is the focus in Work package 5 (WP5) of the COHIBA project. The approach used in WP4 is described in the WP background paper, available on the project website <http://www.cohiba-project.net/>.

1.3 National summary

This report summarises the results in Estonia. These results will be used in WP4 to make a joint assessment of the most important sources of hazardous substances in the Baltic Sea region.

The project collected existing data on production, use volumes and discharges, emissions and losses of the target substances, which formed the basis for the substance flow analysis.

The screening analysis of the 11 substances of specific concern to the Baltic Sea in the anthropogenic sources was the first to estimate discharges of MCCP, SCCP, PFOS, PFOA, HBCDD, NP, NPE, OP, OPE into the Estonian environment. For that reason, it was impossible to retrieve older information on those substances. Hence the work done in the COHIBA project is a very useful starting point for future studies of the fate of those substances in Estonia.

2 Substance flow analysis (SFA) for Estonia

A substance flow analysis (SFA) aims at tracing flows of a substance or group of substances through a system defined in time and space. It is a mapping of how the substance enters the system, the pathways within the system and identification of the receiving compartment in the environment (Figure 1).

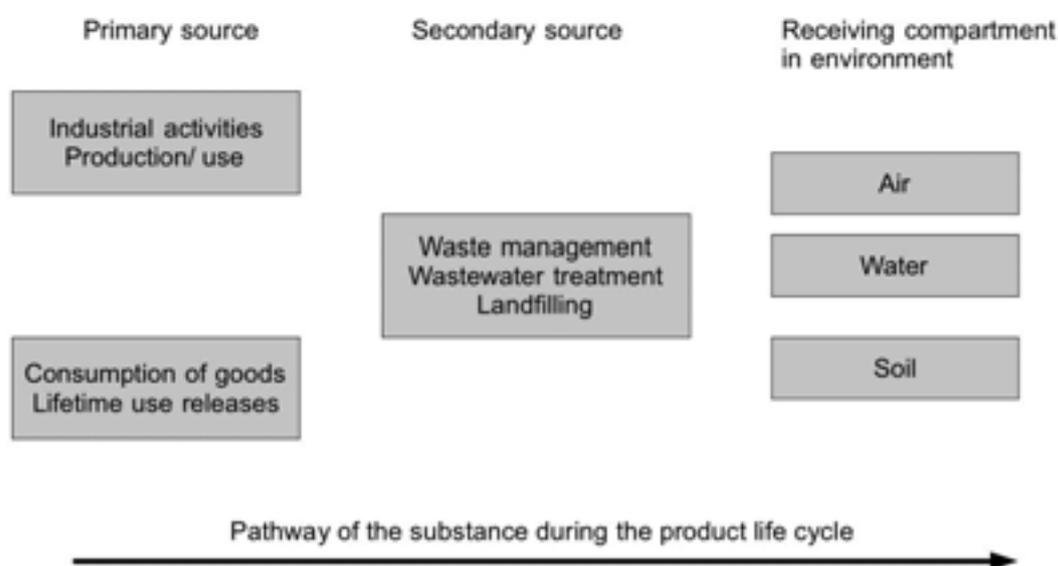


Figure 1. A simplified diagram of Substance flow analysis.

SFAs were conducted on the European scale as a first step in the present project. The EU SFAs functioned as templates for SFAs developed in the different countries in the Baltic Sea region, thus making it possible to achieve comparable results. Project partners were using national, regional and local data obtained from industry, chemical registers, scientific studies etc. to describe the pathways and to estimate emissions of the target substances from their country.

The main calculations were made with the formula:

$$\text{Emission Factor} \times \text{Used/Produced Amount} = \text{Annual Load}$$

The emission factor is the estimated average emission rate of a given pollutant for a given source, relative to the units of activity". For example, an emission factor can be expressed as g/inhabitant

and year, or g/ton produced unit of X. The used or produced amount of the given product is the emission factor multiplier. The emission factor multiplier quantifies a certain activity to which an emission factor is related, for example, tons of PVC produced per year. Results from each source were given as yearly loads.

If there were existing monitoring or research data on a given source, calculations were not necessary. However, as it was stated earlier, such kind of data were rarely available as there was virtually no earlier research on those substances in Estonia.

Exact calculations of each source of each substance are described in SFA reports given in Annexes A-N. In this summary only a general overview is given.

Receiving environmental compartment

Not all the receiving compartments used in the study are defined as the first impression is. The data collected with those SFAs are used in fate modelling that is used to characterise and quantify the total loads of hazardous substances to the Baltic Sea from all the countries. For those reasons, some modifications and simplifications were made when defining the receiving compartments in this study:

- **air**

- outdoor air (OA);

- indoor air (IA)

- **surface water**

- fresh (or inland) surface water (FSW);

- coastal surface water (CSW)

- **land**

- agricultural soil (AS)

- forest soil (FS)

Agricultural soil is defined as soil that is used for agricultural application (data was combined from the Estonian Environment Information Centre and Statistics Estonia). **Forest soil** is defined as all soil that is not agricultural soil.

In the calculations, there were more compartments used (e.g. wastewater WW and Waste), but air, water and land are the final compartments where hazardous substances end up.

The loads to **coastal surface water** were mostly calculated with a fate model in a separated part of the project. An approximate estimate of 1/3 of the effluents from the wastewater treatment plants (WWTPs) being discharged directly to the Baltic Sea was used for some cases. Sea sites where the

discharge of pollutants is historically known were considered to be CSW. All other discharges related to water were defined as (inland) **fresh surface water** (FSW).

The distributions between compartments were calculated according to available scientific data. If no previous studies were found, an approximate distribution was made. For example, 50% to air and 50% water if the substance emissions were estimated to those compartments but the exact proportion was not known. Those estimates were based on specific actions and expert evaluations of the similarities with other activities and substance properties.

Expression of results

The results calculated on gathered data were given as yearly loads for each specific source or action of a substance. The results were shown in three ways: 1) “0” if given source was considered to be unimportant or negligible in Estonia; 2) “?” if given source was assumed to be (potentially) important in Estonia but no load could be quantified due to lack of data; 3) a numerical value when it was possible to calculate a load.

Uncertainties

The data variability of reliability of the data was big, since only a limited amount of data was available for many cases. In most cases, the sources contained information in a way that makes it unreliable for this kind of analysis. Hence, general information was mainly used. Due to limited time of the project, it wasn't possible to perform thorough inventories and studies on safety sheets or environmental permits that are actually needed. Product based information for Estonia is practically missing. Only import data for goods imported from third countries is available, but the data is not substance specific. The product based data bases how different substances are used exist for Estonia.

Therefore, the results of this project cannot be considered as describing the actual emissions or giving an accurate description of the actual situation. The collected data is useful mainly for planning monitoring or for future studies to specify the results to determine the actual situation.

The uncertainties were mostly given as four letter combinations, using letters from A to C. The first letter represents uncertainty for emission factor (EF), the second one for emission factor multiplier (EFM), the third one for division into compartments and the fourth one for the yearly load as total. If no calculations were used (e.g. when the yearly load was retrieved from emission data), uncertainty was given as one letter, representing the uncertainty for the yearly load as a total.

Letter A stands for the most reliable data and C for unreliable or extremely limited data. Uncertainty was classified according to the principles described in “Dealing with uncertainty in substance flow analysis within the COHIBA project”, a project manual describing how data uncertainty is graded in WP4 of the COHIBA project.

In our work for Estonia we grouped the activities as following:

- **Industrial uses**
- **Consumption of products**

- Waste management
- Activities outside Estonia

2.1 Calculation of loads from industrial uses

In that section it is explained how the industrial scale use of products and uses of substances in production were calculated. A scheme on our work is given on Figure 2.

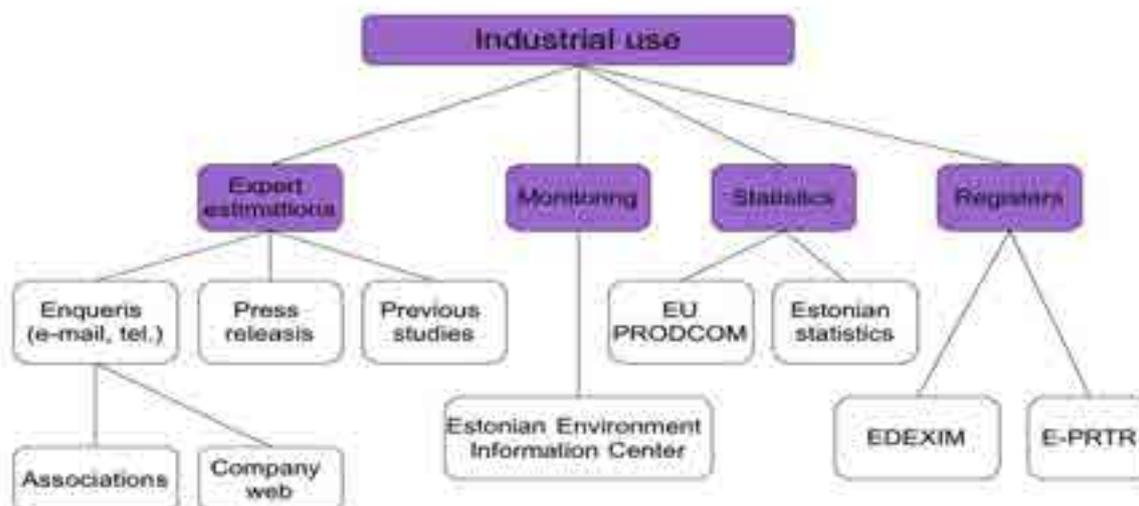


Figure 2. Data collection diagram for industrial applications.

In the EU SFAs the industrial uses were all indicated with the NACE code and the NACE description (for explanations of NACE codes, see chapter “1.2 Description of main data sources for the study”).

All activities were checked from Prodcum database that consolidates European statistics on the production of goods (for further explanations of Prodcum database see chapter “1.2 Description of main data sources for the study”). This database was a tool for deciding whether given activities were potentially relevant for Estonia or not.

If there was no data about given activity in that statistical register, it was safe to this source to be non-existent in Estonia, making the yearly load “0”. No further investigation was made. If there were activities under given NACE, we took a closer look and consulted with experts to decide if this source was relevant for Estonia or not.

Numerical values were rarely given for yearly loads due to lack of data, the yearly loads from industrial sources were mostly given as “?”.

Scaling of EU data could not be used for

industrial uses as it was impossible to compare the production schemes and therefore potential loads from similar sources of other countries. Another reason for general lack of numerical results was insufficient data. There are thorough industrial and product registers in Scandinavian countries that can be used for retrieving information. In Estonia, there are no such registers or these are insufficient.

Hence, during this project we mainly detected the most likely sources where BSAP 11 hazardous substances or substance groups may be used in Estonia, i.e. had qualitative results. However, further studies are needed to make reliable quantitative estimations.

Nowadays the availability of information isn't always a problem, but deciding whether the data source is a reliable one, is definitely a critical point. We consulted several experts from many fields to decide whether found information was reliable and usable for our work.

We also made inquiries to get Estonian specific data on the use of substances in Estonia. For that we contacted the companies and associations on the target field directly. This way we got information about uses of substances, market shares, other companies on the field etc. Company websites, journalistic sources, and other public information were also used for this purpose. Also, it should be kept in mind that Estonia is a small country and quite often the companies and their activities are well known for the public.

Sometimes, some specific factors could be found from Estonian statistic or other studies, e.g. the amount of fuel used in Estonia, units for production etc. In these cases this kind of data was used with appropriate EU emission factors to calculate a yearly load.

2.2 Consumption activities (Private consumption)

As private uses and emissions during service life are comparable or similar in all the EU countries, the yearly loads were mostly scaled from the EU yearly loads to Estonian population or area, as appropriate. If Estonian specific data was available, these were used instead. A simplified picture of work flows are given on Figure 3.

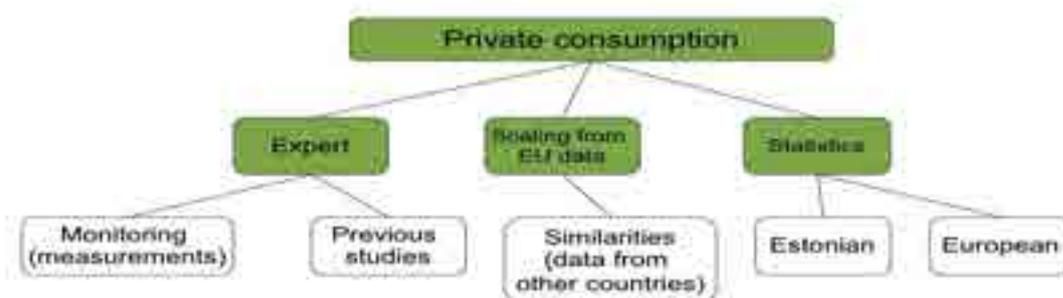


Figure 3. Data collection for private consumption in Estonia.

In the field of private consumption, the biggest data gap comes from the fact that there is no information on product level, i.e. appropriate registers in Estonia. Also, the information about the movements of products between countries within the EU is not available.

The main scaling factors were the 0,3% for the population and 1% for the area to simplify the calculations. Estonian population is approximately 0,3% from EU total and Estonian area is about 1% of EU area. This accuracy level was considered to be enough for given study; especially considering the overall very high uncertainty levels in all other emission strings.

2.3 Waste management

In waste management part landfilling, wastewater treatment, waste incineration and all other related activities were considered.

HELCOM hazardous substances are not monitored in Estonian landfills or wastewater treatment plants – and that creates the main data gap for that field. In COHIBA project WP3, the effluents and landfill leachates were analysed for those substances and the results could be used in the SFAs. Waste scenario calculation model provided by IVL was used to calculate yearly loads.

We used our own modified calculation base to get the loads from WWTPs. In both cases the data from COHIBA project WP3 were used because we did not have any previous measurements of those substances in Estonia before. A simplified work flow chart is given on Figure 4.

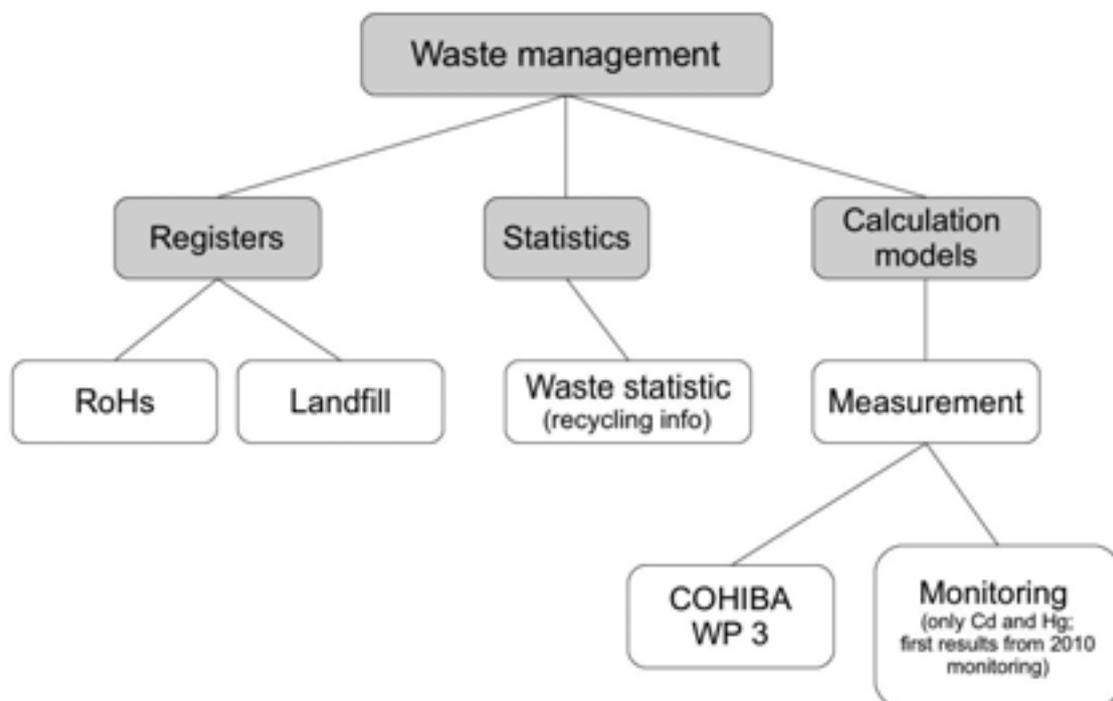


Figure 4. The schematic flow of data collection for waste management in Estonia.

Waste scenarios – calculation of yearly loads from the landfills

Within COHIBA WP3 sludge and water samples from WWTPs in the Baltic Sea region were analyzed for the 11 target substances/substance groups. The results from the screening conducted within WP3 were used to assess loads of the target substances to inland surface waters and coastal surface waters from municipal WWTPs.

The source data on effluent concentrations of the target substances, as measured in WP3, were used in the template to calculate a flow weighted average concentration load estimations. Total loads to surface waters were calculated using water volumes as given in the PLC4 report (HELCOM 2004). In cases where additional data on effluent concentrations are available, these were also used to make a more reliable estimation. The detailed explanation about the calculations are given in a WP4 background paper (http://www.cohiba-project.net/publications/en_GB/publications/).

There was almost no information on the landfill leachates; therefore we decided to use the model to be able to have at least approximate estimations of the potential loads of these substances to the environment.

For some substances, the emissions from landfills to water and land are calculated as a load for leachate and leakages. Leachate is assumed to be the emissions coming to the environment after the treatment from the landfills, whereas leakage is estimated to be the direct emissions to the

environment without treatment. For new and operating landfills, there are leachate collection systems and the leachate from landfills is treated before entering to the environment. Leakages are considered to happen from old and already closed landfills and historical sites.

Waste water treatment plant (WWTP) load calculations

The calculations were done using the data from COHIBA WP3 and preliminary results from another project that was conducted on the hazardous substances at the same time – BaltActHaz. An average result was quantified and that gave us an EF. If results were under the LOQ (limit of quantification), as was often the case, the results were given as a range - minimum and maximum. For minimum scenario, the results under LOQ were considered to be 0. For maximum scenario, the results below LOQ were considered to be LOQ. The EF was then multiplied by the EFM, i.e. the amount of effluents produced per person a day – 125 litres (according to Statistics Estonia 2010), the number of inhabitants (1 340 021 according to Statistics Estonia 2010), and the number of days a year (365).

A calculation sheet for waste-water treatment plants was also provided in the project (WP4 background paper). However, we decided not to use the calculation sheet as most of the measured effluents are mixed in Estonia, but the model was for municipal WWTPs only. When we also considered the sources that was used for base data for that model, we assumed our own way of calculations to be more precise.

Sewage sludge calculations

In the statistical report by Wieland (2003) sludge disposal in the EU member states is described. According to this report 32 % of the sludge was used within agriculture, 13 % was composted, 25 % landfilled, 13 % incinerated and 17 % was disposed using other methods.

As a calculation exercise the amount of substance disposed in the sewage sludge could be estimated. According to the EU statistics (Wieland 2003) the yearly production of sewage sludge is approximately 23 kg dry solid per capita. In the statistics from the year 2002 (Wieland 2003) 32 % of the sewage sludge is used within agriculture. When calculating the results, disposal on landfill, compost and other are designated to the compartment FS.

The calculations for Estonian yearly load were done using the data from COHIBA WP3 and the preliminary results from BaltActHaz project that gave us the EF. The EF was considered to be the average result of all WWTPs. The representability is highly uncertain due to limited data. The EFM is 23 kg of dry solid per capita as in the EU SFAs, as this data was considered to be representative to Estonia by Mr Kõrgmaa (EERC), an expert of WWTPs and sewage sludge (personal communication). The yearly load was calculated by multiplying EF with EFM and number of inhabitants in Estonia.

2.4 Activities outside Estonia as a source

The loads from long-range transport were also estimated in this study. If Estonian specific data (like EMEP data) were available, we used these. In many cases we used the Swedish monitoring data on deposition numbers from Swedish air database (summary made by IVL partners – Swedish Environmental Protection Agency: National Air Monitoring National Air Database, www.ivl.se) to calculate the annual loads. An average value of this data was used after consulting with air monitoring specialist Mr Teinmaa (EERC). The Swedish monitoring stations are located on similar latitude and

therefore the results can be considered to be comparable.

If no other data were available then, we scaled the results from the EU yearly loads to Estonian area and divided the loads in between compartments according to Estonian landscape. The description of the assumptions made when dividing the results into compartments is given above in chapter “1.1. Substance flow analysis (SFA) for Estonia”. Exact data and calculations are given in SFA reports.

3 Description of main data sources for the study

We can divide the data sources in that study into following categories:

- **Substance-based information**
- **Activity based information**
- **Pollutant based information**

The use of collected data was decided by experts. The most probable scenario was decided according to the data available at given moment by experts, meaning that the results given in this study may greatly differ from any new results that may be calculated when new data is available. It was necessary to use experts from different fields as, quite often, there was more than one source with the same reliability factor and a final decision on what to use had to be made considering other factors known to experts.

3.1 Substance based information

The regulatory status for many substances of specific concern for the Baltic Sea has changed over the years. In many cases, the European risk assessment documents were used for EU template SFAs. However, some new bans and restrictions have entered into force for many substances since and the use patterns have also been changed. A detailed substance specific regulatory situation is given in Annexes A-N of this document.

3.1.1 Registered uses of hazardous substances

The use of hazardous substances is regulated by many different documents; one of them is the regulation on export and import of dangerous chemicals 689/2008/EC. There are no registrations under that regulation and there is only one registered use of substances under REACH regulation 1907/2006/EC in Estonia. There are also no registrations of substance use in European Database Export Import of Dangerous Chemicals (EDEXIM). The data are available starting from 2010 (<http://edexim.jrc.it/>). (e-mail conversation with Enda Veskimäe from Health Board Department of Chemical Safety, which is the responsible authority of chemical control in Estonia; 20.12.2010 Mailis Laht)

The authorities from the Ministry of Social Affairs noted that there cannot be registered use of banned substances. Also, if illegal activities take place, these cannot be found from registers or databases. Hence, the real inventories and measurements are needed to control the activity.

3.2 Activity based information

In that section mainly statistical data was collected in different levels and for different purposes (economy, environment etc.).

3.2.1 European statistics

Production Statistics Database (Prodcom database)

Prodcom is a database that offers statistics on the production of goods. European production statistics is based on a certain classification of goods known as the Prodcom list, which includes approximately 4500 product categories. All products are assigned an 8-digit Prodcom code. The first four digits of this code correspond with the NACE code (Statistical classification of economic activities in the European Community) of the economic sector to which businesses that usually produce the respective product generally belong (<http://www.eds-destatis.de/en/theme4/prodcom.php>).

The Prodcom data were used to detect the activities relevant for Estonia. The main hindrance using the Prodcom data for calculations of quantitative results was that some of the data were confidential.

3.2.2 Estonian statistics

If EU emission factors and Estonian-specific data could be used, official Estonian statistics was used for more precise calculations.

Statistics Estonia

Statistics Estonia is a government agency at the area of administration of the Ministry of Finance. The main task of Statistics Estonia is to provide the public institutions, business and research spheres, international organisations and individuals with reliable and objective information service on economic, demographic, social and environmental situation and trends in Estonia. Official statistics is in compliance with international classifications and methods (<http://www.stat.ee/>).

The Estonian Environment Information Centre (EEIC)

The Estonian Environment Information Centre (EEIC) aims to collect, process and generalise data on Estonian nature, state of environment and the factors influencing it. The Information Centre provides reliable environmental information for Estonia's decision-makers, public both in Estonian and abroad, and for various organisations (<http://www.keskkonnainfo.ee/main/index.php>).

3.2.3 Special registers

There are also specific databases in many fields, e.g. there is a specific "Probleemtoodeteregister" (PROTO http://proto.keskkonnainfo.ee/?page=pub_startup&u=20110930165127) that was created under the RoHS directive 2011/65/EU on the restriction of the use of certain hazardous substances in electrical and electronic equipment and that collects information about the uses and products regulated with RoHS directive. Other commonly known register is the pesticide register – the data about pesticide uses, sales etc are registered in that database according to many EU regulations ("Taimekaitsevahendite register" <http://www.pma.agri.ee/index.php?id=104&sub=132&sub2=242>). Environmental permits are listed in KLIS (<http://klis.envir.ee/klis>).

3.2.4 Inquiries

During the project, the enquiries were used to collect data and specify the data found from other sources. Target groups were the companies and associations. We e-mailed, sent official letters with questionnaires, and also called the companies to get information about the possible uses of hazardous substances.

We contacted companies with IPPC permits and those that we found from the Estonian Trade Catalogue (<http://www.estoniantrade.ee>). Estoniantrade.ee is a commercial website and the data about companies can be found using the NACE code.

It was not possible to make these kinds of very time consuming inquiries on every field. We chose companies that could potentially hold the most information for a number or even all the substances, e.g. suppliers of the chemicals and waste management companies etc. The most important sources were checked by personal communication. We checked such fields as textile and leather, chemicals, plastics and rubber, metal, paints and crematoriums this way.

The data collected in this kind of way is not always reliable and the response was also not guaranteed. In our case about half of the companies answered. Exact calculation methods and expert estimations are given in substance-based SFAs case by case (Annexes A-N) if the method was used to estimate the loads.

3.3 Pollutant based information

3.3.1 Registered data about the pollutant release and monitoring data

The collection of pollutant releases and different monitoring data is well regulated and many registers are made to get better overview of the environmental status in Europe.

Monitoring in Estonia

In national monitoring programs only mercury and cadmium have already been measured for years. Other HELCOM priority substances are not included in Estonian monitoring programs and there are very limited numbers of studies the substances have actually been measured in Estonian environment. The monitoring data for metals was used in this study.

The European Pollutant Release and Transfer Register (E-PRTR)

A facility has to report data to E-PRTR (<http://prtr.ec.europa.eu/Home.aspx>) if it fulfils the following criteria:

- the facility falls under at least one of the 65 E-PRTR economic activities listed in Annex I of the E-PRTR Regulation (Regulation (EC) No 166/2006 of the European Parliament and of the Council of 18 January 2006) and exceeds at least one of the E-PRTR capacity thresholds
- the facility transfers waste off-site which exceed specific thresholds set out in Article 5 of the

Regulation. Article 5

- The facility releases pollutants which exceed specific thresholds specified for each media - air, water and land - in Annex II of the E-PRTR Regulation.

There are several COHIBA substances listed in Annex II of the E-PRTR Regulation (Table 3).

Table 3. The HELCOM substances in E-PRTR register. (All notes are left as they are in the original document)

| CAS number | Pollutant (1) | Threshold for releases (column 1) | | | Comments |
|------------|---|-----------------------------------|------------------------------|-----------------------------|--|
| | | to air (column 1a) kg/year | to water (column 1b) kg/year | to land (column 1c) kg/year | |
| | Cadmium and compounds (as Cd) (8) | 10 | 5 | 5 | (1) Unless otherwise specified any pollutants specified in Annex I shall be reported as the total mass of that pollutant or, where the pollutant |
| | Mercury and compounds (as Hg) (8) | 10 | 1 | 1 | (8) All metals shall be reported as the total mass of the element in all chemical forms present in the release. |
| 115-29-7 | Endosulphan | - | 1 | 1 | |
| | PCDD + PCDF (dioxins + furans)(as Teq) (10) | 0,0001 | 0,0001 | 0,0001 | (10) Expressed as I-TEQ. |
| | Brominated diphenylethers (PBDE) (12) | - | 1 | 1 | (12) Total mass of the following brominated diphenylethers: penta-BDE, octa-BDE and deca-BDE. |
| | Nonylphenol and Nonylphenol ethoxylates (NP/NPEs) | - | 1 | 1 | |
| | Organotin compounds(as total Sn) | - | 50 | 50 | |
| | Tributyltin and compounds (15) | - | 1 | 1 | (15) Total mass of tributyltin compounds, expressed as mass of tributyltin. |
| 1806-26-4 | Octylphenols and Octylphenol ethoxylates | - | 1 | - | |

The data to be reported annually by each facility for which the applicable thresholds are exceeded are

as follows:

- Releases to air, water and land of any of the 91 E-PRTR pollutants ;
- Off-site transfers of any of the 91 E-PRTR pollutants in waste water destined for waste-water treatment outside the facility;
- Off-site transfers of waste (reported as tonnes per year) for recovery or disposal. For transboundary movements of hazardous waste outside the reporting country, details of the waste receivers have to be provided.

The reported releases include any introduction of any of the listed pollutants into the environment as a result of any human activity, whether deliberate, accidental, routine or non-routine, at the site of the facility.

E-PRTR also contains information on releases from diffuse sources into water which will be upgraded and extended gradually.

Integrated Pollution Prevention and Control (IPPC)

IPPC - a permitting system for industrial plants based on an EU directive of the same name - IPPC directive, 96/61/EC. The directive concerns the most polluting industry sectors. Some sectors are only covered if exceeding certain capacities. The six categories are:

- Energy industry
- Production and processing of metals
- Mineral industry
- Chemical industry
- Waste management
- Other activities (pulp & paper, textile, tanneries, slaughter houses, food production, intensive rearing of poultry or pigs, surface treatment using organic solvents, production of hard burnt coal or electrographite)

There are about 35 industrial enterprises, 20 combustion plants, 30 landfills and more than 50 pig and poultry farms that are listed as IPPC enterprises in Estonia (<http://www.ippc.envir.ee/english/aboutippc.htm>). Altogether, there are 258 facilities with IPPC permit in Estonia (<http://www.ippc.envir.ee/estonian/tegevusvaldkonnad.htm>).

The applications, the draft permits, the permits and the results of the monitoring of emissions will be public. The applications and the permits will be published in the newspaper and the public will have an opportunity to comment on the application before the permit is issued. The draft Estonian act transposing the directive might also include the possibility of appealing the permits to an appeal committee.

The directive also puts heavy emphasis on the (operational and emission) control – by the company itself and also compliance check-ups by the authorities which are obliged to control, on a regular basis, that the terms in the permits are not exceeded. The company will have to report the monitoring results to the authorities. (<http://www.ippc.envir.ee/english/aboutippc.htm>).

European Monitoring and Evaluation Programme (EMEP)

EMEP (European Monitoring and Evaluation Programme) is a scientifically based and policy driven programme under the Convention on Long-range Transboundary Air Pollution for international co-operation to solve transboundary air pollution problems. In some cases also the data from EMEP Meteorological Synthesizing Centre-East databases were used (<http://www.msceast.org/about.html>).

3.4 Conclusions from registered data for Estonia

There are clear contradictions and data gaps between different sources of data. For example, there are 12 reporting facilities reporting to E-PRTR in Energy sector, even though only two of them report for Cd and Hg. No other COHIBA substances were reported for 2009, which was the latest available data for the time of that study. However, according to IPPC, there are 15 facilities in Energy sector. The biggest difference is in the total number – according to the E-PRTR, there are 38 facilities altogether in Estonia, but the total number of IPPC installations in Estonia is actually 258.

According to E-PRTR there are 31 facilities emitting to air, 7 to water and none to soil in Estonia. The data available in the E-PRTR do not give a reliable picture of the real situation in Estonia.

One important reason for such kind of data gaps is that the environmental permits (IPPC) themselves do not contain data needed to report to the E-PRTR. For future studies, it should be kept in mind that when collecting data, it shouldn't be concluded that there are no emissions from that particular source in Estonia even if it is marked as non-existent in E-PRTR. If data were found in E-PRTR then they were used also in this study.

3.5 Data gaps

One of the outcomes of the study was the detection of data gaps and missing links that now provides a basis for future improvements of the hazardous substances control system. Since most of the hazardous substances are regulated by several legislative acts, the pathways and flows of these substances should be very well documented. In reality, gathering and matching the information obtained from various sources has proven to be very difficult and time-consuming. Quite often, the systems are not fully operational, and therefore obtaining the data is impossible.

Many such bottlenecks were detected and future improvements need to be made in the system. It should also be noted that many of the registers were started in 2010 in Estonia, therefore results from only one year were available for our study.

4 Sources and flows of the target substances

4.1 Dioxins (PCDD), furans (PCDF) and dioxin-like polychlorinated biphenyls (PCBs)

In Estonia, 65% of the dioxin emissions to air originate from local sources, such as incineration of wastes and fuels in power plants (Figure 5).

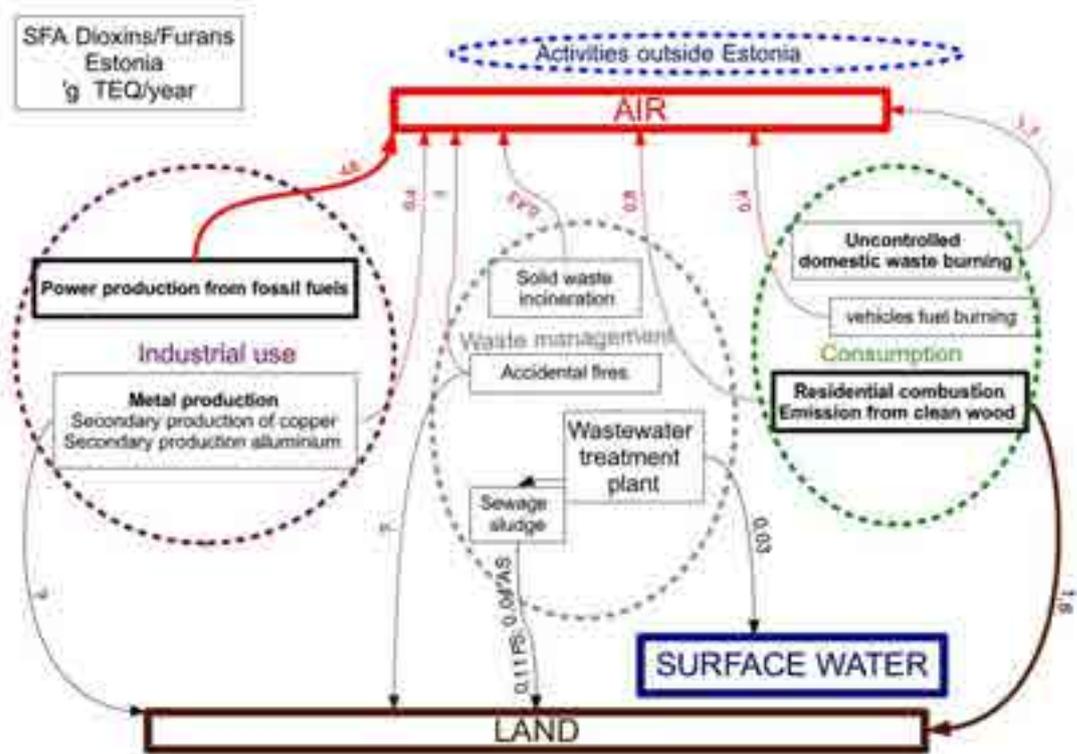


Figure 5. SFA diagram for dioxins and furans in Estonia.

The most meaningful measures for reducing emissions will be to secure and control efficiently incineration and to use best available technologies in the industry. To achieve the reduction of non-industrial emissions, the most effective way is to prevent open fires – education of population is needed.

The fluxes coming from the sources outside Estonia are greater than the ones coming from the country itself. However, it is impossible to control these sources by usual means; the only possibilities are international agreements etc.

According to international agreements, Estonia has taken a responsibility to reduce the emissions to emission projection 3,5 g I TEQ/y by 2015.

4.2 Tributyltin compounds (TBT), triphenyltin compounds (TPhT)

TBT has been used in a great variety of materials and products; hence the potential number of sources is great. Estonia has no data at the moment to quantify the loads to the environment. No product registers and so on.

The biggest quantitatively estimated source for TBT are related to consumption of goods : coatings (used in household appliances, office furniture, architectural uses, lawn/garden equipment, heating and air condition systems etc.) emissions to air 0,5 kg and to WW 0,5 kg year; Polyurethanes (used in upholstered furniture, mattress fillings, car seats, printing, surface coating, engineering components etc.) emissions to air 0,4 kg and to waste water 0,4 kg. The biggest quantitatively estimated source to land is sewage sludge (0,2 kg) and to surface water the waste water treatment plant effluents (0,1 kg).

TBT is found as a biocide in antifouling paints and wood preservation products, and as an impurity in PVC products and catalysts, in textiles, consumer products, silicones, and paints. We assume the emissions from industrial uses mainly end up in the wastewater or outdoor air. Emissions from municipal uses end up in air, WWTPs or soil.

Repairing of ships (removal of old anti-fouling paints) and residual pollution in the sediments of ports and harbours is a significant source of TBT pollution in Estonia. Pollution from this source affects the coastal water directly. Many industrial activities are also possible for Estonia, but there is no data to quantify the loads.

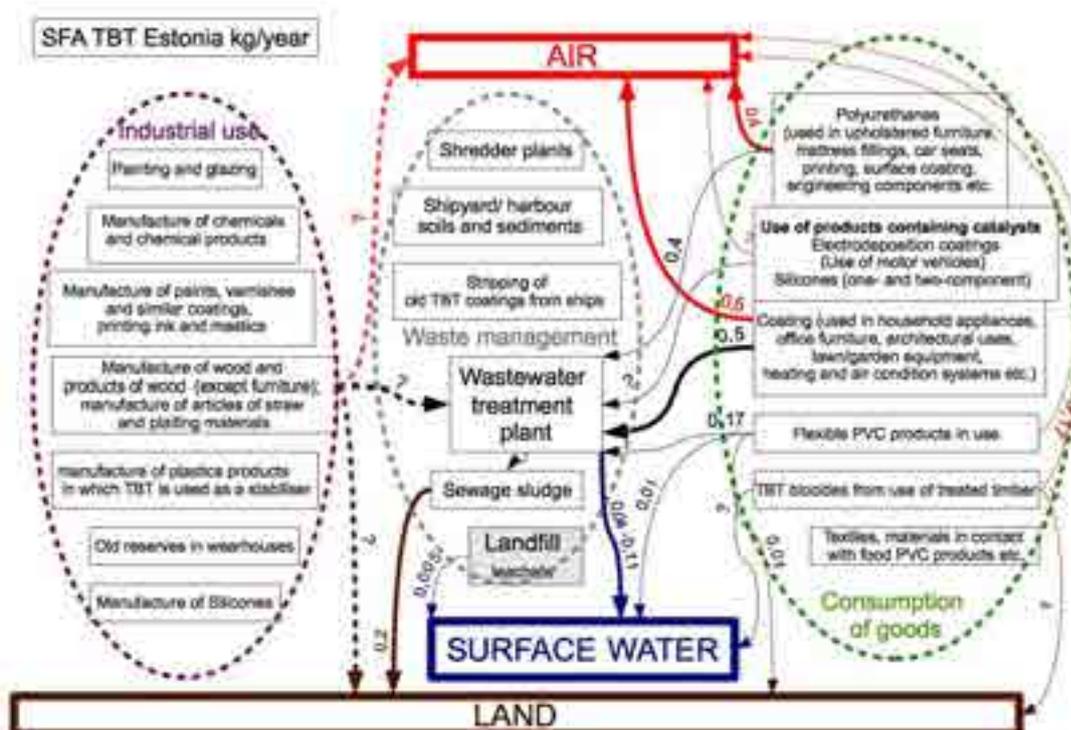


Figure 6. SFA diagram for TBTs in Estonia.

Possible means for reducing the emissions of TBT are mainly administrative. It is not possible to make future plans for reducing TBTs in Estonia as the mapping of the current situation is insufficient.

It is of utmost importance to further research the situation of the moment and make an inventory of the amounts of TBTs in products and environment to plan further actions and measures. It is also important to have a better control over products (such as textiles) imported to Estonia from non-EU countries, i.e. have a better monitoring at the border as imported products may be an important source of TBTs. Also, raising of general awareness is of utmost importance. It is also necessary to add TBTs to the national monitoring.

For industries, it is necessary to use BATs and perhaps find alternatives for the use of TBTs. As most of the emissions of TBTs are led to WWTPs, it is also important to find technologies that help to stop the pollution at this point. Proper waste and sewage treatment will hopefully remove the substance entering the environment from this source.

The removal of polluted sediments from harbours and docks is one possible measure for reducing the effects of TBTs on the marine environment. If this cannot be done, the highly possible presence of TBTs in sediments must be kept in mind when planning future dredging or building new quays and docks.

It is safe to say that it is necessary to work with TBTs more. It is also safe to say the impacts of the TBTs on the environment will be far-flung.

4.3 Pentabromodiphenyl ether (pentaBDE), octabromodiphenyl ether (octaBDE), decabromodiphenyl ether (decaBDE)

The most common congeners found in Estonia were BDE-47, BDE-99, and BDE-209.

For many cases we could not calculate the load but if we compare our results from WP3 and studies from other countries, it seems like the most possible sources are products containing these substances. The results of WP3 indicate that the level of pBDEs detected, is in correlation with the number of inhabitants in the area and also that the level is similar for all city areas.

The most important source for pentaBDEs in Estonia is the consumption of products containing pBDEs like electronic appliances (emissions from TV sets 3,8 kg to indoor air and PC sets 17 kg to indoor air). The calculated load from indoor air to outdoor air were 0,01 – 0,07 kg/year.

Also, burning activities release pBDEs to the environment. Accidental fires are not an easily predictable source, but there are some smaller or bigger scale fires every year. Based on statistics and available measurement data the load from different waste fires was calculated and the emissions to the air are estimated as 1,56 kg.

The detected emissions from secondary sources wastewater treatment plants with effluent water and landfill leachate gave a total emission of 0,4 kg to the surface water and 0,7 kg to the land. Air

deposition from long-range transport of pollutants can also be an important source of pentaBDEs in Estonia (0,17 kg to land and 0,015 kg to surface water) but the quantitatively detected sources have higher loads.

PentaBDEs are banned and the loads from industrial activities are stopped but the critical point to avoid environmental damages is the proper waste management. Avoiding uncontrolled burning of waste and preventing accidental fires is a possible way to reduce the emissions from waste string to the environment. Incineration of municipal waste and dismantling of wrecks and electronic equipment are also the possible sources of pentaBDEs in Estonia and those activities need to be further studied to calculate the loads to the environment and propose possible measures to reduce the discharges.

The most important source inside Estonia of decaBDEs to air are incineration activities and accidental fires of electronic waste. The load of 0,2 kg was calculated from statistical data.

The most important quantitatively detected source to land is sewage sludge (7,35 kg AS and 15,62 kg FS). To avoid the pBDEs entering the environment again, proper sewage sludge treatment and control of burning events and thermal processes is needed. Some local land pollution can come from fire incidence and also the sites of dismantling wrecks. The recycling and dismantling of cars and electronic equipment is assumed to be an important source for Estonia (other countries like Denmark have showed studies in the frame of COHIBA that it could be relevant for pBDEs). However, there are no emission factors available so we could not calculate the load for that string. Further studies and also monitoring measures for dismantling activities are needed.

Based on measurements done in COHIBA WP3, we can assume that in some cities industrial use of decaBDE can also be an important source in Estonia, but we could not detect the field or company, where the substance is used.

The most important quantitatively detected source to air is indoor air (0,05 kg/year) and the sources to the indoor air are electronic appliances (0,1 kg/year) especially the plastic housing (pBDE-s are used as flame-retardant). Fire activities have a major risk releasing the substances to the air.

The most important quantitatively detected source to surface water are the secondary sources like wastewater treatment plant effluents (0,04 kg/year) and the landfill leachate (0,005 kg/year). The numbers can look small but the EQS for pBDEs in freshwater is 0,0005 µg/l. It means the substances are toxic and the measures to reduce the discharges are needed.

Activities outside Estonia have also impact to the loads in Estonia (0,69 kg/y AS and 1,48 kg FS; 1,4 kg FSW).

Considering the literature we can also assume that load of pBDEs from Estonia is higher than the amounts calculated in this study as certain amounts of pBDEs may be released from oil shale mining and oil shale thermal processing. More research is needed on that issue.

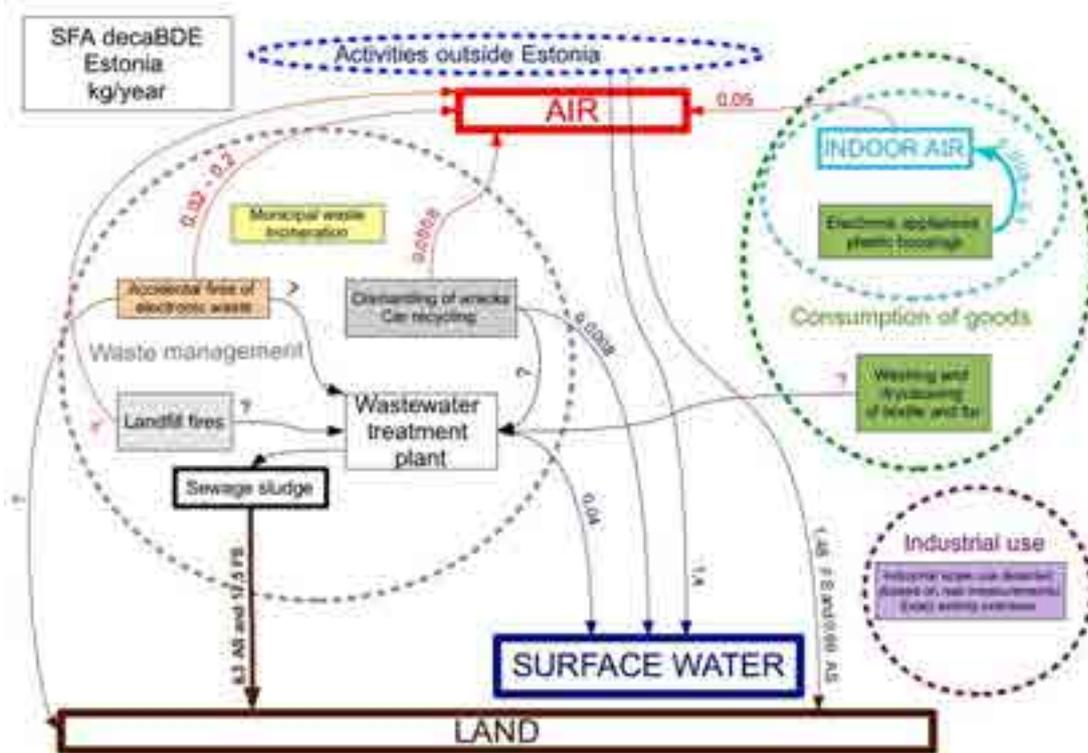


Figure 7. SFA diagram for decaBDEs in Estonia.

There are many international agreements that Estonia is a part of that aim to decrease the level of pBDEs. The main goal is to create a proper waste management system. Also, to raise of awareness should not be underestimated due to the use of those substances in everyday products and the fact that public has direct contact with them daily. If everyone can understand, that the proper waste management will help to avoid pollution, then we will have a good basis for the next steps. Possible loads from municipal waste incineration are the critical point for the future (emissions to air 0,00147 - 26,43 kg the load is calculated with today's produced waste amounts). Municipal waste is not incinerated in Estonia yet, but there are some plants under development. That's the reason why we have calculated the possible loads from that string.

4.4 Perfluorooctane sulfonate (PFOS), Perfluorooctanoic acid (PFOA)

Important sources for Estonia are use of products containing PFOS and PFOA. For PFOS is the most important source the impregnated goods. The emissions are to the waste -water but the loads can affect land and surface water through the waste-water systems. At the moment the quantitatively biggest source to the land and surface water is the landfill leachate (0,11 kg to land and 0,11 kg to water). Loads could be decreased by proper waste management and sewage treatment.

The atmospheric deposition is also important source for Estonia and at the moment quantitatively the loads are bigger than the loads from different sources in Estonia. But we should take in account that

the industrial sources were not possible to quantify.

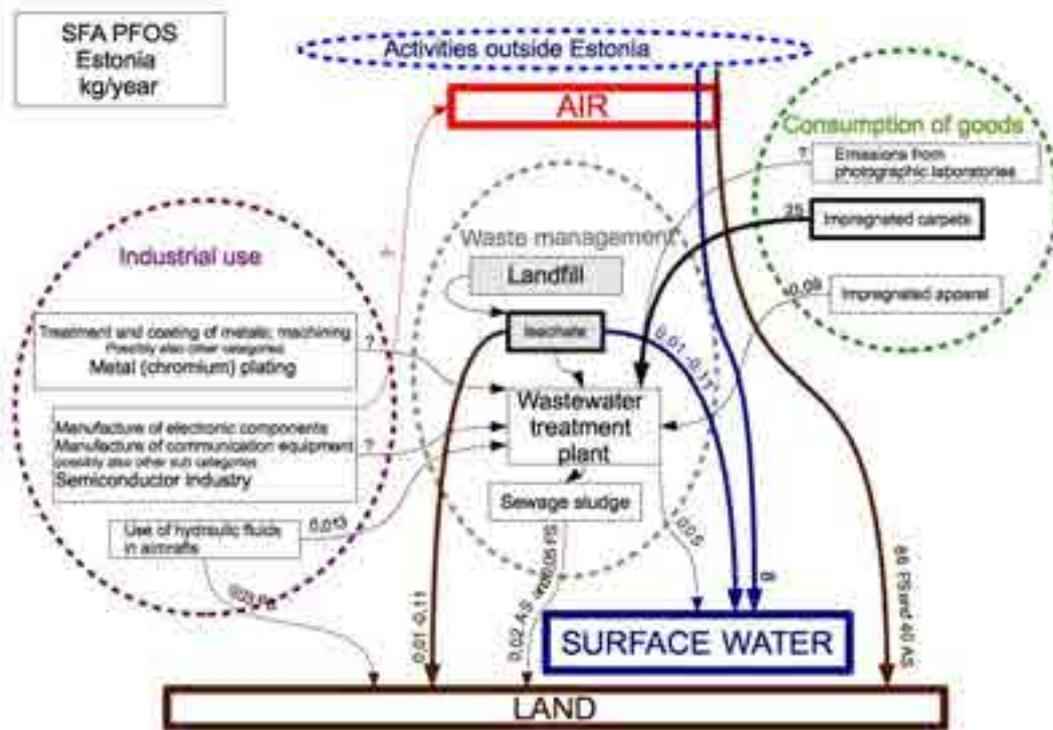


Figure 8. SFA diagram for PFOS in Estonia.

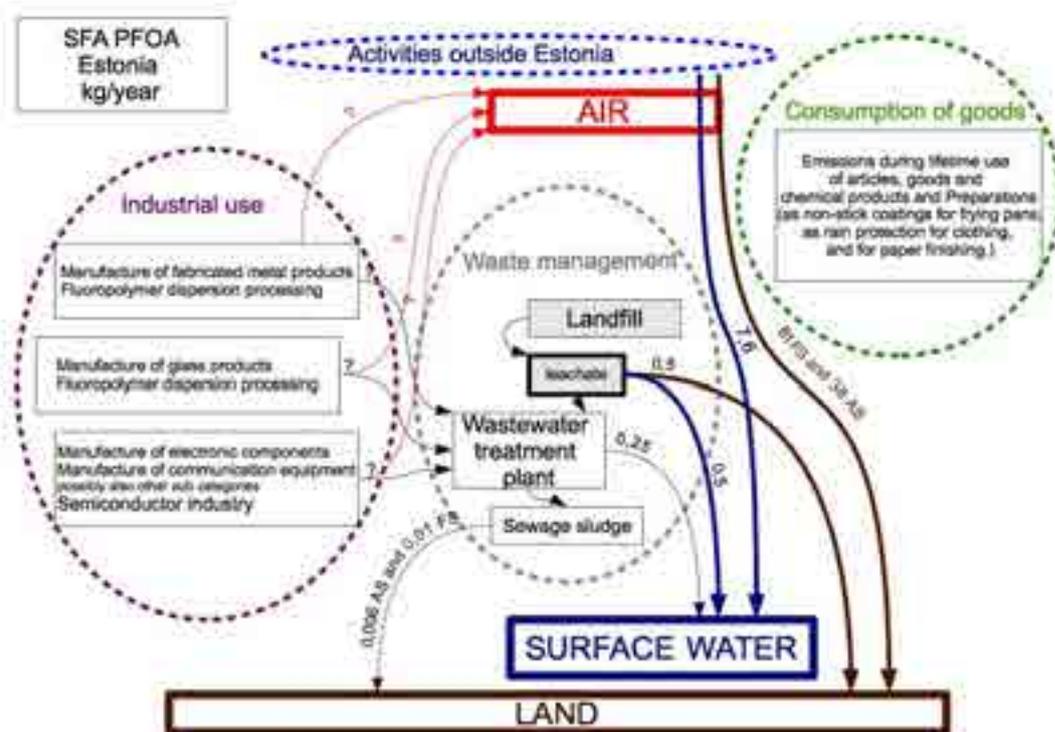


Figure 9. SFA diagram for PFOA in Estonia.

Possible means for reducing the emissions of PFOS and PFOA are administrative. It is not possible to make future plans for reducing perfluorinated substances in Estonia as the mapping of the current situation is insufficient.

4.5 Hexabromocyclododecane (HBCDD)

The most important source of HBCDD in Estonia is usage of products containing HBCDD. One portion of this will end up in WWTPs. The yearly load from WWTP effluents is 96,51 kg. It is possible to reduce the load entering the environment from this source by improving or using more innovative treatment processes.

The sources that have the biggest impact are the construction and demolition. The yearly load from demolition is 8 kg to SW and 8 kg to OA.

Another important source of HBCDD-s in Estonia is atmospheric deposition from which the HBCDD-s will enter the environment directly (0,01 - 4,5 kg to SW, 0,158 – 98,7 kg to AS and 0,168 – 115,5 kg to FS). This source is extremely difficult to control.

There are plastic industries in Estonia that might have a use of the raw materials that contain HBCDD-s, but there is no data available at the moment (as of December 2010).

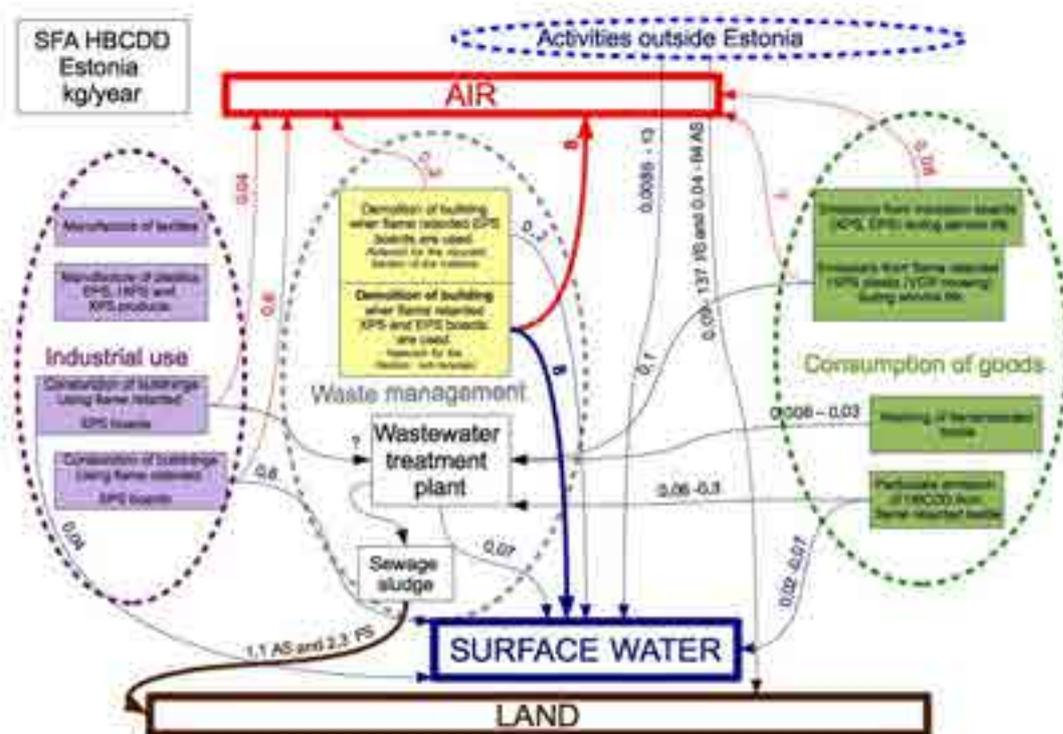


Figure 10. SFA diagram for HBCDDs in Estonia.

It is near impossible to give any qualitative estimation of time trends for future scenarios because the data is insufficient. More thorough inventories on both industrial and municipal usage are needed. It is also necessary to add HBCDD to the national monitoring. It is safe to say that it is necessary to work with HBCDDs more. It is also safe to say the the impacts of the HBCDD on the environment will be far-flung, as HBCDDs are used in many products that have a long-term use.

4.6 Nonylphenols (NP), nonylphenol ethoxylates (NPE)

It was not possible to identify the most important sources of NPs in Estonia as most of the data from industrial sources is missing due to the poor registers and chemical control in Estonia. We have data from many industrial activities that might use the NP in processing but no reliable information. The reason for that is the use of different products that contain NP. Estonia has no product register and so the quantitative estimation was not possible to carry out in the frame of this work. In the future it can be possible to detect the products that are in use and then using the information from companies, environmental permits and product safety data sheets the quantitative estimation is also possible.

NP emissions are also coming from private consumption in Estonia and the most important sources are the washing and cleaning activities. The use of NPs and NPEs is forbidden in the EU, but the substances are still present in the imported clothes and cleaning products. The use of imported cleaning products has a great impact of 216 kg/year. Cosmetic products emit 0,4 -12 kg of NPs yearly. Also washing of imported textiles gives a great amount of emissions of NPs, but this is

considered in the SFA of NPE.

The most important compartment is wastewater, but the NPs may also end up in surface waters through the wastewater system.

In our opinion, the most relevant reduction possibilities are in the industrial sector, with the use of BAT and BEP. Also, raising the awareness of the general public and the industry managers is an important step to be taken. By our experience, the managers in the industry are not aware of their potential use of hazardous substances, which can be additives and may be often detected only by thorough research through the safety cards. This is also one reason why we didn't consider the information straight from the producers to be of A-type accuracy.

Also the proper treatment of wastewater would give a good effort to protect the environment from NP releases.

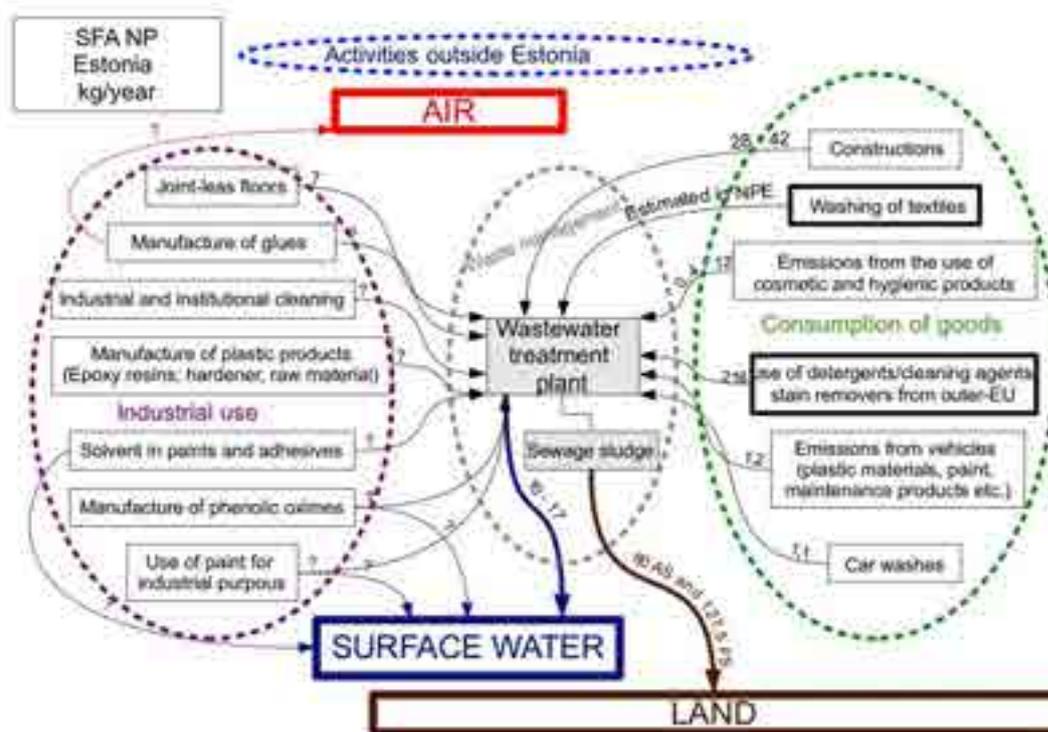


Figure 11. SFA diagram for NP in Estonia. Please note that on this SFA diagram the atmospheric deposition is missing – it is included on the NPE SFA diagram.

Possible means for reducing the emissions of NPs are administrative. It is not possible to make future plans for reducing NPs in Estonia because the mapping of current situation is insufficient.

The main sources of NPEs in the private consumption are cleaning activities. The highest load of NPEs comes from the washing of imported textiles – up to 2,8 t to WW.

The wastewater treatment systems are also a relevant secondary source of NPEs and that source has

also the biggest potential to reduce the pollutant entering the environment. At the moment the loads from the WWTPs with effluent water are estimated as 1,7 – 59 kg to FSW and 0,75 – 25,3 to CSW. Contaminated sludge ends up in agricultural soil 13 – 87 kg and forest soil 28 – 185 kg annually. The proper sludge treatment can prevent the pollutant entering the environment.

No proper quantitative estimation was possible to make about the industrial sources during the study due to limited data, incomplete registers and poor product and chemical control in Estonia.

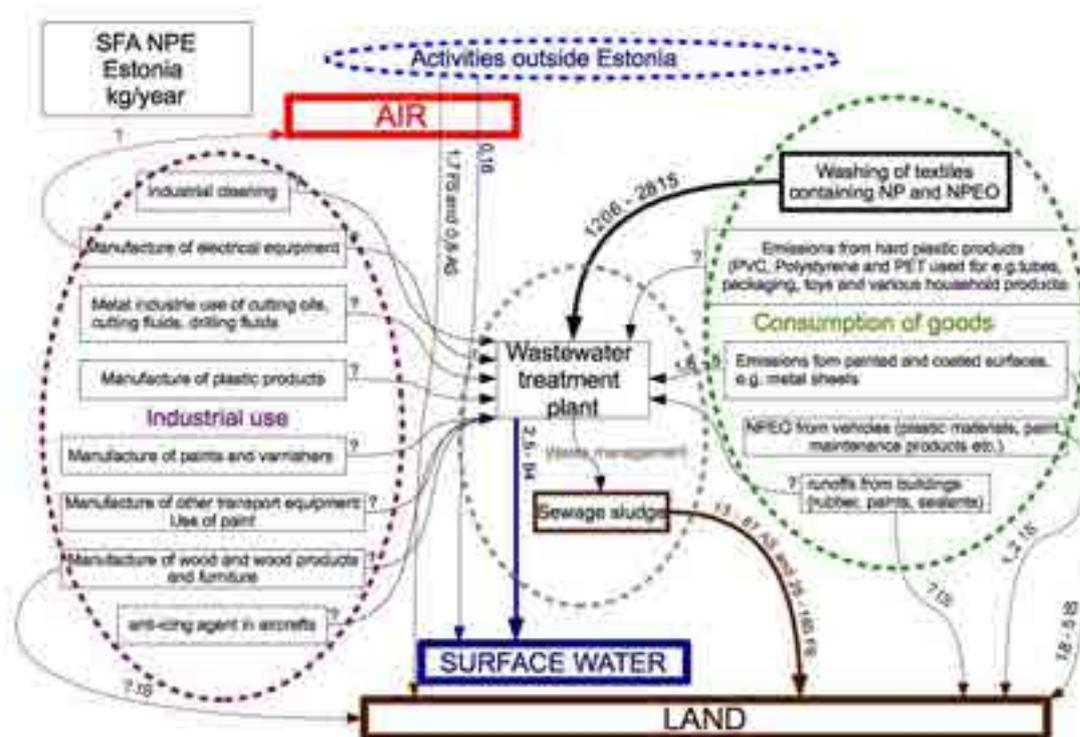


Figure 12. SFA diagram for NPEs in Estonia. Please note that the atmospheric depositions of both NP and NPEs are used on this graph.

It would be possible to reduce the use of NPEs by different measures. However, as we have no good overview of the present situation, it is difficult to predict future scenarios. It is important to continue mapping of the substance in Estonia.

4.7 Octylphenols (OP), octylphenol ethoxylates (OPE)

The main source of OPs is the private consumption – abrasion from tyres 41 – 125 kg to FS and 41 – 125 kg FSW. Other big source is washing of imported textiles containing OP 285 kg to WW. The main receiving compartments for OP are FS and FSW. Several industrial uses are also possible, but quantitative estimation is not possible to make at the moment.

We assume the atmospheric deposition to be also relevant for Estonia. However, there is no

quantitative data to prove or disapprove it at the moment.

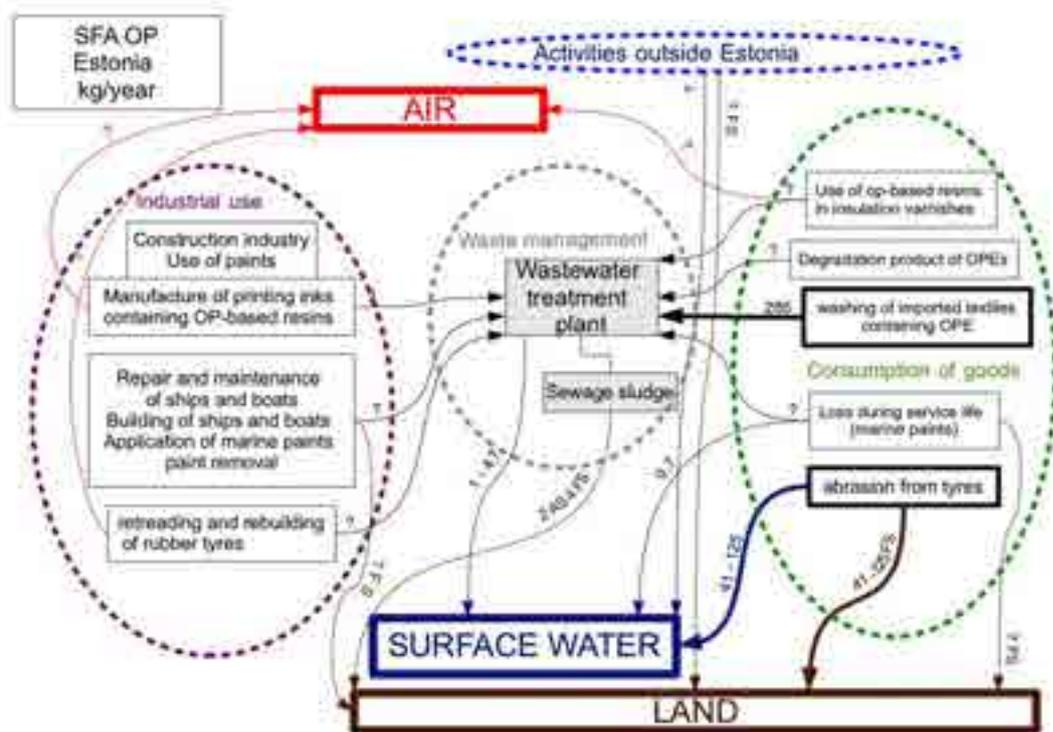


Figure 13. SFA diagram for OP in Estonia.

New national measures are considered to reduce the emissions of OPs, but they are not in force yet. It is of utmost importance to make a further research and an inventory of the amounts of OPs and OPEs in products, in order to plan further actions and measures. It is also important to have better control over products imported to Estonia from third countries (non-EU countries), i.e. have a better monitoring at the border.

The industrial use of products containing OPEs could be a relevant source for Estonia. At the moment the sources are not detected. There is no proper product register in Estonia and product based uses are not known. Further and thorough investigation is needed in the future in order to identify the potential sources of OPEs in Estonia.

OPEs mostly end up in WWTPs that means it is possible to remove and prevent from entering the environment again. If it is not done, the surface water will be contaminated.

The most important source for Estonia at the moment is the usage of products containing OPEs. It was possible to calculate the number for washing the imported textiles and yearly load was found 11,4 t/year to WW.

Direct emissions to the land may come from veterinary medicaments used for goats and sheep. Calculated load to AS from this source was 87,5 kg. The loads may also come from pesticides used in agriculture, then the receiving compartments are AS and FSW. The sewage sludge is also a

possible source for land contamination: 0,1 - 19 kg AS and 0,3 - 40 kg to FS.

It was not possible to calculate air emissions as there is no monitoring data. However, the potential air emissions are probably mostly related to the industrial activities.

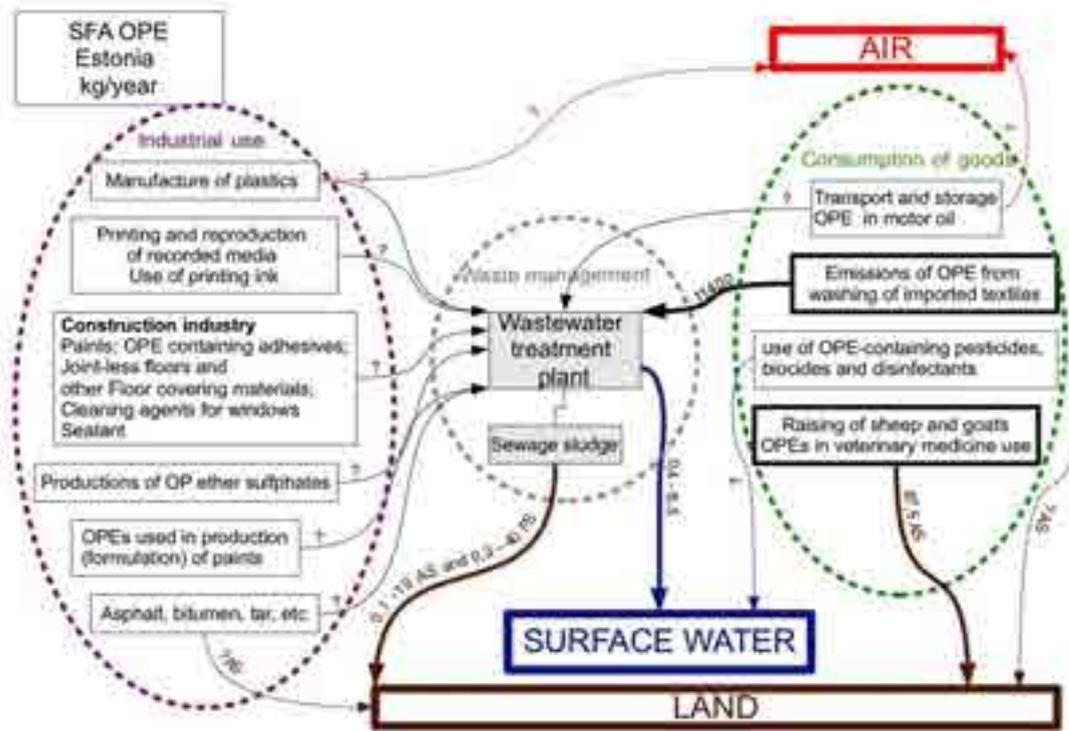


Figure 14. SFA diagram for OPEs in Estonia.

It is important to map the use of OPEs and OPs in the industry in order to plan potential measures to reduce the emissions of OPEs. At the moment the data from industry is extremely scarce and it is difficult to take any measures.

It is also important to strengthen the control of customs and check the products imported from non-EU countries as imported products (such as textiles) may be an important source of OPEs.

Also, raising of general awareness is of utmost importance. Reducing the use of pesticides and finding alternatives for veterinary medicines and pesticides is a potential measure for reducing the emissions of OPEs.

As most of the emissions of OPEs are led to WWTPs, it is also important to find technologies that help to stop the pollution at this point. Proper waste and sewage treatment will hopefully remove the substance entering the environment from this source.

4.8 Short-chain chlorinated paraffins (SCCP), medium-chain

chlorinated paraffins (MCCP)

The most important source of emissions of short chain chlorinated paraffins is the use of products containing short chain chlorinated paraffins. The majority of the short chain chlorinated paraffins from products end up in the water compartment and the rest is emitted to air. Volatile and leaching loss over lifetime from products to waste water is 118 – 321 kg/year and to indoor air 8 – 29 kg.

The most important sources to surface water are waste-water treatment plants (40 -47 kg/year) and waste remaining in the environment (28 – 58 kg/year).

The most important source to land is also the waste remaining in the environment (88 -175 kg/year) and second largest source for land is the sewage sludge (12 -14 kg to AS and 24 – 30 kg to FS)

The emissions to air are not so important for Estonia. We should keep in mind that SCCP is highly regulated also under The 1998 Aarhus Protocol on Persistent Organic Pollutants (POP Protocol) to the regional UNECE The 1979 Geneva Convention on Long-range Transboundary Air Pollution (CLRTAP) and also in our study the deposition data from activities outside Estonia are really high exceeding even the loads from local sources (95 – 4015 kg to FS and 45 – 1882 kg AS and (9 – 376kg to surface water). Estonian emissions to air can be underestimated in that study or we just did not know the possible sources.

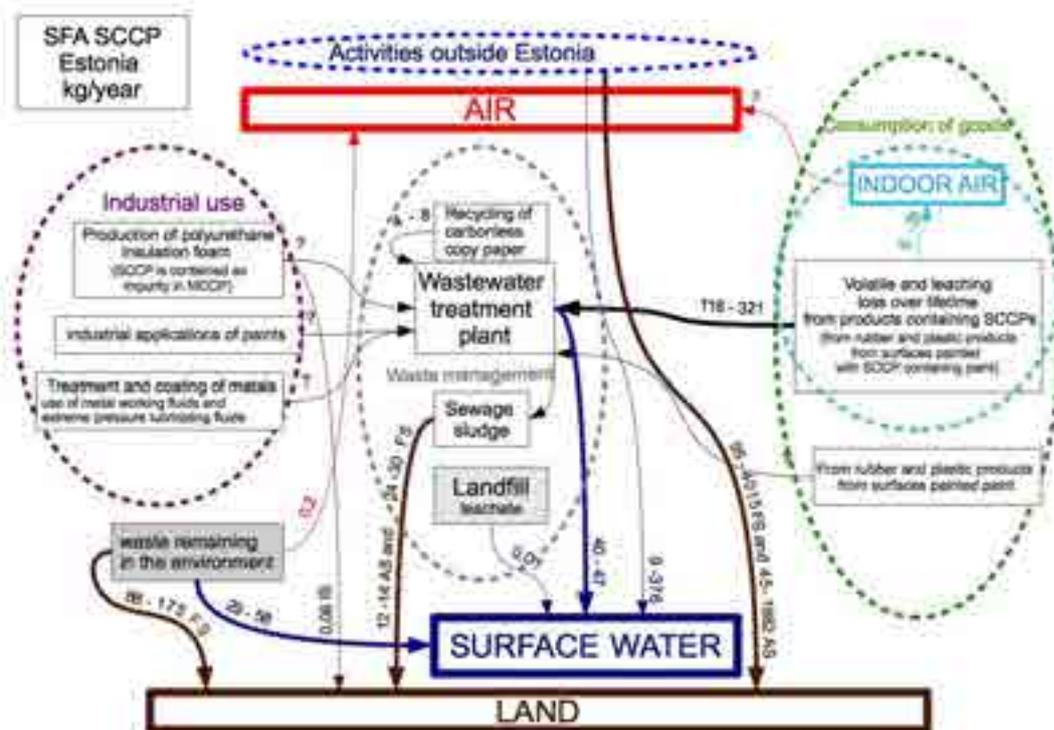


Figure 15. SFA diagram for SCCPs in Estonia.

The estimated emissions presented in this report are mainly based on data from 2001. Since the emission estimates mainly are based on old data it is likely that the situation has changed. Some of the sources mentioned here may not be relevant and some may be missing. The proportions between different uses may also have changed.

In the addendum to the EU RAR it is said that Euro Chlor have indicated that the use of short chain chlorinated paraffins in the EU 2003 was around three times lower than 2001. Due to the fact that short chain chlorinated paraffins have been proposed to be added to the list of substances subjected to authorization under the REACH-regulation (1907/2006), a further reduction can be expected. The situation can be expected to be similar in Estonia.

However, as the main sources of emissions are sources with sometimes a long service-life, there will be a delay in the effect of reduced use on the yearly releases to the environment. The proper waste management is really important for reducing the SCCP loads to the environment. Also the recycling activities should be under better control.

Raising the awareness of the general public and the industry managers is an important step to be taken.

Also the proper treatment of wastewater especially the sludge treatment would give a good effort to protect that the SCCPs would not end up in the environment.

4.9 Endosulfan

As the major field of application for endosulfan, i.e. the use as a plant protection product is now banned within EU. Hence the agricultural use is not longer a source of the substance within EU27. Thus diffuse sources originating from activities outside EU have instead become more important. Long-range atmospheric transport of endosulfan and subsequent deposition on land and surface water and endosulfan on imported foodstuffs have been identified as two possible important sources. The yearly load of endosulfan from atmospheric deposition to surface water in Estonia was estimated to be 0.05-1,77 kg and 0.7-27 kg for the yearly load of endosulfan from atmosphere to land. The load to wastewater originating from endosulfan residues in foodstuffs was considered to be insignificant. The contribution of endosulfan via imported foodstuffs could thus be underestimated; the emissions from the WWTP overestimated or a source of endosulfan may be missing.

All of the estimations are associated with large uncertainties and the data presented should be interpreted with caution.

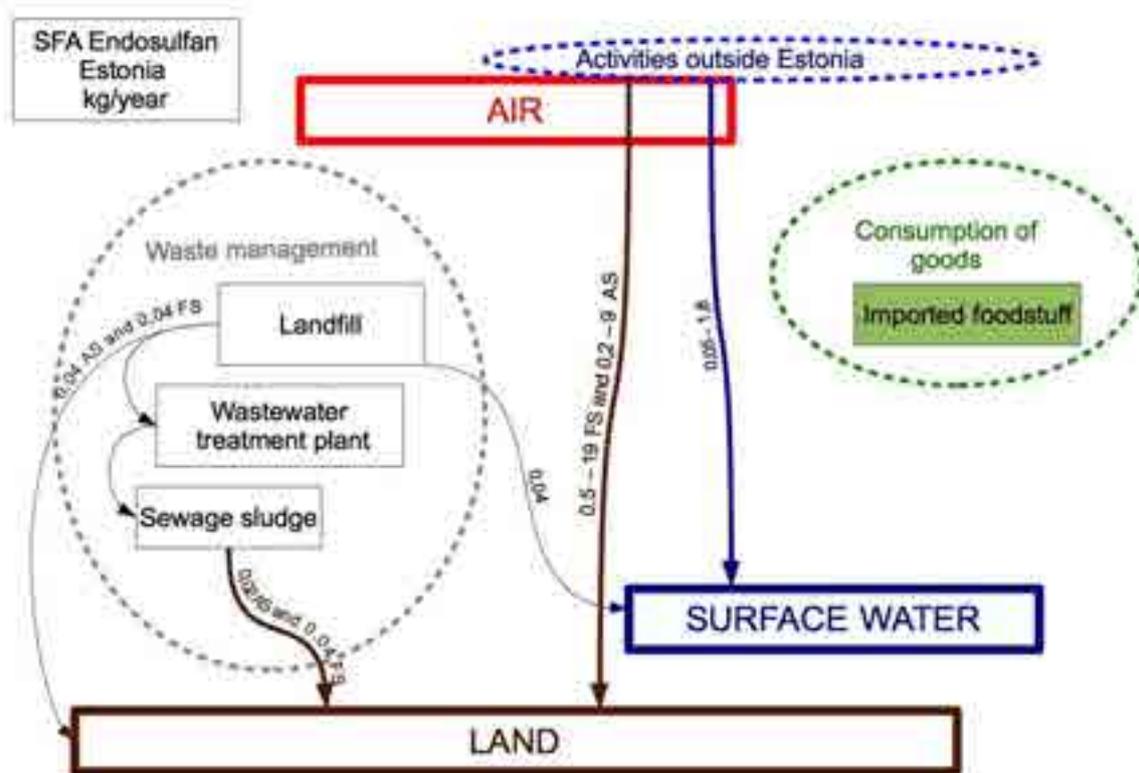


Figure 16. SFA diagram for endosulfan in Estonia.

Recognition of the hazardousness of endosulfan, as well as its potential for long range transport in the atmosphere, will probably lead to further decreased emissions of the substance. The fact that active use of endosulfan should already have been discontinued within EU does however mean that the rate and character of further decreased emissions are difficult to foresee.

4.10 Mercury

The most relevant source to air is thermal power installations (501 kg). Wood burning stoves are also an important source in Estonia as many people use wood for heating their houses. This source gives 168 kg of Hg a year to air.

Even though amalgam is mostly no longer used as a dental filling (only for fixing old fillings), many people still have old fillings and this together gives a significant load of 122 kg to wastewater.

Main loads to surface waters are not that obvious as many of the potential sources could not be quantified. At the moment it seems like the most important load to FSW comes from erosion of roads (26 kg), but production of paper and board and other primary wood products also give a load to FSW (4,9 kg), as does the load from wastewater treatment plants (1,6 kg). Wastewater treatment plants seem to be generally a significant point to monitor as sludge from wastewater treatment plants also

gives a significant load (15 kg) to soil.

Atmospheric deposition of Hg is also high and gives a load of 410 kg a year to land and 26 kg to water a year.

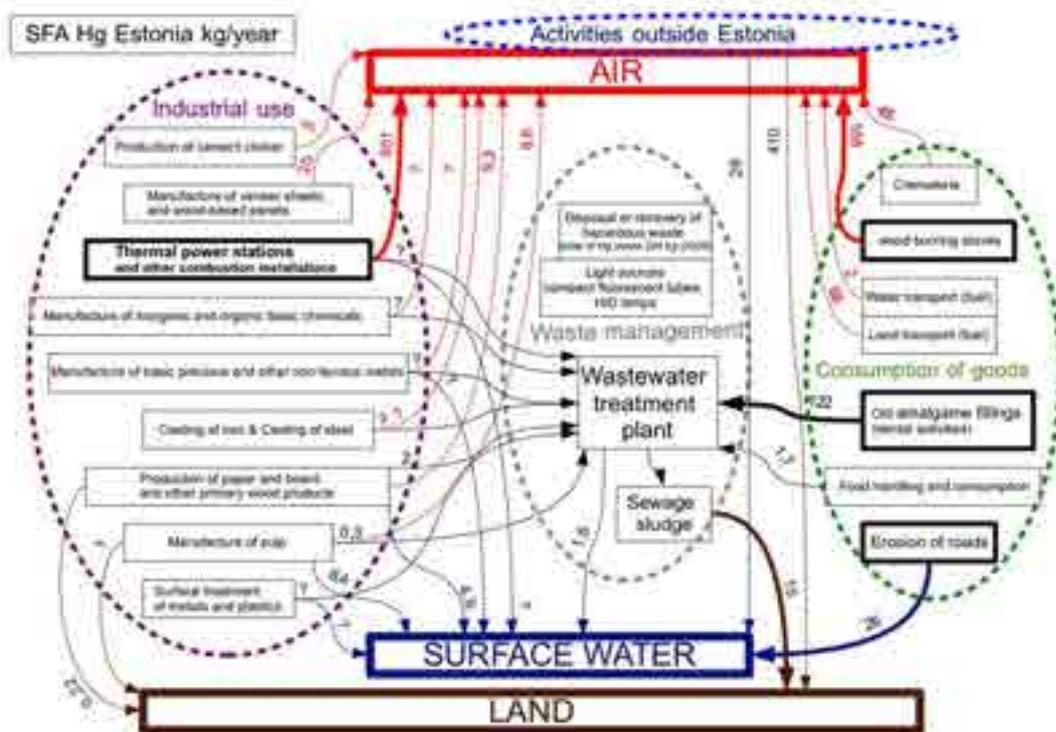


Figure 17. SFA diagram for Hg in Estonia.

Due to global efforts to decrease the mercury uses and emissions, a future scenario is that these should be lower. Dental use of Hg amalgam fillings is decreasing, as is the content of Mercury in consumer products, which will affect the concentration in wastewater. Emissions to air by point sources, especially power plants, will be decreased, which will also affect atmospheric deposition.

It is quite clear that wastewater treatment plants are an important secondary source of Hg, which means that monitoring the effluents and sludge and restricting the use of sludge is an important step that helps to reduce the amount of Hg circling in the environment. Innovative technologies that help to increase the efficiency of removing hazardous substances could also be used.

4.11 Cadmium

In E-PRTR, four facilities reported Cd releases to the register in 2008, 3 facilities releasing to air, 2 to water and 0 to soil.

The main source of Cd emissions in Estonia is definitely the thermal power stations and other

combustion installations that altogether give emissions of 597 kg to air, 22 kg to soil and 560 kg to surface water, making this source the biggest emitter to air and surface water.

Great emissions to air also come from the production of cement clinker that emits 34 kg of Cd to air. It should be kept in mind that most of the emissions to air are not quantified; however, it is safe to say that the thermal power stations and other combustion installations are the main source.

The sources to wastewater are probably diffuse and mainly not quantified. According to available data, the biggest source is car washing and degreasing that emits 13,4 kg to WW, but this is unlikely to be the most important source altogether as several sources can be expected to be of the same order of magnitude.

The main source of Cd to soil originates from sludge from the WWTPs (50 kg a year) as Cd is a heavy metal and tends to settle in the sludge. A range of 1 to 98 kg Cd a year goes from wastewater treatment plants to surface water.

Besides those sources, atmospheric deposition is also a significant source, giving 2359 kg a year to soil and 150 kg to surface water.

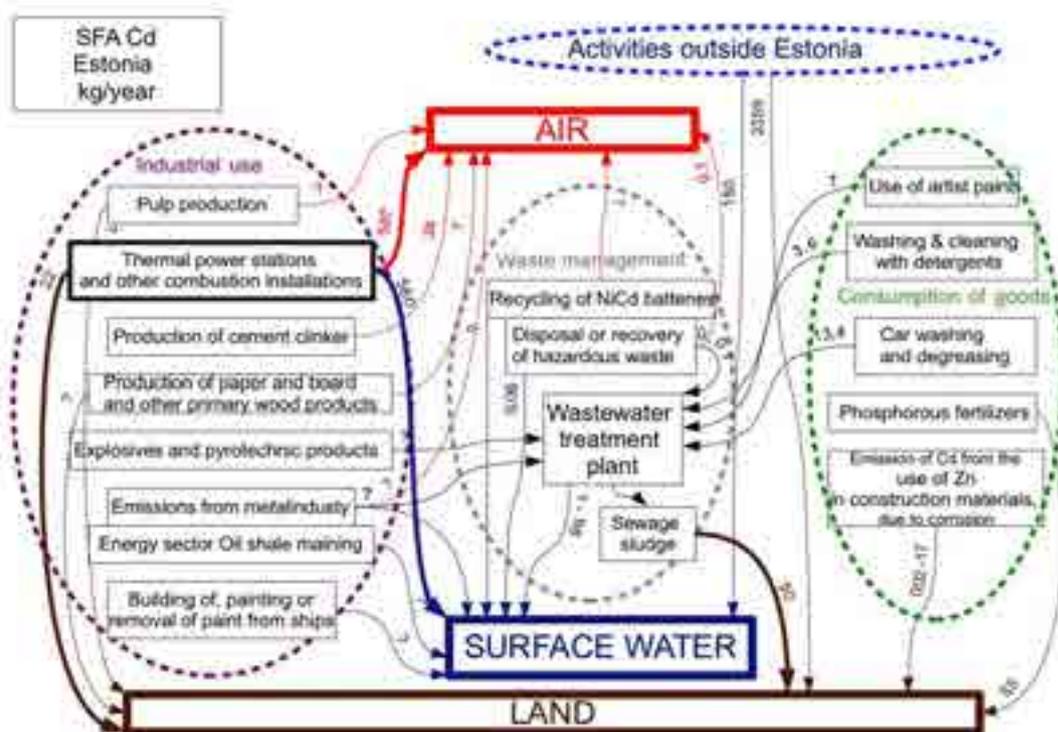


Figure 18. SFA diagram for Cd in Estonia.

Decreasing emissions to air (worldwide) would be an important measure as atmospheric deposition is such an important source of Cd. When it comes to point sources, such as thermal power stations, better treatment, BAT, more monitoring and regulations should be managed.

Better treatment processes for WWTPs and regulations on sludge use are important measures to be taken as well. As with all hazardous substances, general raising of awareness is also needed to reduce the emissions from diffuse sources.

5 Summary and conclusions

5.1 Emissions to the environment

A short text commenting the results in Table 4.

Table 4. Summary of emissions to environmental matrices (kg/year).

| Substance/ substance group | Total emissions to: | | | | |
|---|------------------------------|---------------|--------------------------|-------------------------|------------|
| | FSW | CSW | FS | AS | AO |
| 1. Dioxins (PCDD), furans (PCDF) and dioxin-like polychlorinated biphenyls (PCBs) | 0,003 - 0,02 (0,25) | 0,004 - 0,03 | 1,72 - 1,73 (1,185) | 0,04 - 0,05 (2,97) | 5 - 9 |
| 2a. Tributyltin compounds (TBT). | 0,1 - 17 | 0,05 - 7 | 0,2 - 50 | 0,07 - 21 | 1 - 95 |
| 2b. Triphenyltin compounds (TPhT) | 0 | 0 | 0 | 0 | 0 |
| 3a. Pentabromodiphenyl ether (pentaBDE) | 0,02 - 0,03 (0,02 - 21) | 0,003 - 0,009 | 0,44 (0,2 - 226) | 0,2 (0,008 - 106) | 1,4 - 14,9 |
| 3b. Octabromodiphenyl ether (octaBDE) | was not estimated separately | | | | |
| 3c. Decabromodiphenyl ether (decaBDE) | 0,04 - 0,05 (1 - 49) | 0,002 | 18 (2 - 518) | 8 (0,7 - 243) | 0,002 - 26 |
| 4a. Perfluorooctane sulfonate (PFOS) | 0,2 - 4 (8) | 0,03 - 2 | 0,1 - 13 (86) | 0,03 - 6 (40) | ? |
| 4b. Perfluorooctanoic acid (PFOA) | 0,3 - 1 (8) | 0,2 | 0,5 (81) | 0,006 (38) | ? |
| 5. Hexabromocyclododecane (HBCDD) | 8 - 9 (0,01 - 13) | 0,04 - 0,06 | 1 - 2 (0,1 - 137) | 0,55 - 1 (0,04 - 64) | 8 - 9 |
| 6a. Nonylphenols (NP). | 7 - 52 (0,2) | 3 - 5 | 128 - 247 (2) | 51 - 111 (1) | ? |
| 6b. Nonylphenol ethoxylates (NPE) | 214 - 577 (in NP) | 90 - 211 | 661 - 1663 (in NP) | 284 - 720 (in NP) | ? |
| 7a. Octylphenols (OP) | 43 - 180 (?) | 0,7 - 23 | 43 - 279 (?) | 2 - 66 (?) | ? |
| 7b. Octylphenol ethoxylates (OPE) | 0,4 - 1995 | 0,1 - 855 | 40 - 6025 | 0,1 - 2671 | ? |
| 8a. Short-chain chlorinated paraffins (SCCP) | 90 - 161 (6 - 263) | 9 - 24 | 174 - 373 (95 - 4015) | 39 - 86 (45 - 1882) | |
| 8b. Medium-chain chlorinated paraffins (MCCP) | 884 - 1088 | 16 - 18 | 2495 - 2661 | 119 - 194 | 170 |
| 9. Endosulfan | 0 (0,05 - 2) | 0 | 0,04 (0,5 - 19) | 0,02 (0,2 - 9) | 0 |
| 10. Mercury | 39 - 61 (26) | 6,4 - 10 | 16 - 82 (279) | 28 (131) | 785 |
| 11. Cadmium | 4 - 658 (150) | 29 - 50 | 107 (1607) | 5 - 10 (752) | 631 |

FSW: Fresh surface water (inland surface water)
CSW: Coastal surface water
AS: Agricultural soil
FS: Forest soil
AO: Air outdoor

It should be kept in mind, however, that only quantitatively estimated emission strings are considered in this summary table.

There were greatest quantitative pollution loads from MCCP, SCCP, NPE, and OPE. There are little quantitative loads for PFPS, PCDD, and HBCDD. However, by no means should it be considered as having little or no environmental hazard. Those substances are very toxic and seriously hazardous to organisms in very little concentrations. It can be said with confidence, however, that triphenyltin and endosulfan are not relevant for Estonia.

Loads that were designated for WW compartment at the beginning were later divided to final compartments. We assumed that there are two kinds of substances: ones that end up in sludge and others that tend to leave WWTPs without any significant decrease in concentrations. The substances that settle to sludge were designated to have a load of 25% to effluents, which was divided to 1/3 of CSW and 2/3 of FSW as usual. The substances that were consider not settling to sludge very significantly the division was the other way round, i.e. 75% of the load going to effluents and 25% to sludge.

5.2 Indoor air

Some of the hazardous substances are emitted to indoor during the service life of products that contain them, e.g. electronic appliances (TV, PC-sets etc.). Such substances are, for example, pBDEs and SCCPs. The impact is direct and the concentrations of hazardous substances can be much higher in small rooms than outdoors. If health risks are to be considered, emissions of hazardous substances from these products must be reduced significantly and health monitoring should be conducted. Those aspects must also be considered in the work safety programs.

5.3 Transfer to waste and sewerage

Hazardous substances contained in consumer products often end up in WWTPs. Calculating these loads is not an easy task, neither is an easy task controlling these diffuse sources. At the same time, the waste water treatment and waste management systems are a good point where effective measures could be taken to reduce the amounts of hazardous substances entering the environment again. In case of wastes, a long detention time should be noted. This means that some loads can become evident in the environmental samples in 10, 20 or even 100 years.

5.4 Conclusions

The COHIBA project changed the way of thinking about hazardous substances in Estonia as it was virtually the first time to perform real analyses of most of the substances covered in this project. Up to now, the prevalent opinion even in official level has been that there are no problems with hazardous substances in Estonia or Estonian environment.

Use patterns and emission delays

Use and emission patterns show regional differences on industrial level but comparing the uses on every day level the patterns are the same for all the Baltic Sea countries. Diffuse sources

(including emissions during the service life of consumer articles) are increasingly important but industrial sources remain to be relevant within the region.

Bans and restrictions of substance use have effects on emissions. Long service life of articles does however lead to the build-up of stocks which causes a delay in the decrease of emissions.

Industrial sources

When gathering data about the industrial sources, we found that it was extremely difficult to find the emission factors for companies or production processes. For this reason, the results from these sources were given without specific values, and are provided only to illustrate the potential sources of hazardous substances in Estonia from industrial applications.

The main activities that involve hazardous substances in industrial applications are related to chemical industry, plastic production (polyurethane foam), construction materials like sealants, insulation boards (EPS, HIPS), paints, etc. Electronic equipment production is also a large potential user of hazardous substances in Estonia.

Substance-based conclusions

pBDEs, HBCDD, PFOS, PFOA, NP, NPE, OP, OPE, TBT are widely used in various products and therefore discarded and found in waste. The biggest impact on Estonian environment comes from diffuse sources. Although industrial use also occurs in Estonia, verifying of the exact sphere is difficult due to the lack of monitoring and production data.

MCCPs have the greatest impact on the Estonian environment according to current data in our study. Medium-chain chlorinated paraffin has an important authorized industrial use in Estonia. MCCPs are used industrially in polyurethane foams and the Estonian production of such montage foams comprises one third of the global market. The calculated loads from private consumption and waste handling are also high. As the group is very large, different trade names and CAS numbers are used, therefore the real extent and impact is difficult to estimate and a certain group of substances was studied in the paper.

NP, NPE, OP and OPE also have a big impact on the Estonian environment according to current data. This is a logical outcome, as the use of phenols has been only recently restricted. TBT is historically a substantial source of pollution in Estonia, but several current insufficiently controlled possible sources of TBT appeared during our study. There is no direct industrial use of both penta- and decaBDE; there is some indirect industrial production and waste handling that should be investigated in more detail in future, as there may be more possible uses and sources. PFOS and PFOA result from both industrial and domestic consumption. The amounts are small but there are limited available and reliable data. Therefore, there may be possible sources in many enterprises in the electronics industry, which could influence the total loads.

The most relevant source of dioxins in Estonia is combustion – the industrial and energy sector that is decreasing and is being controlled using the best available techniques and filters at the point sources. Diffuse sources such as households, transport and products etc. are having an increasing impact. Heavy metals as pollution sources are still relevant. Although the number of unknown heavy metal sources is not very great and is decreasing due to a better monitoring program, a better control

program and cessation of emissions is still needed.

Atmospheric deposition

Long-range atmospheric transport is an important pathway into the region for several of the substances and it is also relevant for many substances in Estonia.

Atmospheric deposition is an important source of PFOS, PFOA, HBCDD, and pentaBDE in Estonia. Also, the only detected relevant source for endosulfan in Estonia is from atmospheric deposition. Heavy metals cadmium and mercury also have big deposition loads to Estonia. Atmospheric deposition is a source that cannot be reduced nationally but cooperation in international level can have effective results.

The loads from atmospheric deposition were greatly during the project because of updated monitoring data from Sweden. The old emission factors were about 10 years old and the situation with many substances has changed dramatically due to new international bans and regulatory measures. However, not all the HELCOM priority substances were monitored and there are new monitoring programs for those substances in only a few countries. The loads from atmospheric deposition can be both under- and overestimated and more studies are definitely needed in the future.

Raising awareness

The work with identification of the major sources and flows of the BSAP substances has led to an increased awareness of the importance and complexity of source tracking in the region. The next step should be seminars and trainings on different levels, so that the information could reach as many target groups as possible. At the moment, the main target group should be environmental specialists, but spreading the information among general public should not be underestimated.

Monitoring and future studies

The COHIBA project has detected that there is a need for measured data both with regards to environmental levels and emission factors. There are high uncertainties because of data gaps and the results from measured data would help to achieve better environmental status for more case studies (substance-based inventories) in the future.

Databases and registers

There is a need for chemical product registers and emission registers covering the BSAP substances in Estonia. Also, the pollutant based registers should be overlooked and the missing data should be corrected in the future. National databases are also needed for many cases, not only the centralized registers. With local scale registers the flexibility for changing needs is more easily accomplished. The registers should cover all the flows in substance life cycle.

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Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC”, OJ L 396, p p. 1–849.

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ANNEX A - Substance flow analysis of dioxins (PCDD), furans (PCDF) and dioxin-like PCB-s for Estonia.

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This study was carried out under the COHIBA study from May 2010 to May 2011. This report is based on the SFA “Dioxins, Furans, dioxin like PCB, Europe” by Institute for Ecology of Industrial Areas. The results are for Estonia. Many of the results are rough approximations that cannot be taken as exact results for Estonia, but more as a base to plan future studies. The results are for Estonia.

1 Introduction

Dioxins and dioxin-like PCBs are substances that belong to POPs (persistent organic pollutants). All of these substances have similar toxicity (EMEP, 2002). These substances are not produced, but are rather by-products of human activities such as industrial processes, fossil fuel combustion or waste destruction (Guerzoni et al., 2004).

Dioxins are a class of structurally and chemically related polyhalogenated aromatic hydrocarbons which mainly includes polychlorinated dibenzo-p-dioxins (PCDDs or dioxins), dibenzofurans (PCDFs or furans) and the “dioxin-like” biphenyls (PCBs). They constitute a group of persistent environmental chemicals and usually occur as congeners.

TEQ values are calculated with Toxicity Equivalency factors (TEFs). Below is the scheme according to calculate of TEQ:

$$\text{TEQ} = \sum [\text{PCDD}_i] \times \text{TEF}_i + \sum [\text{PCDF}_i] \times \text{TEF}_i + \sum [\text{PCB}_i] \times \text{TEF}_i + \dots$$

TEQ – toxicity equivalent 2,3,7,8 - TCDD

[PCDD_i], [PCDF_i] i [PCB_i] – concentration of i congener PCDD, PCDF i PCB

TEF_i – indicator of congener toxicity PCDD, PCDF i PCB according to 2,3,7,8-TCDD (Toxic Equivalent Factor). These values are shown in Table 1 and Table 2.





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Table 1. Differences in TEF values for PCDD/Fs.

| Congener | I-TEF ¹⁾ | WHO 1997-TEF ²⁾ | WHO 2005-TEF ³⁾ |
|---|---------------------|----------------------------|----------------------------|
| Polychlorinated dibenzo-p-dioxins (PCDD) | | | |
| 2,3,7,8-TCDD | 1.0 | 1.0 | 1.0 |
| 1,2,3,7,8-PeCDD | 0.5 | 1.0 | 1.0 |
| 1,2,3,6,7,8-HxCDD | 0.1 | 0.1 | 0.1 |
| 1,2,3,7,8,9-HxCDD | 0.1 | 0.1 | 0.1 |
| 1,2,3,4,7,8-HxCDD | 0.1 | 0.1 | 0.1 |
| 1,2,3,4,6,7,8-HpCDD | 0.01 | 0.01 | 0.01 |
| 1,2,3,4,6,7,8,9-OCDD | 0.001 | 0.0001 | 0.0003 |
| Polychlorinated dibenzo furans (PCDF) | | | |
| 2,3,7,8-TCDF | 0.1 | 0.1 | 0.1 |
| 1,2,3,7,8-PeCDF | 0.05 | 0.05 | 0.03 |
| 2,3,4,7,8-PeCDF | 0.5 | 0.5 | 0.5 |
| 1,2,3,6,7,8-HxCDF | 0.1 | 0.1 | 0.1 |
| 1,2,3,7,8,9-HxCDF | 0.1 | 0.1 | 0.1 |
| 1,2,3,4,7,8-HxCDF | 0.1 | 0.1 | 0.1 |
| 2,3,4,6,7,8-HxCDF | 0.1 | 0.1 | 0.1 |
| 1,2,3,4,6,7,8-HpCDF | 0.01 | 0.01 | 0.01 |
| 1,2,3,4,7,8,9-HpCDF | 0.01 | 0.01 | 0.01 |
| 1,2,3,4,6,7,8,9-OCDF | 0.001 | 0.0001 | 0.0003 |

1) I-TEF: NATO/CCMS (1992). Scientific basis for the development of the International Toxicity Equivalency Factor (I-TEF) Method of risk assessment for complex mixtures of dioxin and related compounds. Report No. 170, Dec.

2) WHO 1997-TEF: Van den Berg et al., (1998) Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for Humans and for Wildlife. Environmental Health Perspectives, 105(12): 775

3) WHO 2005-TEF: Van den Berg et al. Toxicological Sciences Advance Access, 7 July 2006



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Table 2. Differences in TEF values for dioxin like PCBs.

| Congener | WHO 1997-TEF [®] | WHO 2005-TEF [®] |
|---------------------------------|---------------------------|---------------------------|
| Non ortho-PCB | | |
| 3,3',4,4'-TetraCB (#77) | 0,0001 | 0,0001 |
| 3,4,4',5-TetraCB (#81) | 0,0001 | 0,0003 |
| 3,3',4,4',5-PentaCB (#126) | 0,1 | 0,1 |
| 3,3',4,4',5,5'-PentaCB (#169) | 0,01 | 0,03 |
| Mono-ortho PCB | | |
| 2,3,3',4,4'-PentaCB (#105) | 0,0001 | 0,00003 |
| 2,3,4,4',5-PentaCB (#114) | 0,0005 | 0,00003 |
| 2,3,4,4',5-PentaCB (#118) | 0,0001 | 0,00003 |
| 2',3,4,4',5-PentaCB (#123) | 0,0001 | 0,00003 |
| 2,3,3',4,4',5-HexaCB (#156) | 0,0005 | 0,00003 |
| 2,3,3',4,4',5-HexaCB (#157) | 0,0005 | 0,00003 |
| 2,3',4,4',5,5'-HexaCB (#167) | 0,00001 | 0,00003 |
| 2,3,3',4,4',5,5'-HeptaCB (#189) | 0,0001 | 0,00003 |
| Di-ortho PCB | | |
| 2,2',3,3',4,4',5-HeptaCB (#170) | - | - |
| 2,2',3,4,4',5,5'-HeptaCB (#180) | - | - |

In this report the values are measured in toxic equivalent values (TEQ). This unit is used as a means of normalizing the toxicity in series of compounds relative to single compound. Dioxin results are reported with TEQs where 2,3,7,8-TCDD is assigned as TEQ of one and the other dioxin isomers and coplanar PCBs are reported as their toxicity relative to 2,3,7,8-TCDD. A TEQ report calculates the concentration of 2,3,7,8-TCDD that would have the same toxicity as the total mixture of analytes found present. TEQ is a calculated value and it can be used for measuring all of 17 congeners of PCDD/F and dioxin-like PCBs with any method.

There are three types of international toxic equivalents: International TEQ (I-TEQ), 1997-WHO-TEQ, 2005-WHO TEQ and toxic equivalent used for Nordic scheme (N-TEQ). All congeners of dioxin-like PCBs are measured in WHO-TEQ (both 1997 and 2005). The situation with dioxins is more complicated, because both I-TEQ and WHO-TEQ are measured. But due to Toolkit and EMEP Report there are no big differences between TEQs for PCDD/Fs, so due to this information in this report they are all marked as TEQs.



1.1 Physical chemical properties

Only 7 of the 75 possible PCDD congeners, and 10 of the 135 possible PCDF congeners, especially those with chlorine substitution in the 2,3,7,8 positions, are toxicologically important. Likewise there are 209 possible congeners of PCBs, only 12 of them have dioxin-like toxicity. These dioxin-like PCB congeners have four or more chlorine atoms and are sometimes referred to as coplanar PCBs, since their rings can rotate into the same plane. Figure 1 presents the basic structural formula of PCDDs, PCDFs, and PCBs together with the numbering convention at the positions on benzene rings where chlorine or other halogen atoms can be substituted.

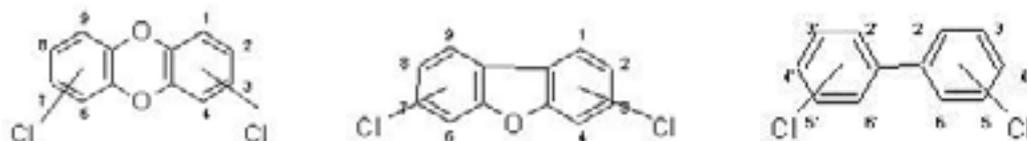


Figure 1. The skeletal formula and substituent numbering scheme of PCDDs, PCDFs and PCBs.

The physio-chemical properties of PCDDs and PCDFs explain the behaviour of these compounds in the environment (Table 3). PCDDs as well as PCDFs have relatively low vapour pressures and high octanol/water partition coefficient (K_{OW}) values which mean they are not very mobile in the environment, and show the tendency of sorption onto soil and sediments. The high K_{OW} values also mean that PCDDs/PCDFs will move easily into the fatty tissues of grazing animals, cows, sheep and fish, who incidentally ingest them in the soil adhering to grass or water and sea sediments. PCDDs/PCDFs bioaccumulate and biomagnify in animal and fish fat.

Because dioxins and furans persist in the body for years, recent significant reductions in dioxins/furans emission into the air are unlikely to reduce overall human health and environmental risks in the near term. Limited exposure might result from breathing air containing trace amounts of dioxins/furans, incidental ingestion of soil containing dioxins/furans, and from absorbing minute levels of dioxins/furans presents in the soil through the skin during field works.



Table 3. Basic of physico-chemical properties for dioxins and furans.

| No | Compound | Melting point [°C] | Solubility in water at 25°C [mg L ⁻¹] | Vapour pressures at 25 °C [Pa] | Henry constants [atm m ³ mol ⁻¹] | log K _{ow} |
|----|----------------------|--------------------|---|--------------------------------|---|---------------------|
| 1 | 2,3,7,8-TCDD | 305 | 1,93 x 10 ⁻⁵ | 2,0 x 10 ⁻⁷ | 3,29 x 10 ⁻⁵ | 7,02 |
| 2 | 1,2,3,7,8- PeCDD | 240 | 1,20 x 10 ⁻⁴ | 5,9 x 10 ⁻⁸ | 2,60 x 10 ⁻⁶ | 7,50 |
| 3 | 1,2,3,4,7,8-HxCDD | 274 | 4,42 x 10 ⁻⁹ | 5,1 x 10 ⁻⁹ | 1,07 x 10 ⁻⁵ | 7,80 |
| 4 | 1,2,3,6,7,8-HxCDD | 285 | 4,40 x 10 ⁻⁶ | 4,8 x 10 ⁻⁹ | 1,10 x 10 ⁻⁵ | 7,80 |
| 5 | 1,2,3,7,8,9-HxCDD | 243 | 4,40 x 10 ⁻⁶ | 6,5 x 10 ⁻⁹ | 1,10 x 10 ⁻³ | 7,80 |
| 6 | 1,2,3,4,6,7,8 -HpCDD | 264 | 2,40 x 10 ⁻⁶ | 2,4 x 10 ⁻⁶ | 2,26 x 10 ⁻³ | 8,20 |
| 7 | OCDD | 325 | 7,40 x 10 ⁻⁶ | 1,1 x 10 ⁻¹⁰ | 6,75 x 10 ⁻⁶ | 8,60 |
| 8 | 2,3,7,8-TCDF | 227 | 4,19 x 10 ⁻⁴ | 2,0 x 10 ⁻⁶ | 1,44 x 10 ⁻⁵ | 6,50 |
| 9 | 1,2,3,7,8- PeCDF | 226 | 2,40 x 10 ⁻⁴ | 2,3 x 10 ⁻⁷ | 5,00 x 10 ⁻⁶ | 7,00 |
| 10 | 2,3,4,7,8 -PeCDF | 196 | 2,36 x 10 ⁻⁴ | 3,5 x 10 ⁻⁷ | 4,98 x 10 ⁻⁶ | 7,00 |
| 11 | 1,2,3,4,7,8-HxCDF | 226 | 8,25 x 10 ⁻⁶ | 3,2 x 10 ⁻⁸ | 1,43 x 10 ⁻⁵ | 7,50 |
| 12 | 1,2,3,6,7,8-HxCDF | 233 | 1,77 x 10 ⁻⁵ | 2,9 x 10 ⁻⁸ | 7,31 x 10 ⁻⁶ | 7,50 |
| 13 | 1,2,3,7,8,9-HxCDF | 248 | 1,30 x 10 ⁻⁶ | 2,7 x 10 ⁻⁸ | 1,10 x 10 ⁻⁵ | 7,50 |
| 14 | 2,3,4,6,7,8- HxCDF | 239 | 1,30 x 10 ⁻⁶ | 2,7 x 10 ⁻⁸ | 1,10 x 10 ⁻⁵ | 7,50 |
| 15 | 1,2,3,4,6,7,8 -HpCDF | 236 | 1,35 x 10 ⁻⁶ | 4,7 x 10 ⁻⁸ | 1,41 x 10 ⁻⁵ | 8,00 |
| 16 | 1,2,3,4,7,8,9-HpCDF | 222 | 1,40 x 10 ⁻⁶ | 1,4 x 10 ⁻⁸ | 1,40 x 10 ⁻⁵ | 8,00 |
| 17 | OCDF | 259 | 1,16 x 10 ⁻⁶ | 5,0 x 10 ⁻¹⁰ | 1,88 x 10 ⁻⁶ | 8,80 |

The most toxic dioxin congener for fish is 2,3,7,8-TCDD/F and most of the total toxicity comes from this congener. In southern Gotland it may come up even to 80%. Another congener found very often is 2,3,4,7,8-PeCDF. In herrings it sometimes constitutes more than TCDF, approximately 50% of total toxicity. On the other hand the most toxic congener of PCBs is PCB 126. In all samples but herring it constitutes more than 60% of total TEQ. In contrast to dioxins there were no big differences between herring from Baltic and North Sea. The only difference was WHO-dl-PCB profile. PCB 118 had a large share in profile of WHO-PCB toxicity (Karl, Ruoff 2007).

1.2 Production

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are of no commercial value and are not intentionally produced, but are the by-products in other chlorinated chemicals production, such as chlorinated wood preservatives and herbicides, and chlorine bleaching of wood pulp for paper. PCDDs/PCDFs are also produced by combustion (wastes, fossil fuels wood) and metal smelting. They may also





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be formed from natural sources such as forest fires.

1.3 Regulatory status

There are no special regulations considering those substances in Estonia. Estonian legislation follows the European legislation and international agreements.

The environmental law concerning dioxins, furans and polychlorinated biphenyls is covered by international law and European Community law. The Stockholm Convention on Persistent Organic Pollutants (POPs) is a primary global treaty setting the goals for Persistent Organic Pollutants (POPs) to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically and accumulate in the fatty tissue of humans and wildlife. It defines Persistent Organic Pollutants (POPs) sources and present best available techniques and best environmental practices of efficient prevention.

According to the Commission Decision of the 17th of July 2000 on the implementation of a European pollutant emission register (EPER), Article 15 of the Council Directive No 96/61/EC concerning integrated pollution prevention and control (IPPC), the EU member states are required to establish a database on emissions to water and air of 50 key pollutants from large and medium-sized industrial point sources in the European Union. The register (Pollutant Release and Transfer Register E-PRTR) is hosted by the European Environment Agency.

PCDDs/PCDFs and PCBs are also subject to two Helsinki Commission's Recommendations, No 28 E/8 adopted on the 15th of November 2007 "Environmentally friendly practices for the reduction and prevention of emissions of dioxins and other hazardous substances from small-scale combustion", and Recommendation No 27/1 adopted on 8th of March 2006 "Limitation of emissions into atmosphere and discharges into water from incineration of waste".

The aim of the first recommendation (no 28 E/8) is to prevent and eliminate pollution of the marine environment by application of Environmentally Friendly Practices for the use of small-scale combustion appliances with a view to limiting emissions of dioxins and other dioxin-like compounds. Recommendations mentioned in this document are:

- Ensure the introduction of the use of an increasing number of low-emission combustion appliances.
- Promotion of environmentally sound combustion appliances for small-scale combustion installations.





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- Suppliers should be made aware of environmentally sound practices for combustion appliances below 50 kW and should be involved in the promotion of Best Environmental Practises (BEP) for households.
- At enterprises, annual internal inspections (by the operator) and regular instructions on the proper use of the technical equipment by authorised experts (e.g. professional chimney sweepers) should be recommended or made mandatory.

Recommendation No 27/1 suggests the application of Best Environmental Practice (BEP) and Best Available Technology (BAT) to waste minimisation, handling and incineration which is efficient in removal of acids, organics and organohalogens, e.g. dioxins, from the flue gases. Dry or semi-dry lime systems as well as wet systems are recommended.

Specific recommendations mentioned here are the following:

- Atmospheric emissions from waste incineration should not exceed the following levels at 11% O₂ (ndg): Dioxins and furans 0.1 ng TEQ m⁻³
- Discharges of waste water from cleaning of exhaust gases should not exceed the following levels (24 h samples): Dioxins and furans – 0.3 ng L⁻¹ The European Union is adopting a strategy to limit the presence of dioxins, furans and polychlorinated biphenyls (PCBs) in the environment to protect human and animal health and the environment. The strategy also establishes a quantitative objective, namely to reduce the human intake levels of these substances to below a certain threshold. Objectives of the strategy are:
 - o To assess the current state of the environment and of the ecosystem,
 - o To reduce human exposure to these substances in the short-term and to maintain human exposure at safe levels in the medium to long term,
 - o To reduce the impact on the environment.

The major European instrument for release control from industrial sources including provisions for POPs has been established with the IPPC Directive 2008/1/EC which contains effective provisions both for release reduction (via the obligation to apply Best Available Technique) and improved knowledge (via the obligation to report on releases). The IPPC Directive provides an integrated approach to establish pollution prevention from stationary "installations", as listed in the Directive, for a wide range of polluting activities.

A legal instrument specifically addressing emissions of PCDDs/PCDFs, PCBs and other POPs is the Waste Incineration Directive 2000/76/EC issued on 4 of December 2000 and setting strict limit values for PCDD/PCDF emissions and establishing obligation to





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monitor in flue gas and waste water for waste incineration and co-incineration facilities.

Requirements on PCDDs/PCDFs and PCBs are included in the following waste legislation acts:

- Directive No 2006/12/EC of the European Parliament and of the Council of 5 April 2006 on waste (modified version of Directive 75/442/EEC),
- Council Directive No 91/689/EEC of 12 December 1991 on hazardous waste, as amended,
- Decision No 2000/532/EC establishing a list of wastes, as amended,
- Regulation (EC) No 1013/2006 of the European Parliament and of the Council of 14 June 2006 on shipments of waste.

The purpose of PCB Directive No 96/59/EC is to approximate the laws of the Member States on the controlled elimination of polychlorinated biphenyls and terphenyls (PCB/PCT). The Member States must take necessary measures concerning controlled disposal of PCBs, the decontamination or disposal of equipment containing PCBs and the disposal of used PCBs in order to eliminate them completely.

The objective of Regulation (EC) No 850/2004 of The European Parliament and of the Council of 29 April 2004 on persistent organic pollutants and amending Directive No 79/117/EEC is to protect human health and the environment from persistent organic pollutants. This document sets limit values for POP content in waste, specific requirements for disposal of POP waste and obligation to conduct release inventories.

Intermediate target levels/maximum allowable concentrations of dioxins & dioxin-like PCBs in fish muscle meant for human consumption are regulated by EC 1881/2006 as follows: dioxins (WHO-PCDD/F-TEQ) $4 \cdot 10^{-3}$, Dioxins and dioxin-like PCBs (WHO-PCDD/F-PCB-TEQ) $8 \cdot 10^{-3}$ ($12 \cdot 10^{-3}$ in eel *Anquilla anquilla*).

1.4 Use

Dioxins have no particular uses. Dioxins are produced intentionally only for laboratory purposes (for e.g. in Germany and Switzerland). They come in the products as impurities of substances used intentionally.

1.5 Environmental fate

Dioxins and furans are substances that easily distribute between environmental





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compartments. The distance of dioxin transport depends on factors connected with height of release, temperature, or particle size (EC, 1999). The distribution of PCDD/Fs between different environmental media (the atmosphere, soil, vegetation and seawater) was estimated for 2003 (Gusev et al., 2005) using the MSCE-POP model EMEP inventory data and monitoring data from 12 monitoring stations. 96% of PCDD in the environment originates from air deposition and is then deposited to plants, soil and water.

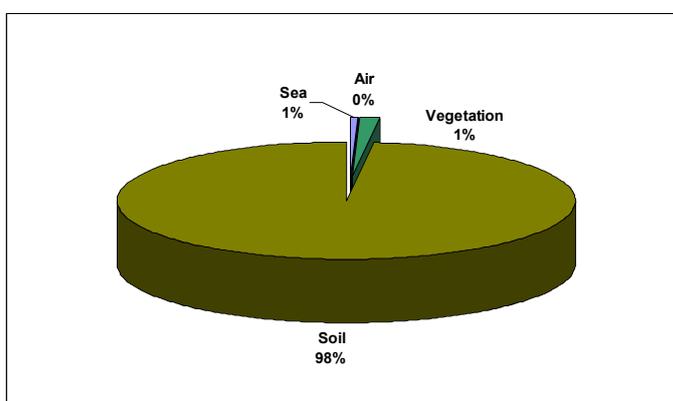


Figure 2. Distribution of PCDD/Fs among main environmental compartments (Gusev, et. al, 2005).

1.5.1 Soil

Dioxins are widely distributed among soils and sediments. The highest levels of them are found in urban areas.



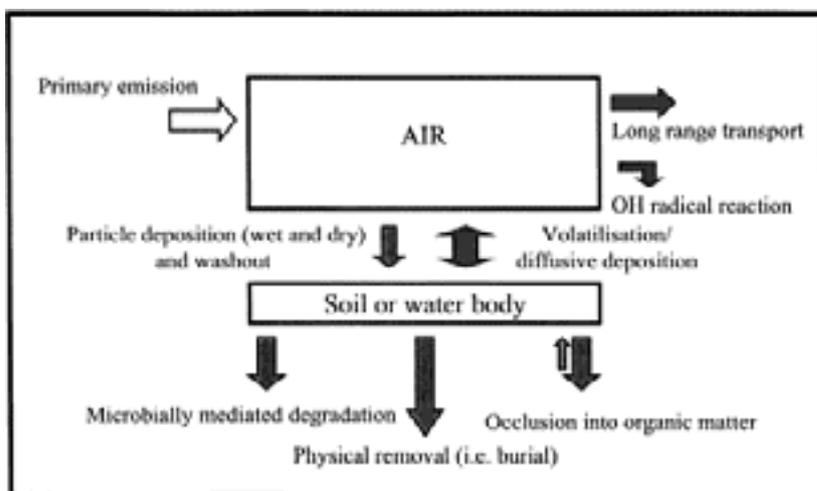


Figure 3. Conceptual representation of the fate processes that effect ambient concentrations and PCDD/Fs in the environment (Alcock et al., 2001).

1.5.2 Air

Air deposition plays a big role in transport of PCDD/Fs and PCBs. These substances are emitted into the air during combustion of such components as solid fuel, biomass, wastes or ashes. In installations with flue gas treatment dioxins and PCB are removed from the gas and accumulated in filter ashes and scrubbing water. Today, the main release pathway of air (smoke) and ashes is domestic combustion and open burning. PCDD/Fs emitted from domestic sources are released close to the ground and the impact is local. Less than 1% of PCDD/F emitted from domestic sources was detected in the gas phase (BiPRO, 2009). The emitted majority is absorbed on dust particles.

TEQs from emission of PCDD/Fs during atmospheric modelling are related to specific mixture (profile) in the air. Concentrations in the air during long range transport are influenced by primary and secondary inputs, losses (deposition, reactions) and mixing/dilution (like advection, turbulence). Particles of PCDD/Fs in the air are distributed with different speed. The quickest weathering processes come in di-CDD/Fs during two days period of time. The longest time is 7 days for hexa-CDD/Fs. The air masses with different congeners are mixing. It is even possible that UK air will have influence on the amount of congeners of PCDD/Fs on the continent (Alcock et al., 2001). The half life of dioxins in the air seems to be 10 times smaller than in water (Sinkkonen, Paasivirta, 2000). From 1980s the emission to the air started decreasing and lowered 5





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times. The emission sources are not fully known, but seem to be from South-Western and Southern Europe. Long range transport causes spread of these substances in EU area and contamination of soil and water.

Soil may be treated as a natural sink and it accumulates dioxins. The persistent and lipophilic substances like dioxins get to soil with such pathways as atmospheric dry and wet deposition, application of sewage sludge and composts, spills or erosion from contaminated areas situated nearby. Other ways are uptake by roots, background concentration, or losses of contaminants through processes such as leaching of volatilisation. Due to this fact there are hardly any clearance factors and due to adsorption of soil organic carbon they will remain relatively immobile (Wyrzykowska et.al, 2007). The soil conditions such as pH, soil structure, characteristics and water content affect distribution and mobility of contaminants. The contaminants may be removed from soil during leaching process (Meneses, 2004). According to model estimates, over 95% of PCDD/Fs residing in the environment will partition to soil (including forest litter as the upper soil layer). The contamination of soil is a very slow process. The emission in the soil started to decrease in 1990, whilst in the air and water this process begun 10 years earlier.

Due to the significant persistence of PCDD/Fs in soil (following the adopted half-life in soil of about 60 years) the pollutant mainly accumulates in this media. In 1960s and 1970s the most important source of dioxins in soil might have been pesticides containing dioxins. Today, the main route of PCDD/Fs load into the soil is wet and dry deposition from the atmosphere. In agricultural soils the source of dioxin may be also sewage sludge. The decrease of contamination in soil takes several decades. Dioxins in the soil gradually degrade into less toxic components. Such residues as fly ashes, bottom ashes and sludge may be left at the site and contaminate land or e.g. water or disposed of in a landfill or used for useful applications.

1.5.3 Water

The water of Baltic Sea is contaminated mainly through wet and dry deposition from air. PCDD/Fs enter Baltic Sea with river input and point sources along the coast. Important source is also releases from soil and river sediments. Concentrations of PCDD/Fs in seas tend to decrease similarly to emissions in the air that is five-fold from 1980 to 2000. The heavier congeners of PCDD/Fs and PCBs tend to absorb on atmospheric aerosols that increases the probability of subsequent deposition and washout with precipitation (MSC-





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E, 2005). The ultimate sink for majority of the compounds is open sea and costal sediments but there is a fraction that enters into the food chain.

Dioxins may be formed in WWTPs during chlorination of wastewater. In wastewater treatment plant if wastewater from wet scrubbers is treated and reintroduced there is no additional release with scrubber effluent of PCDD/Fs into the environment (United Nations Environment Programme, 2005). In wastewater plants the PCDD/F profile changes with vast transformation of dioxins into furans. Dioxin like PCBs remains rather intact after wastewater treatment.

1.5.4 Sediments

PCDDs accumulate quickly in the sediments as they have high affinity to organic matter. The vertical profiles in sediments show the changes in past accumulation and inputs of PCDD/Fs, although modifying factors confound. Analyses of sediments have been used for studies of trends in dioxin pollution in freshwater, estuaries and oceans (Verta et al., 2007). Dioxins disintegrate very slowly. The half-lives of dioxin congeners in the Baltic are estimated in between 20 and 275 years. In general the half-life in Baltic sediments seems to be even more than 100 years. In the case of TeCD/F the half-life is about 80 years. Data collected for PCB content in sediments show that most often half-life was 9 years. The shortest half-life in sediments was measured for PCB105 that is 4.4 years, and the longest is 18.8 years for PCB 118 and PCB 153 (Sinkkonen, Paasivirta, 2000).

The level of dioxins generally peaked in the 1970s after which a significant decrease (60%) was observed. Data on archived samples together with recent analyses show that main inputs of PCDD/Fs to the environment were in 1960s and early 1970s.

The problem connected with contamination is presented in Finnish research of sediments from river Kymijoki (Salo et al. 2008). In this area wood preservative Ky-5 was used since 1940 till 1984, which caused high levels of PCDD/Fs in the river's sediments.

1.5.5 Biota

This substance accumulates in aquatic fauna. The concentration of dioxins increases in fish up the food chain (biomagnification). PCDD/Fs tend to accumulate in fatty tissues and milk of animals (MSC-E, 2005). The differences between species may be explained by differences in feeding habits. Body size (weight) of the fish and seasonal changes are





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also important factors (Szlinder-Richter et al. 2009).

The most important source of dioxins for human is oral route. Contamination of food is caused by deposition of emission of various sources of farmland and bioaccumulation in food chain especially associated with fat (Leishout et al., 2001). The half-life of PCDD/Fs in human is 3.5-15.7 years for dioxins and 3-19.6 for furans. These values are different for TCDD that has half-life 7.1 years with the range of 2.9-26.9 years (Hensley et al., 2007).

1.6 Environmental levels

1.6.1 Air

Estonia's contribution to the total annual emission of PCDD/Fs into the Baltic Sea is the lowest among the Baltic countries. In 1990-2008 it showed a 10,5% decrease presenting 5,1 g TEQ/year in (Gusev 2010). Still, because of uncontrolled burning of oil shale in oil shale industry and power plants and lack of incineration devices attention is to be paid to monitor and control PCDD/Fs atmospheric levels. Only some non-systematic measurements of PCDD/Fs concentration in air over Estonian territory have been made. At the beginning of 2000 in the frame of the project Dioxin in Candidate Countries with financial support of the European Commission PCDD/F concentrations were measured in some samples near a potential emission source – cement industry in Kunda, northern Estonia. PCDD/Fs concentration was 0,018 ng I-TEQ/m³ giving for annual release 47 mg I-TEQ/year (Roots, Sweetman 2007).

1.6.2 Soil

Only some data is available on PCDD/Fs concentrations in soil in Estonia. In 2004 (Roots et al. 2004) 4 samples from the vicinity of Laguja landfill (south-eastern Estonia) were analysed. Samples were taken in the distance of 300 m from the landfill. The PCDD/Fs concentrations were at background level (0,64-2,33 pg I-TEQ/g dry weight). There are also some data concerning PCDD/Fs content in shale oil and fly ash. These materials are considered to potentially be major PCDD/Fs sources in Estonia (Roots 2004). Concentrations in shale oil samples for most of congeners were below the detection limits; in fly ash they were slightly higher. Dioxin emission measurements from two oil shale fired power plants, producing more than 90% of electricity consumption in Estonia gave 160-300 mg I-TEQ/year for the total estimated emission of dioxins.





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1.6.3 Fish

PCDD/Fs studies of fish in Estonia begin in 2002 and they concern mainly Baltic fish. From year 2007 the Veterinary and Food Board is responsible for regular monitoring of harmful substances in food, including fish. Monitoring programs are designed to match the Estonian and European legal requirements. The results so far show that PCDD/Fs levels are below 4 pg WHO1998 TEQ/g wet weight, the average concentration remaining about 3 pg WHO1998 TEQ/g wet weight. As Estonia has no necessary equipment for PCDD/Fs analyses, these data are ordered from other EU countries. All data presented below are upperbound concentrations.

Dependence of PCDD/Fs in fish (sprat, herring) on age, weight and gender is shown (Roots, Simm 2007; Simm et al. 2006; Pandelova et al. 2008; Roots et al. 2008). Latest data (Estonian Environmental Research Centre 2010) of 17 PCDD/Fs and 12 DL PCBs in 2009 showed that dioxins content in Baltic herring in Estonian catchments areas is as a rule lower than EU norm even for 8-years old herring from the Gulf of Finland and even for the 9-year-old herring from the Gulf of Riga. (4,0 pg/g for PCDD/F-TEQ or 8 pg/g for PCDD/F-PCB-TEQ). Like in earlier years the concentration of several congeners was below LOD. Dominant congeners in herring on weight basis were 2,3,4,7,8-PeCDF and 2,3,7,8-TCDF (39 and 38% respectively). On the toxicity basis also PCDFs prevail. Of PCBs in weight basis CB-118 and CB105 are predominate but CB-126 gives about 60% to the total toxicity Mean concentration in medium size/age herring of PCDD/F and DL PCB was 1,72 and 1,86 pg WHO1998-TEQ/g w.w. what gives for the total PCDD/Fs DL PCB content 3,58 pg WHO-TEQ/g w.w. This number coincides quite well with the earlier results for 3-4 year-old herring.

1.6.4 Other food

PCDD/Fs and DL PCB concentrations in pork in 2009 were near the LOQ. Dominating congeners of PCDD/Fs were 2,3,7,8-TCDF and 1,2,3,6,7,8-HxCDF. CB118 was the most abundant PCB congener (it formed about an half of total DL-PCBs).

In mutton concentrations of 4 congeners exceeded LOQ: 2,3,4,7,8-PeCDF; 1,2,3,4,7,8-HxCDF; 1,2,3,6,7,8-HxCDF and 1,2,3,4,6,7,8-HpCDF. Dominating CB was CB118. On concentration basis PCBs formed 99% of the sum of PCDD/Fs and DL PCBs, but contribution to total toxicity of these 2 groups was comparable. In rape oil only concentrations of 2,3,7,8-TCDF and CB77 were above LOQ.





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Table 4. Concentrations of PCDD/Fs and DL PCBs in food (2009 data).

| Concentration pg/g fat wt | | | | |
|---------------------------------------|-----------|-----------|----------|-----------|
| | Pork | Mutton | Rape oil | Butter |
| PCDD/Fs | 0,16-2,45 | 0,67-1,67 | 0,04 | 2,30-2,76 |
| DL PCBs | 46-99 | 590-595 | 1-27,3 | 457-668 |
| pg/g WHO ₁₉₉₈ TEQ/g fat wt | | | | |
| PCDD/Fs | 0-0,22 | 0,17-0,35 | 0-0,24 | 0,36-0,48 |
| DL PCBs | 0,01-0,03 | 0,47 | 0-0,02 | 0,33 |

In analysed food concentrations were considerably lower than EU norms for PCDD/Fs and DL PCBs for food (EC regulation 199/2006/EC).

1.6.5 Wastewater

In the frame of COHIBA project WP3 PCDD/Fs waste water analyses from WWTP-s located in different parts of Estonia have been performed. The results for the majority of PCDD/Fs congeners in all analysed samples were below LOQ except for 1,2,3,4,6,7,8-HpCDF- 0,13 pg/l in one sample and OCDD 0,8- 1,8 pg/l in three samples. On toxicity basis the results were below 13,2 fg WHO TEQ /l.

According to the data from the Meteorological Synthesizing Centre – East (2010), the mean annual concentrations in the main environmental compartments in Estonia are: soil 0,0005 – 0,00217 pg/TEQ/g, air 0,14 – 0,62 pg/TEQ/m³, vegetation 0,35 – 1,51 pg/TEQ/g.



2 Sources of emissions of PCDD/F in Estonia

The uncertainties in the following emission strings are given with four letters, the first letter representing uncertainty for EF, the second for EFM, the third for division into compartments and the fourth for the yearly load. Uncertainty is classified according to the principles described in “Dealing with uncertainty in substance flow analysis within the COHIBA project”, a PM describing how data uncertainty is graded in WP4 of the COHIBA project.

If the Estonian yearly loads were scaled from the EU yearly load to Estonian population, the Estonian population was considered to be 0,3% of the EU population. If the Estonian yearly loads were scaled from the EU yearly load to Estonian area, the Estonian area was considered to be 1% of the EU area. This accuracy level was considered to be enough for given study; especially considering the very high uncertainty levels in other emission strings.

The estimate of total emissions of PCDD/F in Estonia to air (distributed by the main sources) based on the EMEP monitoring data (Estonian Environment Information Centre 2010).

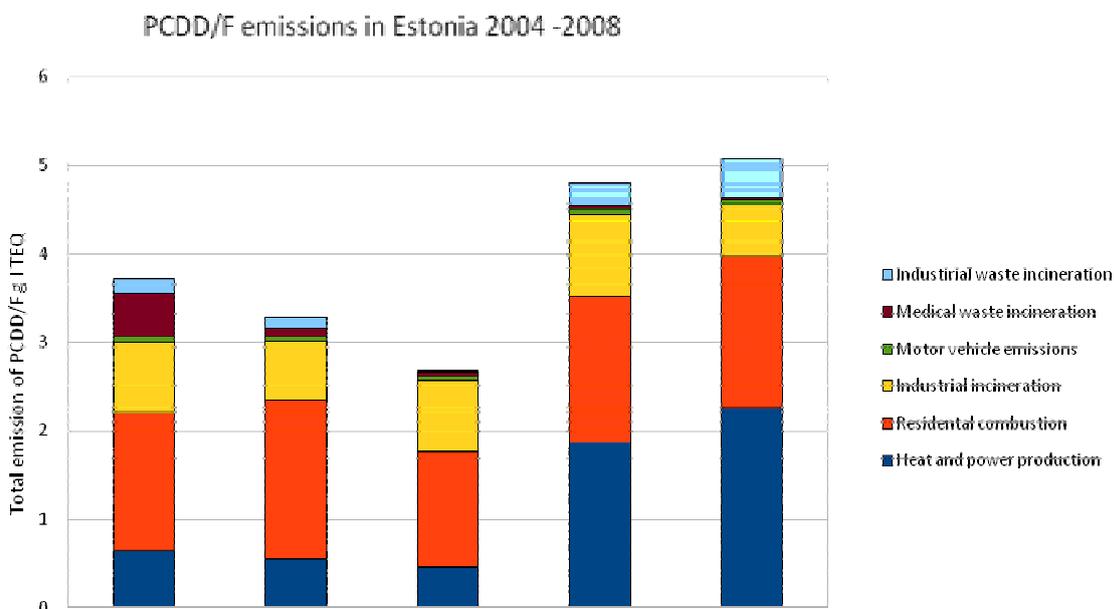


Figure 4. PCDD/F emissions in Estonia 2004 -2008.



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2.1 Solid waste incineration

NACE 38.2

Total air emission from waste incineration

Yearly load 0,43 g I TEQ/y to AO

Uncertainty: CCCC

Emissions from industrial waste incineration for 2008 (Estonian Environment Information Centre 2010).

At this time, the **municipal waste incineration** systems are under development in Estonia (Estonian Ministry of Environment 2010).

2.2 Medical waste incineration

NACE 38.2

General air emission from clinical waste incineration

Yearly load 0,026 g I TEQ/y to AO

Uncertainty: CCCC

This estimation is based on EMEP monitoring data 2008.

The PCDD/Fs formation potential in medical waste burning is generally higher than for municipal solid waste. The major release vectors of concern are air and residue (fly ash is taken into account due to the lack of data for bottom ash). Emissions from clinical waste incineration depend strongly on the applied technology.

2.3 Non Ferrous Metal

NACE 24.4

Secondary production of copper

Yearly load – 0,038 g TEQ/y to AO

Yearly load low – 0,002 g TEQ/y to AO



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Yearly load high – 0,381 g TEQ/y to AO

Uncertainty: CCCC

The EF is the European EF (UNEP 2006). The EFM is from Prodcum 2008 database: Copper and copper alloy tube/pipe fittings including couplings, elbows, sleeves, tees and joints excluding bolts and nuts used for as-sembling/fixing pipes/tubes, fittings with taps, cocks, valves. 477 t of products are produced in Estonia (PRODCOM 2008).

Secondary aluminium production, emission to the air;

Secondary aluminium production, emission to waste;

Secondary lead production, emission to the air

Yearly load - ?

According to Prodcum 2008, there are such activities in Estonia, but the data is classified and it is not possible to calculate the yearly loads.

2.4 Heat and power production

NACE 40.10

Power production from fossil fuels – general air emission

Yearly load 4,6 g I-TEQ/y to AO

Uncertainty: CCCC

According to the Estonian Informative Inventory Report 2008, this is the amount of dioxins from Public Electricity and heat production for 2008. This data is from EMEP monitoring data.

Oil shale is the main fuel used in power and heat production in Estonia. 88% of power in Estonia is produced from oil shale, 3% from the biomass, whereas the same plants actually use both fuels. Alternatively, hydro- and wind energy is produced.

Power production from biomass – air emission;

Primary power production from biomass – lowest air emission;

Yearly load - ?

Emission factor multiplier for primary power production from biomass - wood pellets and briquettes were used for 2009 to produce primary power – data from Statistics Estonia 2009.





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Power production from coal – air emission

Included in “Power production from fossil fuels – general air emission”

2.5 Chemical industry

NACE codes: 24

Emission from production of chemicals – air emission

Yearly load - ? to AO

Uncertainty: N/A

Emission from production of chemicals – water emission

Yearly load ? – to FSW

Uncertainty: N/A

PCDD/Fs are produced as impurities during the manufacture of chlorine, chlorophenols, chlorobenzenes and chlorobiphenyls. The production, use and disposal of such compounds are now banned or strictly regulated in most countries including Estonia. There are some activities taking place in Estonia under those NACE codes, according to Prodcom 2008 database, however, the data is classified and it is impossible to calculate the results.

2.6 Cement and lime

NACE 26.5

Estimation for new cement production installations

Yearly load – 0,03 g TEQ/y to AO

Yearly load high – 0,0564 g TEQ/y to AO

Uncertainty: CCCC

The yearly load high is calculated with the old installation EF as there is no data on the number of new installations in the sense of COHIBA project.

The data is from Estonian Informative Inventory Report 2010.

Emission from lime production

Yearly load – 0,004 g I TEQ to AO



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Uncertainty: CCCC

Emission from lime production for new installations

Yearly load - ? to AO

Uncertainty: N/A

Total production of cement, lime, bricks and tiles in Estonia is 978581 tons in total. 59400 tons of lime and 806100 tons of cement were produced on 2008.

2.7 Motor vehicle emissions

NACE: 60

Emissions from vehicles fuel burning

Yearly load 0,031 – 0,395 g TEQ/y to AO

Uncertainty: CCCC

Calculated from the EU yearly load using road transport mileage in Estonia for 2008 – 8780 million km/y¹ (Estonian Informative Inventory Report 2010).

Road transport is a significant source of dioxins to the atmosphere. Because of the significant differences in quality of vehicles it is difficult to clearly determine the emission factor for this source. Values of air emission factors vary between 0.00 – 507 g TEQ km⁻¹. Moreover, emissions from motor vehicles are difficult to estimate as they are highly variable according to driving conditions e.g. the steady state of long journeys vs. stopping and starting of urban driving conditions². The majority of PCDD/F emissions from gasoline-powered vehicles are attributed to vehicles running on leaded petrol, where PCDD/F generation is related to the use of halogenated scavengers. The estimated average emission factor for leaded fuel is 45 pg I-TEQ km⁻¹ compared with 1.5 pg I-TEQ km⁻¹ for unleaded petrol. The addition of a catalytic converter also has an impact on PCDD/F emissions. It should be noted that the emission factors from road transport are provided on average base for Europe. The same EF was used for calculating the Estonian yearly load from this source.

¹ Estonian Informative Inventory Report 2010

² Motor vehicle emissions are quantified using two types of monitoring technique: direct monitoring of the vehicle exhaust and studies on tunnel air. The tunnel method gives a good random sample of a large number of cars but relies on indirect measurements and can lead to overestimation of emissions due to re-suspended particulates being sampled.



2.8 Accidental Fires

NACE: 02.40

Accidental fires can be an important temporary source of PCDD/F emission to the air. The emission depends on the material burned. For example an estimated mid-range air emission factor for PVC is 500-750 $\mu\text{g I-TEQ t}^{-1}$ and for wood, 25-50 $\mu\text{g I-TEQ t}^{-1}$ of burned material. Also, other materials in the household, when burned can contribute to PCDD/F formation. Many of the wood burning studies were conducted under good combustion conditions, which would result in an overestimate compared with the relatively poor combustion conditions involved during a house fire.

The total number of fires in Estonia on 2009 was 8421 (Estonian Rescue Service 2010). There is data available on the number of buildings that had caught fire, but not the data on the magnitude of the fires or how much of dioxins and furans were emitted to the air.

On Figure 5, the number of accidental fires of residential buildings in Estonia 2005-2008 is shown. The figure is made using the data from the Estonian Rescue Board. The total number of fires of buildings was used. There were 2598 fires of buildings in 2009 in Estonia, 598 of these were in Public buildings (except Industry), and 302 were in Industrial buildings³.

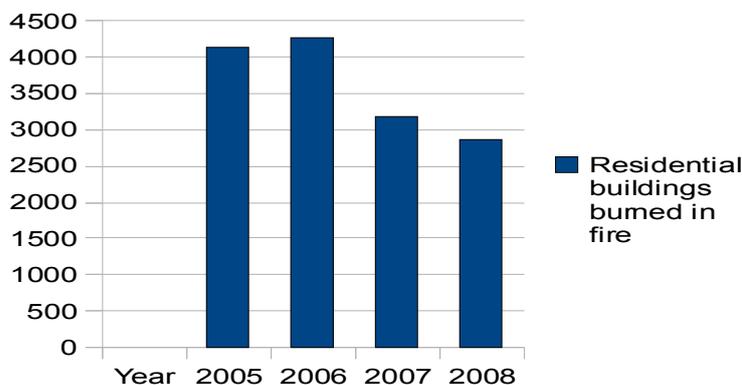


Figure 5. Accidental fires of residential buildings in Estonia 2005-2008 (Estonian Rescue Board 2009).

³ http://issuu.com/estonianrescueboard/docs/v2/p__ste_s_ndmuste_statistika_2009





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Emission from burning PVC in accidental fires

Yearly load 0 – 0,00918 g TEQ/y to AO

Uncertainty: CCCC

The yearly load was derived from the European yearly load, using the Estonian population as a basis for calculation. The EF data is from Carroll 2001.

Emission from burning wood in accidental fires

Yearly load – 0 – 0,027 g TEQ/y to AO

Uncertainty: CCCC

The yearly load was derived from the European yearly load, using the Estonian population as a basis for calculation. The EF data is from Carroll 2001.

General emission from accidental fires of buildings

Yearly load – 0,0026 g TEQ/y to AO

Uncertainty: CCCC

The yearly load estimation is based on EMEP report (Total number of burned buildings includes both residential and industrial buildings).

Emission from detached house fires

Yearly load - ? to AO

Uncertainty: N/A

No information.

Emission from other non residential buildings

Yearly load – 0,0004 g TEQ/y

Uncertainty: CCCC

The European EF was used. The EFM is from Estonian Rescue Service 2010.

Emission from other waste and apartment building fire (other fires)

Yearly load – 0,0008 g TEQ/y

Uncertainty: CCCC

The European EF was used. The EFM is from Estonian Rescue Service 2010.





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Emission from other waste and industrial building fire

Yearly load – 0,0014 g TEQ/y

Uncertainty: CCCC

The European EF was used. The EFM is from Estonian Rescue Service 2010.

This number also includes the emissions from the car fires. There is data available on the number of car fires and the number of waste fires in total, but none of the statistics includes data on the magnitude of the incidents.

There were 387 car fires in Estonia in 2008. This number is calculated from the 109 car fires that were registered in Tallinn in 2008⁴ to Estonian average 412 cars per 1000 inhabitants⁵. Using the population of Tallinn (400 000) and the number of fires (109), we get that 0,07% of the cars used in Estonia catch fire in one year. The total number was added to the string „Emissions from other waste and industrial building fire“.

In 2008, 444 waste fires were reported in Harju County (10% of total Estonian area and 1/3 of population). To get the number to the whole country, the calculation was done on an area basis. The total number of waste fires Estonia was 4440. The number was added to the string „Emission from other waste and industrial building fire“.

Emission from forest fires

Yearly load – 0,004 g TEQ/y

Uncertainty: CCCC

The European EF (based on EMEP data) was used. The EFM is from Estonian Environment Information Centre 2010.

The number is recalculated from EU numbers. 174 189 hectares was burnt in EU 2008. In Estonia, the total amount of forest fires was 1280 ha in 2008. The main reasons were negligence, ignition and breaking of electrical lines (Estonian Environment Information Centre -

<http://www.keskkonnainfo.ee/index.phpplan=EE&sid=888&tid=809&l2=463&l1=29>).

⁴http://www.pepk.ee/public/resources/editor/File/statistikaraamat_2008.pdf

⁵<http://www.keskkonnainfo.ee/index.phpplan=EE&sid=202&tid=192&l3=26&l2=22&l1=2>





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2.9 Residential combustion

NACE: 27.52

General emission for residential combustion

Yearly load – 1,67 g TEQ/y

Uncertainty: CCCC

This calculation is based on the data taken from Statistics Estonia for 2009 (residential combustion in tonnes) and emissions for PCDD/PCDF for 2008 taken from Estonian Informative Inventory Report, 2010.

The following ES-s are sub-strings for this ES.

Emission from clean wood

Yearly load – 0,835 g TEQ/y

Uncertainty: CCCC

Calculation is derived from EMEP monitoring data and divided to fuel types, using percent distribution of used fuel types (Statistics Estonia 2010). Clean wood was used in 50% of the times.

Emission from wood heavily contaminated with PCP

Yearly load - ? to AO

Uncertainty: N/A

No information available.

Emission from burned coal

Yearly load – 0,004 g TEQ/y

Uncertainty: CCCC

Calculation is derived from EMEP monitoring data and divided to fuel types, using percent distribution of used fuel types (Statistics Estonia 2010). Of the total fuels used, 0,21% was coal.

Annual emissions in Estonia for new installations;

Annual emissions in Estonia for old installations;

Emission from brown and hard coal;



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**Emission from coal burning in old installations;
General emission for coal combustion in stoves**

Yearly load - ? to AO

Uncertainty: N/A

Only hard coal is used in Estonia, not brown coal – 7000 t (Statistics Estonia 2010).

Emission to soil from wood burning

Yearly load – 1,6 g TEQ/y to FS

Uncertainty: CCCC

Derived from the European yearly load, using the area of Estonia as a basis for calculation.

Uncontrolled domestic waste burning

Yearly load – 1,74 g TEQ/y to AO

Uncertainty: CCCC

Derived from the European yearly load, using the area of Estonia as a basis for calculation.

Air emission from wood preservation

Yearly load - ? to AO

Uncertainty: N/A

2.10 Activities outside Estonia

Deposition from transboundary fluxes

Yearly load 4,2 g TEQ/y

Uncertainty: CCCC

Data from Meteorological Synthesizing Centre – East (2010)

(<http://www.msceast.org/countries/Estonia/index.html>).

2.11 Mean annual concentration in main environmental compartments in Estonia



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Soil

Yearly load - ? to FS

Uncertainty: N/A

Air

Yearly load - ? to AO

Uncertainty: N/A

Vegetation

Yearly load - ? to FS

Uncertainty: N/A

EFs for these ESs are: 0,0005 pg/TEQ/g for Soil, 0,14 pg/TEQ/m³ for Air, and 0,35 pg/TEQ/g for Vegetation. Data from MSC-E.

2.12 Sewerage

NACE: 37

Municipal wastewater treatment plants – effluent

Yearly load – 0,0037 – 0,0314 g WHO-TEQ (1998) to CSW

Yearly load – 0,0024 – 0,0209 g WHO-TEQ (1998) to FSW

Uncertainty: CCCC

Yearly load was calculated from the COHIBA WP3 results.

The EFs are the average concentrations of all WWTPs. For EF low, the results <LOQ were considered to be 0. For EF high, the results <LOQ were considered to be LOQ.

The EFM of 125 l is the average amount of effluents created by inhabitant a day (Statistics Estonia 2010). Estonian population is considered to be 1340021 (Statistics Estonia 2010).

Sludge

Yearly load – 0,03790 g WHO TEQ (2005) to AS

Yearly load – 0,11206 g WHO TEQ (2005) to FS

Uncertainty: CCCC

(The yearly load of PCBs and Co-PCBs to sludge:

0,00206 g WHO TEQ (2005) to AS



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0,00608 g WHO TEQ (2005) to FS
Uncertainty: CCCC

The EF is calculated from the Polish results as there were no results for the dioxins in sludge for Estonia and we considered the results to be similar enough to give an overall idea of the possible concentrations, especially considering the overall extremely high uncertainty. Lowerbound results were used.

The EFM is the one from European SFA-s, considered to be representative to Estonia by Mr Kõrgmaa, an expert of WWTPs and sewage sludge (personal communication). The yearly load was calculated by multiplying EF with EFM and number of inhabitants in Estonia.

2.13 Waste treatment and disposal

NACE: 38.2

Landfill leachate

Yearly load – 0,0008 – 0,0010 g WHO (1998) TEQ to WW

Yearly load – 0,0002 g WHO (1998) TEQ to FS

Yearly load – 0,0002 g WHO (1998) TEQ to FSW

Uncertainty: CCCC

2.14 Other - Worldwide activities outside the region, for example atmospheric deposition of long range transport

Atmospheric deposition

Yearly load 0,0005 – 0,0013 g WHO TEQ to FSW

Yearly load 0,0023 – 0,0066 g WHO TEQ to AS

Yearly load 0,0053 – 0,014 g WHO TEQ to FS

Uncertainty: CCCC

Calculated with Swedish EFs as it these were considered to be similar enough for Estonia (especially considering the latitude and the essence of atmospheric deposition of substances) by Erik Teinmaa, EERCs air monitoring head specialist (personal communication, May 2011).

The basis for calculation was the territory of Estonia. The division into the compartments



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was made according to the data from Estonian Environment Information Centre.



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3 Conclusions

3.1 Quantitative estimation of the most relevant sources to each environmental compartment (Soil, water and air)

In Estonia, 65% of the dioxin emissions to air originate from local sources such as incineration of wastes and fuels in power plants.

The most meaningful measures for reducing emissions would be to secure and control efficient incineration and to use best available technologies in the industry. To achieve the reduction of non-industrial emissions, the most efficient way is to prevent open fires – educating the population is needed.

The fluxes coming from the sources outside Estonia are greater than the ones coming from the country itself. However, it is impossible to control these sources by usual means, the only possibilities being international agreements etc.

3.2 A qualitative estimation of time trends for future scenarios.

According to international agreements, Estonia has taken a responsibility to reduce the emissions to emission projection 3,5 g I TEQ/y by 2015.



4 SFA diagram

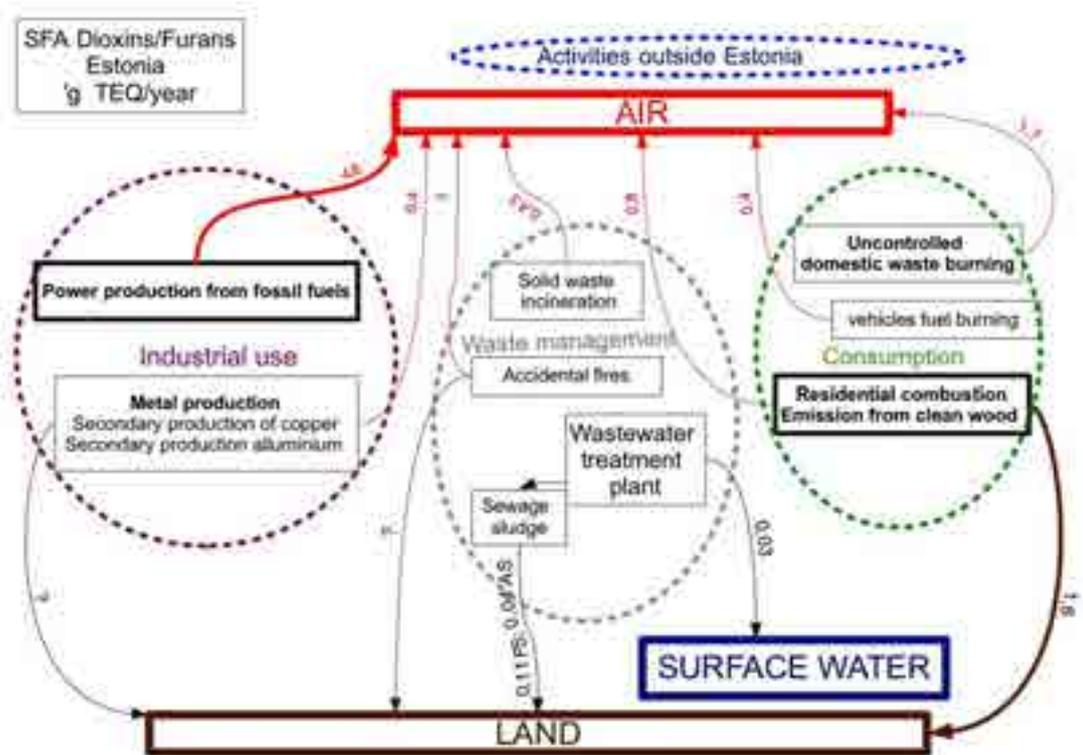


Figure 6. SFA diagram for dioxins in Estonia.



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ANNEX B – Substances flow analysis for TBT in Estonia

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This study was carried out under the COHIBA study from May 2010 to May 2011. This report is based on the SFA Tri-organotins (EU27) by Environment and Health Administration, City of Stockholm. The results are for Estonia. Many of the results are rough approximations that cannot be taken as exact results for Estonia, but more as a base to plan future studies. The results are for Estonia.

1 Introduction

Organotin compounds are substances with a number of organic groups bound to a tin atom (RPA 2005, p 1). Depending on the number of groups, the organotin compound can be called di-substituted (two organic groups) or tri-substituted (three organic groups) etc. Mono- and Di-substituted organotins are used as stabilisers for PVC products and as different types of catalysts, but it can also be found as impurities in mono- and di-substituted compounds. Tri-substituted organotins was historically most used in pesticides and biocides. Most uses of tri-substituted organotins, like Tributyltin (TBT) and Triphenyltin (TPhT), have since a few years back been banned within EU.

TBT is mainly found as a biocide in antifouling paints and wood preservation products, but can also be present as impurities in PVC products and catalysts, in textiles and consumer products. As such it can be imported to Europe from over seas. TBT is a substance which shows a high toxic effect on aquatic life, causing chronic and acute poisoning of organisms such as zooplankton, algae and invertebrates (Hoch 2001, p 721). The European Community has classified TBT as toxic and dangerous for the environment (Feenestra et al. 2009, p 11).

TBT is rarely appearing as pure TBT, but combined with other substances (Feenestra et al 2009, p 10). The most industrially commonly used TBT compounds (on which this report will focus) are; Tributyltin benzoate, Tributyltin chloride, Tributyltin fluoride, Tributyltin linoleate, Tributyltin methacrylate, Tributyltin naphthenate and Tributyltin oxide. Their abbreviations and CAS numbers are presented in Table 1.1.

Table 1. CAS number for TBT compounds, source: HELCOM (2009)

| Chemical compound : | Abbreviation | CAS no |
|----------------------------|--------------|------------|
| Tributyltin compounds | TBT | 688-73-3 |
| - Tributyltin benzoate | TBTB | 4342-36-3 |
| - Tributyltin chloride | TBTC | 1461-22-9 |
| - Tributyltin fluoride | TBTF | 1983-10-4 |
| - Tributyltin linoleate | TBTL | 24124-25-2 |
| - Tributyltin methacrylate | TBTM | 2155-70-6 |
| - Tributyltin naphthenate | TBTN | 85409-17-2 |
| - Tributyltin oxide | TBTO | 56-35-9 |

TPhT is mainly used as agricultural fungicide and pesticide, usually called fentin, but has also been present in antifouling paints.

TPhT is rarely appearing as pure TPhT, but combined with other substances (HELCOM 2009, p 13). The most commonly used TPhT compounds (which this report will focus on) are; Triphenyltin acetate, Triphenyltin chloride, Triphenyltin fluoride and Triphenyltin hydroxide. Their abbreviation and CAS# is presented in Table 1.2.

Table 2. CAS number for TPhT compounds, source: HELCOM (2009)

| Chemical compound: | Abbreviation | CAS no |
|------------------------|--------------|-------------------|
| Triphenyltin | TPhT | 668-34-8/892-20-6 |
| Triphenyltin acetate | TPhTA | 900-95-8 |
| Triphenyltin chloride | TPhTC | 639-58-7 |
| Triphenyltin fluoride | TPhTF | 379-52-2 |
| Triphenyltin hydroxide | TPhTH | 76-87-9 |

The substance flow analysis presented in this report is for EU27. The time frame used is one year. The analysis does not refer to a specific year, but the most recent available data have been used, and sometimes older data have been updated to 2009 conditions.

According to the Council Directive 67/548/EEC tributyltin compounds are classified as: T (toxic): R25 - toxic if swallowed; R48/23/25 - toxic, danger of serious damage to health by prolonged exposure through inhalation and if swallowed; N (dangerous for the environment): R50/53 - very toxic to aquatic organisms, may cause long-term adverse effect in the aquatic environment; Xn (harmful): R21 - harmful in contact with skin; Xi (irritant): R36/38 - irritating to eyes and skin.

1.1 Physical chemical properties

Organotins are moderately hydrophobic. TBT and TPhT adsorb strongly to suspended matter in the aquatic environment and binds in the sediment (HELCOM, 2009, p 19). In the marine environment the major TBT compounds at pH 8 are TBT hydroxide and TBT carbonate (HELCOM 2009, p19). TBTO, which is commonly used, is hydrolysed to TBT cation in water.

The chemical structure of TBT derivatives is shown in Figure 1.1 (UNEP 2009). The molecular formula is $(C_4H_9)_3Sn-X$ where X is a group or an anion (Feenestra et al. 2009, p 10). Physical and chemical properties of some TBT-compounds are presented in Table 1.2.

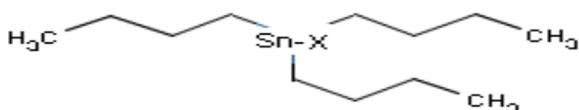


Figure 1. Chemical structure of TBT Source: UNEP (2009)

Table 3. Physical and chemical properties of TBT. Due to lack on information, this table is incomplete IPCS (1990).

| Property | TBT | TBTB | TBTC | TBTF | TBTL | TBTM | TBTN | TBTO |
|--|----------------------------|----------------------------|-------------------|------------------|--------------------------------|--------------------------|------------------------------|----------------------------------|
| Physical state at npt | | Clear, yellow liquid | | Crystal | | | Yellow/brown liquid | Liquid |
| Molecular formula/ simplified structural formula | $(C_4H_9)_3Sn-X$ | $(C_4H_9)_3Sn-COO(C_6H_5)$ | $(C_4H_9)_3Sn-Cl$ | $(C_4H_9)_3Sn-F$ | $(C_4H_9)_3Sn-COOC_{17}H_{35}$ | $(C_4H_9)_3Sn-COOC_3H_7$ | $(C_4H_9)_3Sn-COO C_7H_{15}$ | $((C_4H_9)_6Sn)_2O$ |
| Molecular weight (g/mol) | - | 411 | 325 | 309 | 569 | 375 | Ca.500 | 596 |
| Melting point (°C) | - | 20 | -16 | 240 | <0 | 16 | <0 | <- 45 |
| Vapour pressure (Pa, at 20°C) | - | 2.0E-04 | | | 9.0E-02 | 3.0E-02 | 9.0E-05 | 1.0E-03 |
| Log octanol-water partition coefficient (log Kow, at pH X) | - | | | | | | | |
| Water solubility (mg/l, at pH X, XX°C) | ca. 4 (at pH 7.0 and 20°C) | | 105 | | | | 1.5 mg/ml | 4.0 (at pH 7.0; 20°C; distilled) |

| | | | | | | | | |
|--|-------|--|------|--|--|--|--|--------|
| | 20°C) | | | | | | | water) |
| Dissociation constant | 6.51 | | | | | | | 6.25 |
| Henry's Law Constant (Pa m ³ /mol, at XX°C) | | | 32.5 | | | | | 17 |

TPhT compounds are triphenyl derivatives of tetravalent tin. It occurs as colourless solid substances with low vapour pressure below 2 mPa at 50°C. TPhT compounds are lipophilic and have low solubility in water, usually with a few mg/l at a neutral pH. The general formula of TPhT is (C₆H₅)₃Sn-X (see Figure 1) where X is an anion or anionic group, such as chloride, hydroxide or acetate. The properties of the TPhT compounds depend on the anion linked to the tin atom, and are presented in Table 1.4 below. TPhTC and TPhTA hydrolyse quickly in aquatic environment to TPhTH (WHO 1999).

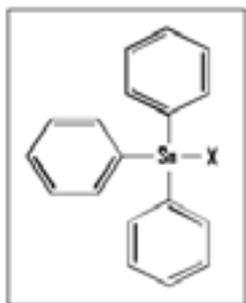


Figure 2. The chemical structure for triphenyltin compounds.

Table 4. Physical and chemical properties of TPhT. Due to lack on information, this table is incomplete. (IPCS INCHEM website, and other references)

| Property | TPhT | TPhTA | TPhTC | TPhTF | TPhTH |
|---|--|--|--|---|--|
| Physical state at npt | | | White solid with no characteristic odour. | | Fine white powder with a characteristic odour |
| Molecular formula/simplified structural formula | (C ₆ H ₅) ₃ Sn-X | (C ₆ H ₅) ₃ SnC ₂ H ₃ O ₂ | (C ₆ H ₅) ₃ SnCl | (C ₆ H ₅) ₃ SnF | (C ₆ H ₅) ₃ SnOH |
| Molecular weight (g/mol) | | 409.1 | 385.5 | 369.0 | 367.0 |
| Melting point (°C) | | 122-124 | 106 | 281 | 122-123.5 |
| Vapour pressure (mPa) | | 1.9 (at 60 °C) | 0.021 | 8.22E-06 mmHg at 25°C | 0.047 (at 50 °C) |



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| | | | | | |
|---|--|----------|-------------------|--|---------------------------------|
| Log octanol-water partition coefficient (log Kow) | | 3.43 | 3.43 | | 3.43 |
| Water solubility (mg/l, 20°C) | | 9 (pH 5) | 40 (pH not given) | | 1 (pH 7, greater at a lower pH) |
| Viscosity (mPa) | | | | | |
| Dissociation constant | | | | | |
| Henry's Law Constant (Pa m ³ /mol) | | | 2.02E-04 | | 1.72 |

1.2 Regulatory status

Legislative or administrative measures:

It is prohibited to place on the market or use plant protection products containing tributyltin compounds, since these active substances are not included in Annex I to Directive 91/414/EEC concerning the placing of plant protection products on the market and in accordance with Commission Regulation (EC) No 2076/2002 of 20 November 2002 extending the time period referred to in Article 8(2) of Council Directive 91/414/EEC and concerning the non-inclusion of certain active substances in Annex I to that Directive and the withdrawal of authorisations for plant protection products containing these substances.

It is prohibited to place on the market or use biocidal products containing tributyltin compounds since these active substances are not included in Annex I to Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market and in accordance with Commission Regulation (EC) No 1451/2007 of 4 December 2007 on the second phase of the 10-year work programme referred to in Article 16(2) of Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market.

Furthermore, it is prohibited to place on the market or use all organostannic compounds for treatment of industrial waters in accordance with point 20 of Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC.



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Tributyltin cations are identified as "priority hazardous substances" under the 2000/60/EC (the Water Framework Directive, WFD). Directive 2008/105/EC (the EQS Directive), which is a daughter directive of WFD, sets the water quality standards for TBT cations in the EU. As Estonian legislation is compliant to the EU legislation, TBT cation is also listed as a priority substance and has set water quality standards under the Estonian law (RT I 2010, 51, 318; RT I 2010, 65, 484).

HELCOM Baltic Sea Action Plan also identifies TBTs and TPhTs as substances of specific concern to the Baltic Sea. TBT has also been of concern in two recommendations from HELCOM; 20/4 Antifouling paints (adopted 23.03.1999) and 19/5 HELCOM Strategy for Hazardous Substances (adopted 26.03.1998).

The use of TPhT hydroxide and acetate as pesticides are no longer authorised in the EU according to Commission Decisions 2002/478/EC and 2002/479/EC.

Restrictions and prohibitions of the TBT and TPhT substances in Europe and worldwide today are described in HELCOM 2009, p 13, RPA 2005, p 10).

1.3 Production

There is no production of TBTs and TPhTs in Estonia.

1.4 Use

No TBTs or TPhTs have been registered under regulation 689/2008/EC (export and import of dangerous chemicals) and there is no registered use under Regulation 1907/2006/EC (REACH regulation) (data from Endla Veskimäe Health Board Department of Chemical Safety – it is the responsible authority of Estonia e-mail conversation 20.12.2010 Mailis Laht).

1.5 Environmental fate and levels

TBT compounds binds easily to particulate matter, and contaminates the sediments (Feenestra et al. 2009, p 16). The reported adsorption coefficient for TBT compounds range from 110 to 55 000 and the half-life is considered to be between 1-2 years in aerobic sediments and up to ten times longer in anaerobic sediments. The adsorption and desorption is consequently depending on the state of the sediment, and the biodegradation is significantly slower in sediment than in water (HELCOM, 2009, p 19). Since there are now regulations and ban of TBT in antifouling paints, there is a consensus that TBT



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concentrations in surface water are declining rapidly. But after many years of use of TBT as a biocide in antifouling paints, there is a risk that sediments, especially in shipyards and harbours, contain high amounts of TBT. In marine harbours and shipyards the decline of TBT concentrations are slow, due to higher concentrations of TBT bound to the sediment. A resuspension of these contaminated sediments may release a high concentration of TBT into the water. It is concluded that still 19 years after TBT in antifouling paints was prohibited for vessels of this size, there is still TBT released to the environment from these vessels (Eklund et al. 2008, p 127).

Because TBT is so easily adsorbed to the sediment, biota on the bottom can be highly exposed to large concentrations of TBT. High concentrations of organotins in seafood other than fish has been detected in several EU countries (EFSA 2004 cited in RPA 2005) and *“the TBT levels in mussels were so high in all marine areas that they pose a considerable risk of adverse effects in animals”* (HELCOM 2009, p 19). A Danish study cited in HELCOM also showed that concentrations of TBT could be found throughout the tropical marine food web, from seaweeds to invertebrates, fish, birds and mammals, where the highest concentrations was found in porpoises, though the accumulation varied between different species at the same level in the food chain. Bioaccumulation of TBT is depending on pH and is considered low below pH 6.5 (ECHA 2008). TBT bioaccumulates more strongly within the liver of fish or marine mammals than in the muscle. Studies on flounder show that the TBT had been ingested from food consumption. TBT is an endocrine disruptor, which affects the endocrine system of certain marine and freshwater molluscs. It can cause imposex (females are masculinised resulting in sterilisation of the population) and intersex (male features on female sex organs, almost entirely specific to the common periwinkle) in marine gastropods (HELCOM 2009, and ECHA 2008, p13).

High levels of TBT (10-500 ng/L) have been measured in industrial storm water in four Swedish cities, and can be assumed to be a significant diffuse emission source of TBT (Junestedt et al. 2003, p 104).

Environmental concentrations of TPhT compounds vary depending on how, when and where the substances were used (WHO 1999). High concentrations can be found in harbours, marinas and bay areas. This is considered as a result of historical use of antifouling paints containing TPhT on ship hulls. Environmental levels of TPhT have decreased recent years in the world due to restrictions on the use of the substances in antifouling paint as well as restrictions of other use of TPhT compounds.

TPhT is a substance which is strongly adsorbed in sediments and soil and desorption is unusual. Half life can be from several days in June to a couple of weeks in November (WHO 1999).

When taken up by biota, TPhT can by dephenylation stepwise be degraded and excreted



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in conjugated forms (di-phenyltin etc.), but it can also bioaccumulate in gastropods and fish with bio concentration factors ranging from several 100 to 32 500. Both TBT and TPhT bioaccumulate in aquatic organisms, but it is believed that TPhT shows greater bioaccumulation than TBT. A Japanese study performed in 2008 on TBT and TPhT in deepwater fish confirms that TPhT concentrations are higher in benthic organisms than in the sediments (Kono et al 2008). This implies that TPhT can be transferred to benthic organisms from the sediment, and then bioaccumulates throughout the food chain. The sediments can in that matter act as a secondary source of TPhT.

TPhT compounds bioaccumulate mainly in the kidney and liver, but other organs may also have smaller amounts present (WHO 1999). The substances exert damaging effects on aquatic organisms at very low concentrations. They are considered to be endocrine disruptors causing imposex (female gastropods develop male sex organs). Though, because TBT and TPhT are present together in the environment, there is no estimation which causes their relative contribution of damage to organisms. Hoch (2001, p 721) presents that TPhT can cause various symptoms on exposed organisms, like thickening shells, failure of spat in oysters, impotence of neogastropods and gastropods, reduction of dogwhelk population, retardation of growth in mussels and immunological dysfunction in fish. WHO (1999) identifies other toxicological effects among various animal species, such as effects on the immune system or reproductive system and developmental effects.

In Estonia, there have not been any exhaustive studies on organotin compounds. The objects of residual pollution have been mapped before, but the residual pollution has considered for other substances (e.g. PAHs), but not for organotin substances.

However, there were three studies where organic tin compounds were analysed in 2010 in Estonia – COHIBA, and BaltActHaz (both co-financed by EU), and a study ordered by Estonian Ministry of Environment (conveyed by MAVES) that was made on the priority hazardous substances of WFD.

The study ordered by Estonian Ministry of Environment analysed TBT cation in the coastal waters and surface waters and found no results of it (all of the results were <LOQ, 0,001 µg/l).

Mono-, di-, tri-, and tetrabutyltin, mono- and dioctyltin, tricyclohexyltin, mono-, di-, and triphenyltin were analysed in the BaltActHaz study in both waters and sediments of municipal and industrial WWTP-s, lakes, rivers, and coastal waters.

The rivers and lakes were mostly free of organotin compounds, some mono- and dibutyltin was found from the waters of bigger rivers (up to concentrations of 5,4 and 1,5 ng/l, respectively).

In the BaltActHaz study, the greatest pollution of mono-, di-, and tributyltin and also



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mono- and diphenyltin was found from the biggest shipyard – from both water (where the TBT was measured up to 9 090 ng/l) and sediments (up to 22 500 µg/kg dw). TPhT was also found from one measurement from the sediments of the shipyard (15 µg/kg dw), being the only finding of TPhT so far in Estonia.

Organotin compounds could not be detected from the effluents of WWTP-s, but some were detected from the sediments. Mostly the findings in the sediments were from mono-, and dibutyltin compounds (up to the concentrations of 237 and 269 µg/kg dw, respectively). Some tributyltin was also found from the sediments (up to µg/kg dw). Triphenyltin was not found in neither the effluents nor sediments of WWTP-s.

Therefore, we can conclude that organotin compounds are being used widely and evenly all over Estonia as the measured levels are quite comparable in all of the WWTP-s measured in the BaltActHaz study.

Mono- (MBT), di- (DBT), tri- (TBT), and tetrabutyltin (TTBT), mono- (MOT), and dioctyltin (DOT), triphenyltin (TPhT), and tricyclohexyltin (TCyT) cations were analysed in the COHIBA WP3 study from the effluents of five WWTPs, one landfill and two samples of urban runoff. The results were quite comparable with the BaltActHaz results.

Table 5. Organotin substances in waste-water and sewage sludge in Estonia 2009-2010 (Data from COHIBA WP3).

| Substance | WWTP1 | WWTP2 | WWTP3 | WWTP4a | WWTP4b |
|-------------|--------------|--------------|--------------|--------------|--------------|
| | Water (ng/l) |
| MBT | <LOQ – 8,9 | <LOQ - 5 | <LOQ - 10 | <LOQ – 2,3 | 3,8 – 7,3 |
| DBT | <LOQ – 7,5 | <LOQ – 1,4 | <LOQ – 5,6 | <LOQ | <LOQ – 1,5 |
| TBT | <LOQ – 2,9 | <LOQ – 2,2 | <LOQ | <LOQ | <LOQ |
| TTBT | <LOQ – 5,5 | <LOQ | <LOQ - 13 | <LOQ | <LOQ – 8,6 |
| MOT | <LOQ – 3,5 | <LOQ – 3,7 | <LOQ – 8,5 | <LOQ | <LOQ – 5,4 |
| DOT | <LOQ | <LOQ – 1,3 | <LOQ | <LOQ | <LOQ |



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| Substance | WWTP1 | WWTP2 | WWTP3 | WWTP4a | WWTP4b |
|-------------|--------------|--------------|--------------|--------------|--------------|
| | Water (ng/l) |
| TPhT | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ |
| TCyT | <LOQ | <LOQ | <LOQ | <LOQ | <LOQ |

Table 6. Organotin substances in Estonian landfill and storm waters (data from COHIBA WP3).

| Substance | Landfill ng/l | Stormwater ng/l |
|-------------|------------------|--------------------|
| MBT | 21 and 58 | <LOQ |
| DBT | <LOQ | 3,4 – 5,4 |
| TBT | <LOQ | <LOQ |
| TTBT | <LOQ | <LOQ |
| MOT | <LOQ - 18 | <LOQ – 1,5 |
| DOT | <LOQ | <LOQ |
| TPhT | <LOQ | <LOQ |
| TCyT | <LOQ | <LOQ |



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2 Sources of emissions of tributyltin compounds in Estonia

The uncertainties in the following emission strings are given with four letters, the first letter representing uncertainty for EF, the second for EFM, the third for division into compartments and the fourth for the yearly load. Uncertainty is classified according to the principles described in “Dealing with uncertainty in substance flow analysis within the COHIBA project”, a PM describing how data uncertainty is graded in WP4 of the COHIBA project.

If the Estonian yearly loads were scaled from the EU yearly load to Estonian population, the Estonian population was considered to be 0,3% of the EU population. This accuracy level was considered to be enough for given study; especially considering the very high uncertainty levels in other emission strings.

2.1 Production of TBT/Organotin compounds

2.1.1 Manufacture of other organic basic chemicals

NACE 20.14

Emissions due to the formulation (secondary production stage) of TBT-containing chemical products other than paints (e.g. surface disinfectants)

Yearly load - ? to OA and WW

Uncertainty: N/A

According to Prodcorn 2008 database, there are several activities taking place in Estonia under that NACE, but we have no information of the use of TBTs.

2.1.2 Manufacture of other chemical products n.e.c.

NACE 20.59

Emission of TBT due to the use of TBT compounds as intermediates in the production of other compounds (e.g. used as a reducing agent for the conversion of alkyl halides to hydrocarbons; for desulfurisation of organic sulfides etc.)

Yearly load - ? to OA and WW

Uncertainty: N/A

Emission due to product manufacture involving catalysts – silicones

Yearly load - ? to FS

Uncertainty: N/A



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Emission due to product manufacture involving catalysts- Esterification and powder coating of plasticisers for PVC

Yearly load - ? to AO and WW

Uncertainty: N/A

Emission due to applications of products containing catalysts - Esterification and powder coating of plasticisers for PVC

Emission due to product manufacture of catalysts - Esterification and powder coating of paint formulation

Yearly load - ? to WW

Uncertainty: N/A

Releases

Yearly load - ? to WW

Uncertainty: N/A

According to Prodcum 2008 database, there are several activities taking place in Estonia under those NACE codes, but we have no information of the use of TBTs.

Mono- and dibutyltin compounds are used as stabilizing agents in PVC plastics, which make the PVC plastics less unstable when influenced by light and heat (Hoch 2001). TBT is present as an impurity in mono- and dibutyltin compounds are used as stabilisers in PVC, polyurethane and polyester, and can therefore be released to the environment (HELCOM 2009 and Kjølholt et al 2007).

The Government of Canada proposed risk management approach (Environment Canada, 2009) assumes there will be no environmental releases from dry blend manufacture of powder coatings.

2.2 Use of products containing catalysts

2.2.1 Manufacture of plastics in primary forms

Emission due to applications of products containing catalysts - silicones (room temperature vulcanisation)

Yearly load - ? to WW

Uncertainty: N/A

According to Prodcum 2008 database, there are several activities taking place in Estonia



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under this NACE code, but we have no information of the use of TBTs.

2.2.2 Other - Emission from (private) consumption; during lifetime use (including tear and wear) of articles, goods and chemical products and preparations.

TBT is present as an impurity in mono- and di-butyltin compounds which are used as stabilisers in PVC, polyurethane and polyester (HELCOM, 2009; Kjølholt et al, 2007, p 13). Silicon products are used in one-component sealants for costumer, two-component sealants for industrial application; esterification and powder coating catalysts are used in household appliances, office furniture, architectural uses, lawn/garden equipment, heating and air condition systems etc.; polyurethanes catalysts are used in upholstered furniture, mattress fillings, car seats, printing, surface coating, engineering components etc. Electrodeposition coatings are used as corrosion prevention of motor vehicles. Losses to soil relate to abrasion during use. Additional losses during removal at vehicle body shop assumed as 1% of all usage, of which 98% passes to landfill and 1% to each of air and waste water (ScorePP database).

Emission due to use of products containing catalysts - electrodeposition coatings. (Use of motor vehicles)

Yearly load - ? to AO, WW, FS

Uncertainty: N/A

Emission due to use of products containing catalysts - silicones (one-component sealants for costumer, two-component sealants for industrial application)

Yearly load - ? to AO, WW

Uncertainty: N/A

According to Prodcum 2008 database, there are several activities taking place in Estonia under those NACE codes, therefore we assume those ESs to be relevant or Estonia. but we have no information of the use of TBTs.

We didn't find it appropriate to calculate the yearly load for Estonia from the EU yearly load as the EU EF didn't see plausible for Estonia. There is no data for the use of TBT chloride and DBTC-dibutyltin chloride and we are not sure if the use of TBT is dependent on the number of population – as the industrial sources are much more important for this particular substance.

Emission due to use of products containing catalysts - Esterification and powder coating (used in household appliances, office furniture, architectural uses,



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lawn/garden equipment, heating and air condition systems etc.)

Yearly load – 54,9 kg to AO

Yearly load – 54,9 kg to WW

Uncertainty: AAAC

Losses to soil relate to abrasion during use. Additional losses during removal at vehicle body shop is assumed to be 1% of all usage, of which 98% passes to landfill and 1% to each of air and waste water. TBT is present as an impurity in mono- and di-butyltin compounds are used as stabilisers in PVC, polyurethane and polyester according to HELCOM (2009) and Kjølholt et al (2007, p 13.)

The yearly load was calculated from the EU SFA, using Estonian population as a basis for scaling.

Emission due to use of products containing catalysts - Polyurethanes (used in upholstered furniture, mattress fillings, car seats, printing, surface coating, engineering components etc.)

Yearly load – 40,26 kg to AO

Yearly load – 40,26 kg to WW

Uncertainty: AAAC

The yearly load was calculated from the EU SFA, using Estonian population as a basis for scaling as we assume this ES considers mostly municipal use, making scaling on population adequate.

2.3 Production/use of paint containing TBT

2.3.1 Manufacture of paints, varnishes and similar coatings, printing ink and mastics¹

NACE: 20.3

Emissions during the formulation (secondary production stage) of TBT-containing paints

Yearly load - ? to AI

Uncertainty: N/A

Emissions to the environment due to use of TBT in mildewcides (used to prevent mildew formation in the dried film of water-based emulsion paints)

¹ For detail on potential products and percentage of active ingredients see http://www.scorecard.org/chemical-profiles/pesticides.tcl?edf_substance_id=56-35-9.



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Yearly load - ? to FS
Uncertainty: N/A

According to Prodcop 2008 database, there are several activities taking place in Estonia under this NACE code, but we have no information of the use of TBTs.

No Emission factors were found for these sources for EU or Estonia. The released emissions from these facilities during manufacture of paint were assumed to be released to forest soil (FS) and indoor air (AI).

There are different types of antifouling paints containing TBT (Hoch 2001, p 725). In the free-association antifouling paint the biocide is mixed physically with the paint, and the release to the environment is by diffusion. The release rate of TBT is high after application of the paint, but over time the release rate decreases. In the self-polishing antifouling paint or copolymer paint the TBT is bonded chemically with a polymer, which causes a delay of the toxic release to the environment. Also this paint has higher concentrations of emission releases when the ship hulls were newly painted, and decreasing over time.

Antifouling paints contained TBT compounds as TBTM, TBTO in the UK in 2001 according to RPA 2002. The production only involves physical mixing of the active ingredient and base, which means that no wastewater or new TBTs produced. Solvents used to clean equipment are added to the paint mixture so no waste solvent is produced. After mixing, the paint discharged to a tank is transferred into 20 litre drums by a closed and automated filling line produced.

2.3.2 Painting and glazing

NACE: 43.34

Emission to air due to volatilisation during application of TBT-containing formulations

Yearly load - ? to AO
Uncertainty: N/A

Emission due to spillage during application of TBT-containing formulations

Yearly load - ? to FS
Uncertainty: N/A

According to Prodcop 2008 database, there are several activities taking place in Estonia under this NACE code, but we have no information of the use of TBTs.



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No Emission factors were found for this source for EU or Estonia. The emissions are assumed to be released to outdoor air (AO) and forest soil (FS) during application of TBT containing paint.

2.3.3 Other - Emission from (private) consumption; during lifetime use (including tear and wear) of articles, goods and chemical products and preparations.

Release due to washing of TBT contaminated paint brushes or equipment

Yearly load - ? to WW

Uncertainty: N/A

No Emission factors were found for these sources, though it is estimated that the leachate from cleaning painting equipment will be distributed to wastewater (WW). Although the European directive banned the use of antifouling paint in 2003 and 2008 (see regulatory status), there is a possibility that not all equipment painted with antifouling paints have been removed /permanently covered.

2.4 Production of metal

2.4.1 Manufacture of basic metals

NACE: 20

Release to the environment due to TBT use in the metal industry (e.g metal ore roasting or sintering installations, installations for the production of ferrous and non-ferrous metals)

Yearly load - ? to WW

Uncertainty: N/A

According to Prodcom 2008, there is a production of “other ferroalloys” in Estonia.

According to Feenestra et al (2009, p17) the release of organotin compounds from production and use of metal is estimated to be 0.274 tonnes/year (TBT not specified) to WWTPs (EPER 2007). Organotin compound emissions is to be reported to EPER only if they exceed the threshold of 0.05 tonnes/year and facility, which means that the total value of unreported emissions may be high (Pacyna 2009).



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2.5 Production of Cement/glue

2.5.1 Manufacture of clay building materials

NACE: 23.3

Release to the environment due to TBT use in production of cement clinker, lime, glass and ceramic products

Yearly load - ? to WW

Uncertainty: N/A

There is clinker production in Estonia, but there is no information about the possible TBT releases.

No emission factors were found for this source for EU and Estonia, and data about this type of facilities and products were scarce. According to Feenestra et al (2009, p17) the release of organotin compounds from production and use of cement, lime, glass and ceramic products etc. is estimated to be 0.106 tonnes/year (TBT not specified) to WWTPs (EPER 2007) in the EU. Organotin compound emissions are to be reported to EPER only if they exceed the threshold of 0.05 tonnes/year and facility, which means that the total value of unreported emissions may be high (Pacyna 2009 p 37).

2.5.2 Unspecified

Emissions of TBT from cement

Yearly load - ? to WW, FS, and AO

Uncertainty: N/A

There is cement production in Estonia, but there is no information about the possible TBT releases. No emission factors were found for this source. However, we suspect this source to be relevant for Estonia.

2.6 Production/use of electronics

2.6.1 Other - Emission from (private) consumption; during lifetime use (including tear and wear) of articles, goods and chemical products and preparations.

Gradual ongoing emission from rodent repellent cable coatings containing TBT. (Former use - but some residual emissions may still remain)

Yearly load - ? to FS

Uncertainty: N/A



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Use for rodent repellent cable coatings is a former use but some residual emissions may still remain. No Emission factors were found for this source. It is estimated that this type of product will be released into forest soil (FS). This information is from the EU SFA, the source is cited as ATSDR (2005).

This source might be a relevant source for Estonia as well, but there is no data to calculate the yearly load.

2.7 Production/use of plastics as PVC containing TBT

According to EU SFA, this is a minor use as tributyltin methacrylate has been used as a stabiliser for PVC. However, it is predominantly dibutyltins which are used for this purpose. Note that even in mono- and di-substituted commercial products used as PVC stabilisers, there can be a small fraction of tri-substituted compounds. Stabilisers are generally quite tightly held in the matrix and leaching from this source should be relatively minimal.

Approx 70% of the annual production of non-pesticidal organotin compounds are used for PVC plastics worldwide (Environment Canada, 2009, p 6), such as in PVC, polyurethane and polyester (Kjølholt et al 2007, p 13.). The stabilizing agents in PVC plastics production are mono- or dibutyltin compounds, which make the PVC plastics less unstable when influenced by light and heat (Hoch 2001). TBT is here present as an impurity.

Rigid products include: food packaging, credit cards, foamed sheeting, thin rigid film, bottles, pipes and mouldings, and profile extrusions (e.g. windows). Flexible products include; flooring, wall covering, steel coating and for example T-shirt printing. European community also reports uses of TBT in modifiers for synthetic rubber polymers (UNEP, 2009).

2.7.1 Manufacture of plastic plates, sheets, tubes and profiles

NACE: 22.21

Release during manufacture of plastics products in which TBT is used as a stabiliser

Yearly load – 0,03 kg to AO

Uncertainty: --AC

According to Prodcum 2008 there are several activities taking place under that NACE in Estonia. The yearly load was calculated from the EU SFA, using Estonian population as a basis for scaling.



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2.7.2 Other - Emission from (private) consumption; during lifetime use (including tear and wear) of articles, goods and chemical products and preparations.

Releases of leaching from rigid and flexible PVC products in use. (Products in which TBT or TBT-contaminated mixtures have been used as stabilisers)

Yearly load – 0,17 kg to AO

Yearly load – 0,17 kg to WW

Yearly load – 0,01 kg to FSW

Yearly load – 0,01 kg to FS

Uncertainty: --AC

The yearly load was calculated from the EU SFA, using Estonian population as a basis for scaling.

2.8 Paper/pulp Industry

2.8.1 Manufacture of pulp

NACE 17.11

Emissions of TBT due to release from slimicides used in pulp and paper mills (e.g from timber or other fibrous materials and paper or board production)

Yearly load - ? to FSW

Uncertainty: N/A

No Emission factors were found for this source and data about this type of facilities and products were scarce. According to Prodcom 2008, there are several pulp and paper factories in Estonia. The possible use of TBTs is unknown.

According to EPER (2007, cited in Pacyna 2009, p 37) the release of organotin compounds from production and use of paper and pulp industry is estimated to be directly to water. These facilities are assumed to have on-site treatment, and the emissions were assumed to be released to fresh surface water (FSW) after on-site treatment. Organotin compound emissions are to be reported to EPER only if they exceed the threshold of 0.05 tonnes/year and facility, which means that the total value of unreported emissions may be high (Pacyna, J.M.).



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2.9 Textile/leather industry/use

2.9.1 Manufacture of textiles

NACE 13

Emissions of TBT due to release from slimicides used in textile mills

Yearly load - ? to WW

Uncertainty: N/A

This is a possible source for Estonia but there is no proper data to calculate the possible yearly loads.

There was only one factory in Estonia for this ES, but it was closed in 2010. However, in WP3 measurements, we found higher TBT concentrations from the WWTP that this factory led its sewage water to. Hence we suspect that this old factory was at least partly the source of this TBT pollution, e.g. from cleaning the old machines. However, there is no way to prove or disapprove that theory.

In EU SFA, the source citing this ES as a possible source for TBT is ATSDR 2005.

2.9.2 Other - Emission from (private) consumption; during lifetime use (including tear and wear) of articles, goods and chemical products and preparations.

Release of TBT due to washing of TBT contaminated skin and/or clothes (can be due both to contamination from handling of TBT and also to the intentional presence of TBT in manufactured clothing materials)

Yearly load - ? to WW

Uncertainty: N/A

No Emission factors were found for this source, and data about this type of products were scarce. It was assumed that the emissions were distributed to wastewater (WW). TBT may also be present in some laundry sanitizers.

2.10 Building/wood industry

TBT oxide, TBT naphthenate and TBT phosphate are used in the fungicidal components of wood impregnation (Hoch 2001 p 726). There are different practices in which impregnation of wood is performed, including dipping, spraying, brushing and vacuum impregnation. The double vacuum impregnation is performed in an impregnation chamber specially designed for the practice, and is the most used and effective way of wood impregnation. These chambers are considered secure from



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leaching TBT to the environment due to the fact that they are closed systems, though there might be a small release from timber treatment facilities into the freshwater environment due to seepage, accidental spill and effluents. According to RPA (2005), TBT emissions from these facilities will be released into outdoor air (AO) and wastewater (WW).

According to Hoch (2001, p 726) TBT is applied as a 1-3 wt% solution in an organic solvent, which makes the fungicidal component in the wood preservation. TBT compounds are present in varying proportions in commercial products. Ready to use wood preservatives can contain as little as 0.3 % TBT, but content may also be considerably higher than this. Even though there might be emissions released from the wood which has been treated, the leakage is considered to be negligible.

Because of the high toxicity of organotins these compounds are increasingly replaced in the formulation. Synthetic pyrethroids, cypermethrin, and permethrin have been progressively used in timber preservation in recent years. However, tributyltin naphthenate (TBTN) is compatible and light organic solvent preservatives have been developed which formulate TBTN in conjunction with pyrethroids.

2.10.1 Manufacture of wood and of products of wood and cork, except furniture; manufacture of articles of straw and plaiting materials

NACE: 16

Emissions from TBT biocides from timber treatment

Yearly load - ? to AO, WW

Uncertainty: N/A

According to Prodcum 2008 there are several activities taking place under that NACE in Estonia, but the use of TBTs is unknown. Side activity no information about the use on TBT in that string. In Sweden, tributyl-, mono(naphthenoyloxy) derivs, has been used in 2007 according to the Swedish product register. We assume that the situation can be similar in Estonia.

Side activity and Estonia has wood and wood product manufacture but no information about the use on TBT in that string.

According to Feenstra et al 2009 (p 15), TBT used as biocide in wood preservatives in 2001 was less than 50 tonnes / year of tributyltin oxide and less than 50 tonnes / year of tributyltin naphthenate is used. Hoch (2001) notes that tributyltin oxide, tributyltin naphthenate and tributyltin phosphate are used as the fungicidal components in wood preservers, applied as a 1–3 wt% solution in an organic solvent. The application methods include dipping, spraying, brushing and double vacuum impregnation in specially



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designed impregnation chambers. The latter is the most effective treatment and is often used in the timber industry. Impregnation chambers are closed systems and it is not likely that they constitute a significant source of environmental pollution. Nevertheless, in spite of care timber treatment facilities can release TBT into the freshwater environment due to seepage, accidental spills and effluents. Because of the high toxicity of organotins these compounds are increasingly replaced in the formulation. Synthetic pyrethroids, cypermethrin, and permethrin have been progressively used in timber preservation in recent years. However, tributyltin naphthenate (TBTN) is compatible and light organic solvent preservatives have been developed which formulate TBTN in conjunction with pyrethroids. TBT compounds are present in varying proportions in commercial products: ready to use wood preservatives can contain as little as 0.3 % TBT but content may also be considerably greater than this. Was not used in paints for wood preservation in France or Germany. TBT leaching from wood that has been applied by a double vacuum treatment is considered to be negligible. After evaporation of the solvent the pollutants remain safely within the wood structure, due to their low vapor pressures. In Sweden, tributyl-, mono(naphthenoyloxy) derivs, has been used in 2007 according to the Swedish product register. (comment from EU tabel)

2.10.2 Other - Emission from (private) consumption; during lifetime use

Emissions from TBT biocides from use of treated timber

Yearly load - ? to AO, FSW, FS

Uncertainty: N/A

In the EU level, the use of treated timber is considered to be the most significant source of TBT to the environment. We suspect this source is also relevant for Estonia, but there is no proper data about that source.

2.10.3 Manufacture of wood and of products of wood and cork, except furniture; manufacture of articles of straw and plaiting materials

NACE: 16

Emissions from construction and demolition of preserved wood, additives in paint and stain

Yearly load - ? to IS

Uncertainty: N/A

According to Feenstra et al (2009, p17) the release of organotin compounds has no estimations.



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2.11 Direct water related emissions as transport or sediment shipyards aso.

2.11.1 Other - Emission from historical activities, for example contaminated land

Because of the use of antifouling paints, and that the release rate for newly painted vessels were so high, the harbour sediments and dockyards have been very exposed for TBT contamination. Since TBT is also adsorbing quickly to particles in the sediment, there are high concentrations of TBT within these sediments. As previously mentioned, the adsorption to sediments is regulated by factors as oxygen, salinity, pH and the mineralogical and chemical composition of the adsorption material (Hoch 2001, p 728).

Leaching of tributyltin to groundwater is restricted by preferential sorption to the solid phase. TBT tends to partition to the solid phase but transport can occur via movement of particles in runoff waters. Resuspension from these sediments are possible through tides, storms and dredging, which is releasing emissions into the water (Feenstra et al. 2009, 17).

While tributyltin concentrations in water have declined in the EU since restrictions on tributyltin use in paints have been in place, concentrations of tributyltin in sediments have remained relatively high. Degradation of tributyltin in sediment is much slower than in the water column. Approximately 95% of tributyltin in the water column has been found to be bound to suspended particles and the remainder associated with dissolved organic matter and organic and inorganic ligands (Gadd 2000 cited in ATSDR, 2005). Due to the slow degradation rates the TBT contaminations are estimated by the Kjølholt et al (2007) to sustain until 2025. All other TBT sources except leakage from sediment to the Baltic Sea has been considered to be negligible (HELCOM 2009). A research conducted by Eklund et al. (2008) also concluded that TBT is still released from pleasure craft even though paints on these vessels had been banned for 19 years before the survey was conducted.

Keithly et al (1999) report mean values of TBT in different types of seafood from around the world, including Europe. Average TBT concentrations for bivalves, pelagic fish, pelagic invertebrates, and flatfish were 40, 16, 906, and 608 g TBT/kg, respectively. There is an assumption that TBT will be released when biota is decomposing.

Tributyltin that is associated with particles in the water column may settle out, which is an important process in the removal of tributyltin from the water column. Different investigations (Anderson et al. 2002 cited in ATSDR, 2005; Maguire et al. 1985 cited in ATSDR, 2005) concluded that the half-life of the desorption reaction was about 10



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months, indicating that tributyltin can be strongly retained by sediments. It has been reported that methylation of inorganic and organotin compounds, such as di- and tributyltin, are likely to occur in sediments, producing potentially volatile organotin compounds. This process may lead to mobilization of tin species into the water column and possibly into the atmosphere. However, there is currently no significant evidence of losses of organotin compounds to the atmosphere (Amouroux et al. 2000 cited in ATSDR, 2005).

It is estimated that the emissions from these sources are distributed to coastal surface water (CSW).

Emissions from contaminated soils/sediments in shipyards where antifouling paints are in use (or have been used)

Yearly load - ? to CSW

Uncertainty: N/A

We calculated a possible EF of **8996,7 µg/kg dw** from the preliminary results of BaltActHaz study, however, we cannot calculate the yearly load as we don't know the extent of the pollution.

Emissions of TBT from contaminated dockyards, harbour sediments

Yearly load - ? to CSW

Uncertainty: N/A

We calculated a possible EF of **8996,7 µg/kg dw** from the preliminary results of BaltActHaz study, however, we cannot calculate the yearly load as we don't know the extent of the pollution.

Emission release to water due to decomposition of biota containing TBT

Yearly load - ? to CSW

Uncertainty: N/A

This ES is likely to be relevant for Estonia; however, there is no data for calculating the yearly loads.

2.11.2 Other - Emission from (private) consumption; during lifetime use

Emission through slow ongoing release of TBT from crab pots, fishnets, cages and other fishing equipment painted with antifouling paint

Yearly load - ? to CSW

Uncertainty: N/A



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This ES is likely to be relevant for Estonia; however, there is no data for calculating the yearly loads.

Emission through slow ongoing release of TBT from quays and buoys painted with antifouling paint

Yearly load - ? to CSW

Uncertainty: N/A

This ES is likely to be relevant for Estonia; however, there is no data for calculating the yearly loads.

2.11.3 Water transport

NACE 50

The emission factor included in the emission strings table was presented by HELCOM report (2009). Because this data (1-10 μ g TBT per cm² of hull surface per day) has been confirmed by other sources, the estimation is that this source is trustworthy and has been given an A as data uncertainty.

TBTO is very effective against algae, gram positive bacteria, fungi and marine organisms (HELCOM, 2009). Therefore, emissions of TBTO are historically associated with maritime activities as from ship hulls. Today emissions of TBTO are mainly from contaminated sediments, especially in shipyards and harbours where boat traffic with antifouling paints have been common. In the HELCOM report (2009) the historical release rate of TBT from antifouling paint has been estimated to around 4 μ g cm² per day. Considering the given release rate and the estimated number of ship hulls, the Finnish ministry of Environment (cited in HELCOM, 2009) assumed that 50 tonnes of TBT was released from ship hulls during 1992-2005. This is considered to historically be the major TBT release to the environment in the Baltic Sea and the significant emissions into the region today is considered to be from the contaminated sediments in the harbours and shipyards. The study conducted by Eklund et al (2008, p 127) concluded that still 19 years after vessels of pleasure boat size were prohibited to use TBT antifouling paints, there is TBT released to the environment from these vessels.

The release of TBT from antifouling paint is due to a chemical reaction with seawater, which triggers the biocide release from the self-polishing antifouling paint or copolymer paint. The copolymer paint was the most generally used antifouling paint in the 1980s, having a release rate of 1.6 μ g (Sn) cm⁻² per day (Hoch 2001, p 725). This paint had higher emissions when the ship hulls were newly painted, and decreasing over time.

Emission due to gradual release from antifouling paint on ships and boats



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Yearly load - ? to CSW
Uncertainty: N/A

This yearly load should be zero as there is a ban on the use (European regulation 782/2003, AFS Convention). From 2008 ships carrying an active TBT based paint will no longer be allowed to enter European harbours. However, there might be some illegal use and hence this ES might be of some relevance for Estonia.

AFS Convention International Convention on the Control of Harmful Anti-Fouling Systems on Ships – AFS Convention (2001) entered into force in 17 September 2008. According to the Convention TBT-based paint must not be applied after 1 January 2003, and by 1 January 2008 no ships must carry active TBT-based paint on their hulls, ships are required to either remove any organotin compounds that are on their surfaces or to ensure that any organotin compounds on their external surfaces are sealed to prevent their leaching into the water.

The ships must have an AFS certificate that proves they are not using anti-fouling paints containing TBTs. Ships flying the flag of a state that has not joined the Convention or the Regulation must demonstrate their compliance to the Convention and the Regulation. Both the AFS Convention and the EU regulation do not apply to any warship, naval auxiliary or other ship owned or operated by a State and used, for the time being, only on government non-commercial service.

The AFS Convention was ratified in Estonia in 3 December 2008 and entered into force in 23 April 2009.

Emission of TBT due to stripping of old TBT coatings from ships and boats

Yearly load - ? to FS, IS, and CSW

Stripping is usually done in dry docks by sandblasting (or blasting with other biodegradable materials such as walnut shell, baking soda etc.), or by chemical stripping. The Farrow System is a patented method using proprietary organic media – natural volcanic pumice the company calls Green Clean and hot water at low pressure. The distribution of emissions between different environmental compartments as a result of paint stripping activities will depend on the particular method used.

2.12 Sewerage

2.12.1 Crop and animal production, hunting and related service activities

NACE: 1



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Release due to spreading of contaminated sewage sludge

This ES is considered in the following ESs

2.12.2 Sewerage

NACE 37

TBT-s in sewerage sludge from municipal WWTP-s

Yearly load – 0,07 kg to AS

Yearly load – 0,16 kg to FS

Uncertainty: BBBC

The calculations were done using the data from COHIBA WP3 and the preliminary results from BaltActHaz project that gave us the EF. The EF was considered to be the average result of all WWTP-s. The representability is highly uncertain due to limited data. The EFM is the one from European SFA-s, considered to be representative to Estonia by Mr Kõrgmaa, an expert of WWTPs and sewage sludge (personal communication). The yearly load was calculated by multiplying EF with EFM and number of inhabitants in Estonia.

Effluents from the WWTP-s

Yearly load – 0,012-0,033 kg to CSW

Yearly load – 0,03-0,08 kg to FSW

Uncertainty: BAAC (The uncertainty of the yearly load is marked as C because the data used for calculation is too limited to be considered reliable)

The calculations were done using the data from COHIBA WP3 and the preliminary results from the BaltActHaz project – that gave us the EF. The EF was considered to be the average result of all WWTP-s. For min scenario, the results under LOQ were considered to be; for max scenario, the results below LOQ were considered to be LOQ. The EF was then multiplied by the EFM, i.e. the amount of effluents produced per person a day – 125 litres (according to Statistics Estonia 2010), the number of inhabitants (1 340 021 according to Statistics Estonia 2010), and the number of days a year (365).

2.12.3 Waste treatment and disposal

NACE 38.2

Leaching from consumer products containing TBT in landfill

Yearly load – 0 –0,005 kg to SW

Yearly load – 0 –0,005 kg to SW



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Uncertainty: C

The calculations were done using the excel sheet provided by IVL. The data used was from the COHIBA WP3 results from the study of landfill leachate. However, this result is considered extremely inaccurate as it is based on two samples from one landfill.

To point out our opinion, the leachate from the hazardous wastes should be in a different ES. However, we didn't find it meaningful to create an additional ES as we have no data from the effluents of leachates of hazardous waste landfills.

Disposal to landfill of waste materials and consumer products containing organotins can result in their presence in landfill leakage (Mersiowsky et al., 2001 cited by WWF).

2.13 Consumer products

2.13.1 Other - Emission from (private) consumption; during lifetime use

There may be TBT emissions released from consumer products as TBT often is present as an impurity in products such as PVC plastics, textiles etc. No Emission factors were found for these sources.

The US NIH Household Products Database indicates use of TBT in consumer products such as interior wall/wood caulk, sidewalk and driveway crack repair, window and door caulk, tub and tile caulk, concrete/mortar repair, tile adhesive, and kitchen and bath caulk. Updated versions of the database no longer show these items however, so it is possible that these products no longer contain TBT. The presence of TBT in households can also be confirmed by data presented in ScorePP (Deliverable 5.2) which showed the presence of TBT in household wastewater. TBT has been used on the inner surfaces of cardboard and cellophane containers for tomatoes. TBT concentrations measured in a range of seafood from around the world are also summarised in ATSDR (2005) and values range from below detection limit to 655 ng TBT/g wet weight.

Emissions from consumer products (e.g textiles, materials in contact with food PVC products etc)

Yearly load - ? to WW

Uncertainty: N/A

Emissions to household wastewater from TBT contaminated food prepared and consumed in the household (e.g. seafood)

This ES is included in total sewerage rows.



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2.14 Others

2.6.1. Warehousing and storage

NACE 52.1

Emission to the environment due to dispersion from stockpiled TBT (i.e. from unused stocks - the use of TBT has now been banned).

Yearly load - ? to FS, WW, and AI

Uncertainty: N/A

No emission factors were found for this source of emissions. The emissions are assumed to be released to indoor air (AI), forest soil (FS) and wastewater (WW) during storage.

The quantity of stockpiled TBT products in the EU is not known. On banning the use of TBT for marine biocidal uses in the EU a short phase-out period was allowed. This was to reduce the risks associated with product recall, storage and disposal and allowed users time to adopt alternatives. However, evidence from France suggests that application continued to occur in some locations following the ban so it is likely that some stockpiling has occurred.

3 SFA diagram

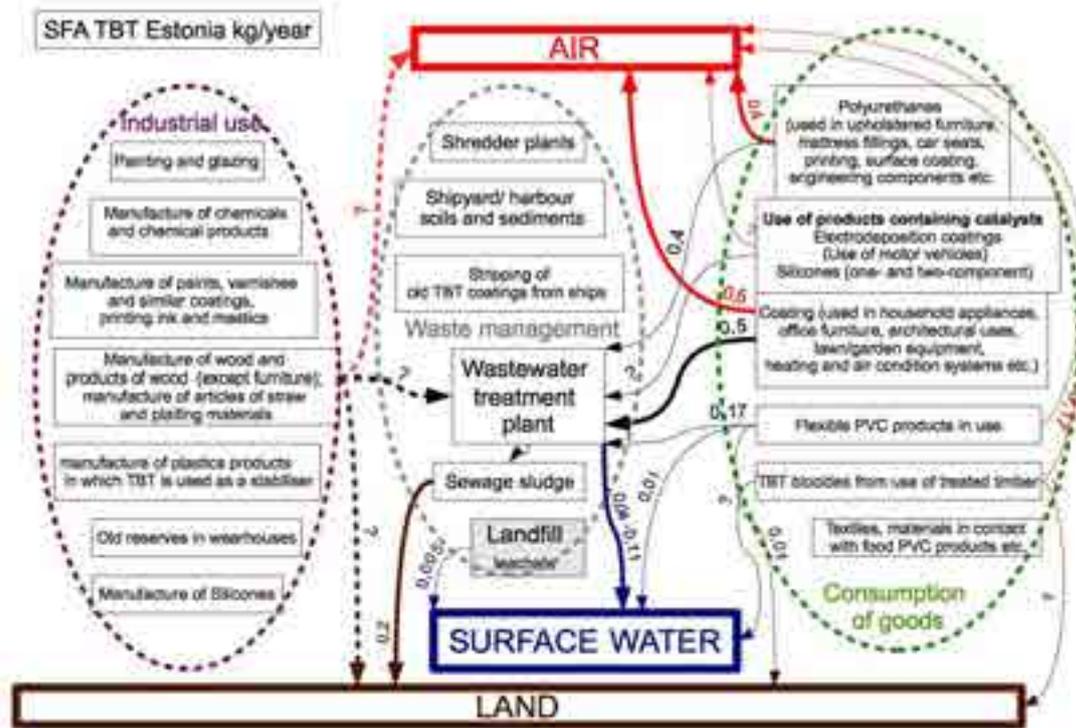


Figure 3. SFA diagram for TBTs in Estonia.



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4 Conclusions

4.1 Quantitative estimation of the most relevant sources to each environmental compartment (Soil, water and air)

TBT has been used in a great variety of materials and products, hence the potential number of sources is great. Estonia has no data at the moment to quantify the loads to the environment. No product registers and so on.

The biggest quantitatively estimated source for TBT are related to consumption of goods : coatings (used in household appliances, office furniture, architectural uses, lawn/garden equipment, heating and air condition systems etc.) emissions to air 0,5 kg and to WW 0,5 kg year; Polyurethanes (used in upholstered furniture, mattress fillings, car seats, printing, surface coating, engineering components etc.) emissions to air 0,4 kg and to waste water 0,4 kg. The biggest quantitatively estimated source to land is sewage sludge (0,2 kg) and to surface water the waste water treatment plant effluents (0,1 kg).

TBT is used in PVC as an additive in both everyday products and industrial use, as a additive.

TBT is found as a biocide in antifouling paints and wood preservation products, and as an impurity in PVC products and catalysts, in textiles, consumer products, silicones, and paints. We assume the emissions from industrial uses mainly end up in the wastewater or outdoor air. Emissions from municipal uses end up in air, WWTPs or soil.

Repairing of ships (removal of old anti-fouling paints) and residual pollution in the sediments of ports and harbours is a significant source of TBT pollution in Estonia. Pollution from this source affects the coastal water directly.

Many industrial activities are also possible for Estonia, but no data to quantify the loads.

4.2 A qualitative estimation of time trends for future scenarios

Possible means for reducing the emissions of TBT are mainly administrative. It is not possible to make future plans for reducing TBTs in Estonia as the mapping of the current situation is insufficient.

It is of utmost importance to further research the situation of the moment and make an inventory of the amounts of TBTs in products and environment to plan further actions and measures. It is also important to have better control over products (such as textiles) imported to Estonia from non-EU countries, i.e. have a better monitoring at the border as imported products may be an important source of TBTs.



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Also, raising of general awareness is of utmost importance. It is also necessary to add TBTs to the national monitoring.

For industries, it is necessary to use BATs and perhaps find alternatives for the use of TBTs. As most of the emissions of TBTs are led to WWTPs, it is also important to find technologies that help to stop the pollution at this point. Proper waste and sewage treatment will hopefully remove the substance entering the environment from this source.

It is safe to say that it is necessary to work with TBTs more. It is also safe to say the impacts of the TBTs on the environment will be far-flung.

The removal of polluted sediments from harbours and docks is one possible measure for reducing the effects of TBTs on the marine environment. If this cannot be done, the highly possible presence of TBTs in sediments must be kept in mind when planning future dredging or building new quays and docks.

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ANNEX C - Substance flow analysis for pBDE-s in Estonia

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This study was carried out under the COHIBA study from May 2010 to May 2011. This report is based on the SFA BDE (EU 27) by IVL Swedish Environmental Research Institute. The results are for Estonia. Many of the results are rough approximations that cannot be taken as exact results for Estonia, but more as a base to plan future studies. The results are for Estonia.

1 Introduction

Polybrominated diphenyl ethers are substances mainly used as flame retardants, with application in products such as plastics, textiles and upholstered furniture. Similar to the case of PCBs, the PBDE (polybrominated diphenyl ethers) group consists of 209 possible congeners of varying degree of bromination, of which only a few accounts for the vast majority of PBDE found in environmental samples. Atmospheric samples are normally dominated by components of lower bromination level (tetra-penta; typically BDEs 47, 99, 100), whereas biotic samples, soils and sediments usually contain higher proportions of the higher brominated congeners (hexa-deca; typically BDEs 153, 183, 209). Data on occurrence in surface water are so far very limited. Because of the varying form of occurrence depending on environmental matrix, as well as the possibility for degradation/transformation from higher to lower brominated components, this report considers all the commercially available technical products; namely penta- octa and decaBDE. The sources for the various components are discussed jointly, as some sources are of similar origin. In addition, it is sometimes hard to distinguish the technical products from one another when they reach the environment, as they all contain a mixture of different congeners, and degradation of higher brominated to lower brominated congeners is possible. Thus, the finding of for example a pentabrominated BDE congener in the environment may be the result of commercial penta usage or usage of octa and/or deca followed by degradation under certain circumstances and in certain matrices, such as biological material. Historically, the use of octaBDE in the EU has been somewhat higher than the commercial use of penta (Palm et al. 2004), but the dominant congeners in the octa mixture have rarely been reported. Therefore, in the current assessment, “pentaBDE” is treated as the sum of tri- to hexabrominated congeners (generally congeners 28, 47, 100, 99, 85, 154, 153, 138) and “decaBDE” is treated as the sum of nona-deca brominated congeners (normally congeners 183, 209). For these two technical products, separate emission factors are derived and two separate flow diagrams constructed.

Real measurements of emissions are scarce. Some studies have recently been performed concerning emissions of PBDEs from various materials (Kemmlin et al., 2003; Wilford



et al., 2003) and activities (Sakai et al., 2006). In addition, attempts have been made to estimate emissions on the European level (ECB, 2000; Palm et al.; 2004, Prevedouros et al. 2004; Alcock et al., 2003). This assessment combines the studies previously performed and where possible, emission/activity figures are updated. Substantial uncertainties are still connected with the quantification of emissions done below. For each emission estimate, a qualitative uncertainty factor is given, the description of which is found in the separate COHIBA document – “Dealing with uncertainty in substance flow analysis within the COHIBA project”.

Table 1. CAS (Chemical Abstract Service) numbers for the polybrominated diphenyl ethers

| Substance name | CAS nr |
|----------------|------------|
| pentaBDE | 32534-81-9 |
| octaBDE | 32536-52-0 |
| decaBDE | 1163-19-5 |

1.1 Physical chemical properties

The physical and chemical properties of the commercial polybrominated diphenyl ether products are presented in Table 2 and the general structure formula is shown in Figure 1. Physical-chemical properties of individual congeners has been reviewed and compiled by Palm et al. (2004).

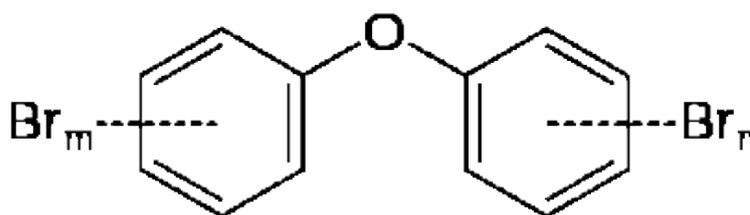


Figure 1. Chemical structure of the polybrominated diphenyl ethers





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Table 2. Physical and chemical properties of polybrominated diphenyl ethers (the commercial products). (Data from the EU risk assessments, ECB 2003a; ECB 2002; ECB 2000).

| Property | pentaBDE | OctaBDE | decaBDE |
|---|--------------------------------------|---|-----------------------|
| Physical state at npt | amber viscous liquid or semi solid | powder or flaked material | crystalline powder |
| Molecular weight (g/mol) | 564.7 | 801.38 | 959.2 |
| Melting point (°C) | -7 to -3 | 167-257 ^a 130-155 ^a 70-150 ^a | 300-310 |
| Vapour pressure (Pa) | 4.69×10 ⁻⁵ | 6.59×10 ⁻⁶ 21 °C | 4.63×10 ⁻⁶ |
| Log octanol-water partition coefficient (log Kow) | 6.57 (measured) 7.88 (calculated) | 6.29 at 25 °C | 6.27 |
| Water solubility (mg/l) | 0.0133 | 0.0005 | <0.0001 |
| Henry's Law Constant (Pa m ³ /mol) | 11 (estimation) | 10.6 (estimation) | >44 (estimation) |

a) The commercial product has a melting range depending on composition

1.2 Regulatory status

Directive 2002/95/EC on the Restriction of the use of certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) and Directive 2002/96/EC on Waste Electrical and Electronic Equipment (WEEE) entered into force on 13 February 2003. Both Directives require Member States to transpose their provisions into national law by 13 August 2004. Estonia joined the EU in May 2004 and has reconciled all the EU directives and has also all the regulations need to observe them.



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Maximum concentration values are set in the RoHS Directive. For the purposes of Article 5(1)(a) (RoHS) the Commission has adopted Decision 2005/618/EC whereby a maximum concentration value of 0.1% by weight in homogeneous materials for polybrominated diphenyl ethers (PBDE) shall be allowed.

In the Decision 2009/1 by parties to the Protocol on POPs, it was decided to amend the 1998 Protocol on Persistent Organic Pollutants (the “POPs Protocol”) with the Convention on Long-Range Trans-boundary Air Pollution. New substances were added including octabromodiphenyl ether and pentabromodiphenyl ether. These amendments have not yet entered into force for the Parties that adopted them¹.

A list of nine additional chemicals as persistent organic pollutants including pBDEs, PFOS and PFOS-F were added to the Stockholm Convention at its fourth meeting held from 4 to 8 May 2009, the Conference of the Parties (COP), by decisions SC-4/10 to SC-4/18, adopted amendments to Annexes A (elimination), B (restriction) and C (unintentional production)².

The objective of the Regulation 850/2004/EC on persistent organic pollutants is to protect human health and the environment from persistent organic pollutants by prohibiting, phasing out as soon as possible, or restricting the production, placing on the market and use of substances subject to the Stockholm Convention on Persistent Organic Pollutants or the 1998 Protocol to the 1979 Convention on Long-Range Trans-boundary. Revised with regulation 756/2010 when the new substances were added.

Regulation 689/2008/EC concerning the export and import of dangerous chemicals to implement the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade.

Regulation (EC) No 304/2003 of the European Parliament and of the Council of 28 January 2003 concerning the export and import of dangerous chemicals implemented the Rotterdam Convention on the prior informed consent procedure for certain hazardous chemicals and pesticides in international trade, which entered into force on 24 February 2004, and replaced Council Regulation (EEC) No 2455/92 of 23 July 1992 concerning the export and import of certain dangerous chemicals. The chemicals covered by the

1 the POPs Protocol - http://www.unece.org/env/lrtap/pops_h1.htm

2 Stockholm Convention new POPs - <http://chm.pops.int/Programmes/New%20POPs/The%209%20new%20POPs/tabid/672/language/en-US/Default.aspx>





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provisions of this Regulation relating to export notification, PIC notification and the PIC procedure respectively shall be as listed in Annex I. This annex I includes also octa- and penta-BDE-s. The data are collected to the EDEXIM database.

1.3 Production

No registered production in Estonia.

1.4 Use

Polybromodiphenyl ether congeners including tetraBDE, pentaBDE, hexaBDE, and heptaBDE inhibit or suppress combustion in organic materials and therefore are used as additive flame retardants. We have no registration under regulation 689/2008/EC (export and import of dangerous chemicals) and also no registered use under regulation 1907/2006/EC (REACH regulation) (personal communication with Endla Veskimäe Health Board Department of Chemical Safety –the responsible authority of Estonia e-mail conversation 20.12.2010 Mailis Laht).

1.5 Environmental fate

The physical-chemical properties of PBDEs generate an environmental behaviour characterised by strong tendencies to partition to organic carbon containing media such as soils and sediments. PBDEs bioaccumulate and sorb to lipid tissues in living organisms. PBDEs are persistent, and therefore last long enough to be transported long distances with the atmosphere, mainly associated with particles, but the lower brominated congeners can also be found in the gaseous phase. A current topic of interest to scientists is to study the transport processes from source to the Arctic, including the movement of small particles, as a large proportion of PBDEs is believed to be emitted from products used indoors. An increasing number of studies focus on the indoor and urban environment as sinks or sources of PBDEs (e.g. Wilford et al., 2005; Hazrati & Harrad, 2006; Harrad et al., 2007; Zhang et al., 2009).

1.6 Environmental levels

Research on environmental levels of PBDEs in Estonia provides only limited information. Single measurements in air from northern and northeastern Estonia (Lahemaa and Kohtla-Järve regions) gave for sum of PBDEs concentrations 22,97 resp.





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47,77 pg/m^3 . Most abundant components were PBDE- 47 and PBDE-99 (Roots et al, 2007).

Wide use of PBDEs in a variety of products together with the fact that in the Estonian Thermal Power Plant oil shale with substantial chlorine content (0,22%) is thermally processed in large quantities allows to anticipate that Estonia might contribute to the load of chlorinated POPs, among others possibly to PBDEs load to the Baltic. The analysis of soil samples from selected urban and rural areas in northern and southern Estonia and from reference areas which served also as EMEP areas (Vilsandi and Lahemaa) showed in most cases the presence of only 4 PBDE congeners – PBDE-30, PBDE-47, PBDE- 99 and PBDE-100, while PBDE-47 was the most abundant in all samples. The highest were the concentration in soil from Kunda and Lahemaa locations. The concentrations of PBDEs in the studied locations are presented in the Table 3 below as the sum of all detected congeners.

Table 3. Concentrations (ng g-1dw) of PBDEs in soil samples from Estonia (Kumar et al., 2009).

| Location | Sum of PBDEs (ng g ⁻¹ dw) |
|---------------------|--------------------------------------|
| Ahja-1 | 0,32 |
| Ahja-2 | 0,03 |
| Eerika-1 | 0,27 |
| Eerika-2 | 0,04 |
| Eerika-3 | 0,07 |
| Eerika-4 | 0,37 |
| Kohtla-Järve 1 | 0,16 |
| Kohtla-Järve-2 | 0,04 |
| Kohtla-Järve city-1 | 1,03 |
| Kohtla-Järve city-2 | ND |
| Muuga Port 1 | 0,03 |
| Muuga Port 2 | 1,70 |
| Kunda-1 | 1,6 |
| Kunda-2 | 1,1 |
| Lahemaa EMEP-1 | 0,70 |
| Lahemaa EMEP-2 | 0,08 |
| Vilsandi EMEP | 0,21 |

The concentrations of PBDEs in Estonian soils are rather low but some increase in the future is possible because of the lack of incineration facilities in Estonia to safely utilize PBDEs containing materials. Therefore further control and monitoring of these substances are necessary.





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As fish is an essential source of accumulation of harmful organic pollutants into human organism, attention has been paid also for investigating PBDEs levels in Baltic fish. Concentration profiles of PBDEs in Baltic herring in 2006-2008 from three different areas of the sea – open Baltic, Gulf of Riga and Gulf of Finland - were studied depending on weight, age and gender of fish (Roots, 2009).

Comparing the concentrations of the sum of PBDEs in Baltic herring to the results obtained earlier by other investigators (Parmanne, 2006) showed that the concentrations between 1999 and 2008 did not change considerably.

Large differences in PBDEs profiles and high concentrations of BDE-209 in some samples were mentioned. Average concentrations for sum of PCDEs in Baltic herring remained in the interval 0,65-0,86 ng g⁻¹ fresh weight. In sprat this interval was 0,67-0,92 and in eel 0,91-1,37 ng g⁻¹ fresh weight (Roots, 2008).

To harmonize activities in the field of food safety with EU first steps in Estonia have been made also to monitor food contamination with persistent organic pollutants, among others with PBDEs (Roots, 2007). PBDEs concentration in Estonian food was found to be below 4 ng g⁻¹, the majority being below 2 ng g⁻¹ (Table 4).

Table 4. Concentrations of PBDEs on Estonian foodstuffs

| Foodstuff | Sum of PCDEs (ng g ⁻¹ fat) |
|-------------|---------------------------------------|
| Meat (pork) | 0,05-3,90 |
| Butter | 0,38-1,80 |
| Milk | 0,02-1,40 |

COHIBA project was one of the first times to measure pBDE-s in WWTP effluents and sludges, landfills, and urban runoff in Estonia. Therefore we mainly used that data for detecting the possible sources of pBDEs.

Short summary of results from those two projects is given below. Congeners 28, 47, 99, 100, 153, and 154 are considered as pentaBDE-s, congeners 183 and 203 as octaBDE-s, and BDE-209 as decaBDE. The most abundant component was BDE-209 followed by BDE-99 and BDE-47.

Table 5. pBDE in waste-water and sewage sludge in Estonia 2009-2010 (Data from COHIBA WP3).





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| Substance | WWTP1 | | WWTP2 | WWTP3 | | WWTP4a | WWTP4b |
|------------|---------------|--------------------|---------------|---------------|--------------------|---------------|---------------|
| | Water ng/l | Sludge µg/kg dw | Water ng/l | Water ng/l | Sludge µg/kg dw | Water ng/l | Water ng/l |
| pentaBDE-s | Nd – 0,57 | 26,58 | Nd – 0,40 | Nd – 0,39 | 27,0 29,86 | – Nd – 0,2 | Nd – 0,35 |
| octaBDE-s | Nd | 2,25 | nd | nd | 1,92 – 2,08 | nd | nd |
| decaBDE-s | 0,13 – 1,70 | 303,60 | 0,17 – 2,16 | 0,17 2,42 | – 1010 – 1183 | 0,2 – 2,76 | 0,24 – 0,76 |

Table 6. *pBDE-s* in Estonian landfills and stormwaters (data from COHIBA WP3).

| Substance | Landfill ng/l | Stormwater ng/l |
|------------|------------------|--------------------|
| pentaBDE-s | 5,94 – 10,67 | Nd – 1,3 |
| octaBDE-s | Nd – 1,36 | Nd – 0,25 |
| decaBDE-s | 3,28 – 3,73 | 3,73 – 10,40 |



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2 Sources of emissions of pBDEs in Estonia

The uncertainties in the following emission strings are given with four letters, the first letter representing uncertainty for EF, the second for EFM, the third for division into compartments and the fourth for the yearly load. Uncertainty is classified according to the principles described in “Dealing with uncertainty in substance flow analysis within the COHIBA project”, a PM describing how data uncertainty is graded in WP4 of the COHIBA project.

If the Estonian yearly loads were scaled from the EU yearly load to Estonian population, the Estonian population was considered to be 0,3% of the EU population. This accuracy level was considered to be enough for given study, especially considering the very high uncertainty levels in other emission strings.

2.1 Dismantling of wrecks

NACE 38.31

Car recycling

Yearly load for both penta- and decaBDEs - ? to ?

Uncertainty – n/a

We assume this ES to be relevant for Estonia but we have no proper information to calculate the yearly loads. There is a register of licensed institutions³ that are allowed to dismantle wrecks (according to Directive 2002/95/EC on the Restriction of the Use of certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) and Directive 2002/96/EC on Waste Electrical and Electronic Equipment (WEEE)). However, there is no information available about the volumes processed.

If we assume that the pBDEs are mainly used in plastic parts, then statistics of Estonia (waste report by formation of waste) shows 638,92 t of plastic waste from car recycling.

Volatilisation and particle release from dismantling plants of electronic equipment

pentaBDE

Yearly load - ? to ?

³ <http://www.envir.ee/108233>, accessed 2.11.2010





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Uncertainty – n/a

decaBDE

Yearly load low – **0,00083 kg** to FSW

Yearly load low – **0,00083 kg** to WW

Uncertainty - BCCC

decaBDE

We used the EU EF-s (Sakai et al. 2006). The yearly load was derived from the EU yearly load, using the Estonian population of 0,3% of the EU population as a basis for calculation.

$$185000 \text{ t} * 0,3\% = 55,5\text{t.}$$

The Statistics Estonia 2010 (Waste report by formation of waste) shows that approximately 3143,855 t of electronic equipment was collected at 2009 (considered relevant only for decaBDE). From that approximately 1500 t was exported. 970t of electronic waste stays in Estonia on what purpose is unknown, also the percentage of potential decaBDEs is unknown. Hence we decided to use extrapolate the EU yearly load for Estonian population. Receiving compartments were assumed to be 50% to WW and 50% to SW.

2.2 Private consumption

Volatilisation from Flexible polyurethane (PUR) in products

PentaBDE (congener 47 only)

Yearly load – **17 kg** to IA

Uncertainty – BBBC

This yearly load was extrapolated from the EU yearly load for Estonian population, which was considered to be 0,3% of the EU population.

Electronic appliances – TV sets

pentaBDE (congeners 28, 47, 66, 99, 100, 153, 154)

Yearly load – 3,75 kg to IA

Uncertainty - BBAC

Calculation: 40 mil m² of housing in Estonia times the European EF 10,7 ng/m² h times 8760 h (hours per year).





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Electronic appliances – PC sets

pentaBDE (congeners 28, 47, 66, 99, 100, 153, 154)

Yearly load 12,28 kg to IA

Uncertainty – BBAB

30% of Estonian families have PC sets at home⁴. Calculation: 40 milj m² of housing in Estonia times the European EF 21,24 ng/m² h times 8760 h (hours per year). Only the living space is considered. Offices and public spaces are left out.

Electronic appliances - plastic housings

pentaBDE (sum of 28,47,66,100,99,153,154)

NB! In excel table it is considered under decaBDE in both EU and also Estonian SFA table!

Yearly load low – 0,005 – 0,1 kg to IA

Uncertainty – BCAC

EU emission factors were used – 0,2 ng/g and 0,48 ng/g. There was no Estonian specific data available on how much plastic housings are in use so we extrapolated the EU EFM to Estonian population, which was considered to be 0,3% of EU population – therefore the Estonian EFM was 72000 t * 0,3% = 2400 t. The EF and EFM were then multiplied. The used amount of plastic is 186 t.

Solid polyurethane foams

pentaBDE

Yearly load - ? to ?

Uncertainty – n/a

We assume this ES to be important in Estonia but we have no information about it.

Emissions from indoor environment

pentaBDE

Yearly load low – 0,007 kg to AO

Uncertainty – BBAC

Yearly load high – 0,073 kg to AO

4 www.riso.ee/et/files/upload/Lairibastrateegia.pdf





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Uncertainty – --AC

decaBDE

Yearly load – 0,05 kg to AO

Uncertainty – BBAC

The yearly loads were calculated as follows: the EU EF was used (for pentaBDE 14 -149 pg/m^3 and for decaBDEs 94 pg/m^3). Estonian housing space of 40 million m^2 was multiplied with average height of rooms (2,5 m), giving 100 000 000 m^3 as EFM.

For comparison, the yearly load low for pentaBDEs was calculated from the EU SFA, extrapolating the result for Estonian population, which was considered to be 0,3% of the EU population. As the results from two different calculations were different by a magnitude, we cannot be sure which one is more correct.

Uncontrolled households burning

PentaBDE

Yearly load – 0,028 kg to OA

Uncertainty – CCAC

The calculations are based on the assumption that this ES doesn't consider accidental fires but burning of wastes in residential areas. We also assumed there is one event per person a year of burnings with wastes. (If the BDEs are mostly used in electronic equipment and not much in everyday waste, then the number is certainly smaller. The number of electronic equipment used per person is not so high that we could burn at least one set per person in a year. Textile and furniture are burnt much more).

Calculation: The European EF 0,022 mg/person event times approximate number of Estonians (i.e. 1 300 000). The reliability of this result is **extremely** low.

2.3 Sewerage

NACE 37.00

Effluents from the WWTPs

pentaBDE (sum of congeners 47, 100, 99, 85, 154, and 153)

Yearly load **0,003 – 0,009 kg** to CSW

Yearly load **0,006 – 0,021 kg** to FSW





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Uncertainty – BABB

decaBDE (considers sum of congeners 183, 203, 209)

Yearly load **0,016 – 0,017 kg** to CSW

Yearly load **0,036 – 0,039 kg** to FSW

Uncertainty - BABB

The calculations were done using the data from COHIBA WP3 that gave us the EF. The EF was considered to be the average result of all WWTPs. For EF low, the results below LOD were considered 0 and the results below the LOQ were considered to be the LOD. For EF high, the results below the LOD were considered to be the LOD and the results below the LOQ were considered to be the LOQ. The EF was then multiplied by the EFM, i.e. the amount of effluents produced per person a day – 125 litres (according to Statistics Estonia 2010), the number of inhabitants (1 340 021 according to Statistics Estonia 2010), and the number of days a year (365).

BDEs in sewage sludge from municipal WWTPs

pentaBDE (sum of congeners congeners 28, 47, 99, 100, 153, 154).

Yearly load – **0,20 kg** to AS

Yearly load – **0,43 kg** to FS

Uncertainty - CBBC

decaBDE (sum of congeners 183, 203, and 209).

Yearly load – **8,23 kg** to AS

Yearly load – **17,48 kg** to FS

Uncertainty – CBBC

The calculations were done using the data from COHIBA WP3 that gave us the EF. The EF was considered to be the average result of all WWTPs. The representability is highly uncertain due to limited data. The EFM is the one from European SFAs, considered to be representative for Estonia by Mr Kõrgmaa, an expert on WWTPs (personal communication). The yearly load was calculated by multiplying the EF with EFM and the number of inhabitants of Estonia.

2.4 Washing and (dry-) cleaning of textile and fur products

NACE 96.01

Yearly load - ? to ?



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Uncertainty – n/a

The yearly load for both penta- and decaBDE-s in all ES-s is unknown at the moment (as of May 2011). We assume it's a relevant ES as this kind of activity definitely takes place in Estonia, but we have no data to approve or disapprove.

2.5 Waste treatment and disposal

NACE 38.2

Landfill fires

Yearly load - ? to AO

Yearly load - ? to WW (for pentaBDEs)

Uncertainty – n/a

The yearly load for both penta- and decaBDE-s in all ES-s is unknown at the moment (as of March 2011). However, we assume this ES to be relevant for Estonia, but we have no data to prove or disapprove.

Landfill leachate

pentaBDE (sum of congeners 28, 47, 99, 100, 153 and 154)

Yearly load **0,0096 – 0,0113 kg** to SW

Yearly load **0,0096 – 0,0113 kg** to FS

Uncertainty - --CC

decaBDE (Sum of congeners 183, 203, and 209)

Yearly load **0,0046 – 0,0052 kg** to SW

Yearly load **0,0046 – 0,0052 kg** to FS

Uncertainty - --CC

The calculations were done using the excel sheet provided by IVL. The data used was from the COHIBA WP3 results from the study of landfill leachate. However, this result is considered extremely inaccurate as it is based on two samples from one landfill. The researchers of this study would expect the loads from the leachate to be much greater, considering the properties, the general use, and overall mass balance of this substance.

Municipal waste incineration

Yearly load - ? to AO

Uncertainty – n/a



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Municipal waste incineration is still under development in Estonia and is irrelevant for Estonia at the moment (as of May 2011). However, this ES will be of importance in the future studies.

Some of the waste is incinerated in Kunda, however, this is not municipal waste (personal communication, Epp Volkov). The waste fuel is made from the municipal waste in landfills (e.g. Jõelähtme, the landfill that serves Tallinn, the capital of Estonia with the population of about 1/3 of Estonian population), however, as the waste incineration system is still under development, this waste fuel is sold to Latvia (personal communication with the manager of Jõelähtme landfill, 13.03.2011, Epp Volkov).

Accidental fires of electronic waste

pentaBDE

Yearly load – **1,53 kg** to AO

Uncertainty – BBAC

Yearly load – ? to AS, FS, WW

Uncertainty – n/a

decaBDE

Yearly load – **0,02 – 0,24 kg** to AO

Uncertainty – BBAC

Yearly load ? to AS, FS, WW

Uncertainty – n/a

The loads for both penta- and decaBDE-s in all ES-s are mostly unknown at the moment (as of May 2011). We assume this ES to be relevant for Estonia but we have no data to approve or disapprove.

The yearly load for BDE-s to AO was calculated from the EU SFA, extrapolating the EU yearly load to Estonian population, which was considered to be about 0,3% of the EU population.

2.6 Worldwide activities outside the region

Atmospheric deposition mainly derived from long-range transport



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pentaBDE

Yearly load – **0,00075 kg** to AS

Yearly load – **0,16 kg** to FS

Yearly load – **0,015 kg** to SW

Uncertainty - BAAC

Yearly loads low and high **0,83 – 106,1 kg** to AS

Yearly loads low and high **1,77 – 226,3 kg** to FS

Yearly loads low and high **0,17 – 21,22 kg** to SW

Uncertainty - CAAC

decaBDE

Yearly load – **0,69 kg** to AS

Yearly load – **1,48 kg** to FS

Yearly load – **1,4 kg** to FSW

Uncertainty – BAAC

Yearly loads low and high – **8,75 – 242,87 kg** to AS

Yearly loads low and high – **18,67 – 518,12 kg** to FS

Yearly loads low and high – **1,75 – 48,57 kg** to FSW

Uncertainty – CAAC

The yearly loads are calculated from the Swedish air monitoring data. The yearly loads low and high are calculated from the EU SFAs.

The deposition numbers from Swedish air database (summary made by IVL partners – Swedish Environmental Protection Agency: National Air Monitoring National Air Database, www.ivl.se) were used to calculate the yearly loads. We used an average value after discussion with our air monitoring specialist Erik Teinmaa. The Swedish monitoring stations are located on the similar latitude and we considered the results to be comparable to Estonia. The calculated emission factor was 51,1 ng/ m² (Average deposition per day 0,14 ng/m²).

As the earlier versions of EU SFAs gave also some emission factors for other congeners that were not monitored, we considered it to be the best option to give three different numbers. Lower boundary considers the sum of 47, 99, 100. Upper boundary also includes congeners 28, 153, 154. For low and high calculations the EU SFA emission factors were used. EU emission factor for decaBDEs is 645 and 17 900 ng/m²; and 61 and 7811 ng/m² pentaBDEs (Deposition data from various studies (see EU SFA report)).





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Estonian territory is 45 000 km². The division into compartments was made, using statistical data from Estonia – 30% AS, 64% FS, 6% FSW⁵.

In the Decision 2009/1 it was decided to amend the 1998 Protocol on Persistent Organic Pollutants (the “POPs Protocol”) with the Convention on Long-Range Trans-boundary Air Pollution. The pBDEs were added to the protocol with this decision. As a consequence, we can assume that the activities outside Estonia are also an important source of pBDEs. Estonia does not monitor the deposition for pBDEs at the moment.

5 Estonian Forestry 2009 – <http://www.keskkonnainfo.ee/failid/forestry2009/EstonianForestry.swf> (last accessed 15.03.2011)



3 SFA diagrams

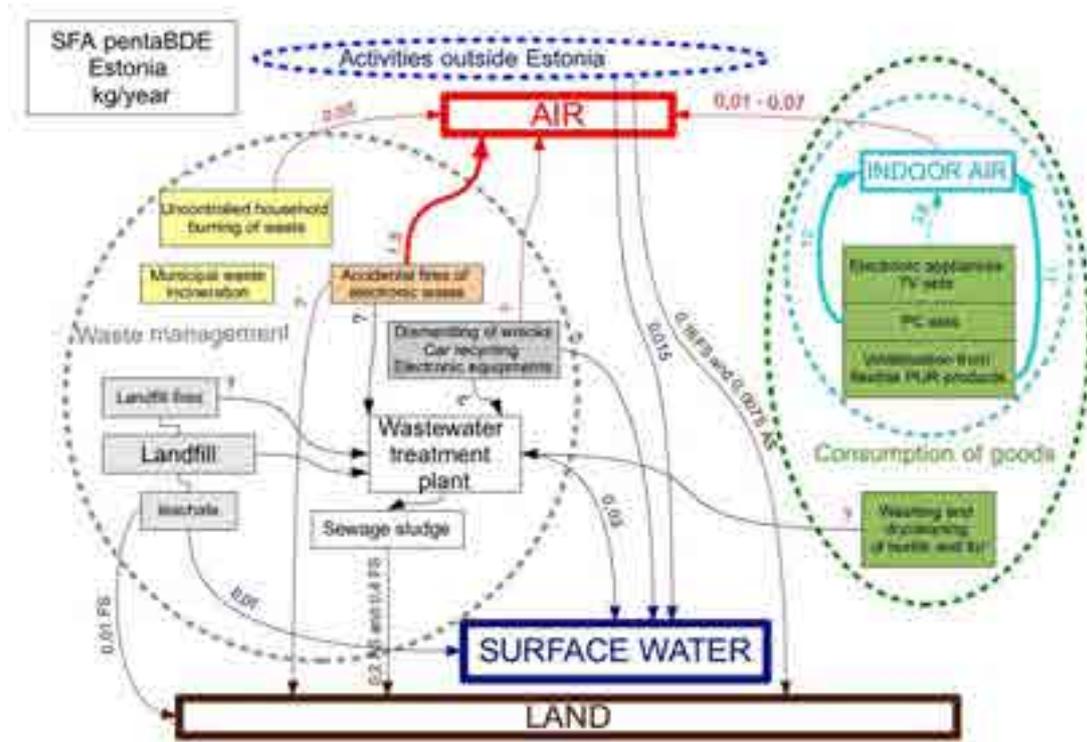


Figure 2. SFA diagram for pentaBDEs in Estonia.

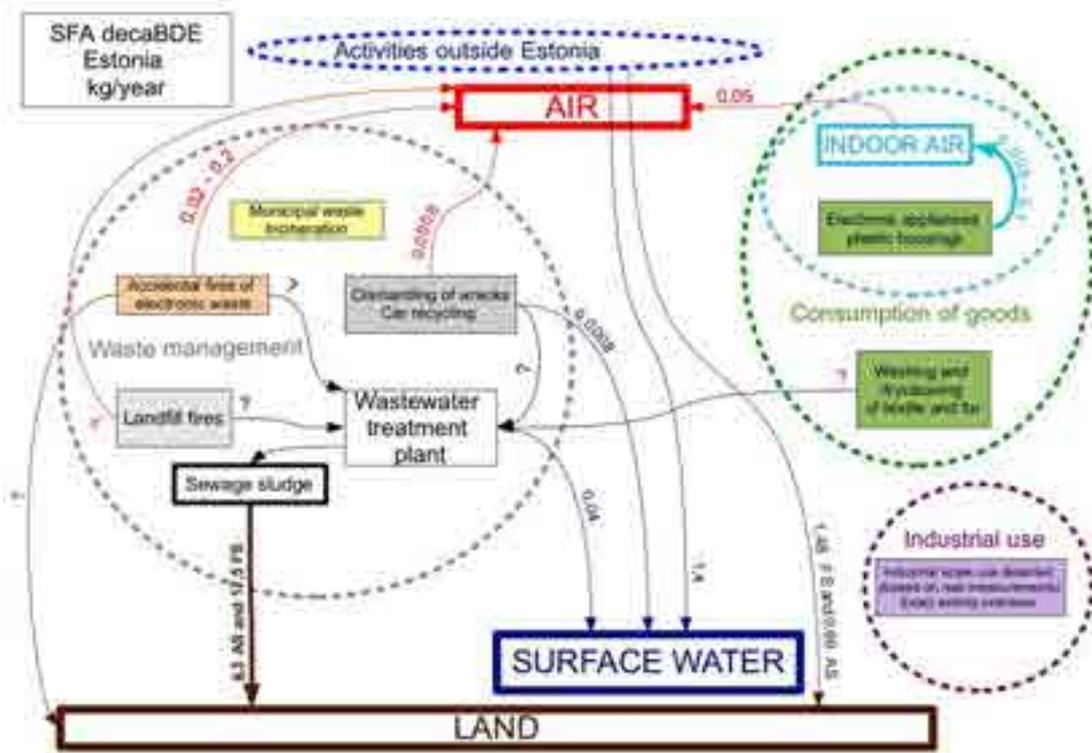


Figure 3. SFA diagram for decaBDEs in Estonia.



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4 Conclusions

4.1 *Quantitative estimation of the most relevant sources to each environmental compartment (Soil, water and air)*

The most common congeners found in Estonia were BDE-47, BDE-99, and BDE-209.

For many cases we could not calculate the load but if we compare our results from WP3 and studies from other countries, it seems like the most possible sources are products containing the substances. The results of WP3 indicate that the level of pBDEs detected is in correlation with the number of inhabitants in the area and also that the level is similar for all the city areas.

The most important source for pentaBDEs in Estonia is the consumption of products containing pBDEs like electronic appliances (emissions from TV sets 3,8 kg to indoor air and PC sets 17 kg to indoor air). The calculated load from indoor air to outdoor air were 0,01 – 0,07 kg/year.

Also, burning activities release pBDEs to the environment. Accidental fires are not an easily predictable source but there are some smaller or bigger scale fires every year. Based on statistics and available measurement data the load from different waste fires was calculated and the emissions to the air are estimated as 1,56 kg.

The detected emissions from secondary sources wastewater treatment plants with effluent water and landfill leachate gave a total emission of 0,4 kg to the surface water and 0,7 kg to the land. Air deposition from long-range transport of pollutants can also be an important source of pentaBDEs in Estonia (0,17 kg to land and 0,015 kg to surface water) but the quantitatively detected sources have higher loads.

PentaBDEs are banned and the loads from industrial activities are stopped but the critical point to avoid environmental damages is the proper waste management. Avoiding uncontrolled burning of waste and preventing accidental fires is a possible way to reduce the emissions from waste string to the environment. Incineration of municipal waste and dismantling of wrecks and electronic equipment are also the possible sources in Estonia and those activities need to be further studied to calculate the loads to the environment and propose possible measures to reduce the discharges.





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The most important source inside Estonia for decaBDEs to air are incineration activities and accidental fires of electronic waste 0,2 kg to air is the load calculated from statistical data.

The most important quantitatively detected source to land is sewage sludge (7,35 kg AS and 15,62 kg FS). To avoid the pBDEs entering the environment again, proper sewage sludge treatment and control of burning events and thermal processes is needed. Some local land pollution can come from fire incidence and also the sites of dismantling wrecks. The recycling and dismantling of cars and electronic equipment is assumed to be an important source for Estonia (other countries like Denmark have showed studies in frame of COHIBA that it could be relevant for pBDEs). However, there are no emission factors available so we could not calculate the load for that string. Further studies and also monitoring measures for dismantling activities are needed.

Based on measurements done in COHIBA WP3, we can assume that in some cities industrial use of decaBDE can also be an important source in Estonia, but we could not detect the field or company where the substance is used.

The most important quantitatively detected source to air is indoor air (0,05 kg/year) and the sources to the indoor air are electronic appliances (0,1 kg/year) especially the plastic housing (pBDE-s are used as flame-retardant). Fire activities are also big risk releasing the substance to the air.

The most important quantitatively detected source to surface water are the secondary sources like waste water treatment plant effluents (0,04 kg/year) and the landfill leachate (0,005 kg/year). The numbers can look small but the EQS for pBDEs in freshwater is 0,0005 µg/l. It means the substances are toxic and the measures to reduce the discharges are needed.

Activities outside Estonia have also impact to the loads in Estonia (0,69 kg/y AS and 1,48 kg FS; 1,4 kg FSW).

Considering the literature we can also assume that load of pBDEs from Estonia is higher than the amounts calculated in this study as certain amounts of pBDEs may be released from oil shale mining and oil shale thermal processing. More research is needed on that issue.





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4.2 A qualitative estimation of time trends for future scenarios.

There are many international agreements that Estonia is a part of that aim to decrease the level of pBDEs. The main goal in Estonia should be a proper waste management system. Also, raising of awareness should not be underestimated due to the use of those substances in everyday products and the fact that public has direct contact with the substance daily. If everyone could understand that the proper waste management can avoid pollution then we could have a good ground for the next steps. Possible loads from municipal waste incineration are the critical point for the future (emissions to air 0,00147 - 26,43 kg the load is calculated with today's waste amount). Municipal waste is not incinerated in Estonia yet, but there are some plants under development. That's the reason why we have calculated the possible loads from that string.

4.2.1 Commission proposes revised laws on recycling and use of hazardous substances in electrical and electronic equipment

Too few products collected and recycled

EU legislation to restrict the use of hazardous substances in electrical and electronic equipment and to promote the collection and recycling of such equipment has been in force since August 2004. More than four years later only about a third of electrical and electronic waste is reported to be treated in line with these laws and the other two thirds is going to landfill and potentially to sub-standard treatment sites in or outside the European Union. Apart from losing out on valuable secondary raw materials, this is especially worrisome since inadequately treated products pose major environmental and health risks. The illegal trade to non-EU countries also continues to be widespread. Moreover many electrical and electronic products not complying with the substance restrictions have been found in the EU.

Legislation on electrical and electronic equipment has proved difficult to implement and enforce by market actors and public authorities. The Commission proposes measures to address these difficulties and reduce the cost of putting into effect the revised directives.

New collection and recycling targets and greater coherence

The objective of the proposed directives is to develop a better regulatory environment, one that is simple, understandable, effective and enforceable. The scope and definitions of both directives would thus be clarified. The proposed directives would also improve their compatibility with other EU legislation such as the Waste Framework Directive and REACH and the recent "Marketing of Products" package. They would enhance the





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implementation and enforcement of current provisions and lessen the administrative burden on businesses. Under the new WEEE directive registration and reporting obligations for producers would be harmonised and national registers would be made interoperable. It is estimated that savings under the proposed revised directives would amount to some €66 million. The directives also seek to better control the illegal trade of electrical and electronic equipment.

The proposed revised RoHS directive would cover medical devices and monitoring and control instruments. A list of "priority" substances posing particular environmental concerns when used in electrical and electronic equipment will be assessed in line with REACH with a view of a possible ban in the future. Complying with the requirements of the directive will also be made easier with the introduction of the CE label for electrical and electronic equipment.

The proposed revised WEEE directive sets a new binding target for the collection of electrical and electronic equipment. The current collection target of 4 kg per person per year does not properly reflect the situation in individual Member States. Some Member States where the consumption of electrical and electronic equipment is widespread would have more ambitious targets under the new directive while others with smaller markets will have less ambitious targets. The Commission proposes to differentiate the targets by setting mandatory collection targets equal to 65% of the average weight of electrical and electronic equipment placed on the market over the two previous years in each Member State. The recycling and recovery targets of such equipment now include the re-use of whole appliances, and weight-base targets will increase by 5%. It is also proposed to set targets for the recovery of medical devices^{6,7}.

6 http://ec.europa.eu/environment/waste/weee/index_en.htm

7

<http://europa.eu/rapid/pressReleasesAction.do?reference=IP/08/1878&format=HTML&aged=0&language=EN&guiLanguage=en>





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ANNEX D - Substance flow analysis for PFOS and PFOA in Estonia

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This study was carried out under the COHIBA study from May 2010 to May 2011. This report is based on the SFA PFOS and PFOA (EU27) by IVL Swedish Environmental Research Institute. The results are for Estonia. Many of the results are rough approximations that cannot be taken as exact results for Estonia, but more as a base to plan future studies.

1 Introduction

Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are as the names imply perfluorinated substances, which means that each hydrogen on the compound's alkyl chain has been exchanged with a fluorine atom. PFAS is the collective name of perfluorinated alkyl sulfonates, and used as such in the present report (the abbreviation is sometimes used to include all perfluorinated substances). These substances are used for their surface active properties; they can form smooth surfaces that repel both fat and water.

There are a vast number of PFOS-related compounds, *i.e.* derivatives containing the PFOS moiety and PFOS-salts. Also PFOA exists in a number of forms of which the most commonly used is an ammonium salt called APFO (KemI 2004). In Table 1 commonly used abbreviations are explained and in Table 2 selected CAS number for PFOS, PFOA and related compounds are listed.

Table 1: Commonly used abbreviations in the present report

| Abbreviation | Explanation |
|----------------|--|
| APFO | Ammonium salt for PFOA, the most commonly used salt of PFOA |
| Fluoropolymers | Fluorocarbon based polymers, <i>e.g.</i> polytetrafluoroethylene (PTFE) |
| Fluorotelomers | Fluorocarbon based telomers |
| PFAS | perfluorinated alkyl sulfonates |
| PFO | perfluorooctanoate |
| PFOA | perfluorooctanoic acid |
| PFOS | perfluorooctane sulfonate |
| PFOSA | perfluorooctane sulfonic acid |
| POSF | perfluorooctane sulfonyl fluoride (CAS nr: 307-35-7); starting material for PFOS-related chemicals |





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| xFOSAs | perfluorooctane sulfonamides (N-methyl and N-ethyl FOSA; xFOSAs) |
| xFOSEs | N-methyl or N-ethyl sulfonamidoethanols |

Table 2: Selected CAS numbers for PFOS and PFOA as listed in Mehtonen 2009.

| Compound | CAS number | Comment |
|--|------------|--|
| PFOS | | The anion does not have a CAS number and is not commercially available (Keml 2004) |
| Perfluorooctane sulfonic acid | 1763-23-1 | |
| Potassium salt for perfluorooctane sulphonic acid | 2795-39-3 | |
| Diethanolamine salt for perfluorooctane sulphonic acid | 70225-14-8 | |
| Ammonium salt for perfluorooctane sulfonic acid | 29081-56-9 | |
| Lithium salt for perfluorooctane sulfonic acid | 29457-72-5 | |
| | | |
| PFOA | 335-67-1 | |
| Ammonium salt for PFOA, APFO | 3825-26-1 | |
| Sodium salt for PFOA | 335-95-5 | |
| Potassium salt for PFOA | 2395-00-8 | |
| Silver salt for PFOA | 335-93-3 | |
| Fluoride salt for PFOA | 335-66-0 | |
| Methyl ester for PFOA | 376-27-2 | |
| Ethyl ester for PFOA | 3108-24-5 | |

1.1 Physical chemical properties

Figure 1 shows the chemical structure of PFOS (Perfluorooctane sulfonic acid) and PFOA. Note that PFOS has eight perfluorinated carbons whereas PFOA has seven. PFOS is the dissociated anionic form of perfluorooctane sulfonic acid (PFOSA). PFOSA or salts of the acid will almost entirely dissociate in the environment due to the low pKa. Both PFOS and PFOA are rather water soluble compounds and may thus accumulate in



surface waters, *i.e.* eventually in the oceans, due to their persistence (Prevedouros *et al.* 2006; Paul *et al.* 2009).

The risk evaluations of PFOS made in the UK and in Sweden have both concluded that PFOS is a PBT substance (persistent, bioaccumulative and toxic) as well as a vPvB substance (very persistent and very bioaccumulative). PFOA on the other hand is as persistent as PFOS and it does fulfil the P and T criteria but not the B criteria (based on today's knowledge) (KemI 2004). In 2006, Canadian EPA finalised the PBT assessment of all 23 000 chemicals on their Domestic Substances List, drawing similar conclusions regarding PFOS and PFOA, with the Potassium-, Diethanolamine-, and ammonium salts of PFOS meeting the PBT criteria, and APFO meeting the P and T criteria with uncertainty regarding the B criterion (CEPA, 2010).

In Table 3 some physical and chemical properties of the substances are listed.

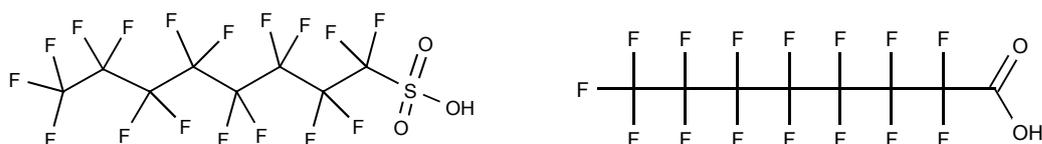


Figure 1: Chemical structure of PFOS (perfluoro sulfonic acid, left) and PFOA (perfluorooctanoic acid, right)

Table 3: Physical and chemical properties of PFOS and PFOA

| Property | PFOS | PFOA |
|--------------------------|--|---|
| Physical state at npt | Solid (Brooke <i>et al.</i> 2004) | Solid (OECD SIDS 2006) |
| Molecular weight (g/mol) | 500 (the acid) | 414.07 |
| Melting point (°C) | | 44-56.5 (Lide 2003 and Beilstein 2005, both quoted in OECD SIDS 2006) |
| Vapour pressure (Pa) | 3.31×10^{-4} (temp. not stated; Brooke <i>et al.</i> 2004) ^a | 4.2 (25°C) 2.3 (20°C) extrapolated from measured data (Kaiser <i>et al.</i> 2005 and Washburn <i>et al.</i> 2005, both quoted in OECD SIDS 2006) |





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| Log octanol-water partition coefficient (log Kow) | Not possible to measure (Brooke <i>et al.</i> 2004) | Not possible to measure (USEPA, 2005 quoted in OECD SIDS 2006) |
| Water solubility (mg/l pH or temp. not stated) | 519 (Brooke <i>et al.</i> 2004) | 9500 (Kauck and Diesslin 1951 quoted in OECD SIDS 2006) |
| Dissociation constant | -3.27, the acid, calculated (Brooke <i>et al.</i> 2004) ^b | 1.5-2.8 (Kissa 2001 quoted in OECD SIDS 2006) |
| Henry's Law Constant (Pa m ³ /mol) | 3.19×10^{-4} , calculated from vapour pressure ^a and water solubility (Brooke <i>et al.</i> 2004) ^c | Cannot be calculated since PFOA is a dissociating substance (OECD SIDS 2006) |

- a) Measured for the potassium salt. According to Brooke *et al.* 2004 the reliability if this value is limited and there are indications that the vapour pressure is lower.
- b) The substance is a strong acid and will in the environment be present in the ionised form (Brooke *et al.* 2004).
- c) The validity of this value is uncertain, see e.g. the comment on Henry's law constant of PFOA

1.2 Regulatory status

The use of PFOS within the EU is regulated with Directive 2006/122/EC from mid 2008 (European Parliament and Council 2006a). Current EU legislation regarding PFOS can be found in Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH, Regulation (EC) No 1907/2006, annex XVII) (European Parliament and Council 2006b), amended by Commission Regulation 552/2009. Perfluorooctane sulfonates (PFOS, C₈F₁₇SO₂X) may not be placed on the market or used as a substance or in preparations in concentrations exceeding the threshold 0.005 % by mass. The threshold concentration by mass for semi-finished products or articles is 0.1 %. The directive exempts several uses from this limitation, but still, the perspective is for PFOS to be phased out and that the derogations shall be reviewed when new information on alternative (safer) substances and/or technologies becomes available.

The EU regulation No 648/2004 on detergents restricts the use of perfluorinated substances to some extent as detergents must be readily or primarily biodegradable, which the perfluorinated substances are not. This only applies to products with a cleaning effect. Thus polishes are not covered by the regulation.

PFOS is listed in Annex III of EQS directive on priority substances 2008/105/EC (European Parliament and Council 2008a), which is a daughter directive to the Water Framework Directive 2000/60/EC (European Parliament and Council 2000). It is listed as a substance subjected to review for possible identification as a priority substance (or priority hazardous substance). As of June 2011, this review process is currently ongoing.





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National bans on the use of PFOS (with the exception of hydraulic oil) have been introduced both in Sweden and in the UK (Prioriteringsguiden PRIO, www.kemi.se). Perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride are classified as POPs (persistent organic pollutants) under the Stockholm Convention (annex B, restriction of production and use) and perfluorooctane sulfonates are included among the substances to be added to the new CLRTAP (Convention on Long-Range Transboundary Air Pollution) POPs Protocol (Stockholm Convention 2010; UNECE 2010).

The US EPA and eight manufacturers have started the PFOA Stewardship programme, which aims to achieve a 95 % reduction of PFOA emissions (and emissions of its precursors and homologues) compared to the baseline year 2000 (US EPA 2010).

1.3 Production

There is no production of PFOS or PFOA in Estonia.

1.4 Use

According to the EDEXIM data (<http://edexim.jrc.it/>), there is no registered use of PFOS and PFOA in Estonia. The data is gathered according to the Regulation 689/2008/EC (European Parliament and Council 2008b) which aims to implement the Rotterdam Convention in the EU.

There is no registered use of PFOS and PFOA according to the regulation 1907/2006 (REACH) in Estonia either (e-mail conversation with Health Board Department of Chemical Safety, Mailis Laht Dec 2010).

According to those sources we can assume there is no industrial use of PFOS and PFOA in Estonia as a pure substance (as of December 2010), but the use of products containing PFOS and PFOA is possible and quite obvious, considering the findings from the screening of substances carried out under COHIBA WP3. There is no product register in Estonia and also the content of products marked to be used in processes is not traceable into content level in environmental permits.

1.5 Environmental fate

Substances produced from POSF have the potential to degrade to PFOS via removal of the non-fluorochemical moiety added to the sulfonyl fluoride group. Thus sulfonyl





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fluorochemicals that remain in the final product as residuals have the potential to degrade or metabolize to form PFOS (3M 1999). PFOS and PFOA precursors may have different physical and chemical properties compared to PFOS and PFOA, affecting emissions, pathways as well as the dominant final recipient. Furthermore degradation rates and patterns of these precursors may differ between substances. Also this influences the final environmental distribution pattern of PFOS and PFOA. (see e.g. Prevedouros et al. 2006; Brooke et al. 2006; Ellis et al. 2004)

1.6 Environmental levels

Perfluorinated substances have not been studied so far in Estonia. The first studies on PFOS and PFOA in Estonia are from 2010 (EU projects COHIBA and BaltActHaz). Neither PFOS nor PFOA were found under BaltActHaz study, but some of the perfluorinated substances were found in COHIBA WP3 consistently and uniformly from all the screening points, referring to common everyday use. However, the LOQs of perfluorinated substances were remarkably higher in BaltActHaz study than those of the COHIBA study (30 ng/l and 0,5 ng/l, respectively), therefore we can assume that the real environmental levels may lie somewhere in between those two levels. The levels were especially high in landfill effluents. In Table 4 and Table 5, summary of COHIBA WP3 results is shown.

Table 4. Perfluorinated substances in waste-water and sewage sludge in Estonia 2009-2010 (Data from COHIBA WP3).

| Substance | WWTP1 | | WWTP2 | WWTP3 | | WWTP4a | WWTP4b |
|-----------------------------------|--------------|----------------|--------------|--------------|----------------|--------------|--------------|
| | Water (ng/l) | Sludge (µg/kg) | Water (ng/l) | Water (ng/l) | Sludge (µg/kg) | Water (ng/l) | Water (ng/l) |
| perfluoro-n-hexanoic acid (PFHxA) | Nd – 3,1 | Nd | <LOQ – 1,5 | 0,6 – 1,8 | <LOQ and 0,2 | <LOQ – 1,0 | <LOQ – 0,8 |
| perfluorooctane sulfonate (PFOS) | Nd – 0,7 | 2,2 | Nd – 1,1 | 0,6 – 2,3 | 2,4 – 3,0 | 0,6 – 1,2 | Nd – 1,3 |
| perfluorooctanoic acid (PFOA) | 2,0 – 5,6 | 0,6 | 1,6 – 11,9 | 3,2 – 13,6 | 0,4 and 0,7 | 2,3 – 5,4 | 1,0 – 2,1 |





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| | | | | | | | |
|----------------------------------|----------|-----|----------|-----------|-----------|------|------|
| c acid (PFOA) | | | | | 0,7 | | |
| perfluoro-n-decanoic acid (PFDA) | Nd – 0,8 | 2,3 | Nd – 4,2 | Nd – 0,42 | 2,4 – 2,7 | <LOQ | <LOQ |

Table 5. Perfluorinated substances in Estonian landfill and stormwaters (data from COHIBA WP3).

| Substance | Landfill ng/l | Stormwater ng/l |
|-----------|---------------|-----------------|
| PFHxA | 570 and 597 | Nd and 0,8 |
| PFOS | 11 and 108 | 1,3 and 1,5 |
| PFOA | 533 and 590 | 0,5 – 1,9 |
| PFDA | 2,2 – 20,7 | nd |





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2 Sources of emissions of PFOS in Estonia

The uncertainties in the following emission strings are given with four letters, the first letter representing uncertainty for EF, the second for EFM, the third for division into compartments and the fourth for the yearly load. Uncertainty is classified according to the principles described in “Dealing with uncertainty in substance flow analysis within the COHIBA project”, a PM describing how data uncertainty is graded in WP4 of the COHIBA project.

If the Estonian yearly loads were scaled from the EU yearly load to Estonian population, the Estonian population was considered to be 0,3% of the EU population. This accuracy level was considered to be enough for given study; especially considering the very high uncertainty levels in other emission strings.

2.1 Emissions during lifetime use of articles, goods and chemical products and preparations.

Impregnated carpets

Yearly load 25 kg to WW (NB! no steady state)

Uncertainty: ACBC

Impregnate apparel

Yearly load 0,09 kg to WW

Uncertainty: BCBC

The purpose of the use of PFOS-related substances on carpets, textile and leather is to give the material soil, water and oil resistance. As such the PFOS-related substance, mainly in the form of PFOS-polymers, is applied to the surface of the material (Brooke *et al.* 2004). These kinds of products are subject to wear and tear, such as washing and vacuum cleaning, which yield direct releases of, *inter alia*, PFOS-related substances to air and water.

For both of the ESs, the yearly loads for Estonia were calculated from the EU yearly load, using the Estonian population (0,3% of the EU population) as a basis for scaling.

2.2 Manufacture of articles of paper and paperboard

NACE 17.2



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Protective coatings for paper and paper products

Yearly load 0 ww

Uncertainty: N/A

A variety of paper types have previously been treated with PFOS-related substances to improve the paper's grease, oil and water resistance. The PFOS related substances were applied to the paper in levels of 1-1.5 % by weight (RIKZ 2002 quoted in Brooke et al. 2004) which means that the used formulation should have had a concentration of PFOS higher than what is now allowed in the EU (0.005 % by mass; REACH annex XVII), which should mean that industrial use of PFOS in this industry should no longer occur within the EU. However, given the poor product and chemical control and incomplete registers, and considering that there are several activities taking place under that NACE in Estonia, according to PRODCOM2008, this ES still could be relevant for Estonia. However, the use of PFOS is not known at the moment. Further research is needed to ensure PFOS is not used indeed. We have put 0 at the moment on assumption that no illegal use is taking place.

2.3 Manufacture of electronic components. Manufacture of communication equipment

NACE 26.3

Manufacture of semi-conductors

Yearly load - ? to WW

Uncertainty: N/A

PFOS-related substances are used in various applications in photolithography, which is the process that produces the circuit on the semi-conductor wafers (Brooke *et al.* 2004). There are several activities taking place in Estonia under those NACE codes, such as: Semiconductor diodes; Semiconductor thyristors, diacs and triacs; Semiconductor light emitting diodes (LEDs); Transmission apparatus for radio-broadcasting and television, with reception apparatus; Telephones for cellular networks or for other wireless networks etc.

The use of PFOS or related substances is not known. However, given the poor product and chemical control and incomplete registers, this ES still could be relevant for Estonia. Further research is needed to ensure these substances are not used indeed.





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2.4 Manufacture of fabricated metal products, except machinery and equipment. Treatment and coating of metals; machining.

NACE 25; 25.6

Metal (chromium) plating

Yearly load ? to WW

Uncertainty: N/A

PFOS-salts are used in metal plating (chromium plating, anodising and acid pickling) to lower the surface tension of the metal plating solution and thus prevent formation of mist (Brooke *et al.* 2004). Losses of the PFOS-salt could occur during the metal plating process (OECD 2004b). Process solution is also lost to wastewater during maintenance and cleaning procedures of the plant's fittings as well as maintenance of the process solution itself. Losses of process solution to wastewater may also occur at disposal of spent bath solutions. According to information in POPRC (2010) PFOS breaks down during the metal plating process.

There are metal industries in Estonia that use chromium substances in the process. In Prodcom 2008 there are several activities mentioned under that NACE as well, such as: *metallic coating by electrolysis or chemical treatments of metals other than zinc (including nickel, copper, chromium, precious metals, etc)* and many other production activities. Hence, we assume this ES could be relevant for Estonia. However, there is no registered use of PFOS and its salts in Estonia, as mentioned above.

We know that sometimes the components used in the industry may contain substances (as additives) that producers themselves are unaware of. It would be necessary to perform a thorough research on this subject, e.g. check the safety cards of companies working under that NACE, but this was impossible under the COHIBA study. Hence, further research is needed to ensure PFOS or PFOS-related substances are indeed not used in Estonia under that ES.

2.5 Manufacture of soap and detergents, cleaning and polishing preparations

NACE 20.4





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Manufacture of industrial and household cleaning products

Yearly load 0 WW

The restrictions in REACH annex XVII should make this a no longer relevant source of PFOS within the EU. However, the PFOS-related substance *glycine, N-ethyl-N-[(heptadecafluorooctyl)sulfonyl]-, potassium salt* (CAS nr 2991-51-7) was registered in the Swedish Products Register for use in polishing agents with a use quantity of 0.0055 tonnes in 2008 (Swedish Chemicals Agency 2010).

Given the poor product and chemical control and incomplete registers, and considering that there are several activities taking place under that NACE in Estonia, according to Prodcom 2008, this ES still could be relevant for Estonia. However, the use of PFOS or PFOS-related substances is not known at the moment. Further research is needed to ensure these substances are not used indeed. We put the 0 at the moment on assumption that no illegal use is going one in Estonia.

2.6 Manufacture of other chemical products n.e.c.

NACE 20.59

Manufacture of liquids for hydraulic transmission

Yearly load – 0 WW

Uncertainty: CB

Hydraulic fluids for aviation are exempted from the ban of PFOS (REACH annex XVII). However, according to Brooke *et al.* (2004) manufacture of these hydraulic oils takes place outside the EU. Hence we can assume this ES is probably irrelevant for Estonia as well, however, further research is needed to ensure PFOS is not used indeed as there are still several activities taking place in Estonia according to Prodcom 2008, such as: *Anti-freezing preparations and prepared de-icing fluids*. It is not related with hydraulic transmissions that why we have considered no emissions from that string.

2.7 Passenger air transport; Freight air transport

NACE 51.10; 51.21

Use of hydraulic fluids in aircrafts

Yearly load 0,038 kg to FS

Yearly load 0,0132 to WW.



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Uncertainty: ABAC

The similarity with other countries is assumed. The planes are the same everywhere. Brooke *et al.* (2004) assumed that one third of the worldwide consumption of PFOS-related substances (classified as a PFOS-salt) in this application was used within the EU (0.73 tonnes/year).

The yearly load for Estonia was scaled from the EU yearly load, assuming that the population of Estonia is 0,3% of EU population. The number could be more accurate if the flying hours or other air transport numbers on Estonian and EU level were done. For the limited time it is not done in this rapport.

2.8 Photographic activities

NACE 74.2

Emissions from photographic laboratories

Yearly load - ? WW

Uncertainty: N/A

In the present report PFOS-related substances in products used in photographic activities are assumed to either remain in the product, which means that it will eventually end up in the waste, or be released from the product but then be treated as hazardous waste. This ES is relevant for Estonia. The assumption was made on bases of similarity with other countries no special photographic technologies for Estonia. However, we have no data to calculate the yearly load. Further research is needed.

2.9 Sewerage

NACE 37

Emissions from municipal sewage treatment plants, effluent water.

Yearly load 0,03-0,04 kg to FSW

Yearly load 0,01-0,02 kg to CSW

Uncertainty: CAAC

PFOS-related substances can be emitted from households and industry via the wastewater, enter the WWTP and subsequently be emitted via the WWTP water effluent and sewage sludge.





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The yearly load was calculated using the data from COHIBA – that gave us the EF. The EF was considered to be the average result of all WWTP-s. For the minimum scenario, the results below the LOQ were considered to be 0; for the maximum scenario, the results under the LOQ were considered to be the LOQ. The EF was then multiplied by the EFM, i.e. the amount of effluents produced per person a day – 125 litres (according to Statistics Estonia 2010), the number of inhabitants (1 340 021 according to Statistics Estonia 2010), and the number of days a year (365).

It should be kept in mind that the presence of PFOS precursors in the effluent water implies that this source might contribute more to PFOS levels in the environment than what the emission calculations above show.

Emissions from municipal sewage treatment plants, sludge

Yearly load – 0,02 kg to AS

Yearly load – 0,05 kg to FS

Uncertainty: CAAC

The calculations were done using the data from COHIBA WP3 that gave us the EF. The EF was considered to be the average result of all WWTP-s. The representability is highly uncertain due to limited data. The EFM is the one from European SFA-s, considered to be representative to Estonia by an Mr Kõrgmaa, an expert on WWTPs and sewage sludge (personal communication, Epp Volkov). The yearly load was calculated multiplying EF with EFM and number of inhabitants in Estonia (Statistics Estonia 2010).

2.10 Waste treatment and disposal

NACE 38.2

Emissions from landfills

Yearly load 0,01-0,11 kg to FSW

Yearly load 0,01-0,11 kg to FS

Uncertainty: C

The calculations were done using the excel sheet provided by IVL. The data used was from the COHIBA WP3 results from the study of landfill leachate. However, this result is considered extremely inaccurate as it is based on two samples from one landfill.





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Emissions from incineration of waste

Yearly load ? OA

Uncertainty: N/A

Waste incineration is still under development in Estonia. Some of the waste is incinerated in Kunda. The waste fuel is made from the municipal waste in landfills (e.g. Jõelähtme, the landfill that serves Tallinn, the capital of Estonia with the population of about 1/3 of Estonian population), however, as the waste incineration system is still under development, this waste fuel is sold to Latvia (personal communication with the manager of Jõelähtme landfill, 13.03.2011, Epp Volkov). According to statistics, in 2009, 224 190 tons of waste was used in energy production in Estonia, 14 685 tons of which was municipal waste¹.

The amount of waste incinerated in Estonia is not known at the moment.

2.11 Worldwide activities outside the region

Atmospheric deposition of PFOS-related substances

Yearly load – 8,2 kg to FSW

Yearly load – 85,58 kg to FS

Yearly load – 40,11 kg to AS

Uncertainty: CAB

The yearly loads were scaled from the Swedish loads, as there is no monitoring data for Estonia, but given the nature of atmospheric pollution, similar latitudes and of the two countries and meteorology, the Swedish data can be considered reliable for Estonia.

The Swedish load was scaled for Estonian territory and divided in between compartments. The compartments were set according to data on the Estonian landscape use from Estonian Informative Inventory Report 1990-2008 (Estonian Environment Information Centre 2010).

¹

<http://www.keskkonnainfo.ee/index.php?lan=EE&sid=115&tid=109&l1=29>





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3 Sources of emissions of PFOA in Estonia

The uncertainties in the following emission strings are given with four letters, the first letter representing uncertainty for EF, the second for EFM, the third for division into compartments and the fourth for the yearly load. Uncertainty is classified according to the principles described in “Dealing with uncertainty in substance flow analysis within the COHIBA project”, a PM describing how data uncertainty is graded in WP4 of the COHIBA project.

If the Estonian yearly loads were scaled from the EU yearly load to Estonian population, the Estonian population was considered to be 0,3% of the EU population. This accuracy level was considered to be enough for given study; especially considering the very high uncertainty levels in other emission strings.

Emissions of salts of PFOA can be regarded as direct emissions. PFOA will hereafter refer to PFOA as well as its salts. The most commonly used is an ammonium salt called APFO (KemI 2004). PFOA may also occur as an impurity in POSF-products manufactured with the ECF (electro-chemical fluorination) process, as well as in fluorotelomer products (Prevedourous *et al.* 2006), which means that such materials could also be a potential source of PFOA. Furthermore, PFOA is a potential degradation product of POSF based products and fluorotelomer based products (OECD 2007).

3.1 Finishing of textiles. Manufacture of glass and glass products. Manufacture of fabricated metal products, except machinery and equipment

NACE 13.3; 23.1; 25

Fluoropolymer dispersion processing

Yearly load - ? to OA

Yearly load - ? to WW

Fluoropolymer products sold as aqueous dispersions (approximately 16 % of fluoropolymer products) still contain APFO (Prevedouros *et al.* 2006). These dispersions are used to coat metal, fabric and glass surfaces and during these treatments heat is applied, often in temperatures that make APFO leave the polymer (Fluoropolymer Manufacturing Group 2005) and sometimes in temperatures degrading APFO (Krusic and Roe 2004; Fluoropolymer Manufacturing Group 2005). We assume this ES to be relevant





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for Estonia. In 2010, the biggest textile industry in Estonia was closed and now there is practically no textile industry in Estonia, hence the code 13.3 can be considered irrelevant for Estonia in the future, but there are several activities taking place under other two NACE codes in Estonia, according to Prodcom 2008. Hence further research is needed.

3.2 Manufacture of electronic components. Manufacture of communication equipment

NACE 26.11; 26.3

Semiconductor industry

Yearly load - ? to WW

Uncertainty: N/A

In some cases PFOA has been the substitute for PFOS, e.g. in photolithography processes, which is the process that produces the circuit on the semi-conductor wafers (Brooke *et al.* 2004). There are several activities taking place in Estonia under those NACE codes, such as: Semiconductor diodes; Semiconductor thyristors, diacs and triacs; Semiconductor light emitting diodes (LEDs); Transmission apparatus for radio-broadcasting and television, with reception apparatus; Telephones for cellular networks or for other wireless networks etc.

The use of PFOA or related substances is not known. However, given the poor product and chemical control and incomplete registers, this ES still could be relevant for Estonia. Further research is needed to ensure these substances are not used indeed.

3.3 Sewerage

NACE 37

Emissions from municipal sewage treatment plants – effluent water

Yearly load – 0,08 kg to CSW

Yearly load – 0,18 kg to FSW

Uncertainty: CAAC

PFOA can be emitted from households and industry via the wastewater, enter the WWTP and subsequently be emitted via the WWTP water effluent and sewage sludge.





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The yearly load was calculated using the data from COHIBA – that gave us the EF. The EF was considered to be the average result of all WWTP-s. For the minimum scenario, the results below the LOQ were considered to be 0; for the maximum scenario, the results under the LOQ were considered to be the LOQ. The EF was then multiplied by the EFM, i.e. the amount of effluents produced per person a day – 125 litres (according to Statistics Estonia 2010), the number of inhabitants (1 340 021 according to Statistics Estonia 2010), and the number of days a year (365).

Emissions from municipal sewage treatment plants – sewage sludge

Yearly load – 0,012 kg to FS

Yearly load - 0,006 kg to AS

Uncertainty: CAAC

The calculations were done using the data from COHIBA WP3 that gave us the EF. The EF was considered to be the average result of all WWTP-s. The representability is highly uncertain due to limited data. The EFM is the one from European SFA-s, considered to be representative to Estonia by an Mr Kõrgmaa, an expert on WWTPs and sewage sludge (personal communication, Epp Volkov). The yearly load was calculated multiplying EF with EFM and number of inhabitants in Estonia (Statistics Estonia 2010).

3.4 Waste collection, treatment and disposal activities; materials recovery

NACE 38

Emissions from landfills

Yearly load 0,53-0,59 kg to FS

Yearly load 0,53-0,59 kg to FSW

Uncertainty: C

The calculations were done using the excel sheet provided by IVL. The data used was from the COHIBA WP3 results from the study of landfill leachate. However, this result is considered extremely inaccurate as it is based on two samples from one landfill.

Emissions from incineration of waste

Yearly load ? OA

Uncertainty: C





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Waste incineration is still under development in Estonia. Some of the waste is incinerated in cement production in Kunda. The waste fuel is made from the municipal waste in landfills (e.g. Jõelähtme, the landfill that serves Tallinn, the capital of Estonia with the population of about 1/3 of Estonian population), however, as the waste incineration system is still under development, this waste fuel is sold to Latvia (personal communication with the manager of Jõelähtme landfill, 13.03.2011, Epp Volkov). According to statistics, in 2009, 224 190 tons of waste was used in energy production in Estonia, 14 685 tons of which was municipal waste². Most of the waste are the oil shale production waste with high calorific value and not related with everyday waste.

The amount of critical waste for that string (could emit the PFOA-related substances) incinerated in Estonia is not known at the moment. Waste incineration (industrial plants) is under development in Estonia.

3.3. Worldwide activities outside the region

Atmospheric deposition of PFOA-related substances

Yearly load – 7,63 kg to FSW

Yearly load – 81,35 kg to FS

Yearly load – 38,13 kg to AS

Uncertainty: CAB

The yearly loads were scaled from the Swedish loads, as there is no monitoring data for Estonia, but given the nature of atmospheric pollution, similar latitudes and of the two countries and meteorology, the Swedish data can be considered reliable for Estonia.

The Swedish load was scaled for Estonian territory and divided in between compartments. The compartments were set according to data on the Estonian landscape use from Estonian Informative Inventory Report 1990-2008 (Estonian Environment Information Centre 2010).

² <http://www.keskkonnainfo.ee/index.php?lan=EE&sid=115&tid=109&l1=29>



4 SFA diagrams

4.1 SFA diagram for PFOS

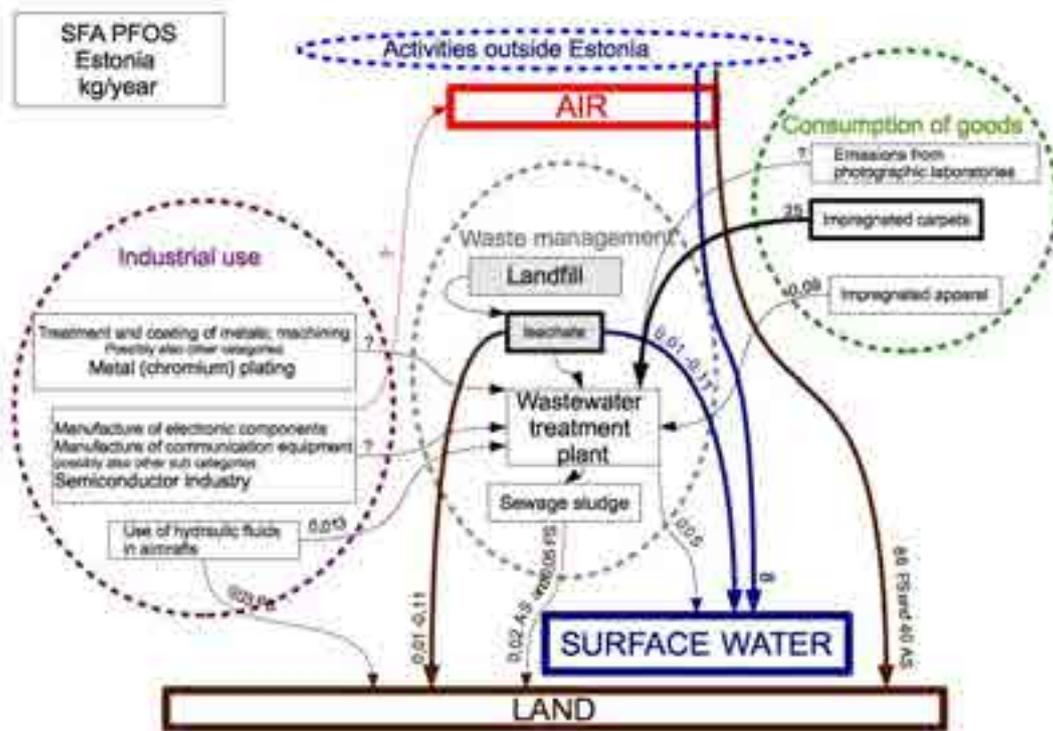


Figure 2. SFA diagram for PFOS in Estonia.

4.2 SFA diagram for PFOA

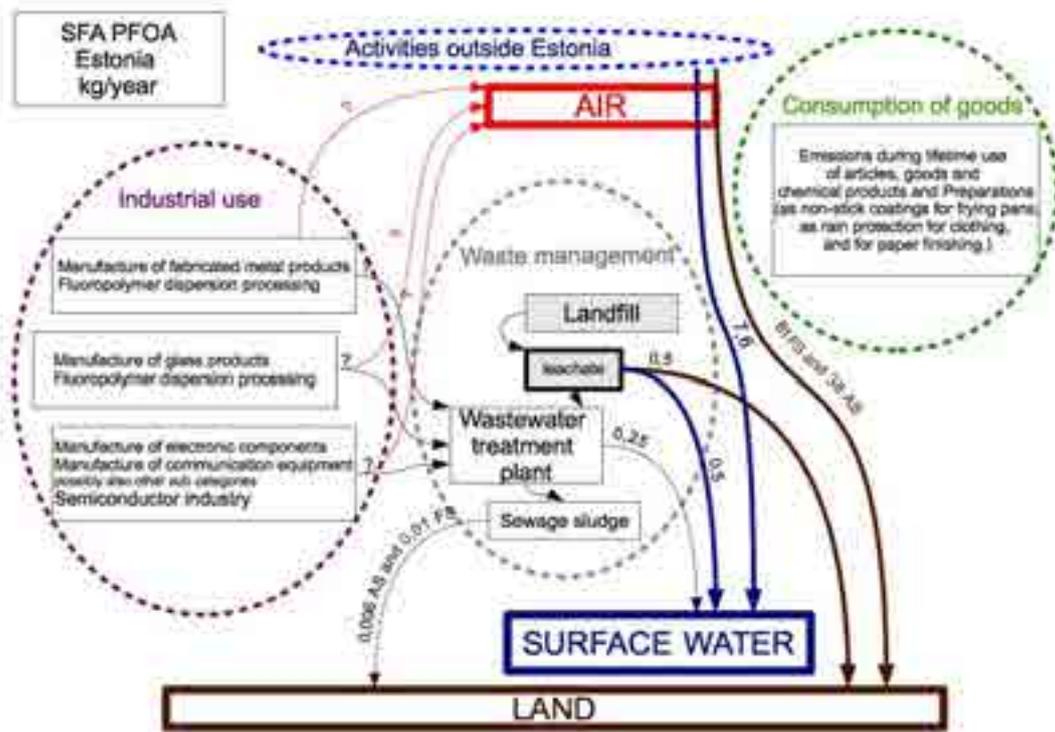


Figure 3. SFA diagram for PFOA in Estonia.



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5 Conclusions

5.1 Quantitative estimation of the most relevant sources to each environmental compartment (Soil, water and air)

Important sources for Estonia are use of products containing PFOS and PFOA. For PFOS is the most important source the impregnated goods. The emissions are to the waste - water but the loads can affect land and surface water through the waste-water systems. At the moment the quantitatively biggest source to the land and surface water is the landfill leachate (0,11 kg to land and 0,11 kg to water). Loads could be decreased by proper waste management and sewage treatment.

The atmospheric deposition is also important source for Estonia and at the moment quantitatively the loads are bigger than the loads from different sources in Estonia. But we should take in account that the industrial sources were not possible to quantified.

5.2 A qualitative estimation of time trends for future scenarios

Possible means for reducing the emissions of PFOS and PFOA are administrative. It is not possible to make future plans for reducing perfluorinated substances in Estonia as the mapping of the current situation is insufficient.





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ANNEX E - Substance flow analysis for HBCDDs in Estonia

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This study was carried out under the COHIBA study from May 2010 to May 2011. This report is based on the SFA HBCDD (EU 27) by IVL Swedish Environmental Research Institute. The results are for Estonia. Many of the results are rough approximations that cannot be taken as exact results for Estonia, but more as a base to plan future studies.

1 Introduction

1.1 Physical chemical properties

HBCDD is a brominated flame retardant. The substance occurs in 16 different stereoisomeric forms of which six pairs are enantiomers (ECB 2008). The technical mixture of J DEFF consists of mainly three diastereomers (α , β and γ) OECU (Echemical Abstract Service) numbers for the different isomers are listed in Table 1.

Table 1: CAS numbers (Chemical Abstract Service) as listed in Methonen (2009)

| Compound | CAS number |
|---|-------------|
| Hexabromocyclododecane (mixture of mainly three diastereomers) | 25637-99-4 |
| | 25495-98-1 |
| 1,2,5,6,9,10-Hexabromocyclododecane | 3194-55-6 |
| α -Hexabromocyclododecane | 134237-50-6 |
| β -Hexabromocyclododecane | 134237-51-7 |
| γ -Hexabromocyclododecane | 134237-52-8 |

The chemical structure of HBCDD is shown in Figure 1. Water solubility of HBCDD is low, as is the vapour pressure. The $\log K_{OW}$ on the other hand is rather high. Physical and chemical properties of the substance are listed in Table 2.

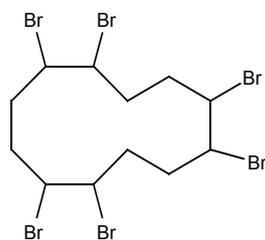


Figure 1: Structure for hexabromocyclododecane CAS number 3194-55-6



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Table 2: Physical and chemical properties of technical hexabromocyclododecane (HBCDD) as listed in ECB (2008).

| Property | HBCDD |
|--|--|
| Physical state at npt | White odourless solid |
| Molecular weight (g/mol) | 641.7 |
| Melting point ^a (°C) | 172-184 to 201-205 |
| Vapour pressure ^b (Pa, at 21 °C) | 6.3×10^{-5} |
| Log octanol-water partition coefficient (log Kow) ^c | 5.62 |
| Water solubility ^d (µg/l at 20 °C) | ∑ (sum of α-Ē - and HBCDD) |
| Henry's Law Constant (Pa m ³ /mol) | 0.75 Calculated from the vapour pressure and the water solubility |

- a) Smith *et al.* (2005) quoted in ECB (2008)
- b) Stenzel and Nixon (1997) quoted in ECB (2008)
- c) MacGregor and Nixon (1997) quoted in ECB (2008)
- d) MacGregor and Nixon (2004)

1.2 Regulatory status

The regulatory status of HBCDD is the same in Estonia as in all of EU. No special regulations in place.

The EU risk assessment of HBCDD, conducted by Sweden, was finalised in 2008 (ECB 2008). In the risk assessment the need to limit the risk for the environmental aquatic, STP, terrestrial and marine compartments was identified for a number of sites. Furthermore it was concluded that: “although HBCDD does not unequivocally fulfil all individual criteria it is concluded that the substance overall fulfils the PBT-criteria of the TGD” (PBT: Persistent Bioaccumulative and Toxic, see ECB 2003), and thus a need to limit the risks due to the PBT characteristics of the substance was identified.

The European Chemicals Agency (ECHA) has identified HBCDD as a substance of very high concern (SVHC) and recommended that HBCDD should be listed in Annex XIV, the list of substances subject to authorisation, of the REACH regulation (European Parliament and Council 2006). HBCDD is also a candidate substance under the Stockholm Convention (2001).

1.3 Production

No production in Estonia. According to the risk assessment (ECB 2008) HBCDD is only produced at one site in EU (EU 15). This site is located in the Netherlands and had an assumed production volume of 6000 tonnes in the year 2005.



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1.4 Use

No information about the industrial use of HBCDD in Estonia at the moment.

1.5 Environmental fate

In the risk assessment of HBCDD (ECB 2008) the rapporteur concluded that chemical degradation of the substance may “not be of quantitative importance in the environment other than in anaerobic, reducing sediments”.

In the EU risk assessment (ECB 2008) also the biodegradability of HBCDD was evaluated. The substance was concluded not to be readily biodegradable in aerobic conditions. Degradation half lives estimated using the EPIWIN model and in two different degradation studies, included in the risk assessment evaluation, are listed in Table 3. The rapporteur of the risk assessment (ECB 2008) regarded one of the studies less reliable as the results could be an over estimation of the degradability of HBCDD (Study 1; Davis *et al.* 2003 quoted in ECB 2008). The half lives calculated from study 2 (Davis *et al.* 2004, 2006 quoted in ECB 2008) were in the risk assessment considered appropriate for a realistic worst case scenario.

Table 3: Estimated degradation half lives for hexabromocyclododecane (HBCDD) as presented in the EU risk assessment (ECB 2008)

| | DT50 at 12 °C ^d (days) | | | |
|----------------------------|-----------------------------------|-------|----------------|--|
| | Air | Water | Soil | Sediment |
| Study 1 ^a | - | - | 119 | 2.8 (anaerobic freshwater sediment) |
| | | | | 21 (aerobic freshwater sediment) |
| Study 2 ^b | - | - | No degradation | 125 (anaerobic freshwater sediment) |
| | | | | 191 (aerobic freshwater sediment) |
| Model results ^c | 2.1 | 60 | 60 | 240 |

a) Aerobic and anaerobic transformation of hexabromocyclododecane in aquatic sediment systems and soil – simulation study 1 (Davis *et al.* 2003 quoted in ECB 2008)

b) Transformation of ¹⁴C-hexabromocyclododecane in sludge, sediment and soil – simulation study 2 (Davis *et al.* 2004, 2006 quoted in ECB 2008)

c) Estimated with EPIWIN (Wania 2003 quoted in ECB 2008)

d) Temperature corrected

The different diastereomers are hard to degrade with different rates, with α -HBCDD degrading with the seemingly slowest rate (ECB 2008). This could be one reason for the different degradation rates listed above (Table 3) since only degradation of the α -diastereomer was measured in study 1. Transformation of HBCDD leads to production of



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the main metabolite 1,5,9-cyclododecatriene (CDT), a substance which is not considered readily biodegradable (ECB 2008).

1.6 Environmental levels

There has been virtually no research on this substance in Estonia. The first data is from 2010 when it was studied in two European funded projects – BaltActHaz¹ and COHIBA. Therefore we mainly used data from these two projects for determining the possible sources of HBCDD.

In BaltActHaz, HBCDD was measured from the effluents and sludge of several municipal WWTPs, waters and sediments of rivers and one point of coast, and waters and sediments from two points of lake Peipsi. All the measured samples were below the LOQ (200 ng/L and 200 µg/kg for water and sediments, respectively). However, it should be noted that these LOQs are rather high compared with the results from COHIBA project.

COHIBA project was another one where HBCDDs were measured for the first time in Estonia from WWTPs (both effluents and sludge), storm waters and one landfill.

For HBCDD analysis HPLC-MS/MS was used. HBCDD was measured as α -, β -, and γ -HBCD isomers. For the substance flow analysis we used the sum of those isomers (if a given isomer was measured under the LOQ, the value of half the LOQ was used). The wastewater contained HBCDD-s up to 3,5 ng/l. The levels HBCDD-s in storm waters was also remarkably high – 6,48 ng/l (Table 4).

Table 4. HBCDD-s in landfills, storm waters, wastewaters and wastewater sewage sludges in Estonia 2009-2010 (Data from COHIBA WP3).

| Landfill | Stormwater | WWTP1 | | WWTP2 | WWTP3 | | WWTP4a | WWTP4b |
|----------|-------------|--------------|-------------------|--------------|--------------|-------------------|--------------|---------------|
| | | Water (ng/l) | Sludge (µg/kg dw) | Water (ng/l) | Water (ng/l) | Sludge (µg/kg dw) | Water (ng/l) | Water (ng/l) |
| 1,07 | 3,94 - 6,48 | 0,44–3,06 | 12,8 | <LOQ – 3,5 | 0,20 – 2,39 | 93,4 | <LOQ – 1,24 | 2,44 and 2,76 |

¹ BaltActHaz web page, available at: <http://www.baltacthaz.bef.ee/>



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2 Sources of emissions of HBCDD in Estonia

Uncertainty is marked with three letters, the first one depicting the uncertainty for EF, the second one for EFM, the third one for the percentage distribution, and the fourth one for the whole load. Uncertainty is classified according to the principles described in “Dealing with uncertainty in substance flow analysis within the COHIBA project”, a PM describing how data uncertainty is graded in WP4 of the COHIBA project.

If the Estonian yearly loads were scaled from the EU yearly load to Estonian population, the Estonian population was considered to be 0,3% of the EU population. This accuracy level was considered to be enough for given study, especially considering the very high uncertainty levels in other emission strings.

2.1 Construction of buildings

NACE 41

Emissions of HBCDD during construction of buildings where flame retarded XPS boards are used.

Yearly load **0,04 kg** to OA

Yearly load **0,04 kg** to SW.

Uncertainty: AACC

All the yearly loads in these strings were calculated, scaling the EU yearly load (that was calculated with the data from 2006) to Estonian population, which is considered to be 0,3% of the EU population. No better data for calculations was available. The uncertainty is thus C.

Emissions of HBCDD during construction of buildings where flame retarded EPS boards are used.

Yearly load **0,6 kg** to OA

Yearly load **0,6 kg** to SW.

Uncertainty: AAAC

All the yearly loads in these strings were calculated, scaling the EU yearly load to Estonian population (1 340 021 – Statistics Estonia 2010). No better data for calculations was available. The uncertainty is thus C.

2.2 Demolition

NACE 43.11

Emissions of HBCDD during demolition of buildings where flame retarded EPS boards are used.



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Yearly load **0,15 kg** to SW

Yearly load **0,15 kg** to OA.

Uncertainty: AAAC

Emissions of HBCDD during demolition of buildings where flame retarded XPS boards are used.

Yearly load ? kg

Uncertainty: n/a

Emissions of HBCDD during demolition of buildings where flame retarded XPS and EPS boards are used.

Yearly load **8,4 kg** to SW

Yearly load **8,4 kg** to OA.

Uncertainty: AAAC

All the yearly loads in these strings were calculated, scaling the EU yearly load to Estonian population. No better data for calculations was available. The uncertainty is C.

For all of the emission strings under that NACE, the comment in the EU SFAs was as follows: “It is unsure to what extent these figures are currently valid as the time from building to demolition could be longer than the time these kinds of polystyrene boards have been in use, which means that steady state might not have been reached and that the actual figure is lower at present.” This is definitely true for Estonian SFA as well, hence the overall uncertainty level of C.

2.3 Emissions during lifetime use (including tear and wear) of articles, goods and chemical products and preparations

NACE X

Particulate emissions of HBCDD from flame retarded textile.

Yearly load **0,0146 – 0,0729 kg** to SW (10%)

Yearly load **0,0578 – 0,289 kg** to WW (40%)

Yearly load 0,0724 – 0,3619 kg to ? (no data for the rest of the 50%)

Uncertainty: AAAC

The EU EF was calculated from emission estimates and used amounts as given in the risk assessment report (ECB 2008). The low loads are calculated based on a decrease in use of 80% (ECHA 2008). The yearly load for Estonia was calculated, scaling the EU yearly load to Estonian population. The uncertainty is thus C.



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Emission of HBCDD to water during washing of flame retarded textile.

Yearly load **0,006 – 0,028 kg** to WW

Uncertainty: AAAC

The emission factor multiplier was calculated assuming a yearly use of 1050 tonnes in EU and that 2% of these textiles were washed. The low loads are calculated based on a decrease in use of 80% (ECHA 2008). The yearly load for Estonia was calculated, scaling the EU yearly load to Estonian population. The uncertainty is thus C.

Emissions of HBCDD to air from insulation boards (XPS and EPS) during service life.

Yearly load **0,084 kg** to OA.

Uncertainty: AAAC

The yearly load for Estonia was calculated, scaling the EU yearly load to Estonian population. The uncertainty is C.

Emissions of HBCDD to air from flame retarded HIPS plastic in e.g. VCR housings, during service life.

Yearly load **0,03 kg** to FSW (10%)

Yearly load **0,11 kg** to WW (40%)

Uncertainty: AAAC

The yearly load for Estonia was calculated, scaling the EU yearly load to Estonian population. The uncertainty is C.

2.4 Manufacture of plastics and plastic products

Manufacture of plastic packing goods

Manufacture of other plastic products

Manufacture of flame retarded EPS products

Manufacture of flame retarded HIPS products

NACE 20.16

Yearly load - ?

Uncertainty: N/A

There are several types of plastic producers and industrial users of plastics in Estonia. However, we have no data on the use of HBCDD. We have contacted the association of plastic producers in Estonia, but have had no answer yet.



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In Prodcom, 2008, there are several activities mentioned as taking place in Estonia under NACE 20.16, such as:

Epoxide resins, in primary forms

Alkyd resins, in primary forms

Urea resins and thiourea resins, in primary forms

Phenolic resins, in primary forms

Silicones, in primary forms

Petroleum resins, coumarone-indene resins, polyterpenes, polysulphides, polysulphones, etc, n.e.c., in primary forms

Data about these activities is mainly classified or considers only the value of production.

We assume these activities don't fall under the specified activities given in the ES-s, which would mean these ES-s to be IRRELEVANT as HBCDD is used mainly in polystyrene plastics (EPS, XPS, HIPS) and in polymer-based dispersions (e.g. acrylic or latex). However, we cannot be sure.

Manufacture of flame retarded XPS products (use of HBCDD as a compound) 22.29

Manufacture of flame retarded XPS products (use of HBCDD as a powder) 22.29

NACE 22.29; NACE 22.22

Yearly load – ?

Uncertainty: N/A

There are several types of plastic producers and industrial users of plastics in Estonia. However, we have no data on the use of HBCDD. We have contacted the association of plastic producers in Estonia, but have had no answer yet.

There are several types of products under NACE 22.20 that are produced in Estonia, according to Prodcom, 2008, such as:

Plastic sacks and bags (including cones) (excluding of polymers of ethylene)

Plastic boxes, cases, crates and similar articles for the conveyance or packing of goods

Plastic carboys, bottles, flasks and similar articles for the conveyance or packing of goods, of a capacity \leq 2 litres

Plastic carboys, bottles, flasks and similar articles for the conveyance or packing of goods, of a capacity $>$ 2 litres

Spools, cops, bobbins and similar supports, of plastics

Plastic caps and capsules for bottles

Plastic stoppers, lids, caps and other closures (excluding for bottles)

Other articles for the conveyance or packing of goods of plastics

Data about these activities is mainly classified or considers only the value of production. However, all of these products might have a content of polystyrene. And even though not



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all of the polystyrene is flame retarded with HBCDD, it is not possible to assess if HBCDD is used as a flame retardant in these cases. Therefore we assume this string might be somewhat relevant for Estonia.

2.5 Sewerage

NACE 37

Emissions of HBCDD with effluent water from municipal WWTP-s.

Yearly load – **0,064 to 0,071 kg** to FSW (70%)

Yearly load – **0,027 to 0,030 kg** to CSW (30%)

Uncertainty: BAAC

The calculations were done using the data from COHIBA WP3 that gave us the EF-s. In COHIBA WP3 three isomers were measured (α -, β -, and γ -HBCD). For the calculations, we used the sum of three isomers. The EF low: if the result was below the LOQ, the result was considered to be 0. The EF high: if the result was below the LOQ, it was considered to be the LOQ (0,1 ng/l). The average of all WWTP-s was taken. The EF was then multiplied by the EFM, i.e. the amount of effluents produced per person a day – 125 litres (according to Statistics Estonia 2010), the number of inhabitants (1 340 021 according to Statistics Estonia 2010), and the number of days a year (365).

According to the principles described in “Dealing with uncertainty in substance flow analysis within the COHIBA project”, the final uncertainty should be B-, however, one should keep in mind that the yearly load is based on only a few analyses, therefore we would like to consider it to be C.

HBCDD in sewage sludge from municipal WWTPs.

Yearly load **1,08 kg** to AS

Yearly load **2,29 kg** to FS

Uncertainty: CBBC

The calculations were done using the data from COHIBA WP3 that gave us the EF. In COHIBA WP3 three isomers were measured (α -, β -, and γ -HBCD). For the calculations, we used the sum of three isomers. The EF was considered to be the average result of all WWTPs. The representability is highly uncertain due to a very limited amount of data. The EFM is the one from European SFAs, considered to be representative to Estonia by an expert (personal communication with Mr Vallo Kõrgmaa, EERC, 10.12.2010). The yearly load was calculated when multiplying EF with EFM and number of inhabitants in Estonia.



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2.6 Waste treatment and disposal

Leaching of HBCDD from landfills

Yearly load **0,0012 kg** to SW.

Yearly load **0,0012 kg** to FS.

Uncertainty: C

The calculations were done using the excel sheet provided by IVL. The data used was from the COHIBA WP3 results from the study of landfill leachate. In COHIBA WP3 three isomers were measured (α -, β -, and γ -HBCD). For the calculations, we used the sum of three isomers. However, this result is considered to be extremely inaccurate as it is based on two samples from one landfill.

For those analyses the comment from the lab was: “Difficult sample to extract, made an awful emulsion, poor recovery (5-8%)!” It is also one reason why we can expect that this is not a true value and due to the poor recovery of the sample the true value is higher than given in this document. When we compared our results to the ones from the other countries the differences were big and it was near to impossible to conclude anything about the average value at the moment. The comparison is given in Table 5.

Table 5. HBCDD results from landfills - sum of isomers.

| Country | Estonia | Latvia | Lithuania | Sweden | Finland | Germany | Poland |
|-------------|---------------------------|--------|--------------|--------|---------|---------|--------|
| HBCD (ng/l) | 1,07 (13) ² | 75,44 | Not detected | < 1 | 3,04 | 0,1 | 3,32 |

Release of HBCDD from polystyrene boards buried and left in the ground after end of use.

Yearly load - ?

Uncertainty: N/A

This ES could be relevant for Estonia, however, there is no data to calculate the results.

2.7 Worldwide activities outside the region, for example atmospheric deposition of long range transport

Atmospheric deposition of HBCDD on land and water surfaces.

Yearly load – **0,01 kg** to FSW (6%)

² Theoretical calculation if the recovery was 100% the measured value is taken as 8%.



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Yearly load – **0,04 kg** to AS (30%)

Yearly load – **0,09 kg** to FS (64%)

Uncertainty: BAAC

Yearly load low **0,02** and high **12,84 kg** to SW (6%).

Yearly load low **0,10** and high **64,20 kg** to AS (30%).

Yearly load low **0,21** and high **137,00 kg** to FS (64%).

Uncertainty: CAAC

The yearly loads are calculated from the Swedish data. The yearly loads low and high are calculated from the EU SFAs.

The deposition numbers are from Swedish air database (summary made by IVL partners – Swedish Environmental Protection Agency: National Air Monitoring National Air Database, www.ivl.se) that were used to calculate the yearly load. We used an average value after discussion with our air monitoring specialist Erik Teinmaa. The Swedish monitoring stations are located on the similar latitude and we considered it comparable to Estonia. The calculated emission factor was $51,1 \text{ ng/m}^2$ (Average deposition per day $0,14 \text{ ng/m}^2$).

The yearly loads low and high are the results that were scaled from the EU yearly loads, using the Estonian territory of $45\,000 \text{ km}^2$ as a basis for calculation. We left it here as a comparison. Also, the EU SFA had considered the deposition data from various studies (see EU SFA report)). However, we believe the calculations done on the Swedish monitoring data to be more accurate.

Estonian territory is $45\,000 \text{ km}^2$. The division into compartments was made, using statistical data from Estonia – 30% AS, 64% FS, 6% FSW.

Due to the fact that HBCDD is in current use in Europe it is difficult to assess which is the origin of these loads. It is possible however that at least part of the deposited amounts originates from sources outside the EU.

3 SFA diagram

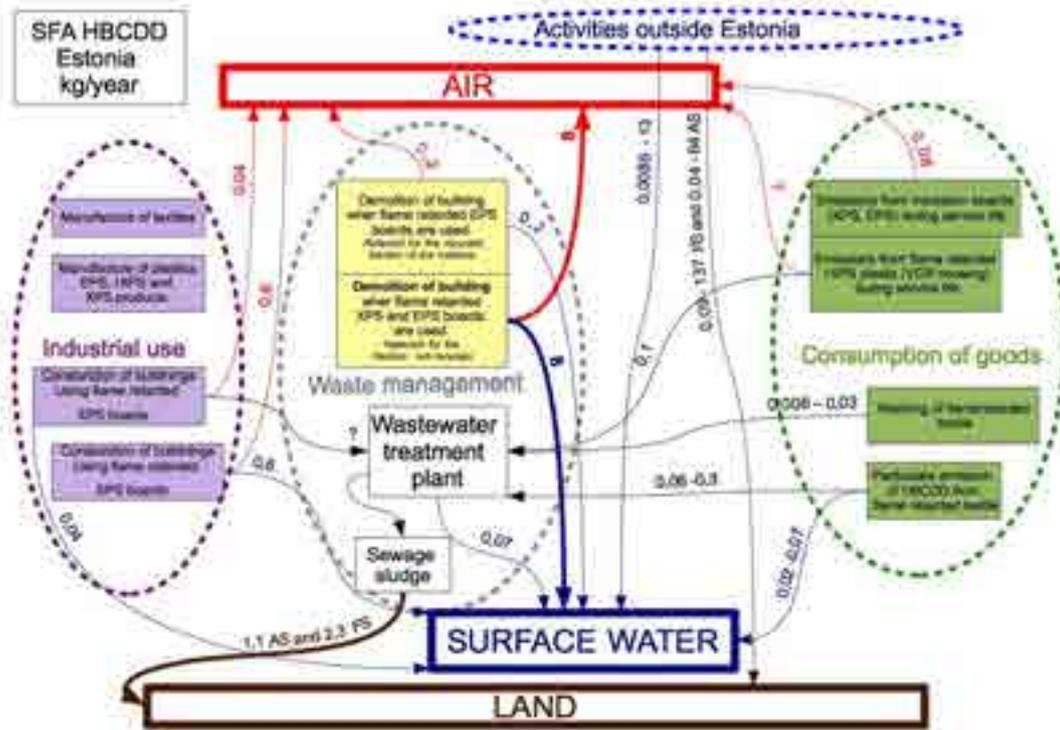


Figure 2. SFA diagram for HBCDDs in Estonia.



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4 Conclusions

4.1 Quantitative estimation of the most relevant sources to each environmental compartment (Soil, water and air)

The most important source of HBCDD-s for Estonia is using the products containing the HBCDD-s. One portion of this will end up in WWTP-s. The yearly load from WWTP effluents is 96,51 kg. It is possible to reduce the load entering the environment from this source by improving or using more innovative treatment processes..

The sources that have the biggest impact are the construction and demolition. The yearly load from demolition is 8 kg to SW and 8 kg to OA.

Another important source of HBCDD-s for Estonia is atmospheric deposition from which the HBCDD-s will enter the environment directly (0,01 - 4,5 kg to SW, 0,158 – 98,7 kg to AS and 0,168 – 115,5 kg to FS). This source is extremely difficult to control.

There are plastic industries in Estonia that might have a use of the raw materials that contain HBCDD-s, but there is no data available for use at the moment (as of December 2010).

4.2 A qualitative estimation of time trends for future scenarios.

It is near impossible to give any qualitative estimation of time trends for future scenarios as the data is just not sufficient. More thorough inventories on both industrial and municipal uses are needed. It is also necessary to add HBCDD to the national monitoring. It is safe to say that it is necessary to work with HBCDDs more. It is also safe to say the the impacts of the HBCDDs on the environment will be far-flung, as HBCDDs are used in many products that have a long-term use.



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IVL Swedish Environmental Research Institute, SFA HBCDD (EU 27)

IVL Swedish Environmental Research Institute, Swedish air monitoring data, COHIBA working material.

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ANNEX F - Substances flow analysis for Nonylphenols in Estonia

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This study was carried out under the COHIBA study from May 2010 to May 2011. This report is based on the SFA NP (EU 27) by IVL Swedish Environmental Research Institute. The results are for Estonia. Many of the results are rough approximations that cannot be taken as exact results for Estonia, but more as a base to plan future studies. The results are for Estonia.

1 Introduction

Nonylphenol (NP) is an organic compound of the wider family alkylphenols, more specific the group long-chain alkylphenols.

The name 'nonylphenol' can be applied to a number of isomer substances having a phenol ring structure and an alkyl chain of C₉H₁₉. Nonylphenols may vary in two ways: the substitution position of the nonyl group on the phenol molecule; and the degree of branching of the nonyl group.

There are several CAS numbers for nonylphenols (Table 1). The CAS No 25154-52-3 previously covered all nonylphenols but later only nonylphenol with a straight alkylchain, and the branched ones have been assigned new CAS-numbers.

Nonylphenol is a breakdown-product of the non-ionic surfactant nonylphenol ethoxylate (NPEO). Nonylphenol ethoxylate and other alkylphenol ethoxylates are widely used as detergents for industry, but also used as softener in the polymer and paint industry. Nonylphenol itself, for example, is used as stabiliser in rubbers and plastics.

Degradation of alkylphenol ethoxylates in wastewater treatment plants (WWTPs) or in the environment generates the more persistent shorter-chain alkylphenols and alkylphenols such as nonylphenol (NP) and octylphenol (OP).

During the literature search for this report it was found that most often it is not distinguished between nonylphenol and nonylphenol ethoxylates when reporting for example content of these compounds in products and articles. It is therefore not easy to differentiate between the emissions of nonylphenol and nonylphenol ethoxylates. Furthermore, as the ethoxylates are easily degraded to phenols in wastewater treatment plants and in the environment, the measured concentrations in wastewater effluents, stormwater or surface water, for example, do not always mirror the emitted amount of the same compound. This is why emissions in this report sometimes are reported as the sum of nonylphenol and nonylphenol ethoxylates or as nonylphenol-equivalents.

Table 1: CAS numbers for nonylphenols.

| Substance | CAS# | Comment |
|--|------------|--|
| 4-Nonylphenol, branched nonylchain in para position | 84852-15-3 | |
| 4-Nonylphenol, branched nonylchain | 90481-04-2 | |
| Isononylphenol (mixed isomers) | 11066-49-2 | |
| 4-Nonylphenol, straight nonylchain in para position | 104-40-5 | |
| Nonylphenol, straight nonylchain, not necessarily in para position | 25154-52-3 | This CAS No. previously covered all nonylphenols |

1.1 Physical chemical properties

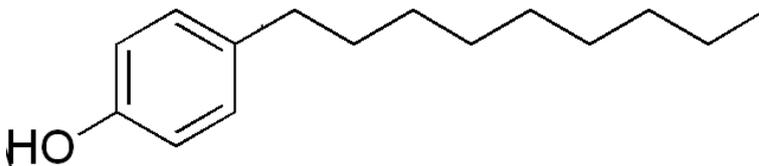


Figure 1: Chemical structure of 4-nonylphenol (straight nonylchain in para position)

Table 2: Physical and chemical properties of nonylphenol

| Property | 4-nonylphenol | Comment |
|--|-----------------------------------|---------------------------------|
| Physical state at npt | | |
| Molecular weight (g/mol) | 220.34 | |
| Molecular formula | C ₁₅ H ₂₄ O | |
| Melting point (°C) | -8 | |
| Vapour pressure (Pa, at XX°C) | | |
| Log octanol-water partition coefficient (log K _{ow}) | 3.28 3.8 – 4.77 4.48 | at 20 °C at 25 °C at ? °C |
| Water solubility (mg/l at 20 °C) | 6 | |
| Viscosity (mPa 20°C) | 2500 | Reported for CAS No 25154-52-3 |
| Dissociation constant | | |
| Henry's Law Constant (Pa m ³ /mol) | 11 | |

The high K_{ow} values of the APEO metabolites (NP, NPEO1–4, OP, OPEO1–4) indicate that they will partition effectively into sediments and sludge, and the aqueous solubility data indicate that they also will be present in water. Data from studies conducted in many regions across the world have shown significant levels in samples of every environmental compartment examined. Nonylphenols are lipophilic, which means that they may



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bioaccumulate in aquatic organisms.

Nonylphenols are classified as injurious to health, hazardous during consumption, and to have a possible risk of impaired fertility and harm to the unborn child. Nonylphenols are persistent in the water environment and are classified as very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment (ESIS, 2009). Furthermore, nonylphenols are shown to be estrogenic to aquatic organisms.

1.2 Regulatory status

Nonylphenol is regulated under the Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community, which is now implemented in the European Water Framework Directive (WFD) (Directive 2000/60/EC). Nonylphenol is one of the substances identified as "priority hazardous substances" under the WFD. Directive 2008/105/EC (the EQS Directive), which is a daughter directive of WFD, sets the water quality standards for nonylphenol in the EU. As Estonian legislation is compliant to the EU legislation, NP is also listed as a priority substance and has set water quality standards under the Estonian law (RT I 2010, 51, 318; RT I 2010, 65, 484).

Furthermore, the use of nonylphenol and nonylphenol ethoxylates are restricted within EU since 2005 by Directive 2003/53/EC. The compounds may not be placed on the market or used as a substance or constituent of preparations in concentrations equal or higher than 0,1 % by mass in applications such as textiles and leather processing, metal industry and industrial cleaning with the exception if it is used in closed systems. This restriction applies also to pulp and paper industry, domestic cleaning, personal care products and co-formulants of pesticides and biocides. Similarly, Regulation 1907/2006 (REACH Regulation) restricts the supply and use of nonylphenol and its ethoxylates. According to the Regulation 689/2008/EC, the export of NP should be notified.

Both NPs and their ethoxylates are listed as 'high concern' on the EU endocrine disrupter priority list (European Commission, 2007). HELCOM Baltic Sea Action Plan also identifies NPs and their ethoxylates as substances of specific concern to the Baltic Sea.

1.3 Production

There is no production of nonylphenols in Estonia.

1.4 Use

Nonylphenols have been used for many applications in textile, metal- and cleaning



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processes in Estonia.

No NPs have been registered under regulation 689/2008/EC (export and import of dangerous chemicals) and there is no registered use under Regulation 1907/2006/EC (REACH regulation) (data from Endla Veskimäe Health Board Department of Chemical Safety – it is the responsible authority of Estonia e-mail conversation 20.12.2010 Mailis Laht).

1.5 Environmental fate

Releases of nonylphenols from production processes are estimated to be very low. The primary source of nonylphenols found in the environment is considered to be nonylphenol ethoxylates, which can break down into nonylphenol in wastewater treatment plants or in the environment. Products containing nonylphenol and nonylphenol ethoxylates are also potential sources of diffuse emissions of nonylphenol and nonylphenol ethoxylates.

The main environmental compartments to which releases of nonylphenol occur are surface waters that receive municipal and industrial wastewater, and soil via spreading of sewage sludge containing nonylphenol. If nonylphenols reach the marine environment this is generally via industrial or municipal wastewater.

Nonylphenols are frequently detected in effluent water and sludge from WWTPs. According to a Finnish screening study referred to in Mehtonen (2009) nonylphenol levels in treated wastewater sometimes exceeded the predicted no effect concentrations (PNEC) for chronic effects and thus, nonylphenol may cause chronic effects in the Finnish aquatic environment. Likewise, a Lithuanian screening study showed that nonylphenol levels in treated wastewater have sometimes exceeded the PNEC for chronic effects (Dudutyte et al. 2007). A Swedish screening study showed that nonylphenol levels in treated wastewater have sometimes been so high that ecotoxicological effects on the aquatic environment are possible (Swedish EPA, 2005).

Nonylphenol is not readily biodegradable and takes months or even longer to degrade in surface waters or in soils and sediments. Non-biological degradation is negligible. Bioconcentration and bioaccumulation of nonylphenol is significant in water dwelling organisms and birds. Because of the bioaccumulation and persistence, it is possible that nonylphenol could be transported significant distances, and therefore potentially have global effects.



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1.6 Environmental levels

The study ordered by Estonian Ministry of Environment (conveyed by AS Maves) was made on the priority hazardous substances of WFD and studied these substances in the coastal waters and surface waters. Iso-nonylphenol and 4-n-nonylphenol were studied under this study.

4-n-nonylphenol was under the LOQ in all analyses ($<0,01$ g/l). The results for iso-nonylphenol were also mainly under the LOQ ($0,1$ µg/l), but were found at some places with the maximum concentration of $1,31$ µg/l.

Iso-nonylphenol was found from Balti SEJ ($0,183$ µg/l), Keila river ($0,292$ µg/l), Peipsi lake ($0,308$ µg/l), Pärnu bay ($0,39$ µg/l) and Liivi bay ($0,178$ µg/l), Mustoja river ($0,48$ µg/l), Emajõe river ($0,664$ µg/l) and Kroodi creek ($1,31$ µg/l). The concentration of iso-nonylphenols was over the annual average EQS in the samples of Kroodi creek, Emajõe river, Pärnu bay and lake Peipsi.



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2 Sources of emissions of nonylphenols in Estonia

The uncertainties in the following emission strings are given with four letters, the first letter representing uncertainty for EF, the second for EFM, the third for division into compartments and the fourth for the yearly load. Uncertainty is classified according to the principles described in “Dealing with uncertainty in substance flow analysis within the COHIBA project”, a PM describing how data uncertainty is graded in WP4 of the COHIBA project.

If the Estonian yearly loads were scaled from the EU yearly load to Estonian population, the Estonian population was considered to be 0,3% of the EU population. This accuracy level was considered to be enough for given study; especially considering the very high uncertainty levels in other emission strings.

2.1 Construction

NACE – F

Emissions of NP from concrete (in which NP is used as hardener), for example as runoffs from buildings

Yearly load 28 – 42 kg to FSW

Uncertainty: CAB

In Denmark the registered total consumption of NP for use in hardeners (including concrete, epoxy and PUR) was around 70 tonnes in 2004 (Kjølholt et al, 2007). According to the Product register the annual Swedish use of NP in hardeners for construction was 6,4 tonnes in 2007 (KemI, 2009). The yearly load was calculated from the EU SFA, using Estonian population as a basis for scaling.

2.2 Emission from (private) consumption; during lifetime use of articles, goods and chemical products and preparations

Emissions from painted and coated surfaces, e.g. metal sheets

Yearly load is considered in the NPE table.

Uncertainty: N/A

Emission due to private use of detergents/cleaning agents/stain removers from outer-EU

Yearly load – 216 kg to WW.



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Uncertainty: BCAC

This ES also includes NPEO, which breaks down to NP. In Stockholm 10% of the NP input to WWTP are estimated to originate from cleaning agents, the rate is probably the same for Estonia, considering the similar living styles of the two countries. The yearly load was calculated from the EU number, using the Estonian population as a basis for scaling.

Emission due to industrial use of detergents and cleaning agents/stains removers from outer EU.

Yearly load ? kg to WW.

Uncertainty: N/A

The biggest producers of textile and leather do not use NP containing products any more (Data from Jelena Lebedeva's personal communication with AS Nakro, Ljubor Varshavskaja, technologist, June 2010). However, if the NPs are used in some other industries (such as car wash) we have no coherent data on that ES.

Emission from the use of cosmetic and hygienic products

Yearly load 0,39– 11,07 kg to WW.

Uncertainty: BAAC

This ES considers both NP and NPE.

NP and NPEO may not be placed on the market or used as a substance or constituent of preparations in concentrations equal or higher than 0,1 % by mass, in preparations which cause direct emissions to the wastewater in EU since 2005 (Directive 2003/53/EC). This legislation is also applicable to cosmetics. The release is possible from old products, illegally imported products, or from the max. 0,1% nonylphenol in the newly produced cosmetics. The yearly load was calculated from the EU yearly load, using the Estonian population as a basis for scaling.

Emission of NP and NPEO from vehicles (plastic materials, paint, maintenance products. Etc.)

Yearly load - 1,23 kg to IS

Uncertainty: BBBB

The Swedish EF was given as 0,14 □g/driven km (Björklund et al (2007)). The same EF was used to calculate the yearly load for Estonia as the two countries can be considered similar enough. EFM was the road transport – total mileage (passenger cars, light duty vehicles, heavy duty vehicles, motorcycles) in Estonia (8780 million km/year) (2008 Estonian Informative Inventory Report, 2010). The EF and EFM were multiplied to get



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the yearly load.

Emission from washing of textiles containing NP and NPEO.

Yearly load is considered in the NPE table.

Uncertainty: N/A

The yearly load was calculated from the EU SFA, using the Estonian population as a basis for scaling. However, the yearly load was added to the NPE yearly load of the same ES and is considered in that table, the reason for that change is the e-mail correspondence with WP4 leaders who stated that NPE is used at this application, not NP.

Use of NPEO in industrial and institutional cleaning

Yearly load - ? kg to FSW

Uncertainty: N/A

Emissions of NP due to degradation of NPEO in WWTPs. This is probably not a relevant source in EU and Estonia at present (2011) as NP and NPEO may not be placed on the market or used as a substance or constituent of preparations in concentrations equal or higher than 0,1 % by mass, in preparations which cause direct emissions to the wastewater in EU since 2005 (Directive 2003/53/EC). This applies also for NP and NPEO used as industrial and institutional cleaning, except controlled closed dry cleaning systems and for special cleaning where the washing liquid is recycled or incinerated.

2.3 Manufacture of basic metals

NACE 24

Emissions of NP due to use of NPEO in metal extraction, refining and processing industries, e.g. from use of cutting oils, cutting fluids, drilling fluids, degreasing etc.

Yearly load - ?

Uncertainty: N/A

Emissions of NP due to degradation of NPEO in WWTPs. According to the Swedish product register (Swedish Chemicals Agency) NP is reported to be in use for this application in Sweden 2007. This situation could be similar in Estonia but there is no data because of the poor product and chemical control and incomplete registers.

However, according to legislation NP and NPEO may not be placed on the market or used as a substance or constituent of preparations in concentrations equal or higher than 0,1 % by mass, in preparations which cause direct emissions to the wastewater in EU since 2005 (Directive 2003/53/EC). This legislation also applies for metal working industries, except for use in controlled closed systems.



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There are several activities taking place in Estonia under that NACE according to Prodcom 2008. We don't know what kind of products they use and if the products might contain NP. Future studies based on the products are needed. For future studies, it should be noted that the following activities are listed as taking place in Estonia in Prodcom:

Hot rolled concrete reinforcing bars;

Hot rolled bars in tool steels;

Tubes and pipes, of circular cross-section, hot or cold formed and welded, of an external diameter ≤ 406.4 mm, of steel other than stainless steel;

Flanges, of steel (excluding cast fittings);

Elbows, bends, couplings, sleeves and other threaded tube or pipe fittings, of steel (excluding cast fittings);

Elbows, bends, couplings and sleeves and other socket welding tube or pipe fittings, of steel (excluding cast fittings);

Iron or non-alloy steel wire containing $<0.25\%$ of carbon including crimping wire excluding stranded wire, barbed wire used for fencing - duplex wire - saw-tooth wire, insulated electric wire;

Unwrought aluminium alloys in secondary form (excluding aluminium powders and flakes);

Aluminium plates, sheets and strips > 0.2 mm thick;

Copper and copper alloy tube/pipe fittings including couplings, elbows, sleeves, tees and joints excluding bolts and nuts used for as-sembling/fixing pipes/tubes, fittings with taps, cocks, valves;

Magnesium and articles thereof (excluding waste and scrap), n.e.c.;

Titanium and articles thereof (excluding waste and scrap), n.e.c.;

Beryllium, chromium, germanium, vanadium, gallium, hafnium (celtium), indium, niobium (columbium), rhenium and thallium, and articles of these metals, n.e.c.; waste and scrap of these metals (excluding of beryllium, chromium and thallium);

Parts for other utilisation (malleable iron casting);

Grey iron castings for locomotives/rolling stock/parts, use other than in land vehicles, bearing housings, plain shaft bearings, piston engines, gearing, pulleys, clutches, machinery;

Steel castings for machinery and mechanical appliances excluding piston engines, turbojets, turboprops, other gas turbines, lifting or handling equipment, construction industry machinery/vehicles;

Light metal castings for land vehicles excluding for locomotives or rolling stock, construction industry vehicles;

Parts for other utilisation.

2.4 Manufacture of electrical equipment

NACE 27



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Use of NPEO in electrical engineering industry

Yearly load ?

Uncertainty: N/A

In this ES, the emissions of NP are a result of degradation of NPEO in WWTPs. This ES could be relevant for Estonia as there are several uses listed under this NACE in Prodcum 2008. We don't know what kind of products they use and if the products might contain NP. Future studies based on the products are needed. For future studies, it should be noted that the following activities are listed as taking place in Estonia in Prodcum:

DC motors and generators of an output > 37.5 W but ≤ 750 W (excluding starter motors for internal combustion engines);

Multi-phase AC motors;

Other transformers, n.e.c., having a power handling capacity ≤ 1 kVA;

Accumulator chargers;

Rectifiers;

Power supply units for telecommunication apparatus, automatic data-processing machines and units thereof;

Inverters having a power handling capacity ≤ 7.5 kVA;

Static converters (excluding polycrystalline semiconductors, converters specially designed for welding, without welding equipment, accumulator chargers, rectifiers, inverters);

Inductors (excluding induction coils, deflection coils for cathode-ray tubes, for discharge lamps and tubes);

Parts suitable for machines of HS 85.01 or 85.02;

Ferrite cores of transformers and inductors;

Parts of transformers and inductors (excluding ferrite cores);

Parts of static converters;

Other apparatus for switching... electrical circuits > 1000 V;

Electrical apparatus for protecting electrical circuits;

Relays and contactors for a voltage > 60 V but ≤ 1 kV;

Programmable memory controllers for a voltage ≤ 1 kV;

Other bases for electric control, distribution of electricity, voltage ≤ 1000 V;

Boards, panels, consoles, desks, cabinets and other bases for apparatus for electric control or the distribution of electricity (excluding those equipped with their apparatus);

Other parts of apparatus of 85.35, 85.36, 85.37;

Primary cells and primary batteries;

Optical fibre cables made up of individually sheathed fibres whether or not assembled with electric conductors or fitted with connectors;

Optical fibres and optical fibre bundles; optical fibre cables (except those made up of individually sheathed fibres);

Insulated coaxial cables and other coaxial electric conductors for data and control



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purposes whether or not fitted with connectors;
Other electric conductors, for a voltage ≤ 1000 V, fitted with connectors;
Insulated electric conductors for voltage >1000 V (excluding winding wire, coaxial cable and other coaxial electric conductors, ignition and other wiring sets used in vehicles, aircraft, ships);
Electrical apparatus for switching electrical circuits for a voltage ≤ 1 kV (including push-button and rotary switches) (excluding relays);
Plugs and sockets for coaxial cables for a voltage ≤ 1 kV;
Prefabricated elements for electrical circuits for a voltage ≤ 1 kV;
Connections and contact elements for wires and cables for a voltage ≤ 1 kV;
Other apparatus for connections to or in electrical circuit, voltage ≤ 1000 V;
Fluorescent hot cathode discharge lamps (excluding ultraviolet lamps, with double ended cap);
Electric table, desk, bedside or floor-standing lamps;
Illuminated signs, illuminated name-plates and the like (including road signs);
Chandeliers and other electric ceiling or wall lighting fittings (excluding those used for lighting public open spaces or thoroughfares);
Electrical lighting or visual signalling equipment for motor vehicles (excluding electric filament or discharge lamps, sealed beam lamp units, ultraviolet, infrared and arc lamps)
Electric lamps and lighting fittings, of plastic and other materials, of a kind used for filament lamps and tubular fluorescent lamps;
Electric water heaters (including storage water heaters) (excluding instantaneous);
Parts for vacuum cleaners;
Parts for electro-mechanical domestic appliances with a self-contained electric motor (excluding parts for vacuum cleaners);
Other domestic cooking appliances and plate warmers, of iron or steel or of copper, non electric;
Iron or steel solid fuel domestic appliances, including heaters, grates, fires and braziers (excluding cooking appliances and plate warmers);
Air heaters or hot air distributors n.e.c., of iron or steel, non-electric;
Electrical signalling, safety or traffic control equipment for roads, inland waterways, parking facilities, port installations or airfields.

2.5 Manufacture of other organic basic chemicals; Manufacture of glues

NACE 20.14 and 20.52



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Use of NP in manufacture of phenolic oximes

Yearly load - ? kg to FSW

Uncertainty: N/A

According to the EU SFA, there was one production site in EU in 1997. This data was for EU15 and therefore didn't cover Estonia. There is no production of phenolic oximes, but there are some activities under that NACE according to the PRODCOM 2008 data. Therefore we consider this ES to be irrelevant for Estonia but we cannot be sure and therefore list this ES as in need for future studies.

Use of NP in phenol and formaldehyde resins

Yearly load - ? kg to AO, WW

Uncertainty: N/A

According to the EU SFA, there were 25 production sites in EU in 1997. This data was for EU15 and therefore didn't cover Estonia. According to Prodcom 2008 data, the activities taking place under that NACE in Estonia are:

Methanal (formaldehyde) 7121 000 kg Estonia; 3570922 000 kg EU total;

Aldehyde-ethers, aldehyde-phenols and aldehydes with other oxygen function – confidential;

Phenols – 663 000 kg.

We don't know if this is relevant for the ES. Future studies are needed.

2.6 Manufacture of other transport equipment

NACE 30

Use of NP in solvent based paint for industrial use

Use of adhesives containing NP

Use of hardeners

Yearly loads - ?

Uncertainty: N/A

According to the Swedish product register (Swedish Chemicals Agency) NP was reported to be in use for these applications in Sweden 2007. The situation could be similar for Estonia but there is no data because of the poor product and chemical controls and incomplete registers. Also, there are several activities taking place under that NACE in Estonia.

However, we have no information on the amount NP containing products used. Product by product research was not possible to do under that study. Therefore, future studies are



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needed.

For future studies, it should be noted that in Prodcom 2008, the following activities are listed under that NACE:

Offshore vessels;

Other floating structures (including rafts, tanks, coffer-dams, landing stages, buoys and beacons);

Conversion and reconstruction of ships, floating platforms and structures;

Sailboats (except inflatable) for pleasure or sports, with or without auxiliary motor;

Motor boats and motor yachts, for pleasure or sports (excluding outboard motor boats);

Other vessels for pleasure or sports n.e.c.; rowing boats and canoes;

Parts of locomotives or rolling-stock;

Reconditioning of railway and tramway locomotives and rolling-stock;

Seats for aircraft; parts thereof;

Vehicles not mechanically propelled including industry trolleys, barrows, luggage trucks, hopper-trucks, hand pulled golf trolleys excluding shopping trolleys.

2.7 Manufacture of paints, vanishes and similar coatings, printing and mastics.

NACE 20.3

Use of NP as a solvent in paints, as hardener and stabilizer, as raw material in plastics, as binders from paints and adhesives and in jointless floors.

Yearly load - ?

Uncertainty: N/A

Use of NPEO in paints, lacquers and varnishes.

Yearly load - ? to FSW.

Uncertainty: N/A

The last two lines are marked as probably relevant because there is some manufacturing of paints in Estonia. However, there is no data on the use of NP-s on that field. Producers who have about 40% of the market share claim they don't use any NP. 60% of the manufacturers are the sub-companies of Finnish paint manufacturers, therefore we might use the Finnish results to calculate Estonian yearly loads later. Unfortunately, we had no time to do this kind of research in this study. Future studies are needed.

For future studies, it must be noted that in Prodcom 2008, the following activities are listed as taking place in Estonia:

Paints and varnishes, based on acrylic or vinyl polymers dispersed or dissolved in an aqueous medium (including enamels and lacquers);

Other paints, varnishes dispersed or dissolved in an aqueous medium;



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*Paints and varnishes, based on polyesters dispersed/dissolved in a non-aqueous medium, weight of the solvent >50% of the weight of the solution including enamels and lacquers;
Paints and varnishes, based on polyesters dispersed/dissolved in a non-aqueous medium including enamels and lacquers excluding weight of the solvent >50% of the weight of the solution;*

Other paints and varnishes based on synthetic polymers n.e.c.;

Glaziers' putty, grafting putty, resin cements, caulking compounds and other mastics;

Painters' fillings;

Non-refractory surfacing preparations for façades, indoor walls, floors, ceilings or the like;

Organic composite solvents and thinners used in conjunction with coatings and inks; based on butyl acetate;

Organic composite solvents and thinners used in conjunction with coatings and inks (excluding those based on butyl acetate).

Most of the production amounts are confidential.

2.8 Manufacture of paper and paper products

NACE 17

Use of NP as surface treatment and in solvent free paint

Yearly load – ?

Uncertainty: N/A

According to the Swedish product register (Swedish Chemicals Agency) NP is reported to be in use for this application in Sweden 2007. The situation could be similar in Estonia, but there is no data because of the poor product and chemical control and incomplete registers. We could not calculate the yearly load in this ES as there was no EF available in the EU SFA.

According to Prodcom 2008, mostly the uncoated paper products are produced (kraft paper etc.), according to Prodcom 2008. Future studies are needed to ensure NPs are not used under these activities. In Prodcom, the following activities are listed as taking place in Estonia:

Other coated mech. graphic paper for writing, printing, graphic purposes, m.f. > 10%, sheets;

Multi-ply paper and paperboard, coated, others;

Corrugated paper and paperboard in rolls or sheets;

Cartons, boxes and cases, of corrugated paper or paperboard;

and many others.



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2.9 Manufacture of plastic products

NACE 22.2

Use of NP in epoxy resins

Use of NP as hardener in plastic products

Yearly load - ?

Uncertainty: N/A

There is plastic industry in Estonia. However, there is no proper data on the relevancy of that ES at the moment. We have contacted the representative of the union of plastic producers and we are waiting for an answer. The NACE covers a wide range of activities, so it can be difficult to make sure if there are hardeners used and if there are NPs used in these hardeners.

According to Prodcum 2008, there are several uses represented in Estonia, but we don't know which could be relevant. Future studies are needed.

Rigid tubes, pipes and hoses of polymers of ethylene;

Rigid tubes, pipes and hoses of polymers of propylene;

Rigid tubes, pipes and hoses of polymers of vinyl chloride;

Rigid tubes, pipes and hoses of plastics (excluding of polymers of ethylene, of polymers of propylene, of polymers of vinyl chloride);

Flexible tubes, pipes and hoses of plastics, with a burst pressure ≥ 27.6 Mpa;

Plastic tubes, pipes and hoses with fittings attached excluding rigid, flexible tubes, pipes or hoses, with minimum burst pressure of 27,6 MPa, reinforced or otherwise combined with other materials;

Plastic tubes, pipes and hoses (excluding artificial guts, sausage skins, rigid, flexible tubes and pipes having a minimum burst pressure of 27.6 MPa);

Plastic fittings for plastic tubes, pipes and hoses (including joints, elbows and flanges);

Other plates..., of polymers of ethylene, not reinforced, thickness ≤ 0.125 mm;

Other plates..., of biaxially orientated polymers of propylene, thickness ≤ 0.10 mm;

Other plates..., of polymers of propylene, thickness ≤ 0.10 mm, others;

Other stripes, thickness > 0.10 mm;

Cellular plates, sheet, film, foil and strip of polymers of styrene;

Cellular plates, sheets, film, foil and strip of polymers of vinyl chloride;

Cellular plates, sheets, film, foil and strip of polyurethanes;

Cellular plates, sheets, film, foil and strip of plastics (excluding of polymers of styrene, of polymers of vinyl chloride, of polyurethanes, of regenerated cellulose).



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2.10 Painting and glazing

NACE 43.34

Emission from application of paints, lacquers and varnishes

Yearly load - ? to FSW

Uncertainty: N/A

This ES would also include NPEOs. This ES is a possible source. Paint application is an exception on the European legislation that states that NP and NPEO may not be placed on the market or used as a substance or constituent of preparations in concentrations equal or higher than 0,1 % by mass, in preparations which cause direct emissions to the wastewater in EU since 2005 (Directive 2003/53/EC). The exception was made because paint is not supposed to cause direct emissions to wastewater.

Emission from paint (application and painted products) for Stockholm was 1-3 kg NP equivalents/yr to the WWTP in 2004 (765 000 inhabitants) (Andersson and Sörme, 2006). The use of NP in paint and lacquers in Denmark were 11 tonnes in 2004. Therefore we can assume that the NP and NPEs are used in paints, lacquers, and varnishes as well in Estonia.

2.11 Sewerage

Emissions of NP with effluent water from municipal WWTP-s

Yearly load 6,8 - 12 kg to FSW

Yearly load 2,9 – 5,1 kg to CSW

Uncertainty: BAAC (The uncertainty of the yearly load is marked as C because the data used for calculation is too limited to be considered reliable)

The calculations were done using the data from COHIBA WP3 and the preliminary results from the BaltActHaz project – that gave us the EF. The EF was considered to be the average result of all WWTP-s. For min scenario, the results under LOQ were considered to be; for max scenario, the results below LOQ were considered to be LOQ. The EF was then multiplied by the EFM, i.e. the amount of effluents produced per person a day – 125 litres (according to Statistics Estonia 2010), the number of inhabitants (1 340 021 according to Statistics Estonia 2010), and the number of days a year (365).

Emission in sewage sludge from municipal WWTP-s

Yearly load 60,0 kg to AS

Yearly load 127,5 kg to FS

Uncertainty: BBBC (The uncertainty of the yearly load is marked as C because the data used for calculation is too limited to be considered reliable)



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The calculations were done using the data from COHIBA WP3 and the preliminary results from BaltActHaz project that gave us the EF. The EF was considered to be the average result of all WWTP-s. The representability is highly uncertain due to limited data. The EFM is the one from European SFA-s, considered to be representative to Estonia by Mr Kõrgmaa, an expert of WWTPs and sewage sludge (personal communication). The yearly load was calculated by multiplying EF with EFM and number of inhabitants in Estonia.

2.12 Support activities for transportation

Emissions of NP and NPEO from car washes

Yearly load 1,06 kg/y to WW.

This ES considers both NP and NPEO.

The EU EF of 0,1 mg/car and washing occasion was used. In Sweden it is assumed that every a car is washed in average 20 times/year, we used the same assumption as the living styles of the two countries are similar enough. Number of cars in Estonia 2009 was 407 cars per 1000 person (Estonian Environment Information Centre 2011¹). The EF, the number of cars and the number of times every car was washed were then multiplied to get the yearly load.

2.13 Treatment and disposal of nonhazardous waste; Treatment and disposal of hazardous waste

NP-s in landfill leachate from the landfills of non-hazardous wastes

Yearly load – 0,0004 to 0,0010 kg to FS

Yearly load – 0,0004 to 0,0010 kg to SW.

Uncertainty: C

The calculations were done using the excel sheet provided by IVL. The data used was from the COHIBA WP3 results from the study of landfill leachate. However, this result is considered extremely inaccurate as it is based on two samples from one landfill.

To point out our opinion, the leachate from the hazardous wastes should be in a different ES. However, we didn't find it meaningful to create an additional ES as we have no data from the effluents of leachates of hazardous waste landfills.

¹ <http://www.keskkonnainfo.ee/index.php?lan=EE&sid=32&tid=34&l2=22&l1=2#auto>



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2.14 Worldwide activities outside the region, for example atmospheric deposition of long range transport.

Atmospheric deposition – (wet + dry)

Yearly load – 0,16 kg to FSW

Yearly load – 1,72 kg FS

Yearly load – 0,8 kg to AS

Uncertainty: BCCC

Both wet and dry depositions are considered in this string. This ES also includes both NP and NPEO. Please note also that on the SFA diagram for NP-s, the atmospheric deposition is missing – it is included on the NPE diagram.

As there is no monitoring data available for Estonia, the EU SFA EFs were used for calculations. The basis for calculation was the territory of Estonia. The division into the compartments was also changed, according to the data from Estonian Environment Information Centre.

3 SFA diagram

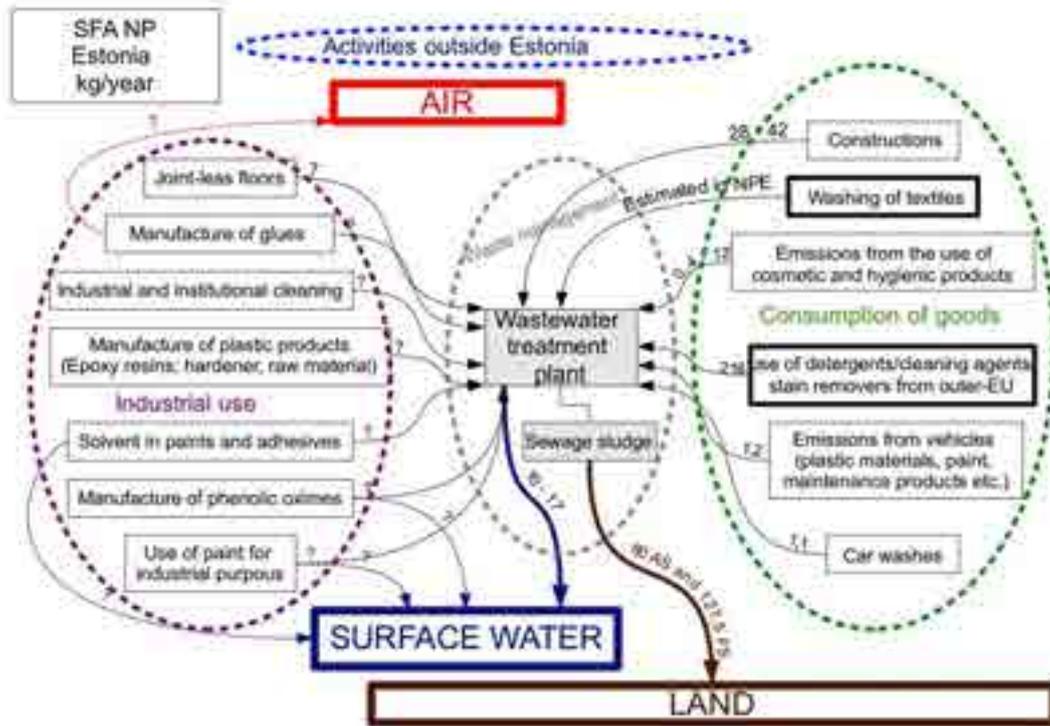


Figure 1. SFA diagram for NP in Estonia.

Please note that on this SFA diagram the atmospheric deposition is missing – it is included on the NPE SFA diagram.



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4 Conclusions

4.1 Quantitative estimation of the most relevant sources to each environmental compartment (Soil, water and air)

It was not possible to identify the most important sources of NPs in Estonia as most of the data from industrial sources is missing due to the poor registers and chemical control in Estonia. We have data from many industrial activities that might use the NP in processing but no reliable information. The reason for that is the use of different products that contain NP. Estonia has no product register and so the quantitative estimation was not possible to carry out in the frame of this work. In the future it can be possible to detect the products that are in use and then using the information from companies, environmental permits and product safety data sheets the quantitative estimation is also possible.

NP emissions are also coming from private consumption in Estonia and the most important sources are the washing and cleaning activities. The use of NPs and NPEs is forbidden in the EU, but the substances are still present in the imported clothes and imported cleaning products. The use of imported cleaning products has a great impact of 216 kg/year. Cosmetic products emit 0,4 -12 kg of NPs yearly. Also washing of imported textiles gives a great amount of emissions of NPs, but this is considered in the SFA of NPE.

The most important compartment is wastewater, but the NPs may also end up in surface waters through the waste water system.

In our opinion, the most relevant reduction possibilities are in the industrial sector, with the use of BAT and BEP. Also, raising the awareness of the general public and the industry managers is an important step to be taken. It has been our and our colleagues' experience that, quite often, the managers in the industry are not aware of their potential use of hazardous substances as the substances are often additives and may be often detected only by thorough research through the safety cards. This is also one reason why we didn't consider the information straight from the producers to be of A-type accuracy.

Also the proper treatment of wastewater would give a good effort to protect that the NP-s would not end up in the environment.

4.2 A qualitative estimation of time trends for future scenarios

Possible means for reducing the emissions of NPs are administrative. It is not possible to make future plans for reducing NPs in Estonia as the mapping of the current situation is insufficient.

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ANNEX G - Substance flow analysis for NPEs in Estonia

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This study was carried out under the COHIBA study from May 2010 to May 2011. This report is based on the SFA NPE (EU 27) by IVL Swedish Environmental Research Institute. The results are for Estonia. Many of the results are rough approximations that cannot be taken as exact results for Estonia, but more as a base to plan future studies. The results are for Estonia.

1 Introduction

Nonylphenol ethoxylate belongs to a class of chemicals called alkylphenol ethoxylates. Nonylphenol ethoxylates (NPEs) are predominantly used as industrial and domestic detergents and cleaning agents. Other uses have included degreasing products, dispersants, humidifying agents and stabilisers. They have also been used as additives in pesticides, in pharmaceuticals, personal care products and cosmetics, plastics and synthetic rubber production, oil additives, textiles, paint and varnishes, agricultural chemicals and in pulp and paper products.

Alkylphenol ethoxylates are commonly found in wastewater discharges and in wastewater treatment plant effluents. Degradation of alkylphenol ethoxylates in wastewater treatment plants (WWTPs) or in the environment generates the more persistent shorter-chain alkylphenols and alkylphenols such as nonylphenol (NP) and octylphenol (OP).

During the literature search for this report it was found that most often it is not distinguished between Nonylphenol and nonylphenol ethoxylates when reporting for example content of these compounds in products and articles. It is therefore not easy to differentiate between the emissions of nonylphenol and nonylphenol ethoxylates. Furthermore, the ethoxylates are easily degraded to phenols in wastewater treatment plants and in the environment, why measured concentrations in for example wastewater effluents, stormwater or surface water not always mirror the emitted amount of the same compound. This is why emissions in this report sometimes are reported as the sum of nonylphenol and nonylphenol ethoxylates or as nonylphenol- equivalents.

Table 1: CAS numbers for nonylphenol ethoxylates (Swedish Chemical Agency, 2010).

| Substance | CAS# |
|------------------------|-------------|
| Nonylphenol etoxylates | 9016-45-9 |
| Nonylphenol etoxylates | 26027-38-3 |
| Nonylphenol etoxylates | 37205-87-1 |
| Nonylphenol etoxylates | 127087-87-0 |
| Nonylphenol etoxylates | 68412-54-4 |

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1.1 Physical chemical properties

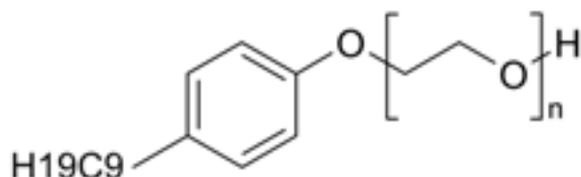


Figure 1: Chemical structure of 4-nonylphenol ethoxylate

Nonylphenol ethoxylates are liquids or waxy solids depending on the number of ethylene oxide substitutions. They are generally colourless to light amber with a varying degree of water solubility. Their physical chemical properties vary with the degree of ethoxylation.

1.2 Regulatory status

Nonylphenol ethoxylates are regulated under the Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community. Furthermore, the use of nonylphenol and nonylphenol ethoxylates are restricted within EU since 2005 by Directive 2003/53/EC. The compounds may not be placed on the market or used as a substance or constituent of preparations in concentrations equal or higher than 0,1 % by mass in applications such as textiles and leather processing, metal industry and industrial cleaning with the exception if it is used in closed systems. This restriction applies also to pulp and paper industry, domestic cleaning, personal care products and co-formulants of pesticides and biocides. Similarly, Regulation 1907/2006 (REACH Regulation) restricts the supply and use of nonylphenol and its ethoxylates. According to the Regulation 689/2008/EC, the export of NP should be notified.

Both NPs and their ethoxylates are listed as 'high concern' on the EU endocrine disrupter priority list (European Commission, 2007). HELCOM Baltic Sea Action Plan also identifies NPs and their ethoxylates as substances of specific concern to the Baltic Sea.

1.3 Production

No production in Estonia.



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1.4 Use

No relevant industrial use detected in Estonia at the moment (May 2011). NPE is detected in Estonian environment and wastewater treatment systems. The use of NPEs in private consumption is important for Estonia. No registered use in Estonia.

We have no registration under regulation 689/2008/EC (export and import of dangerous chemicals) and also no registered use under regulation 1907/2006/EC (REACH regulation). (data from Endla Veskimäe Health Board Department of Chemical Safety – it is the responsible authority of Estonia e-mail conversation 20.12.2010 Mailis Laht)

1.5 Environmental fate

The main environmental compartments to which releases of nonylphenol ethoxylates occur are surface waters that receive municipal and industrial wastewater, and soil via spreading of sewage sludge containing nonylphenol ethoxylates. If nonylphenol ethoxylates reach the marine environment this is generally via industrial wastewater from different industrial activities e.g. production of nonylphenol ethoxylates, industrial uses nonylphenol ethoxylates in the formulation of other chemical products and articles, and via municipal wastewater.

Nonylphenol ethoxylates are very toxic to fish and other water dwelling organisms and is considered a hormone disrupting substance, mimicking oestrogen. It degrades relatively readily in the environment to form the even more harmful nonylphenol.

1.6 Environmental levels

There has been virtually no research on NPEs in Estonia. The first data is from 2010 when it was studied in two European funded projects – BaltActHaz¹ and COHIBA. Therefore we mainly used data from these two projects for determining the possible sources of NPEs.

In BaltActHaz, NPEs were measured from the effluents and sludge of several municipal WWTPs, waters and sediments of rivers and one point on the coast, and waters and sediments from two points of lake Peipsi.

Iso-Nonylphenolmonoethoxylates and iso-Nonylphenoldiethoxylates were analysed from the water samples; iso-Nonylphenolmonoethoxylates, iso-Nonylphenoldiethoxylates, iso-Nonylphenoltriethoxylates, iso-Nonylphenoltetraethoxylate, iso-

¹ BaltActHaz web page, available at: <http://www.baltacthaz.bef.ee/>

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Nonylphenolpentaethoxylates and iso-Nonylphenolhexaethoxylates were measured from the sediments.

Mono- and diethoxylates were found from a few measurements from several WWTP effluents (461 and 1420 ng/l for monoethoxylates, 862 ng/l in one sample for diethoxylates), mostly the results were below the LOQ (100 ng/l). In industrial WWTP, both mono- and diethoxylates were found in higher concentrations (up to 8510 ng/l of monoethoxylates and 5040 ng/l of diethoxylates). Mono- and diethoxylates (but not the other ethoxylates) were found from the sludge of one WWTP as well (interestingly, it was different from those WWTPs where the NPEs were measured from the effluents). NPEs were not found from the waters or sediments of rivers, coast or lake.

COHIBA project was another one where NPEs were measured for the first time in Estonia from WWTPs (both effluents and sludge), storm waters and one landfill.

In COHIBA WP3 analysis NPEs were measured as mono- and diethoxylates. For the substance flow analysis we used the sum of those. The wastewater contained NPEs up to 13,21 ng/l.

Table 2. NPEs in landfills, storm waters, wastewaters and wastewater sewage sludges in Estonia 2009-2010 (Data from COHIBA WP3).

| | Landfill | Stormwater | WWTP1 | | WWTP2 | WWTP3 | | WWTP4a | WWTP4b |
|-------------------------------------|---------------|---------------|--------------|-------------------|--------------|--------------|-------------------|--------------|--------------|
| Substance | ng/l | ng/l | Water (ng/l) | Sludge (µg/kg dw) | Water (ng/l) | Water (ng/l) | Sludge (µg/kg dw) | Water (ng/l) | Water (ng/l) |
| 4-nonylphenol monoethoxylate (mix.) | nd | <LOQ | <LOQ | <LOQ | <LOQ | 0,38 – 6,43 | 7,53 and 31,1 | <LOQ | <LOQ |
| 4-nonylphenol diethoxylate (mix.) | <LOQ and 0,09 | <LOQ and 0,09 | Nd – 0,19 | <LOQ | <LOQ | 0,61 – 6,96 | 13,88 – 26,4 | <LOQ | <LOQ – 0,2 |



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2 Sources of emissions of Nonylphenol ethoxylates in Estonia

The uncertainties in the following emission strings are given with four letters, the first letter representing uncertainty for EF, the second for EFM, the third for division into compartments and the fourth for the yearly load. Uncertainty is classified according to the principles described in “Dealing with uncertainty in substance flow analysis within the COHIBA project”, a PM describing how data uncertainty is graded in WP4 of the COHIBA project.

If the Estonian yearly loads were scaled from the EU yearly load to Estonian population, the Estonian population was considered to be 0,3% of the EU population. This accuracy level was considered to be enough for given study; especially considering the very high uncertainty levels in other emission strings.

2.1 Air transport

NACE 51

Use as anti-icing agent in aircrafts

Yearly load ? to IS

Uncertainty: N/A

There is some reported use in Finland 2002-2004. Professional use in airports is classified as a risk use (Mehtonen, 2009). No data for Estonia, but this string is likely to be a source.

2.2 Cleaning activities

NACE 81.2

Use of NPEO in industrial and institutional cleaning

Yearly load ? to WW

Uncertainty: N/A

No data for Estonia, but we assume this ES is not relevant for Estonia as it is probably not a relevant source at present (2009) in EU either, according to the EU SFA. NP and NPEO may not be placed on the market or used as a substance or constituent of preparations in concentrations equal or higher than 0,1 % by mass in EU since 2005



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(Directive 2003/53/EC). This legislation applies also to industrial and institutional cleaning except when closed systems are used.

2.3 Construction

Emissions of NPEO from concrete (in which NPEO is used as hardener), for example as runoffs from buildings

Yearly load - ? to IS

Uncertainty: N/A

There is no regulation of NPEO usage in concrete in EU today (2008), but the suppliers have voluntarily reduced/stopped the usage according to Hansson et al (2008). NPEO has been used as an additive in concrete since around 1930. Because of this historical use there are large stocks of built-in NPEO-concrete and concrete is therefore still a possible source. Concrete with NPEO as an additive is mainly used for road elements, bridges, parking lots, balconies and other bearing structures. We have no data for Estonia, but this ES is probably relevant.

Use of adhesives, sealants, binders, dustbinding agent, fillers, containing NPEO

Yearly load - ? to WW

Uncertainty: N/A

We have no information about Estonia, but we assume this ES to be relevant.

2.4 Emission from (private) consumption; during lifetime use of articles, goods and chemical products and preparations.

Emissions from hard plastic products containing NP and/or NPEO (PVC, Polystyrene and PET used for e.g. tubes, packaging, toys and various household products)

Yearly load - ? to WW

Uncertainty: N/A

NP and NPEO has mainly been used in PVC. According to Björklund et al. a reduction of use of NP and NPEO was initiated already 20-25 years ago, therefore it is assumed that the levels of NP/NPEO in PVC today are not above 0.1%. We have no information about Estonia, but we assume this ES to be relevant.

Emissions from the use of cosmetic and hygienic products

Yearly load considered in NP SFA



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Uncertainty: N/A

Emissions of NP and NPEO from vehicles (plastic materials, paint, maintenance products etc.)

Yearly load – 1,23 kg to IS

Uncertainty: --CC

This yearly load was calculated with the EU SFA EF. The EFM was the road transport – total mileage (passenger cars, light duty vehicles, heavy duty vehicles, motorcycles) in Estonia (8780 million km/year) (2008 Estonian Informative Inventory Report, 2010). The EF and EFM were multiplied to get the yearly load.

Emissions from painted and coated surfaces, e.g. metal sheets

Yearly load – 1,75 – 5,25 kg to WW

Yearly load – 1,75 – 5,25 kg to IS

Uncertainty: BACC

This ES includes both NP and NPEO and is a possible source. NPEO can be present as a component in paint and lacquers. After application most of the NPEO ends up in the paint layer from where it can be emitted via wear and tear, and leaching. Paint application is an exception on the European legislation that NP and NPEO may not be placed on the market or used as a substance or constituent of preparations in concentrations equal or higher than 0,1 % by mass, in preparations which cause direct emissions to the wastewater in EU since 2005 (Directive 2003/53/EC), because paint is not supposed to cause direct emissions to wastewater. The Stockholm example was used to estimate the Estonian numbers in the string as the living styles city of Stockholm and Estonia can be considered similar. The Estonian population was used as a basis for scaling.

Emissions from parking lots (due to spill of motor vehicle products containing NPEO)

Yearly load - ? to IS

Uncertainty: N/A

NPEO accumulated on parking lots is assumed to mainly come from spill of motor oil, but also from remaining maintenance products rinsed of by rain. We have no information about Estonia, but we assume this ES to be relevant for Estonia.

Emissions from washing of textiles containing NP and NPEO

Yearly load – 2680 kg to WW

Yearly load low – 1206 kg to WW

Yearly load high – 2815 kg to WW

Uncertainty: BAAC



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This ES considers both NP and NPE. The loads of both of these substances are considered under NPE as, according to the e-mail correspondence with WP4 leaders, NPE is used at this application, not NP.

Since 2005 NP may not be placed on the market or used as a substance or constituent of preparations in concentrations equal or higher than 0,1 % by mass, in preparations which cause direct emissions to the wastewater in EU since 2005 (Directive 2003/53/EC). Release is still possible from old products or illegally imported products. The release pattern is made with the assumption that NP is released every time a household washes imported textiles.

The yearly load is derived from the EU SFA yearly load, using the population of Estonia as a basis for calculation.

At first, we considered the result to be too big compared to the total load from wastewater treatment systems, but after consultation with Swedish partners (Hanna Anderson and Katrin Holmström) we agree – if the source is relevant for other EU members it is also relevant to Estonia.

2.5 Forestry and logging

NACE 2

Emissions from use as wood preservative

Yearly load - ? to FS

Uncertainty: N/A

According to the Swedish product register (Swedish Chemicals Agency 2010) NPEO was reported to be in use for this application in Sweden in 2008. The situation could be similar in Estonia and therefore this ES could be somewhat relevant for Estonia, but we have no data to prove or disapprove. Further research is needed.

2.6 Maintenance and repair of motor vehicles

NACE 45.20

Maintenance and repair of motor vehicles

Yearly load ? WW

Uncertainty: N/A

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Reported use in Latvia 2005 (Mehtonen, 2009). According to the Swedish product register (Swedish Chemicals Agency) NPEO was reported to be in use for this application in Sweden 2007. We have no data for Estonia, but this ES could be relevant.

2.7 Manufacture of basic metals

NACE 24

Use of NPEO in metal extraction, refining and processing industries, e.g. from use of cutting oils, cutting fluids, drilling fluids, degreasing etc.

Yearly load ? to WW

Uncertainty: N/A

According to EU SFA, this should not be a source any more as the use of nonylphenol and nonylphenol ethoxylates is prohibited in EU since 2005 due to Directive 2003/53/EC. However, according to the Swedish product register (Swedish Chemicals Agency) NPEO was reported to be in use for this application in Sweden 2007, so this could be the situation in Estonia as well, as there are several activities taking place under that NACE in Estonia, the product and chemical control is very poor, and the registers have very limited data. We consider this ES to be irrelevant for Estonia, but future studies are needed to exclude this ES confidently.

For future studies, it should be noted that the following activities are listed as taking place in Estonia under Prodcom 2008:

Hot rolled concrete reinforcing bars;

Hot rolled bars in tool steels;

Tubes and pipes, of circular cross-section, hot or cold formed and welded, of an external diameter ≤ 406.4 mm, of steel other than stainless steel;

Flanges, of steel (excluding cast fittings);

Elbows, bends, couplings, sleeves and other threaded tube or pipe fittings, of steel (excluding cast fittings);

Elbows, bends, couplings and sleeves and other socket welding tube or pipe fittings, of steel (excluding cast fittings);

Iron or non-alloy steel wire containing $<0.25\%$ of carbon including crimping wire excluding stranded wire, barbed wire used for fencing - duplex wire - saw-tooth wire, insulated electric wire;

Unwrought aluminium alloys in secondary form (excluding aluminium powders and flakes);

Aluminium plates, sheets and strips > 0.2 mm thick;

Copper and copper alloy tube/pipe fittings including couplings, elbows, sleeves, tees and joints excluding bolts and nuts used for as-sembling/fixing pipes/tubes, fittings with taps, cocks, valves;



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Magnesium and articles thereof (excluding waste and scrap), n.e.c.;
Titanium and articles thereof (excluding waste and scrap), n.e.c.;
Beryllium, chromium, germanium, vanadium, gallium, hafnium (celtium), indium, niobium (columbium), rhenium and thallium, and articles of these metals, n.e.c.; waste and scrap of these metals (excluding of beryllium, chromium and thallium);
Parts for other utilisation (malleable iron casting);
Grey iron castings for locomotives/rolling stock/parts, use other than in land vehicles, bearing housings, plain shaft bearings, piston engines, gearing, pulleys, clutches, machinery;
Steel castings for machinery and mechanical appliances excluding piston engines, turbojets, turboprops, other gas turbines, lifting or handling equipment, construction industry machinery/vehicles;
Light metal castings for land vehicles excluding for locomotives or rolling stock, construction industry vehicles;
Parts for other utilisation.

2.8 Manufacture of electrical equipment

NACE 27

Use of NPEO in electrical engineering industry

Yearly load - ? kg to WW, AO

Uncertainty: N/A

NPEO is used in fluxes in manufacture of circuit boards, in chemical baths and may also be present in cleaning products for electrical components. In 1994 the total use of NPEO in EU for electrical engineering industry was 93 tonnes/yr, giving rise to emissions of 0,378 tonnes/year divided between waste water (91%) and outdoor air (9%) (EU RAR 2002). This source is probably relevant for Estonia as well as there are many activities taking place in Estonia under that NACE. However, we have no proper information on the possible amount of NPEs used under these activities. More thorough research is needed.

For future references, it should be noted that in Prodcum 2008, the following activities are listed as taking place in Estonia under NACE 27:

DC motors and generators of an output > 37.5 W but ≤ 750 W (excluding starter motors for internal combustion engines);

Multi-phase AC motors ;

Other transformers, n.e.c., having a power handling capacity ≤ 1 kVA;

Accumulator chargers;

Rectifiers;



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Power supply units for telecommunication apparatus, automatic data-processing machines and units thereof;

Inverters having a power handling capacity ≤ 7.5 kVA;

Static converters (excluding polycrystalline semiconductors, converters specially designed for welding, without welding equipment, accumulator chargers, rectifiers, inverters);

Inductors (excluding induction coils, deflection coils for cathode-ray tubes, for discharge lamps and tubes);

Parts suitable for machines of HS 85.01 or 85.02;

Ferrite cores of transformers and inductors;

Parts of transformers and inductors (excluding ferrite cores);

Parts of static converters;

Other apparatus for switching... electrical circuits > 1000 V;

Electrical apparatus for protecting electrical circuits;

Relays and contactors for a voltage > 60 V but ≤ 1 kV;

Programmable memory controllers for a voltage ≤ 1 kV;

Other bases for electric control, distribution of electricity, voltage ≤ 1000 V;

Boards, panels, consoles, desks, cabinets and other bases for apparatus for electric control or the distribution of electricity (excluding those equipped with their apparatus)

Other parts of apparatus of 85.35, 85.36, 85.37;

Primary cells and primary batteries;

Optical fibre cables made up of individually sheathed fibres whether or not assembled with electric conductors or fitted with connectors;

Optical fibres and optical fibre bundles; optical fibre cables (except those made up of individually sheathed fibres);

Insulated coaxial cables and other coaxial electric conductors for data and control purposes whether or not fitted with connectors;

Other electric conductors, for a voltage ≤ 1000 V, fitted with connectors;

Insulated electric conductors for voltage > 1000 V (excluding winding wire, coaxial cable and other coaxial electric conductors, ignition and other wiring sets used in vehicles, aircraft, ships);

Electrical apparatus for switching electrical circuits for a voltage ≤ 1 kV (including push-button and rotary switches) (excluding relays);

Plugs and sockets for coaxial cables for a voltage ≤ 1 kV;

Prefabricated elements for electrical circuits for a voltage ≤ 1 kV;

Connections and contact elements for wires and cables for a voltage ≤ 1 kV;

Other apparatus for connections to or in electrical circuit, voltage ≤ 1000 V;

Fluorescent hot cathode discharge lamps (excluding ultraviolet lamps, with double ended cap);

Electric table, desk, bedside or floor-standing lamps;

Illuminated signs, illuminated name-plates and the like (including road signs);



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Chandeliers and other electric ceiling or wall lighting fittings (excluding those used for lighting public open spaces or thoroughfares);

Electrical lighting or visual signalling equipment for motor vehicles (excluding electric filament or discharge lamps, sealed beam lamp units, ultraviolet, infrared and arc lamps);

Electric lamps and lighting fittings, of plastic and other materials, of a kind used for filament lamps and tubular fluorescent lamps;

Electric water heaters (including storage water heaters) (excluding instantaneous);

Parts for vacuum cleaners;

Parts for electro-mechanical domestic appliances with a self-contained electric motor (excluding parts for vacuum cleaners);

Other domestic cooking appliances and plate warmers, of iron or steel or of copper, non electric;

Iron or steel solid fuel domestic appliances, including heaters, grates, fires and braziers (excluding cooking appliances and plate warmers);

Air heaters or hot air distributors n.e.c., of iron or steel, non-electric;

Electrical signalling, safety or traffic control equipment for roads, inland waterways, parking facilities, port installations or airfields.

2.9 Manufacture of furniture

NACE 31

Use in binders for paints and adhesives

Yearly load - ? to WW

Uncertainty: N/A

According to the Swedish product register (Swedish Chemicals Agency) NPEO was reported to be in use for this application in Sweden 2007. Several activities are listed as taking place in Estonia under that NACE, according to Prodcom 2008, therefore this ES could be relevant for Estonia. Further investigation on product level is needed to detect possible uses in that string. In the timeframe of that project it was not possible. In the future the product registers could be used for that work.

In Prodcom 2008, the following activities are listed as taking place in Estonia:

Upholstered swivel seats with variable height adjustment, with backrest and fitted with castors or glides excluding medical, surgical, dental or veterinary seats - barbers' or similar chairs;

Upholstered seats with metal frames (excluding swivel seats, medical, surgical, dental or veterinary seats, barbers' or similar chairs, for motor vehicles, for aircraft);

Non-upholstered seats with metal frames (excluding medical, surgical, dental or veterinary seats, barbers' or similar chairs, swivel seats);



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*Seats convertible into beds (excluding garden seats or camping equipment);
Upholstered seats with wooden frames (including three piece suites) (excluding swivel seats);
Non-upholstered seats with wooden frames (excluding swivel seats);
Other seats, of HS 94.01, n.e.c.;
Parts of seats;
Parts of metal furniture excluding for medical, surgical, dental or veterinary furniture, seats, barbers' chairs - for specially designed furniture for hi-fi systems, videos or televisions;
Parts of wooden furniture excluding for medical, surgical, dental or veterinary furniture, seats - for specially designed furniture for hi-fi systems, videos or televisions;
Parts of furniture other than of wood or metal excluding for medical, surgical, dental or veterinary furniture, seats, barbers' chairs - for furniture designed for hi-fi, videos or televisions;
Metal furniture of a kind used in offices, of a height ≤ 80 cm;
Metal furniture of a kind used in offices, of a height > 80 cm;
Wooden furniture of a kind used in offices;
Wooden furniture for shops;
Kitchen furniture;
Mattress supports (including wooden or metal frames fitted with springs or steel wire mesh, upholstered mattress bases, with wooden slats, divans);
Mattresses of cellular rubber (including with a metal frame) (excluding water-mattresses, pneumatic mattresses);
Mattresses of cellular plastics (including with a metal frame) (excluding water-mattresses, pneumatic mattresses);
Mattresses with spring interiors (excluding of cellular rubber or plastics);
Mattresses (excluding with spring interiors, of cellular rubber or plastics);
Metal furniture (excluding office, medical, surgical, dental or veterinary furniture; barbers' chairs - cases and cabinets specially designed for hi-fi systems, videos or televisions);
Wooden bedroom furniture (excluding builders' fittings for cupboards to be built into walls, mattress supports, lamps and lighting fittings, floor standing mirrors, seats);
Wooden furniture for the dining-room and living-room (excluding floor standing mirrors, seats);
Other wooden furniture (excluding bedroom, dining-, living-room, kitchen office, shop, medical, surgical, dental/veterinary furniture, cases and cabinets designed for hi-fi, videos and televisions);
Furniture of materials other than metal, wood or plastic (excluding seats, cases and cabinets specially designed for hi-fi systems, videos and televisions).*



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2.10 Manufacture of motor vehicles, trailers and semi-trailers; Manufacture of other transport equipment

NACE 29

NACE 30

Use of paint and adhesives

Yearly load ? to WW

Uncertainty: N/A

According to the Swedish product register (Swedish Chemicals Agency) NPEO was reported to be in use for this application in Sweden 2007. We have no data for Estonia, but this ES is likely to be relevant for Estonia.

There are several activities under that NACE that take place in Estonia, but there is no information about the possible quantity of NP containing products used. Product by product research was not possible to do under that study. Future research is needed.

For future references, it should be noted that the following activities are listed as taking place in Estonia, according to Prodcom 2008:

Bodies for lorries, vans, buses, coaches, tractors, dumpers and special purpose motor vehicles including completely equipped and incomplete bodies, vehicles for the transport of ≥ 10 persons;

Containers specially designed and equipped for carriage by one or more modes of transport (including containers for transporting fluids);

Other trailers and semi-trailers for the transport of goods;

Chassis for trailers, semi-trailers and other vehicles which are not mechanically propelled;

Bodies of trailers, semi-trailers and other vehicles which are not mechanically propelled;

Axles of trailers, semi-trailers and other vehicles which are not mechanically propelled;

Parts for trailers, semi-trailers and other vehicles which are not mechanically propelled (excluding chassis, bodies, axles);

Insulated ignition wiring sets and other wiring sets of a kind used in vehicles, aircraft or ships;

Parts of equipment of 85.12;

Seats for motor vehicles;

Parts and accessories of bodies (including cabs), n.e.c.;

Bumpers and parts thereof (including plastic bumpers);

Road wheels and parts and accessories thereof;

Silencers and exhaust pipes; parts thereof;

Other parts and accessories, n.e.c., for vehicles of HS 87.01 to 87.05; parts thereof;



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Activities under NACE 30 taking place in Estonia, according to Prodcom 2008:

Offshore vessels;

Other floating structures (including rafts, tanks, coffer-dams, landing stages, buoys and beacons);

Conversion and reconstruction of ships, floating platforms and structures;

Sailboats (except inflatable) for pleasure or sports, with or without auxiliary motor;

Motor boats and motor yachts, for pleasure or sports (excluding outboard motor boats);

Other vessels for pleasure or sports n.e.c.; rowing boats and canoes;

Parts of locomotives or rolling-stock;

Reconditioning of railway and tramway locomotives and rolling-stock;

Seats for aircraft; parts thereof;

Vehicles not mechanically propelled including industry trolleys, barrows, luggage trucks, hopper-trucks, hand pulled golf trolleys excluding shopping trolleys;

Manufacture of motor vehicles, trailers and semi-trailers;

Manufacture of other transport equipment.

2.11 Manufacture of other organic basic chemicals

NACE 20.14

Captive use of NPEO by chemical industry

Yearly load - ? to WW

Uncertainty: N/A

Within EU ten companies produced nonylphenol ether sulphates (emulsifiers) and eight companies produced NPEO phosphates (emulsifiers) in 1997, and the total use of nonylphenol ethoxylates in this production was 7000 tonnes (EU RAR, 2002). We assume this doesn't consider Estonia and therefore this string would be irrelevant for Estonia, but we cannot be sure. There are several activities listed as taking place in Estonia under that NACE and we cannot be sure if NPEO is used. Further research is needed.

2.12 Manufacture of paints, vanishes and similar coatings, printing and mastics.

NACE 20.3

Use of NPEO in paints, lacquers and varnishes

Yearly load - ? to FSW.

Yearly load ? to WW



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Uncertainty: N/A

NPEOs are used in preparation of paint resins and are also present as stabiliser/emulsifier in paints. There is no quantitative data on the use of NPEs found at the moment, however, this string could be relevant. 60% of the manufacturers are the sub-companies of Finnish paint manufacturers; therefore we might use the Finnish results to calculate Estonian yearly loads later. Product-based research is needed in that area.

For future reference, it should be noted that according to Prodcum 2008, the following activities are listed as taking place in Estonia:

Paints and varnishes, based on acrylic or vinyl polymers dispersed or dissolved in an aqueous medium (including enamels and lacquers);

Other paints, varnishes dispersed or dissolved in an aqueous medium;

Paints and varnishes, based on polyesters dispersed/dissolved in a non-aqueous medium, weight of the solvent >50% of the weight of the solution including enamels and lacquers;

Paints and varnishes, based on polyesters dispersed/dissolved in a non-aqueous medium including enamels and lacquers excluding weight of the solvent >50% of the weight of the solution;

Other paints and varnishes based on synthetic polymers n.e.c.;

Glaziers' putty, grafting putty, resin cements, caulking compounds and other mastics;

Painters' fillings;

Non-refractory surfacing preparations for façades, indoor walls, floors, ceilings or the like;

Organic composite solvents and thinners used in conjunction with coatings and inks; based on butyl acetate;

Organic composite solvents and thinners used in conjunction with coatings and inks (excluding those based on butyl acetate);

2.13 Manufacture of plastics products

NACE 22.2

Use of NPEO in polymer industry (as processing aids in formulation of for example polyvinyl acetates and acrylic acids)

Yearly load - ? to WW

Uncertainty: N/A

In 1997 total use of NPEO in polymer industry in EU was 9000 tonnes/year, and production was estimated to take place at 50 sites, giving rise to emissions of 0,66 tonnes/year to wastewater. There is some plastic industry in Estonia as well, however, there is no proper data on the relevancy of that ES at the moment. We are waiting for



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some more information. The NACE code is too general and makes it difficult to do research. Future studies are needed.

2.14 Manufacture of rubber products

NACE 22.1

Use of NPEO in activators, binders, lubricants, surface treatments, process regulators and release agents

Yearly load - ? to WW

Uncertainty: N/A

According to the Swedish product register (Swedish Chemicals Agency) NPEO was reported to be in use for this application in Sweden 2007. Therefore this ES could also be relevant for Estonia. We have no information about Estonia. Future research is needed.

The following activities are listed as taking place in Estonia, according to Prodcum 2008:

Retreaded tyres of rubber of a kind used on motor cars;

Retreaded tyres of rubber of a kind used on buses and lorries;

Other compounded rubber, unvulcanised, in primary forms or in plates, sheets or strip;

Plates, sheets and strip of vulcanized rubber;

Extruded rods and profile shapes of cellular vulcanized rubber;

Extruded solid rubber rods and profiles;

Rubber tubing not reinforced;

Rubber hose reinforced with metal;

Rubber hose reinforced or combined with other materials (excluding rubber hose reinforced with metal or textiles);

Rubber hose assemblies;

Seals, of vulcanized rubber;

Expansion joints for pipes;

Rubber-to-metal bonded articles for tractors and motor vehicles;

Rubber-to-metal bonded articles for other uses than for tractors and motor vehicles;

Articles of vulcanized solid rubber (including rubber bands, tobacco-pouches, characters for date stamps and the like, stoppers and rings for bottles; excluding hard rubber);

Hard rubber, hard rubber scrap; waste and powder and articles of hard rubber;

2.15 Manufacture of soap and detergents, cleaning and polishing preparations

NACE 20.14



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Production of soap, detergents and cleaning preparations

Yearly load - ? to WW

Uncertainty: N/A

According to the Swedish product register (Swedish Chemicals Agency, 2010) NPEO was reported to be in use for this application in Sweden 2007. There is no data for Estonia, but this ES could be relevant for Estonia.

2.16 Manufacture of wood and of products of wood and cork, except furniture; manufacture of articles of straw and plaiting materials

NACE 16

Emissions from wood and products of wood in which NPEO have been used as adhesives, dyes, insecticides and preservatives

Yearly load - ? to FSW, FS

Uncertainty: N/A

According to the Swedish product register (Swedish Chemicals Agency) NPEO was reported to be in use for this application in Sweden 2007. According to Prodcom 2008, the following activities are listed as taking place in Estonia under NACE 16. Therefore this situation could be similar in Estonia and the ES could be relevant. Future research is needed.

For future references, it should be noted that the following activities are listed as taking place in Estonia, according to Prodcom 2008:

Treatment; impregnation and preservation of wood (including seasoning and drying);

Veneered panels and similar laminated wood with blockboard, laminboard or battenboard;

Particle board, of wood;

Waferboard and similar board, of wood (excluding particle board and oriented strand board [OSB]);

Medium density fibreboard (MDF), of wood or other ligneous materials, whether or not bonded with resins or other organic substances, of a thickness not exceeding 5 mm;

Fibreboard of wood or other ligneous materials (excluding medium density fibreboard [MDF]), whether or not bonded with resins or other organic substances, of a density not exceeding 0.5 g/cm³;

Parquet panels of wood (excluding those for mosaic floors);

Windows, French-windows and their frames, of wood;

Doors and their frames and thresholds, of wood;



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Builders' joinery and carpentry of wood (excluding windows, French-windows and doors, their frames and thresholds, parquet panels, shuttering for concrete constructional work, shingles and shakes);

Prefabricated buildings of wood;

Flat pallets and pallet collars of wood;

Box pallets and load boards of wood (excluding flat pallets);

Cases, boxes, crates, drums and similar packings of wood (excluding cable drums).

2.17 Painting and glazing

NACE 43.34

Emission from application of paints, lacquers and varnishes

Yearly load - ? to WW

Uncertainty: N/A

This ES would be considered in NP SFA, but we have no information on the amounts of used NPs or NPEs.

2.18 Photographic activities

NACE 74.2

Use of NPEO in photographic industry, use of NPEO as stabiliser and developer agent in developing photos

Yearly load - ? to WW

Uncertainty: N/A

Information from the photographic industry suggests that NPEs are used in products intended for home use by the amateur photographer, photo developers who develop film for amateur photographers and in some professional products. The concentration of NPEs in these products is between 3-5% w/w. According to the Swedish product register (Swedish Chemicals Agency, 2010) NP was reported to be in use for this application in Sweden 2006. We assume this ES to be relevant for Estonia, however, there is no data to calculate the yearly loads.

2.19 Printing and reproduction of recorded media

NACE 18



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Use of NPEO as dyestuffs, printing ink, finishing agents, dressing agents and binders for paints.

Yearly load - ? to WW

Uncertainty: N/A

According to the Swedish product register (Swedish Chemicals Agency) NPEO was reported to be in use for this application in Sweden 2007. The situation could be similar in Estonia, as there are several activities taking place in Estonia under that NACE according to Prodcom 2008. Therefore we assume this ES to be relevant for Estonia. However, future research is needed to find out if NPEO is used in Estonia.

For future reference, it should be noted that the following activities are listed as taking place in Estonia, according to Prodcom 2008:

Printed newspapers, journals and periodicals, appearing at least four times a week;

Printed new stamps, stamp-impressed paper, cheque forms, banknotes, etc;

Printed commercial catalogues;

Printed trade advertising material (excluding commercial catalogues);

Printed newspapers, journals and periodicals, appearing less than four times a week;

Printed books, brochures, leaflets and similar printed matter, in single sheets;

Printed books, brochures, leaflets and similar printed matter (excluding in single sheets);

Printed maps, hydrographic or similar charts, in book-form;

Printed postcards, whether or not illustrated;

Printed pictures, designs and photographs;

Printed calendars of any kind, including calendar blocks;

Other printed matter, n.e.c.;

Composition, plate-making services, typesetting and phototypesetting;

Printing components;

Bookbinding and finishing of books and similar articles (folding, assembling, stitching, glue, cutting, cover laying);

Binding and finishing of brochures, magazines, catalogues, samples and advertising literature including folding, assembling, stitching, gluing, cutting cover laying;

Binding and finishing including finishing of printed paper/cardboard excluding finishing of books, brochures, magazines, catalogues, samples, advertising literature;

Reproduction of sound on compact discs;

2.20 Scientific research and development

NACE 72

Use of NPEO as laboratory chemical

Yearly load - ? kg to WW

Uncertainty: N/A



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Reported use in Finland 2002-2004 (Mehtonen, 2009) and reported to be in use for this application in Sweden 2007 according to the Swedish product register (Swedish Chemicals Agency 2010). This situation could be similar in Estonia, and therefore we assume this ES to be somewhat relevant for Estonia, yet we have no data to prove or disapprove due to limited registers and chemicals and product control in Estonia. Further research is needed.

2.21 Sewerage

NACE 37

Emissions of NPEs with effluent water from municipal STPs

Yearly load – 1,74-58,95 kg to FSW

Yearly load – 0,75-25,26 kg to CSW

Uncertainty: BAAC

We used the COHIBA and BaltActHaz preliminary results to calculate the EFs. The EF low is for the municipal WWTPs only. The EF high includes the results from the WWTPs where the industrial content is also high. The EF was considered to be the average result of all WWTPs. For EF low, the results under the LOQ were considered to be 0. For max scenario, the results under the LOQ were considered to be LOQ. The sum on mono- and diethoxylates was used for calculation. The EF was then multiplied by the EFM, i.e. the amount of effluents produced per person a day – 125 litres (according to Statistics Estonia 2010), the number of inhabitants (1 340 021 according to Statistics Estonia 2010), and the number of days a year (365). The division between compartments is done according to expert opinions: in Estonia, 30% of the effluents are directed directly to the Baltic Sea.

Emission of NPEs in sewage sludge from municipal STPs.

Yearly load – 13,31-86,90 kg to AS

Yearly load – 28,29-184,66 kg to FS

Uncertainty: CAAC

The calculations were done using the data from COHIBA WP3 and the preliminary results from the BaltActHaz project that gave us the EF. The sum on mono- and diethoxylates was used for calculation. The EF was considered to be the average result of all WWTPs. The EF low is for the municipal WWTPs only. The EF high includes the results from the WWTPs where the industrial content is also high. The representability is highly uncertain due to limited data. The EFM is the one from European SFA-s, considered to be representative to Estonia by Mr Kõrgmaa, an expert on WWTPs and



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sewage sludge. The yearly load was calculated by multiplying EF with EFM and number of inhabitants in Estonia.

2.22 Support activities for transportation

NACE 52.2

Emissions of NPEO from car washes

Included in the NP table

Uncertainty: N/A

2.23 Treatment and disposal of non-hazardous waste; Treatment and disposal of hazardous waste

NACE 38.21

NPE s in landfill leachate

Yearly load 0,09 g – 0,26 g to SW

Yearly load 0,09 g – 0,26 g to FS

Uncertainty: C

Yearly loads calculated with the excel sheet provided by IVL. The sum on mono- and diethoxylates was used for calculation. The results from COHIBA WP3 were used.

To point out our opinion, the leachate from the hazardous wastes should be in a different ES. However, we didn't find it meaningful to create an additional ES as we have no data from the effluents of leachates of hazardous waste landfills.

2.24 Worldwide activities outside the region, for example atmospheric deposition of long range transport

Atmospheric deposition

Yearly load – indicated in NP table

Uncertainty: N/A

Please note that although the yearly load of NPE atmospheric deposition is added to the NP deposition and both are considered in the NP SFA table and report, the load is still shown on the NPE graph for practical reasons.



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3 SFA diagram

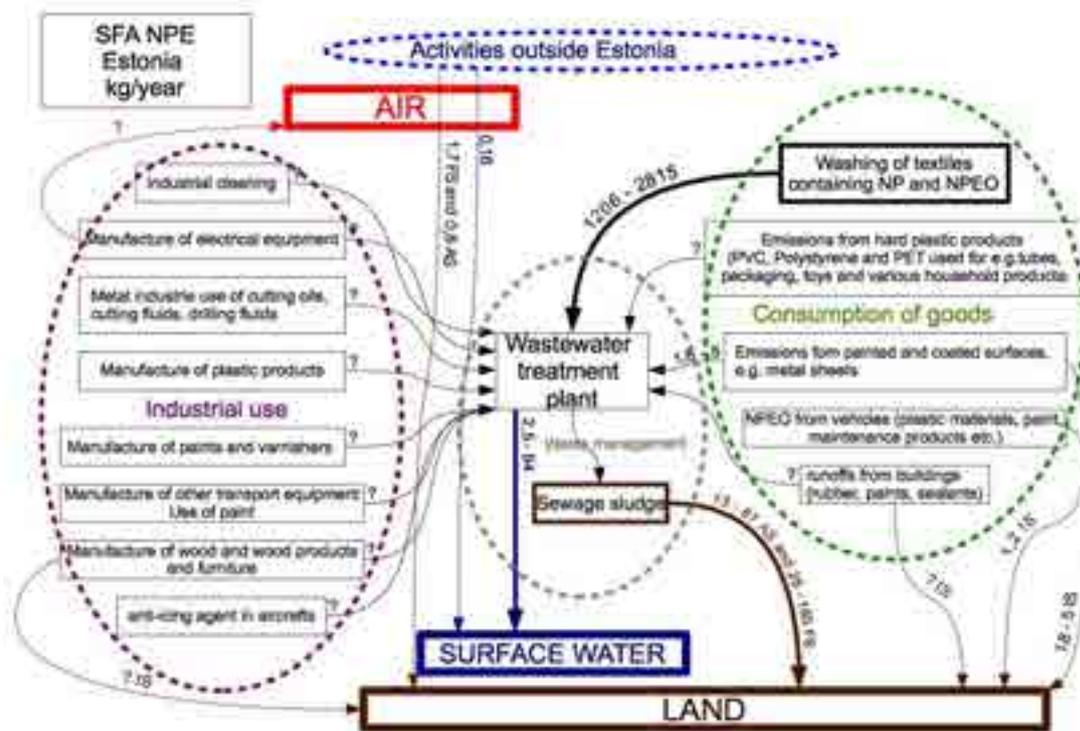


Figure 1. SFA diagram for NPEs in Estonia.

Please note that the atmospheric depositions of both NP and NPEs are used on this graph.



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4 Conclusions

4.1 Quantitative estimation of the most relevant sources to each environmental compartment

The main sources of NPEs in the private consumption are cleaning activities. The highest load of NPEs comes from the washing of imported textiles – up to 2,8 t to WW.

The wastewater treatment systems are also a relevant secondary source of NPEs and that source has also the biggest potential to reduce the pollutant entering the environment. At the moment the loads from the WWTPs with effluent water are estimated as 1,7 – 59 kg to FSW and 0,75 – 25,3 to CSW. Contaminated sludge ends up in agricultural soil 13 – 87 kg and forest soil 28 – 185 kg annually. The proper sludge treatment can prevent the pollutant entering the environment.

No proper quantitative estimation was possible to make about the industrial sources during the study due to limited data, incomplete registers and poor product and chemical control in Estonia.

4.2 A qualitative estimation of time trends for future scenarios

It would be possible to reduce the use of NPEs with different measures. However, as we have no good overview of the present situation, it is difficult to predict future scenarios. It is important to continue mapping of the substance in Estonia.



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ANNEX H – Substances flow analysis for OP in Estonia

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This study was carried out under the COHIBA study from May 2010 to May 2011. This report is based on the SFA OP (EU 27) by IVL Swedish Environmental Research Institute. The results are for Estonia. Many of the results are rough approximations that cannot be taken as exact results for Estonia, but more as a base to plan future studies. The results are for Estonia.

1 Introduction

Octylphenol (OP) is a high production-volume substance of the wider family alkylphenols. In 2000 it was estimated that nonylphenols and their ethoxylates made up 90% of all alkylphenols with the remainder being mostly OP and octylphenol ethoxylates (OPEs). The name octylphenol refers to a large number of isomeric compounds of the general formula $C_6H_4(OH)C_8H_{17}$. However, the 4-tert-octylphenol with CAS no 140-66-9 has been identified by European industry representatives as the only isomer currently commercially available in Europe (RPA 2008). CAS numbers for different OPs are listed in Table 1.

European Union (EU) consumption of 4-tert-Octylphenol (CAS no. 140-66-9) was approximately 23,000 tonnes in 2001, and demand was expected to grow. It is a chemical intermediate mainly used to make phenolic resins. The remainder is converted into octylphenols ethoxylates (OPEs) to produce surfactants. The phenolic resins are mainly used in rubber processing to make tyres. Minor uses include components in printing inks and electrical insulation varnishes, and in the production of ethoxylated resin for offshore oil recovery.

Table 1: CAS numbers and chemical names for different octylphenol isomers.

| Substance | CAS # | Comment |
|------------------------------------|------------|---|
| 4-tert-octylphenol | 140-66-9 | High production volume substance (HPV). In use within EU |
| 4-tert-octylphenol | 27193-28-8 | From Swedish Chemicals Agency 2010 |
| iso-octylphenol | 11081-15-5 | High production volume substance (HPV). Not in use within EU |
| 4-octylphenol | 1806-26-4 | |
| 4-iso-octylphenol | 27103-89-4 | |
| 4-sec-octylphenol | 27214-47-7 | |
| phenol, 4-octyl-, branched | 99561-03-2 | |
| 2-octylphenol | 949-13-3 | |
| 2-(1,1,3,3-tetramethylbutyl)phenol | 3884-95-5 | |
| 2-sec-octylphenol | 26401-75-2 | |



1.1 Physical chemical properties

Octylphenols can be made up of a large number of isomeric compounds of the general formula $C_6H_4(OH)C_8H_{17}$. The molecular structure of 4-*tert*-octylphenol, the most commonly occurring OP, is shown in Figure 1. Physical chemical properties for 4-*tert*-octylphenol are summarised in Table 2.

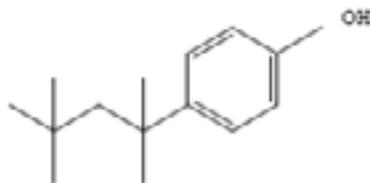


Figure 1. Chemical structure of 4-*tert*-octylphenol (RPA 2008).

Table 2: Physical and chemical properties of octylphenols (info from RPA 2008)

| Property | 4- <i>tert</i> -octylphenol | Comment |
|---|------------------------------|--|
| Physical state at npt | White or light pink flakes | |
| Molecular weight (g/mol) | 206.3 g/mole | |
| Melting point (°C) | 80.5 °C | |
| Vapour pressure (Pa) | 0.21 Pa | At 20 °C |
| Log octanol-water partition coefficient (log Kow) | 4.12 | at 20.5 °C, pH not known |
| Water solubility (mg/L) | 19 mg/L | at 22 °C, pH not known |
| Viscosity (mPa XX°C) | | |
| Dissociation constant | >9.9 and <12.19 | |
| Henry's Law Constant (Pa m ³ /mol) | 0.52 Pa. m ³ /mol | at 25 °C (measured by shake flask method OECD) |

1.2 Regulatory status

Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community, which is now implemented in the European Water Framework Directive (WFD) (Directive 2000/60/EC). Octylphenol is one of the substances identified as "priority hazardous substances" under the WFD.



Directive 2008/105/EC (the EQS Directive), which is a daughter directive of WFD, sets the water quality standards for octylphenol in the EU. As Estonian legislation is compliant to the EU legislation, OP is also listed as a priority substance and has set water quality standards under the Estonian law (RT I 2010, 51, 318; RT I 2010, 65, 484).

Octylphenols and their ethoxylates are listed as “high concern” on the EU endocrine disrupter priority list (European Commission, 2007). HELCOM Baltic Sea Action Plan also identifies OPs and their ethoxylates as substances of specific concern to the Baltic Sea.

OP and OPE has been suggested for inclusion in the Candidate List in REACH (Regulation 1907/2006) since they have been considered to fulfil the criteria for substances of very high concern (SVHC). Subsequently they could also be included Annex XIV, the Authorisation List of REACH (proposal envisaged for Feb 2011, personal communication with Swedish Chemicals Agency).

Due to its high production volume, there are plans to register 4-*tert*-octylphenol by 30 November 2010 by industry (ECHA, 2010).

1.3 Production

No production in Estonia.

1.4 Use

There is no registered use of substance in Estonia. There is no product register in Estonia, therefore any data about use in products.

OPEs have a wider area of usage including emulsion polymerisation, paints, textiles, and pesticides. OPE production is thought to be a minor use of 4-*tert*-octylphenol, accounting for 400 tonnes in 2001 in EU (2% of the total use volume in 2001). OPs can be reformed again in the environment or in WWTP via degradation of the ethoxylate chain of the OPEs which is important for the emission of OPs.

1.5 Environmental fate

The available data indicate that 4-*tert*-octylphenol is of low volatility. If released directly to the atmosphere, degradation occurs rapidly through hydroxyl radical attack. The



potential for transport of 4-tert-octylphenol in the atmosphere is likely to be low, with resulting rainwater concentrations being low. As the lifetime of 4-tert-octylphenol in the atmosphere is relatively short it is unlikely to be transported a long distance from its point of emission and therefore concentrations due to precipitation of 4-tert-octylphenol from the atmosphere are likely to be greatest near the point of emission.

The main environmental compartments to which releases of octylphenol occur are surface waters that receive municipal and industrial wastewater. OPs have low water solubility and when released to the environment they will sorb to organic matter in soil, sediment and sludge. The spreading of sludge from WWTP that treat effluent that contains 4-tert-octylphenol is a route of exposure to soil via spreading of sewage sludge containing OP and OPE. It is estimated that 2,5% of the OPE released to wastewater will reach surface waters as octylphenol, and 19% will reach the sludge as OP. Degradation of OPEs to OPs can occur in WWTP and also in the environment, both under anaerobic conditions.

Degradation processes for OP in water and soil (biotic and abiotic) are predicted to be relatively slow. The environmental risk evaluation report on OPs (EA RER, 2005) reports a half-life of 150 days for water and 300 days for soil in accordance with the recommendations in the Technical guidance document (ECB, 2003). OPs meet the persistence criterion outlined in TGD (ECB 2003) for Persistent, Bioaccumulative, and Toxic (PBT) Substances.

OPs can be considered acutely toxic to aquatic organisms, and may cause long-term adverse effects in the aquatic environment. 4-tert-Octylphenol can also adversely affect the endocrine systems of certain organisms (EA RER 2005). OP meets the toxicity criterion outlined in TGD (ECB 2003) for PBT substances.

Several log K_{ow} have been reported for OP. The value of 4.12 is used in the EA RER (2005). Measured bioconcentration factors (BCF) shows that the potential for bioaccumulation of OP in aquatic organisms is low to moderate and OP does not meet the criterion for bioaccumulation for PBT substances (EA RER 2005, ECB 2003). To summarize, 4-tert-Octylphenol meets two of the PBT criteria; it can be considered to be potentially persistent or very persistent and toxic, but it does not exceed the bioaccumulation criterion given in the TGD (ECB 2003).





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1.6 Environmental levels

The study ordered by Estonian Ministry of Environment (conveyed by MAVES) was made on the priority hazardous substances of WFD and studied these substances in the coastal waters and surface waters.

4-n-octylphenols and 4-tert-octylphenols were analysed under this study. All the results of 4-n-octylphenols were <LOQ (0,01 µg/l) in this study. Most of the results for 4-tert-octylphenol were also <LOQ (0,01 µg/l), but were found in some places (Mustoja river - 0,015 µg/l and Kroodi creek - 0,101 µg/l). Both of the findings were from the samples taken in spring.



2 Sources of emissions of Octylphenols in Estonia

The uncertainties in the following emission strings are given with four letters, the first letter representing uncertainty for EF, the second for EFM, the third for division into compartments and the fourth for the yearly load. Uncertainty is classified according to the principles described in “Dealing with uncertainty in substance flow analysis within the COHIBA project”, a PM describing how data uncertainty is graded in WP4 of the COHIBA project.

If the Estonian yearly loads were scaled from the EU yearly load to Estonian population, the Estonian population was considered to be 0,3% of the EU population. This accuracy level was considered to be enough for given study; especially considering the very high uncertainty levels in other emission strings.

2.1 Construction industry

NACE: F

Use of putty containing OP

Yearly load - ? to WW

Uncertainty: N/A

This use was reported in the Swedish Product register (Swedish Chemicals Agency 2010) for the construction industry during 2008. The products contains > 1% OPE and the SPR data indicates a use volume in Sweden between 2 and 200 tonnes of OP/year in this use. No emission factors were found for this use. This activity is likely to take place in Estonia as well, therefore this ES was considered relevant for Estonia, but it was impossible to calculate the potential yearly load.

Use of paint containing OP

Yearly load - ? kg to WW

Uncertainty: N/A

This use was reported within the construction industry for 2008 in SPR (Swedish Chemicals Agency 2010). Reported paint use for 2007 also included industry for electrical machinery and apparatus (NACE: C27) Industry for fabricated metal products (C25). An emission factor of 0.00013 kg OP released/kg paint used was derived from information in EA RER (2005). We assume that the use of paint in Estonia is similar to



other EU countries, therefore this ES is relevant for Estonia, but as there is no EFM, it is impossible to calculate the potential yearly load.

2.2 Crop and animal production, hunting and related service activities

Dispersion of sludge on farmland

This ES is included in 7a_023 (Sewage - OPs in sewage sludge from municipal STPs).

2.3 Emission from (private) consumption; during lifetime use (including tear and wear) of articles, goods and chemical products and preparations

Emissions from abrasion from tyres

Yearly load 125 kg FSW and 125 kg to FS

Yearly load low 40,76 kg FSW and 40,76 kg to FS

Yearly load high 49,42 kg FSW and 49,42 kg to FS

Uncertainty: BCBC

Two different methods for calculation were used and the differences are very high.

“Yearly load” calculation was based on the EU yearly load, assuming that the population of Estonia is 0,3% of EU population and that the use of tyres is no different than the average use of EU. This was later confirmed by Scrap Tyre Statistics for Europe 2006 by European Tyre and Rubber Manufacturers Association 2006¹. There were 3 212 thousands of tons of scrap tyres in EU in 2006. 11 000 of this was in Estonia, about 2000 tons of this would go to recycling, 7000 tons to landfills and 2000 would be exported. The EU EF was from the data of Environmental Risk Evaluation Report: 4-tert-Octylphenol. (2005) Environment Agency UK. Bristol. ISBN: 1 84432 410 9. And 4-tert-octylphenol. Risk reduction strategy. (2008). UK RPA.

“Yearly load low” and “Yearly load high” were calculated, using the average OP concentration of scrap tyres (33 700 – 27 800 mg/kg) given in the EU SFA and assuming that 15% of the rubber is lost every year.

¹ http://hansabiodiesel.ee/est/wp-content/uploads/2010/07/Rehvid_kasutatud_2006.jpg



In the EU SFA report it was stated that 18500 tonnes of resin was used in rubber tyres in 2001 (EA RER, 2005). In the calculations it is estimated that 15% of the rubber is lost during service life of the tyre. It is assumed that the resin and unreacted OP are lost at the same rate. Thus 15% of 18500 tonnes of resin is lost /year. In the resin there is 3% residual OP. Thus 83 tonnes of OP is possibly abraded/year, spread to surface water (50%) and soil (50%). All abraded material goes out to the environment, but the bioavailability of this abraded material is not known.

Yearly load low and high calculation was made on estimation that about there are about 17 000 tons of scrap tyres in Estonia (Statistics Estonia 2010). 2550 tons is the 15% of it that, as stated previously is the amount assumed to be lost during service life of the tyre. The amount of OP in these tyres was calculated with the assumption given in the EU SFA report: Measurements of OP in reused tyres show concentrations of 33 700-27 800 mg/kg (Swedish Chemicals Agency 2006). According to this logic, the yearly load would be 81,52 – 98,84 kg.

In both cases, the division into compartments was assumed to be 50% to FS and 50% to FSW in absence of better information.

Emissions of OP from washing of imported textiles containing OPE

Yearly load – 285 kg to WW

Uncertainty: C-AC

This yearly load was calculated from the OPE load from a similar ES. The load was considered to be 2,5% of the OPE load as according to RER 2005 about 2.5% of OPE emitted to wastewater is degraded to OP in the WWTP. See OPE SFA and ES table for more information on calculations.

Loss during service life (marine paints)

Yearly load 0,65 kg to CSW

Uncertainty:

The yearly load was calculated from the EU yearly load, using the Estonian population for scaling. In the EU SFA, the yearly load was considered to be 0.0075% of the annual amount of paint used, according to data from RER 2005.



2.4 Manufacture of glues

NACE: 20.52

Complexing agents

Yearly load - ? to WW

Uncertainty: N/A

The Swedish Product Register (Swedish Chemicals Agency 2010) report uses within the glue industry (2007) including complexing agents, raw materials for production of rubber, viscosity regulating agents, and vulcanizing agents. No emissions estimates can be made for these uses.

According to Prodcom 2008 database, there are several activities taking place under that NACE in Estonia, where OP for manufacture of glues can take place, such as:

Glues based on starches, dextrans or other modified starches;

Prepared glues and other prepared adhesives, n.e.c.

In absence of other data, we consider this ES to be relevant for Estonia, but cannot calculate a yearly load.

2.5 Manufacture of paints, varnishes and similar coatings, printing ink and mastics

NACE: 20.3

There are several activities under that NACE that take place in Estonia, according to Prodcom 2008. However, there is no data on the use of OPs on that field. 60% of the manufacturers are the sub-companies of Finnish paint manufacturers. In order to obtain more information, more thorough research on the product information is needed, but there was no time for that under the COHIBA project.

For future studies, we list the activities taking place under NACE 20.3 that could be researched further:

Paints and varnishes, based on acrylic or vinyl polymers dispersed or dissolved in an aqueous medium (including enamels and lacquers);

Other paints, varnishes dispersed or dissolved in an aqueous medium;



*Paints and varnishes, based on polyesters dispersed/dissolved in a non-aqueous medium, weight of the solvent >50% of the weight of the solution including enamels and lacquers;
Paints and varnishes, based on polyesters dispersed/dissolved in a non-aqueous medium including enamels and lacquers excluding weight of the solvent >50% of the weight of the solution;*

Other paints and varnishes based on synthetic polymers n.e.c.;

Glaziers' putty, grafting putty, resin cements, caulking compounds and other mastics;

Painters' fillings;

Non-refractory surfacing preparations for façades, indoor walls, floors, ceilings or the like;

Organic composite solvents and thinners used in conjunction with coatings and inks; based on butyl acetate;

Organic composite solvents and thinners used in conjunction with coatings and inks (excluding those based on butyl acetate).

Use of OP-based resins in insulation varnishes

Yearly load - ? to AO, WW

Uncertainty: N/A

2000 tonnes of resin was used in this application in 2001 in Europe. As Estonia is quite similar to other EU countries, this kind of activity could have been taken place in Estonia as well and this ES could be relevant for Estonia. Most of the OP in the resins is chemically bound and cannot be released, but the resins may also contain a small proportion of unreacted OP (3-4%) (RPA 2008). It is assumed that the content of residual OP in the resins is 3% of the total OPs used for this application.

Manufacture of printing inks containing OP-based resins

Yearly load - ? to AO, WW

Uncertainty: N/A

1000 tonnes of resin was used in this application in 2001 in the EU. As Estonia is quite similar to other EU countries, this kind of activity could have been taken place in Estonia as well and this ES could be relevant for Estonia. Most of the OP in the resins is chemically bound and cannot be released, but the resins may also contain a small proportion of unreacted OP (3-4%) (RPA 2008). It is assumed that the content of residual OP in the resins is 3% of the total OPs used for this application.





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The resin makes up 7-8% of the ink concentrate. Due to reactions in the production process there will be no significant traces of OP left in the finished ink. Thus there will be no significant release from printing or recycling of paper printed with inks.

Manufacture of marine paints containing OP-based resins

Yearly load - ? to AO, WW, Waste

Uncertainty: N/A

There is only one formulator operating in EU and thus this ES may not be of importance for the Baltic.

2.6 Manufacture of plastics in primary forms

NACE: 20.16

OP-based resin manufacture

Ethoxylated resin production

Yearly load - ? to AO, WW

Uncertainty: N/A

There are several activities taking place under that NACE in Estonia according to Prodcom 2008, but there is no information of the use of OPs in the sector. We have contacted Estonian Plastics Association, but have no answer.

There are 10-15 companies producing such resins in Europe, it is unknown if any of these are located in Estonia.

For future studies, we list the activities taking place under NACE 20.16 that could be researched further:

Epoxide resins, in primary forms

Alkyd resins, in primary forms

Urea resins and thiourea resins, in primary forms

Phenolic resins, in primary forms

Petroleum resins, coumarone-indene resins, polyterpenes, polysulphides, polysulphones, etc, n.e.c., in primary forms



2.7 Manufacture of rubber tyres and tubes; retreading and rebuilding of rubber tyres

NACE: 22.11

Use of OP-based resins in rubber formulation

Yearly load - ? to AO; WW

Uncertainty: N/A

Most of the OP in the resins is chemically bound and cannot be released, but the resins may also contain a small proportion of unreacted OP (3-4%) (RPA 2008). The unreacted OP can be emitted during use. In these calculations it is assumed that the content of residual OP in the resins is 3% of the total OPs used for this application. The emission factors for this application are 0.0005 to air (ECB2003) and 0.000015 to waste water (calculated from data in EA RER 2005).

There are several activities taking place in Estonia under that NACE according to Prodcom 2008 database, but there is no information about amounts of retreated tyres. For future studies, we list the activities taking place under NACE 22.11 that could be researched further:

Retreaded tyres of rubber of a kind used on motor cars

Retreaded tyres of rubber of a kind used on buses and lorries

2.8 Repair and maintenance of ships and boats; Building of ships and boats

NACE: 33.15 and 30.1

Application of marine paints

Marine paint removal

Yearly load - ? kg to WW

Yearly load - ? kg to FS

Compartment CSW could be relevant also in Estonia, but there is no data to use yet.

Application of paints:

An Emission Scenario Document (ESD) on coatings quoted in EA RER assumes a transfer efficiency of 65% for the application of paint. Of the remaining 35%, 90% is capture for disposal and the remainder (3.5%) is lost to land and water. It is not clear from the information in EA RER (2005) where the disposed paint ends up. An industrial



situation is assumed in the EA RER (2005). Emission factors derived from information in EA RER (2005) are 0.000135 kg OP released/kg paint used to soil and wastewater (EA RER 2005).

Removal of paints:

This route considers losses that occur when the paint is removed at the end of its service life. Most of the coating removed is assumed to go to waste but a little loss is assumed to go to water and soil. It is also assumed that the old paint is removed at a similar rate to the application of new paint. Emission factors were estimated from information in EA RER (2005) and were 0.00024 kg OP released/kg paint used to both waste water and soil.

There are companies that build and repair the ships and boats in Estonia, but we do not have data about the use of paints containing OPs. We have contacted the biggest companies and they have no information about that (Jelena Lebedeva personal communication June 2010 - AS BLRT Grupp and Loksa Laevatehase AS). It is a common problem in Estonia that in some cases the producers themselves do not know the exact content of products that they are using. The safety sheets are old and the quality of suppliers varies highly.

2.9 Retail sale of hardware, paints and glass in specialised stores

NACE: 47.52

Adhesives, solvent based for consumer use

Yearly load - ? to WW

Use of adhesives, solvent based for consumer use was reported in SPR for 2007 (Swedish Chemicals Agency 2010) for Sweden. We can assume the situation in Estonia to be similar as the consumer behavior is quite common in those two countries. However, there is no information to calculate yearly load from this ES.

2.10 Sewerage

NACE: 37

Emissions of OPs with effluent water from municipal STPs

Yearly load – 0,34-1,40 kg to CSW

Yearly load – 0,79-3,26 kg to FSW





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Uncertainty: BAAC (The uncertainty of the yearly load is marked as C because the data used for calculation is too limited to be considered reliable)

The calculations were done using the data from COHIBA WP3 and the preliminary results from the BaltActHaz project – that gave us the EF. The EF was considered to be the average result of all WWTP-s. For min scenario, the results under LOQ were considered to be; for max scenario, the results below LOQ were considered to be LOQ. The EF was then multiplied by the EFM, i.e. the amount of effluents produced per person a day – 125 litres (according to Statistics Estonia 2010), the number of inhabitants (1 340 021 according to Statistics Estonia 2010), and the number of days a year (365).

OPs in sewage sludge for municipal STP-s

Yearly load – 1,94-2,10 kg to AS

Yearly load – 4,12-4,46 kg to FS

Uncertainty: BAAC (The uncertainty of the yearly load is marked as C because the data used for calculation is too limited to be considered reliable)

The calculations were done using the data from COHIBA WP3 and the preliminary results from BaltActHaz project that gave us the EF. The EF was considered to be the average result of all WWTP-s. The representability is highly uncertain due to limited data. The EFM is the one from European SFA-s, considered to be representative to Estonia by Mr Kõrgmaa, an expert of WWTPs and sewage sludge (personal communication). The yearly load was calculated by multiplying EF with EFM and number of inhabitants in Estonia.

Degradation product of OPEs

Yearly load - ? to WW

One of the indirect inputs of alkylphenols to the environment is via the biodegradation of alkylphenol ethoxylates (APE). The overall conversion is likely to have a fairly long half-life, probably of the order of 100 days in water and 30 days in soil. The key assumptions are that the release of OPEs to WWTP leads to the release of 2.5% of the input as octylphenol to water, and 19.5% of the input as octylphenol to sludge.

We have only one calculated emission (OPEs released from the washing of textiles) to the WWTP-s and decided not to calculate the yearly load based on that as this is only one



source and is also considered in another string (the OPs degraded during the washing of textiles). But if the biodegradation takes place this is also relevant for Estonia.

2.11 Treatment and disposal of non-hazardous waste

NACE: 38.21

OPs in landfill leachate

Yearly load 0 – 0,00017 kg to FSW

Yearly load 0 – 0,00017 kg to FS

Uncertainty: C

The calculations were done using the excel sheet provided by IVL. The data used was from the COHIBA WP3 results from the study of landfill leachate. However, this result is considered extremely inaccurate as it is based on two samples from one landfill.

To point out our opinion, the leachate from the hazardous wastes should be in a different ES. However, we didn't find it meaningful to create an additional ES as we have no data from the effluents of leachates of hazardous waste landfills.

2.12 Worldwide activities outside the region, for example atmospheric deposition of long range transport.

Atmospheric deposition wet + dry

Yearly load - ? to FSW, FS, AS

Uncertainty: N/A

Atmospheric deposition is a possible source of OP to the environment, but according to EA RER degradation of OP occurs rapidly through hydroxyl radical attack in air. However, there are reports on concentrations of OP measured in air (Xie 2006). As the lifetime of 4-tert-octylphenol in the atmosphere is relatively short it is unlikely to be transported a long distance from its point of emission and therefore concentrations due to precipitation of 4-tert-octylphenol from the atmosphere are likely to be greatest near the point of emission. There is no monitoring data available for OPs.





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For future studies, for times when there will be monitoring data, we have divided the possible loads into the compartments was done according to the data from Estonian Environment Information Centre.

2.13 Other

Emissions from impurities in commercial nonylphenol products (5%)

Yearly load - ? to WW

Uncertainty: N/A

Branched OP isomers similar to 4-tert-octylphenol have been identified as a potentially significant impurity in commercial NP with exposure arising during the production and use of NP. A typical impurity level of 5% has been assumed. There is no data to calculate the yearly load from this potential source.



3 SFA diagram

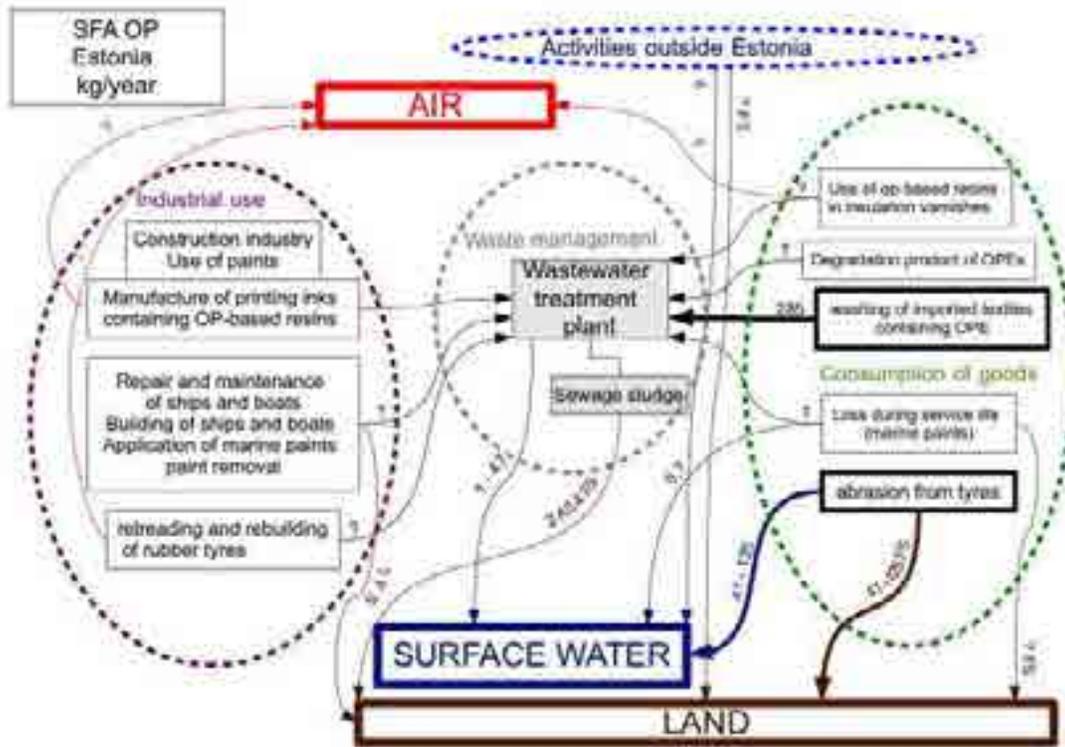


Figure 2. SFA diagram for OP in Estonia.

4 Conclusions

4.1 Quantitative estimation of the most relevant sources to each environmental compartment

The main source of OPs is the private consumption – abrasion from tyres 41 – 125 kg to FS and 41 – 125 kg FSW. Other big source is washing of imported textiles containing OP 285 kg to WW.

The main receiving compartments for OP are FS and FSW.

Several industrial uses are also possible, but quantitative estimation is not possible to make at the moment.

We assume the atmospheric deposition to be also relevant for Estonia. However, there is no quantitative data to prove or disapprove it at the moment.

4.2 A qualitative estimation of time trends for future scenarios

New national measures are considered to reduce the emissions of OPs, but they are not in force yet. It is of utmost importance to further research the situation of the moment and make an inventory of the amounts of OPs and OPEs in products in order to plan further actions and measures. It is also important to have better control over products imported to Estonia from third countries (non-EU countries), i.e. have a better monitoring at the border.



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ANNEX I - Substances flow analysis for OPEs in Estonia

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This study was carried out under the COHIBA study from May 2010 to May 2011. This report is based on the SFA OPE (EU 27) by IVL Swedish Environmental Research Institute. The results are for Estonia. Many of the results are rough approximations that cannot be taken as exact results for Estonia, but more as a base to plan future studies. The results are for Estonia.

1 Introduction

Octylphenol etoxylates (OPEs) are substances of the wider family alkylphenols. In 2000 it was estimated that nonylphenols and their etoxylates made up 90% of all alkylphenols with the remainder being mostly octylphenol (OP) and OPEs.

OPEs are manufactured by the addition of ethylene oxide to octylphenol (OP) under pressure; OP is thus an intermediate in this use. The ethoxylated chain can vary in length which gives rise to a large number of isomers (Figure 1 and Figure 2). The total EU consumption of OPEs was estimated to 1050 tonnes in 2001

OPEs are mainly used as a stabiliser in emulsion polymerisation but also as emulsifiers in textile processing, water-based paints, pesticide and veterinary medicine formulations, and to produce octylphenol ether sulphates. Importantly, by degradation of the ethoxylate chain the parent substance OP can be reformed in the environment, and OPEs are thus a source of OP in the environment.

Table 1. CAS numbers for octylphenoletoxylates (information from Swedish Product Register, SPR, Swedish Chemicals Agency 2010 and Klecka et al. 2005).

| Substance | Cas # | Comment |
|---|------------|-------------------|
| Polyethylene glycol octylphenol ether | 9002-93-1 | Original Polymers |
| Ethoxylated octylphenol | 9036-19-5 | Original Polymers |
| Poly (oxy-1, 2-ethanediyl), alpha- (octylphenyl)-omega-hydroxy-, branched | 68987-90-6 | UVCB Polymers |

1.1 Physical chemical properties

OPEs generally range from 4 moles of ethoxylation (OPE4) up to 80 moles of ethoxylates (OPE80). Some branching of the octyl group results in additional structural isomers, although the isomer shown In Figure 1 is predominant (Klecka et al 2005). Little



information is available on physio-chemical properties of OPEs. The available information is summarised in Table 2.

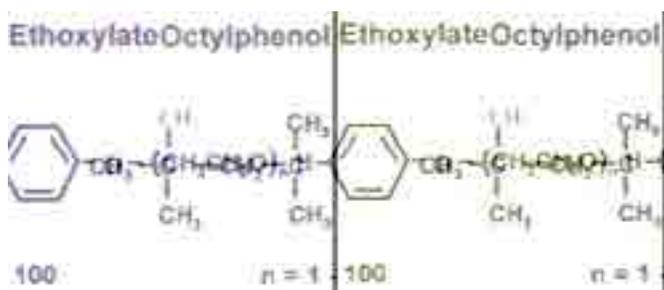


Figure 1. Chemical structure of an octylphenol ethoxylate with CAS # 9036-19-5. (Source: Sigma-Aldrich web page). The ethoxylated chain can vary in length (symbolised by n) which gives rise to a large number of isomers.

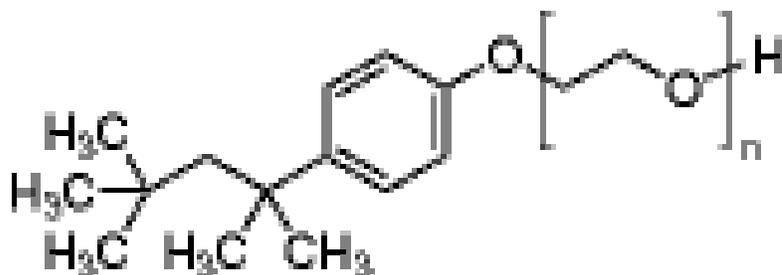


Figure 2. Chemical structure of an octylphenol ethoxylate with CAS # 9036-19-5. (Source: Sigma-Aldrich web page). The ethoxylated chain can vary in length (symbolised by n) which gives rise to a large number of isomers.

Table 2. Physical and chemical properties of octylphenol ethoxylates (information from Material Safety Data Sheet from Fisher Scientific).

| Property | CAS # 9002-93-1 |
|--------------------------|-------------------------------|
| Physical state at npt | clear to slightly hazy liquid |
| Molecular weight (g/mol) | Dependent on isomer |
| Melting point (°C) | 7 °C |
| Vapour pressure (Pa, at | < 1 mm Hg |



| | |
|---|-------------------|
| 20 °C) | |
| Log octanol-water partition coefficient | |
| Water solubility (mg/l at pH X, 22°C) | Soluble >100 mg/L |
| Viscosity (mPa XX°C) | 240 cP at 25 °C |
| Dissociation constant | |
| Henry's Law Constant | |

1.2 Regulatory status

There are no restrictions for 4-*tert*-octylphenol or its ethoxylates are in force yet.

Octylphenols and their ethoxylates are listed as “high concern” on the EU endocrine disrupter priority list (European Commission, 2007). HELCOM Baltic Sea Action Plan also identifies OPs and their ethoxylates as substances of specific concern to the Baltic Sea.

OP and OPE has been suggested for inclusion in the Candidate List in REACH (Regulation 1907/2006) since they have been considered to fulfil the criteria for substances of very high concern (SVHC). Subsequently they could also be included Annex XIV, the Authorisation List of REACH (proposal envisaged for Feb 2011, personal communication with Swedish Chemicals Agency).

There are no local regulation in Estonia for OPE.

1.3 Production

No production of OPE- in Estonia.

1.4 Use

There is no registered use of substance in Estonia. There is no product register in Estonia, therefore any data about use in products. However, OPE-s are detected in Estonian environment and wastewater systems, therefore the use of OPE-s in private consumption is important in Estonia.



OPEs have a wide area of usage including emulsion polymerisation, paints, textiles, and pesticides. OPE production is thought to be a minor use of 4-*tert*-octylphenol, accounting for 400 tonnes in 2001 in EU (2% of the total use volume in 2001). The end applications for polymer dispersions include in paints and coatings (27%), paper (23%), inks, adhesives (22%), and carpet backings (11%). The major classes of emulsion polymers are styrene-butadiene latex (32%), acrylics (27%), vinyl acrylics (15%), vinyl acetate polymers (14%), and ethylene vinyl acetates (7%) (European polymer council, in RPA 2006).

RPA suggests that paint is the most relevant application. 210 tonnes of OPEs were used as emulsifiers or dispersants in water-based paints in 2001 (RPA 2006).

In 2001 an estimated 150 tonnes of OPE were used in finishing agents for the textile and leather industry in EU. Finishing agents are used to cover textiles and leather with a thin polymer film to make the material more resistant to water, dust and light and provide a shiny appearance.

OPEs are also used in pesticides (for plant protection) and veterinary medicine (against ectoparasites) where they act as emulsifiers and dispersants. 140 tonnes were estimated for this use in 2001 in EU. More recent information indicate that 300 tonnes of OPEs were sold across the EU for pesticide use in 2005.

1.5 Environmental levels

The first studies on OPE-s in Estonia are from 2010 (EU projects COHIBA and BaltActHaz).

In BaltAcHaz study, OPE-s were found only from both the water and sludge of some waste water treatment plants, but not from the lakes, rivers nor coastal waters. Only monoethoxylates were detected with an exception of one WWTP where both mono- and diethoxylates were detected at some sampling rounds. Given WWTP is coincidentally the very same WWTP that was a case study in the COHIBA project under the name WWTP3. Therefore, we can see some correlations between the BaltActHaz and COHIBA study.

Table x. OPE-s in waste-water and sewage sludge in Estonia 2009-2010 (Data from COHIBA WP3).

| Substance | WWTP1 | WWTP2 | WWTP3 | WWTP4a | WWTP4b |
|-----------|-------|-------|-------|--------|--------|
| | | | | | |



| | Water (ng/l) | Sludge (µg/kg) | Water (ng/l) | Water (ng/l) | Sludge (µg/kg) | Water (ng/l) | Water (ng/l) |
|-----------------------------------|-----------------|-------------------|-----------------|-----------------|-------------------|-----------------|-----------------|
| octylphenol monoethoxyl ate | <LOQ | nd | <LOQ | Nd 1,29 | <LOQ 5,08 | <LOQ | <LOQ |
| octylphenol diethoxylate | nd | nd | nd | Nd 3,62 | <LOQ 9,64 | nd | nd |

In the COHIBA project, landfill effluent and storm waters were also analysed. The results proved the same – some monoethoxylates were detected but not in quantities big enough to get exact results. The diethoxylates were not detected.

Table x. OPE- in Estonian landfill and storm waters (data from COHIBA WP3).

| Substance | Landfill ng/l | Storm water ng/l |
|-----------------------------------|------------------|---------------------|
| octylphenol monoethox ylate | <LOQ | <LOQ |
| octylphenol diethoxylate | nd | nd |



2 Sources of emissions of OPEs in Estonia

The uncertainties in the following emission strings are given with four letters, the first letter representing uncertainty for EF, the second for EFM, the third for division into compartments and the fourth for the yearly load. Uncertainty is classified according to the principles described in “Dealing with uncertainty in substance flow analysis within the COHIBA project”, a PM describing how data uncertainty is graded in WP4 of the COHIBA project.

If the Estonian yearly loads were scaled from the EU yearly load to Estonian population, the Estonian population was considered to be 0,3% of the EU population. This accuracy level was considered to be enough for given study; especially considering the very high uncertainty levels in other emission strings.

2.1 Agriculture

NACE: 01

Use of OPE-containing pesticides, biocides and disinfectants

Yearly load - ? to AS and FSW

Uncertainty: N/A

OPEs act as emulsifiers and dispersants in pesticides, biocides and disinfectants. 140 tonnes of OPEs were used for this application within EU in 2001. Reported use in 2007 also included wood impregnation agents (Wholesale trade, others, NACE: G46.9) (Swedish Chemicals Agency 2010). In this application, all of the applied substance will reach the environment, 96% to agricultural soil and 4% to surface waters (estimation in EA RER 2005). We assume that the use of products in Estonia is similar to Sweden. Therefore this ES might be relevant for Estonia, but there is no proper data for calculating the results.

2.2 Construction industry

NACE: F

Use of paint (industrial)

Use of OPE containing adhesives

Joint-less floors



Cleaning agents for windows

Floor covering materials, other than joint-less floors

Sealant

Yearly load - ? to WW

Uncertainty: N/A

Asphalt, bitumen, tar, etc

Yearly load - ? to FS

Uncertainty: N/A

There are reported uses for all of those ES-s in Sweden in 2008 (Swedish Chemicals Agency 2010 – see SFA Octylphenol Ethoxylates (EU27) for more information). We assume that the use of products in Estonia is similar to Sweden. Therefore these ESs might be relevant for Estonia, but there is no proper data to calculate the results.

2.3 Crop and animal production, hunting and related service activities

NACE: 01

Dispersion of sludge on farmland

The substance adsorbs to sewage sludge, and the spreading of sludge from WWTP that treat effluent that contains 4-tert-octylphenol can be a route of exposure to soil. However, in Estonian SFA, the spreading of sludge to farmlands is considered in another ES (Sewerage - OPEs in sewage sludge from municipal STPs).

2.4 Emission from (private) consumption; during lifetime use (including tear and wear) of articles, goods and chemical products and preparations

Emissions of OPE from washing of textiles

Yearly load - ? to WW

Uncertainty: N/A

Release from the polymers in the coatings is considered unlikely by EA RER (2005). However, the potential significance of this route is recognised by RPA (RPA 2006). It may be assumed that these additional releases would take place to surface water via a



waste water treatment. The amount of OPEs in textiles has been estimated 0.5-1 g/kg textile (if present) (RPA 2006).

There is no data to calculate the yearly loads, but we consider this ES to be relevant for Estonia.

Emissions of OPE from washing of imported textiles

Yearly load – 0 – 11 400 kg to WW

Uncertainty: CAAC

Release from the polymers in the coatings is considered unlikely by EA RER (2005). However, the potential significance of this route is recognised by RPA (RPA 2006). It may be assumed that these additional releases would take place to surface water via a waste water treatment. The amount of OPEs in textiles has been estimated 0.5-1 g/kg textile (if present) (RPA 2006). One study measured a concentration of 99 mg/kg of OPE in a children's pyjamas. However the extraction method described in the study may overestimate the releases.

The amount of textiles imported per person from outside the EU was estimated to 17 kg/year. An amount of 0.5 g/kg textile would give an emission factor of 8.5 g OPEs/person/year. Still, it is unlikely that all imported textiles contain OPE.

The yearly load for Estonia was calculated using the EU emission factor of 8,5 g/person/year and Estonian population 1,3 million people. As there is no proper data and we consider this EF to be far too high, taking into account the OPE loads from other potential sources, we are giving this load as an interval.

2.5 Industry for fabricated metal products

NACE: 25

Used in production of metal products

Yearly load - ? to WW

Uncertainty: N/A

In the Sweden it is reported from 2007 that OPEs are used in rust preventives, coolants, and lubricants for metal processing, paint, binders for paint, and Galvano-technical agents (C25.6) within this industry. No figures on emission factors could be found for this use.



According to Prodcum 2008 database there are several such activities taking place in Estonia, but there is no data to calculate the potential yearly load from this source. However, as the two countries are quite similar, similar use of OPEs can be suspected.

2.6 Industry for inorganic basic chemicals

NACE: 20.13

Use of surface active agents containing OPEs

Yearly load - ? to WW

Uncertainty: N/A

This application was reported in Sweden for 2007. This use has also been reported from companies for technical testing and analysis (NACE: M71.2), Industry for glues (C20.52), Paint industry (C20.3), and production of other chemical products but synthetic fibres (C20.59). No figures on emission factors could be found for these uses.

According to Prodcum 2008 database there are several such activities taking place in Estonia, but there is no data to calculate the potential yearly load from this source. However, as the two countries are quite similar, similar use of OPEs can be suspected.

2.7 Industry/Manufacture for plastics in primary forms

NACE: 20.16

Use of surface active agents containing OPEs

Yearly load - ? to WW

Uncertainty: N/A

This application was reported in Sweden in 2007 (Swedish Chemicals Agency 2010). This use has also been reported from companies for technical testing and analysis (NACE: M71.2), Industry for glues (C20.52), Paint industry (C20.3), and production of other chemical products but synthetic fibres (C20.59). No figures on emission factors could be found for these uses.

According to Prodcum 2008 database there are several such activities taking place in Estonia, but there is no data to calculate the potential yearly load from this source.



However, as the two countries are quite similar, similar use of OPEs can be suspected. We have also contacted Estonian Plastics Association, but have no answer.

For future studies, we list the activities taking place under NACE 20.16 that could be researched further:

Epoxide resins, in primary forms;

Alkyd resins, in primary forms;

Urea resins and thiourea resins, in primary forms;

Phenolic resins, in primary forms;

Petroleum resins, coumarone-indene resins, polyterpenes, polysulphides, polysulphones, etc, n.e.c., in primary forms.

(Prodcom 2008)

OPEs formulated for paints, textiles and agrochemicals

Yearly load - ? to AO, WW

There are several activities taking place under that NACE in Estonia, but there is no information available about potential use of OPEs. In some applications OPEs are formulated with other components before use. This is likely to take place at different locations to the production of OPEs and to the use of the formulated products.

Use of OPEs in emulsion polymerisation

Yearly load - ? to WW

Uncertainty: N/A

The end applications for polymer dispersions include paints, paper, inks, adhesives and carpet backings. Releases to air are reported as zero. Releases to water during manufacture are reported as being very low and a conservative estimate of the amount released gives an emission factor of 0.1 kg /tonne produced, emitted to waste water. There are several activities taking place under that NACE in Estonia, however, the use of OPEs is not known and it is impossible to calculate the potential loads from this source.

2.8 Manufacture of other organic basic chemicals

NACE: 20.14

Productions of OP ether sulphates

Yearly load - ? to WW

Uncertainty: N/A



This is a specialist application performed only in few sites. Default emission factors (ECB 2003) are 0.007 kg OPE released/kg OPE used to waste water, (zero to air) giving rise to a total yearly load of 1.4 tonnes/year. (EA RER, RPA). According to Prodcum 2008, the activities taking place under that NACE in Estonia are: *Aldehyde-ethers, aldehyde-phenols and aldehydes with other oxygen function production*. Whether OP is used in these applications, is not known to us. We suspect this ES to be irrelevant for Estonia, but more research is needed to exclude this ES for sure.

2.9 Manufacture of paints, varnishes and similar coatings, printing ink and mastics

NACE: 20.3

OPEs used in production (formulation) of paints

Yearly load - ? to WW

Uncertainty: N/A

EA RER (2005) estimates that 210 tonnes of OPEs were used in this application in 2001 in EU. The use of OPEs might be similar in Estonia, considering the similarity of industrial processes, therefore this ES might be relevant for Estonia. However, there is no quantitative data at the moment. 60% of the manufacturers are the sub companies of Finnish paint manufacturers, therefore Finnish studies might be used in future researches to calculate potential Estonian loads. Unfortunately, researching of this subject was out of the scope of this study.

EU Emission factors derived from nonylphenol in a similar application are zero to air and 0.005 kg OPE released/kg OPE used to waste water.

For future studies, we list the activities taking place under NACE 20.16 that could be researched further:

Paints and varnishes, based on acrylic or vinyl polymers dispersed or dissolved in an aqueous medium (including enamels and lacquers);

Other paints, varnishes dispersed or dissolved in an aqueous medium;

Paints and varnishes, based on polyesters dispersed/dissolved in a non-aqueous medium, weight of the solvent >50% of the weight of the solution including enamels and lacquers;

Paints and varnishes, based on polyesters dispersed/dissolved in a non-aqueous medium including enamels and lacquers excluding weight of the solvent >50% of the weight of the solution;



Other paints and varnishes based on synthetic polymers n.e.c.;
Glaziers' putty, grafting putty, resin cements, caulking compounds and other mastics;
Painters' fillings;
Non-refractory surfacing preparations for façades, indoor walls, floors, ceilings or the like;
Organic composite solvents and thinners used in conjunction with coatings and inks; based on butyl acetate;
Organic composite solvents and thinners used in conjunction with coatings and inks (excluding those based on butyl acetate);
(Prodcom 2008)

2.10 Printing and reproduction of recorded media

NACE: 18

Use of printing ink

Yearly load - ? to WW

Uncertainty: N/A

This application was reported in Sweden in 2007 (Swedish Chemicals Agency 2010). Use within the industry also includes use in anti-static agents, degreasing agents and adhesives. Emission factors derived from nonylphenol in a similar application (use of paint) are zero to air and 0.005 kg OPE released/kg OPE used to waste water.

According to Prodcom 2008 database there are several such activities taking place in Estonia, but there is no data to calculate the potential yearly load from this source. However, as the two countries are quite similar, similar use of OPEs can be suspected.

For future studies, we list the activities taking place under NACE 20.16 that could be researched further:

Printed newspapers, journals and periodicals, appearing at least four times a week;
Printed new stamps, stamp-impressed paper, cheque forms, banknotes, etc;
Printed commercial catalogues;
Printed trade advertising material (excluding commercial catalogues);
Printed newspapers, journals and periodicals, appearing less than four times a week;
Printed books, brochures, leaflets and similar printed matter, in single sheets;
Printed books, brochures, leaflets and similar printed matter (excluding in single sheets);
Printed maps, hydrographic or similar charts, in book-form;
Printed postcards, whether or not illustrated;



Printed pictures, designs and photographs;
Printed calendars of any kind, including calendar blocks;
Other printed matter, n.e.c.;
Composition, plate-making services, typesetting and phototypesetting;
Printing components;
Bookbinding and finishing of books and similar articles (folding, assembling, stitching, glue, cutting, cover laying);
Binding and finishing of brochures, magazines, catalogues, samples and advertising literature including folding, assembling, stitching, gluing, cutting cover laying;
Binding and finishing including finishing of printed paper/cardboard excluding finishing of books, brochures, magazines, catalogues, samples, advertising literature;
Reproduction of sound on compact discs
(Prodcom 2008).

2.11 Raising of sheep and goats

NACE: 01.45

OPEs in veterinary medicine use

Yearly load – 87,5 kg AS

Uncertainty: CCAC

OPEs are used in a pour-on treatment for sheep to prevent blow fly strike. The treatment is used mainly in the summer months, and has an intermittent use pattern as one dose provides protection for 10 weeks. In this application, all of the applied substance will reach the environment. Amount of OPE in treatment of 1 sheep = 50 mL x 2% (wet weight) \approx 1 g OPE per sheep and treatment. Still, it is expected that many manufacturers throughout EU are replacing OPEs in their products for this application.

We assume that the use of products in Estonia is similar to Sweden's. Also, as the number of sheep has grown in Estonia during the last few years (Statistics Estonia 2010), the probability of different medicines for them is also increasing.

Table 3. Number of Sheep and Goats in Estonia 2001 – 2007 (Statistics Estonia 2010).

| | Sheep | Goats |
|------|--------------|--------------|
| 2001 | 43775 | 4107 |
| 2003 | 46892 | 4396 |



| | | |
|------|-------|------|
| 2005 | 65592 | 5132 |
| 2007 | 83179 | 4359 |

When calculating the yearly load for this ES, we used the EU EF, as this can be assumed to be the same. The EFM was the number of sheep, as we assumed that there would be one treatment per animal a year. This load is probably too high.

2.12 Real estate companies

NACE: 84.2

Use of OPE containing waxes and other floor polishes, and polish

Yearly load - ? to WW

Uncertainty: N/A

Use of OPE containing waxes and other floor polishes was reported from Real estate companies and public administration in 2008 in EU. Reported use from 2007 also include cleaning companies and chimney-sweepers (N81.2), and paint shops (G47.523). Emission factors derived from nonylphenol in a similar application (use of paint) are zero to air and 0.005 kg OPE released/kg OPE used to waste water. Industrial uses of different products might also be a relevant source of OPEs for Estonia, but there is not enough data available at the moment.

2.13 Sewerage

NACE 37

Emissions of OPEs with effluent water from municipal STPs.

Yearly load – 0,13 – 2,53 kg to CSW

Yearly load – 0,3 – 5,91 kg to FSW

Uncertainty: BAAC (The uncertainty of the yearly load is marked as C because the data used for calculation is too limited to be considered reliable)

The calculations were done using the data from COHIBA WP3 and the preliminary results from the BaltActHaz project – that gave us the EF. The sum on mono- and diethoxylates was used for calculation. The EF was considered to be the average result of all WWTP-s. For min scenario, the results under LOQ were considered to be; for max scenario, the results below LOQ were considered to be LOQ. The EF was then multiplied



by the EFM, i.e. the amount of effluents produced per person a day – 125 litres (according to Statistics Estonia 2010), the number of inhabitants (1 340 021 according to Statistics Estonia 2010), and the number of days a year (365).

Emissions of OPEs with sewage sludge from municipal STPs.

Yearly load – 0,29 – 39,46 kg to FS

Yearly load – 0,13 – 18,57 kg to AS

Uncertainty: BAAC (The uncertainty of the yearly load is marked as C because the data used for calculation is too limited to be considered reliable)

The substance adsorbs to sewage sludge, and the spreading of sludge from WWTP that treat effluent that contains 4-tert-octylphenol can be a route of exposure to soil. The spreading of sludge to farmlands is considered under AS compartment in this string; disposal on landfill and use in landscaping is designated to the compartment FS. The sludge is not incinerated in Estonia.

The calculations were done using the data from COHIBA WP3 and the preliminary results from BaltActHaz project that gave us the EF. The sum on mono- and diethoxylates was used for calculation. The EF was considered to be the average result of all WWTP-s. The representability is highly uncertain due to limited data. The EFM is the one from European SFA-s, considered to be representative to Estonia by Mr Kõrgmaa, an expert of WWTPs and sewage sludge (personal communication). The yearly load was calculated by multiplying EF with EFM and number of inhabitants in Estonia.

2.14 Transport and storage

NACE: H

OPE in motor oil

Yearly load - ? to AO

Uncertainty: N/A

This application was reported in Sweden for 2008. Reported use for the application in 2007 also included wholesale trade except of motor vehicles (G46) (Swedish Chemicals Agency 2010). According to Prodcom 2008 database there are several such activities taking place in Estonia, but there is no data to calculate the potential yearly load from this source. However, as the two countries are quite similar, similar use of OPEs can be suspected.





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2.15 Treatment and disposal of non-hazardous waste

NACE: 38.21, 38.22

OPEs in landfill leachate

Yearly load – 0 – 0,00014 kg to FSW

Yearly load – 0 – 0,00014 kg to FS

Uncertainty: C

The calculations were done using the excel sheet provided by IVL. The data used was from the COHIBA WP3 results from the study of landfill leachate. The sum on mono- and diethoxylates was used for calculation. However, this result is considered extremely inaccurate as it is based on two samples from one landfill.

To point out our opinion, the leachate from the hazardous wastes should be in a different ES. However, we didn't find it meaningful to create an additional ES as we have no data from the effluents of leachates of hazardous waste landfills.



3 SFA diagram

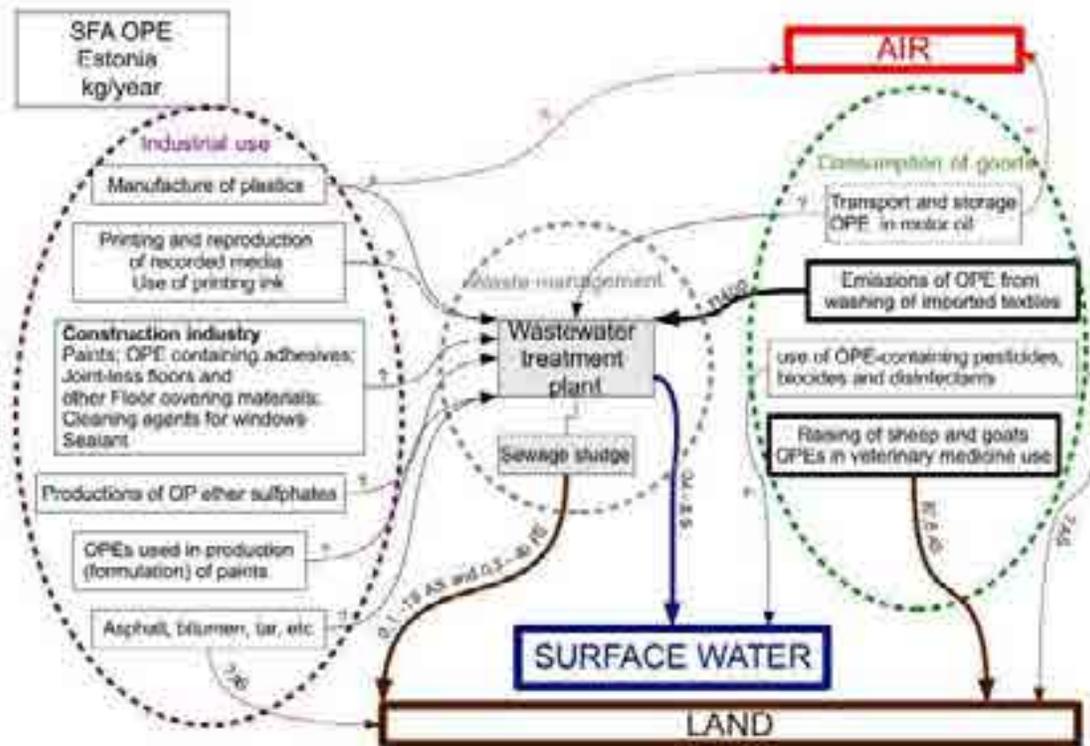


Figure 3. SFA diagram for OPEs in Estonia.

4 Conclusions

4.1 Quantitative estimation of the most relevant sources to each environmental compartment (Soil, water and air)

The industrial use of products containing OPEs could be a relevant source for Estonia. At the moment the sources are not detected. There is no proper product register in Estonia and product based uses are not known. Further and thorough investigation is needed in the future in order to identify the potential sources of OPEs in Estonia.

OPEs mostly end up in WWTPs and it means they could be removed and prevented from entering the environment again. If this is not done, the surface water would be contaminated.

The most important source for Estonia at the moment is the usage of products containing OPEs. It was possible to calculate the number for washing the imported textiles and yearly load from there is 11,4 t/year to WW.

Direct emissions to the land can come from veterinary medicaments used for goats and sheep. Calculated load to AS from this source was 87,5 kg. The loads can also come from pesticides used in agriculture then the receiving compartments are AS and FSW. The sewage sludge is also a big possible source for land contamination: 0,1 - 19 kg AS and 0,3 - 40 kg to FS.

It was not possible to calculate air emissions as there is no monitoring data. However, the potential air emissions are probably mostly related to the industrial activities.

4.2 A qualitative estimation of time trends for future scenarios.

It is important to map the use of OPEs and OPs in the industry in order to plan potential measures to reduce the emissions of OPEs. At the moment the data from industry is extremely scarce and it is difficult to take any measures.

It is also important to strengthen the control of customs and check the products imported from non-EU countries as imported products (such as textiles) may be an important source of OPEs.





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Also, raising of general awareness is of utmost importance. Reducing the use of pesticides and finding alternatives for veterinary medicines and pesticides is a potential measure for reducing the emissions of OPEs.

As most of the emissions of OPEs are led to WWTPs, it is also important to find technologies that help to stop the pollution at this point. Proper waste and sewage treatment will hopefully remove the substance entering the environment from this source.



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ANNEX J - Substance flow analysis for Short chain chlorinated paraffins (C₁₀₋₁₃) in Estonia

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This study was carried out under the COHIBA study from May 2010 to May 2011. This report is based on the SFA Chloroalkanes, C10-13 (EU27) by Environment and Health Administration, City of Stockholm. The results are for Estonia. Many of the results are rough approximations that cannot be taken as exact results for Estonia, but more as a base to plan future studies.

1 Introduction

There is a range of commercially available C₁₀₋₁₃ chlorinated paraffins, commonly referred to as short chain chlorinated paraffins. They are usually mixtures of different carbon chain lengths and different degrees of chlorination; although all have a common structure in that no secondary carbon atom carries more than one chlorine atom. Two other groups of chlorinated paraffins are made commercially – these are known as “mid, medium or intermediate chain” (typically C₁₄₋₁₇) and “long chain” (typically C₂₀₋₃₀).

According to the EU risk assessment report (EU RAR 2008) around 40 CAS numbers have been used to describe the whole chlorinated paraffin family at one time or another (Table 1), although the most typical CAS number for SCCPs is usually 85535-84-8.

Table 1. Substances that might contain short and medium-chain chlorinated paraffins (EU RAR 2005).

| Substance | CAS no. |
|--|-------------|
| Alkanes, C6-18, chloro | 68920-70-7 |
| Alkanes, C10-12, chloro | 108171-26-2 |
| Alkanes, C10-14, chloro | 85681-73-8 |
| Alkanes, C12-13, chloro | 71011-12-6 |
| Alkanes, C12-14, chloro | 85536-22-7 |
| Alkanes, C10-21, chloro | 84082-38-2 |
| Alkanes, C10-26, chloro | 97659-46-6 |
| Alkanes, C10-32, chloro | 84776-06-7 |
| Paraffins (petroleum), normal C>10, chloro | 97553-43-0 |
| Alkanes, chloro | 61788-76-9 |



1.1 Physical chemical properties

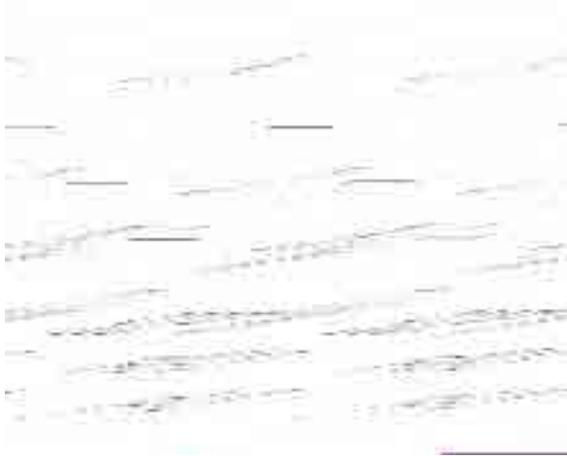


Figure 1. Chemical structure of short chain chlorinated paraffins.

Chlorinated paraffins were designed to be photo-stable, chemical- and temperature-resistant (up to 200°C), and to have low flammability which makes them very persistent. Due to their characteristics of having low water solubility but high lipophilic behaviour, chlorinated paraffins are bio-accumulative. For aquatic organisms chlorinated paraffins are toxic, especially for concentrations above their water solubility. With decreasing chain-length and increasing chlorination content, the toxicity increases.

The physical and chemical properties of the short chain chlorinated paraffins are determined by the chlorine content (typically 49-70% for commercial substances). There are a wide number of possible chlorinated paraffins (of different chain length, degrees of chlorination and position of the chlorine atoms along the carbon chain) present in any given commercial product. Increasing chlorine leads to an increase in viscosity and a decrease in volatility. The short chain chlorinated paraffins are relatively inert substances, which are resistant to chemical attack and are hydrolytically stable. They are chemically very stable but release detectable quantities of hydrogen chloride when heated to high temperatures (or for prolonged periods). Dehydrochlorination also occurs on prolonged exposure to light.

All chlorinated paraffins have low solubility in water but C₁₀₋₁₃ types are significantly more soluble than the other classes which show decreased solubility with increasing chain length. Chlorinated paraffins are capable of mixing with many organic solvents such as aliphatic and aromatic hydrocarbons, chlorinated solvents, ketones and esters.



Studies have confirmed that chlorinated paraffins adsorb strongly onto suspended materials or sediments in an aqueous environment.

Table 2. Physical and chemical properties of short chain chlorinated paraffins according to Böhm et al. (2002).

| Property | SCCP |
|--|---|
| Elemental formula | $C_xH_{2x+2-y}Cl_y$, where $x=10-13$ and $y=1-13$ |
| Physical state at npt | liquid |
| Density | 1.18 - 1.59 g/cm ³ (20°C) |
| Molecular weight (g/mol) | 320 – 500 |
| Melting point (°C) | -30.5°C (49% Cl) 20.5°C (70%) |
| Boiling point | Decay at > 200°C |
| Vapour pressure (Pa, at XX°C) | 0.3 – 1.4 x10 ⁻⁸ Pa at 25°C (51 – 71% Cl, C 10-13) 0.021 Pa at 40°C (50% Cl, C 10-13) |
| Log octanol-water partition coefficient (log Kow, at pH X) | 4,39 – 6,93 (49 % Cl, C10-C13) 5,47 – 7,30 (63 % Cl, C10-C13) 5,37 – 8,69 (71 % Cl, C10-C13) |
| Water solubility (mg/l at pH X, 20°C) | 6,4 – 2.370 mg/l (51 – 71 % Cl, C10-13) 150-470 µg/l (59% Cl, C10-13) |
| Henry's Law Constant (Pa m ³ /mol, at XX°C) | 0,68 - 648 Pa*m ³ /mol (C10 bis C12) |
| Biotic and abiotic decomposition | Persistent |
| Bioaccumulation | High (Bioconcentrationfactor up to > 100.000) |
| PNEC _{water} | 0,5 µg/l |
| PNEC _{microorganisms} | 6 mg/l |

1.2 Regulatory status

No specific regulation on state level in Estonia, but all the EU regulations are valid also for Estonia.

Short chain chlorinated paraffins have been identified as priority hazardous substances under the EU Environmental Quality Standard (EQS) Directive (2008/105/EC). Additionally, it is a chemical for which a risk profile is currently being prepared under the Stockholm Convention on POPs. Under the REACH-regulation (1907/2006), short chain chlorinated paraffins has been proposed to be added to the list of substances subjected to authorization. According to Annex XVII in the same regulation, shall short chain chlorinate paraffins not be placed on the market for use as substances or as constituents of other substances or preparations in concentrations higher than 1% in metalworking or for fat liquoring of leather.



HELCOM Recommendation 19/5 also identifies SCCPs as substances of specific concern to the Baltic Sea.

1.3 Production

There is no registered production in Estonia according to Estonian Health Board.

1.4 Use

The main uses of short chain chlorinated paraffins are as flame retardants in rubbers and textiles, and as plasticisers in paints and coatings. Additionally, still some use of short chain chlorinated paraffins in sealants and adhesives may occur as these are products with long service life.

Another major application for short chain chlorinated paraffins has been in the formulation of metalworking lubricants where they have been used in a wide range of machining and engineering operations (Euro Chlor, 2009). However, short chain chlorinated paraffins are no longer used for this application (EU RAR, 2008).

1.5 Environmental fate

Short chain chlorinated paraffins with low chlorine contents (<50% wt Cl) may biodegrade slowly in the environment, particularly in the presence of adapted microorganisms. Certain bacteria have also been shown to dechlorinate short chain chlorinated paraffins with high chlorine contents. Hence, biodegradation of these compounds may occur slowly in the environment (EU RAR, 2000). No information on the anaerobic biodegradation of short chain chlorinated paraffins has been found.

The potential environmental distribution of short chain chlorinated paraffins has been studied with a generic level III fugacity model. According to the modelling results, once released into the environment, short chain chlorinated paraffins are expected to distribute mainly onto the soil and sediment phases. The results also show that if the substance is mainly released to air or water, it is likely that it is then transferred to soil or sediment. This is also indicated in the measured levels and the calculated predicted environmental concentrations (PECs).

However, it should be noted that since short chain chlorinated paraffins are complex mixtures, individual components of the mixture may have different physico-chemical



properties than used in modelling and these components may distribute slightly differently in the environment (EU RAR 2000).

1.6 Environmental levels

There has been virtually no research on SCCPs in Estonia. The first data is from 2010 when it was studied in two European funded projects – BaltActHaz¹ and COHIBA. Therefore we mainly used data from these two projects for determining the possible sources of SCCPs.

In BaltActHaz, SCCP was measured from the effluents and sludge of several municipal WWTPs, waters and sediments of rivers, and sediments from one point on the coast and two points of Lake Peipsi. All the measured samples were below the LOQ (0,3 µg/l and 0,3 mg/kg for water and sediments, respectively).

However, these results are in contrast with analyses done under COHIBA study, where SCCPs were found in concentrations over the LOQ from all the effluents and sludge samples. In effluents, the concentrations varied from 0,32 to 2,94 µg/l, with the median concentration being 1,01 µg/l. SCCPs were also found in concentrations over the LOQ from the sludge samples of WWTPs, varying from 5,99 to 10,50 mg/kg.

SCCPs were measured in concentrations up to 10,38 µg/l from landfills and up to 1,84 µg/l from storm waters.

Table 3. SCCPs in landfills, storm waters, wastewaters and wastewater sewage sludge samples in Estonia 2009-2010 (Data from COHIBA WP3).

| Landfill | Stormwater | WWTP1 | | WWTP2 | WWTP3 | | WWTP4a | WWTP4b |
|----------------|---------------|--------------|-------------------|--------------|--------------|-------------------|--------------|--------------|
| | | Water (µg/l) | Sludge (mg/kg dw) | Water (µg/l) | Water (µg/l) | Sludge (mg/kg dw) | Water (µg/l) | Water (µg/l) |
| 3,57 and 10,38 | 0,85 and 1,84 | 0,73 – 4,80 | 1,23 | 0,38 – 1,98 | 0,48 – 2,94 | 5,99 and 6,37 | 0,32 - 0,64 | 1,04 - 2,85 |

¹ BaltActHaz web page, available at: <http://www.baltacthaz.bef.ee/>





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It must be noted that three of the WWTPs overlapped in both projects, also the sampling times were roughly similar, and therefore we can suspect that the results of one project are not reliable as two different laboratories performed analyses for the projects. However, deciding, which of the results are more reliable, is out of the scope of this study.





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The uncertainties in the following emission strings are given with four letters, the first letter representing uncertainty for EF, the second for EFM, the third for division into compartments and the fourth for the yearly load. Uncertainty is classified according to the principles described in “Dealing with uncertainty in substance flow analysis within the COHIBA project”, a PM describing how data uncertainty is graded in WP4 of the COHIBA project.

If the Estonian yearly loads were scaled from the EU yearly load to Estonian population, the Estonian population was considered to be 0,3% of the EU population. This accuracy level was considered to be enough for given study; especially considering the very high uncertainty levels in other emission strings.

2 Sources of emissions of SCCPs in Estonia

2.1 Manufacture of rubber products

NACE: 22.1

Emissions during use as flame retardant in rubber formulations

Yearly load - ? to WW

Uncertainty: N/A

In the EU short chain chlorinated paraffins with chlorine contents of around 70-71% are only supplied for use in rubber. The main application of the treated rubber is conveyor belts for use in mines where specific safety requirements need to be met (EU RAR, 2008). The estimated release from the use of short chain chlorinated paraffins as flame retardant in rubber formulations is 0.001% or 0.01 kg/produced tonne of rubber products (EU RAR, 2000).

The receiving compartment for emissions from use of rubber formulations is not described anywhere, but the guess is that the emission is distributed only to wastewater as wastewater is the main receiving compartment for other industrial emissions of short chain chlorinated paraffins.

In Estonia, there is no registered data of SCCP use in official databases that get their data from 10 tons onward. However, there are several activities taking place in Estonia under that NACE according to Prodcom 2008. We don't know what kind of products they use and if the products might contain SCCP. The biggest producer of rubber and plastics claimed not using SCCPs in the process. However, according to our experience, the



producers are often unaware of the substances used, especially if the substances are used as additives. Future studies based on the products are needed.

2.2 Forging, pressing, stamping and roll-forming of metal; powder metallurgy; Treatment and coating of metals

NACE: 25.50; 25.61

Emissions during use of metal working fluids and extreme pressure lubricating fluids

Emissions from blending and formulation of metal working fluids

Yearly load - ? to WW

Uncertainty: N/A

According to the EU RAR Addendum (2008) there is no longer any use of short chain chlorinated paraffins in metal cutting/working in the EU, hence it is assumed that the emissions from these sources are reduced.

It can be assumed that there is no volume of the substance in the given string in Estonia because there are only few companies in the field and the biggest of them confirmed that they do not use the substance in the process. However, to be sure future studies based on the products are needed.

2.3 Manufacturing of polyuretan insulating foam (building materials)

NACE: 20.5

Emissions from industrial applications from production of polyurethane insulation foam

Yearly load - ? to WW

Uncertainty: N/A

Losses during loading

Yearly load – 0,08 kg to IS

Uncertainty: B-CC





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Estonia was the third biggest producer of insulating foams in the world (after China and USA) in 2007. The production was 45 million bottles of foam in Estonia (60 million in China, 50 million in USA). It means that Estonia holds up to 29% from world market share of insulating foams (Ehitusuudised 11.10.2010²). The insulating foams are used in construction for mounting window- and doorframes, filling of cavities, sealing of openings in roof constructions and insulation materials, creating soundproof screens, filling of cavities around pipes, fixing and insulating of wall panels, roof tiles, etc.

MCCP is used as a raw material for foam production, but SCCP is in the MCCP mixture as an additive (< 1%).

1880 t of MCCP was used in Estonia in 2007, according to data from the web-page of Estonian Ministry of the Environment³ where 50 most common chemical substances in Estonia are given. This use is also registered in Chemicals Notification Centre (Estonian Health Board)⁴.

Producers claim that there are no emissions of MCCPs or SCCPs to air during production. The amount of emissions to the wastewater is unknown at the moment. The amount of about 8 kg of spillage during loading is the producers' own estimation (taking into account the amount of substance used per year).

When calculating the yearly load of SCCPs, we used the assumption that 1% of the total usage of MCCP in foam production is SCCPs, i.e. we first calculated the MCCP loads and used 1% of the load to find the load for SCCPs. Yearly amount will be 18,8 t of SCCP used in foam production.

Further research is needed on that ES to calculate proper emission factors and hence calculate more accurate yearly loads to the environment.

2.4 Manufacturing

NACE: C

2 <http://www.ehitusuudised.ee/>

3 <http://www.envir.ee/964088>

4 <http://piksel.ee/kemikaalid/index.php?tid=sJfTXJ8iTThfYITkj7oHXgIZU00aKZggJdljUs8>



Emissions from industrial applications of paints containing SCCP

Yearly load - ? to WW

Uncertainty: N/A

No proper data to calculate the yearly loads, but the use of paints containing SCCPs can be assumed, hence we consider this ES to be relevant for Estonia.

2.5 Emission from (private) consumption; during lifetime use of articles, goods and chemical products and preparations.

NACE: X

Although short chain chlorinated paraffins are of low vapour pressure at ambient temperatures, the vapour pressure is not low enough to exclude the possibility of volatilisation from plastics, paints, rubber, sealants, adhesives and textiles during their service life. Losses are also thought to occur through leaching and as a result of wear and tear of articles (for example particulate losses) during their service life (EU RAR, 2000).

Volatile and leaching losses over lifetime from rubber and plastic products containing SCCPs are estimated to be 0.001 kg/kg product and year and distributed 50:50 to air and wastewater. The service life for rubber and plastic products is estimated to be 5 years (Fridén and McLachlan, 2007). Volatile and leaching losses (due to wear and tear, and erosion) over lifetime from surfaces painted with SCCP containing paint are estimated to be 0.0055 kg/kg paint and year distributed with 27 percent to wastewater and 73 percent to air. The service life for painted surfaces is estimated to be 5 – 7 years (Fridén and McLachlan, 2007).

Volatile and leaching loss over lifetime from products containing SCCPs

Yearly load – 7,72 – 28,54 kg to IA

Yearly load – 117,80 – 320,71 kg to WW

Uncertainty: N/A

The yearly load was calculated from the EU SFA, using the Estonian population as a basis for scaling.

Volatile and leaching loss over lifetime from rubber and plastic products containing SCCPs

Yearly load - ? to IA, WW

Uncertainty: N/A





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No data that could be used for calculating the yearly loads.

Volatile and leaching loss (due to wear & tear and erosion) over lifetime from surfaces painted with SCCP containing paint

Yearly load - ? to OA, WW

Uncertainty: N/A

No data that could be used for calculating the yearly loads.

Emissions from waste remaining in the environment

Yearly load – 88,29 – 175,23 kg to FS

Yearly load – 29,16 – 58,05 kg to FSW

Yearly load – 0,116 – 0,232 kg to OA

Uncertainty: N/A

No emission factors were found for these sources of emissions. However, the estimated yearly release in EU 2001 waste remaining in the environment 32.7-64.9 tonnes to soil, 10.8-21.5 to air and 43-86 kg to surface water. The yearly load for Estonia was calculated from the EU SFA, using the Estonian population as a basis for scaling.

2.6 Materials recovery

NACE: 38.3

Recycling of carbonless copy paper

Yearly load – 4 – 8 kg to WW

Uncertainty: CBAC

Leaching losses during recycling of carbonless copy paper containing SCCPs are estimated to be 0.1 – 0.2 kg/kg product and year and distributed to wastewater (Fridén and McLachlan, 2007).

The rate of paper recycling is many times lower in Estonia (17,5%) than in Western and Northern Europe. The majority of the waste paper collected in Estonia is exported (55,6%) (Maves 2008), 39% is used for making new paper, cardboard, insulation materials or packaging. 3000 tons of waste paper is used by Räpina Paper Mill a year (10% from collected paper).



Räpina Paper Mill is a paper production plant, which uses scrap paper collected in Estonia as a raw material. Räpina Paper Mill does not accept waste paper soiled with lubricant, freshed and waxed paper, carbonless (NCR) and carbon paper, parchment, glassine, and photo paper. But they use material from confidential documents that are disposed and can contain copy paper. The other paper mill does not recycle paper (information from their IPPC permit⁵). Therefore we can assume that some of the SCCPs can be recycled.

The assumption here is that the carbonless copy paper that contains MCCP also contains SCCP and that the percentage is about the same, i.e. About 4% by weight. Therefore, if 0,1-0,2 kg per kg is lost to WW, we get the yearly loads.

2.7 Sewerage

NACE: 37

Emissions of SCCP with effluent water from municipal STPs.

Yearly load – 11,77 – 14,24 to CSW

Yearly load – 27,47 – 33,24 to FSW

Uncertainty: CAAC

The calculations were done using the data from COHIBA WP3 and the preliminary results from the BaltActHaz project – that gave us the EF. The EF was considered to be the average result of all WWTP-s. For min scenario, the results under LOQ were considered to be 0; for max scenario, the results below LOQ were considered to be LOQ. The EF was then multiplied by the EFM, i.e. the amount of effluents produced per person a day – 125 litres (according to Statistics Estonia 2010), the number of inhabitants (1 340 021 according to Statistics Estonia 2010), and the number of days a year (365).

SCCP in sewage sludge from municipal STPs.

Yearly load – 11,55 – 14,08 to AS

Yearly load – 24,54 – 29,91 kg to FS

Uncertainty: CAAC

FOR COMPARISON:

Yearly load – 56,22 to AS

Yearly load – 119,46 to FS

5 <http://www.ippc.envir.ee/english/index.htm>



In the statistical report by Wieland (2003) sludge disposal in the EU member states is described. According to this report 32 % of the sludge was used within agriculture, 13 % was composted, 25 % landfilled, 13 % incinerated and 17 % was disposed using other methods. The situation in the candidate countries at the time (CZ, HU, PL, SI and SK) was rather similar, the biggest difference being less incineration (1 %) and more landfilling (39 %).

As a calculation exercise the amount of SCCP disposed in the sewage sludge can be estimated. According to the EU statistics (Wieland 2003) the yearly production of sewage sludge is approximately 23 kg dry solid per capita. In the statistics from the year 2002 (Wieland 2003) 32 % of the sewage sludge is used within agriculture. When calculating the results, disposal on landfill, compost and other are designated to the compartment FS, incineration is assumed to achieve complete combustion.

The calculations for Estonian yearly load were done using the data from COHIBA WP3 and the preliminary results from BaltActHaz project that gave us the EF. The EF was considered to be the average result of all WWTP-s. The representability is highly uncertain due to limited data. The EFM is the one from European SFA-s, considered to be representative to Estonia by Mr Kõrgmaa, an expert of WWTPs and sewage sludge (personal communication). The yearly load was calculated by multiplying EF with EFM and number of inhabitants in Estonia.

2.8 Treatment and disposal of non-hazardous waste; Treatment and disposal of hazardous waste

NACE: 38.21; 38.22

SCCPs in landfill leachate

Yearly load – 0,0036 – 0,0104 kg to FSW

Yearly load – 0,0036 – 0,0104 kg to FS

Uncertainty: C

The calculations were done using the excel sheet provided by IVL. The data used was from the COHIBA WP3 results from the study of landfill leachate. However, this result is considered extremely inaccurate. We assume the load to be higher, considering the high amounts of SCCPs used in different products.



We also think that the leachate from the hazardous wastes should be in a different ES. However, we didn't find it meaningful to create an additional ES as we have no data from the effluents of leachates of hazardous waste landfills.

2.9 Worldwide activities within and outside Estonia

NACE: Y

Atmospheric deposition of SCCP
Yearly load – 45 – 1882 kg to AS
Yearly load – 95 – 4015 kg to FS
Yearly load – 9 – 376 kg to FSW
Uncertainty: CAAC

Deposition numbers from Swedish air database (summary made by IVL partners – Swedish Environmental Protection Agency: National Air Monitoring National Air Database, www.ivl.se) were used to calculate the yearly load. The Swedish monitoring stations are located on the similar latitude and we considered it comparable to Estonia. Minimum and maximum values are calculated with Swedish emission factors the lowest periodical deposition value and the highest value.

Estonian territory is 45 000 km². The division into compartments was made, using statistical data from Estonia – 30% AS, 64% FS, 6% FSW⁶.

6 Estonian Forestry 2009 – <http://www.keskkonnainfo.ee/failid/forestry2009/EstonianForestry.swf> (last accessed 15.03.2011)



3 SFA diagram

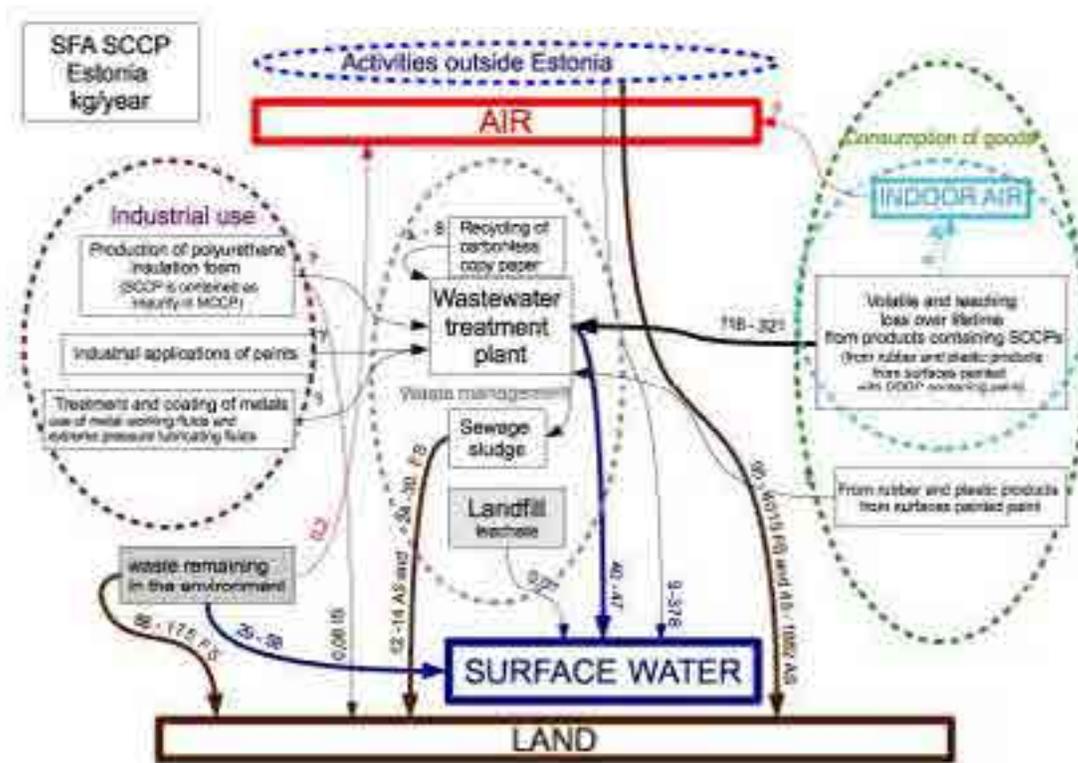


Figure 2. SFA diagram for SCCPs in Estonia.

4 Conclusions

4.1 Quantitative estimation of the most relevant sources to each environmental compartment (Soil, water and air)

The most important source of emissions of short chain chlorinated paraffins is the use of products containing short chain chlorinated paraffins. The majority of the short chain chlorinated paraffins from products end up in the water compartment and the rest is emitted to air. Volatile and leaching loss over lifetime from products to waste water is 118 – 321 kg/year and to indoor air 8 – 29 kg.

The most important sources to surface water are waste-water treatment plants (40 -47 kg/year) and waste remaining in the environment (28 – 58 kg/year).

The most important source to land is also the waste remaining in the environment (88 - 175 kg/year) and second largest source for land is the sewage sludge (12 -14 kg to AS and 24 – 30 kg to FS)

The emissions to air are not so important for Estonia. We should keep in mind that SCCP is highly regulated also under The 1998 Aarhus Protocol on Persistent Organic Pollutants (POP Protocol) to the regional UNECE The 1979 Geneva Convention on Long-range Transboundary Air Pollution (CLRTAP) and also in our study the deposition data from activities outside Estonia are really high exceeding even the loads from local sources (95 – 4015 kg to FS and 45 – 1882 kg AS and (9 – 376kg to surface water). Estonian emissions to air can be underestimated in that study or we just did not know the possible sources.

4.2 A qualitative estimation of time trends for future scenarios.

The estimated emissions presented in this report are mainly based on data from 2001. Since the emission estimates mainly are based on old data it is likely that the situation has changed. Some of the sources mentioned here may not be relevant and some may be missing. The proportions between different uses may also have changed.

In the addendum to the EU RAR it is said that Euro Chlor have indicated that the use of short chain chlorinated paraffins in the EU 2003 was around three times lower than 2001. Due to the fact that short chain chlorinated paraffins have been proposed to be added to





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the list of substances subjected to authorization under the REACH-regulation (1907/2006), a further reduction can be expected. The situation can be expected to be similar in Estonia.

However, as the main sources of emissions are sources with sometimes a long service-life, there will be a delay in the effect of reduced use on the yearly releases to the environment. The proper waste management is really important for reducing the SCCP loads to the environment. Also the recycling activities should be under better control.

Raising the awareness of the general public and the industry managers is an important step to be taken.

Also the proper treatment of wastewater especially the sludge treatment would give a good effort to protect that the SCCPs would not end up in the environment.



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ANNEX K - Substance flow analysis for Medium chain chlorinated paraffins (C₁₄₋₁₇) in Estonia

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This study was carried out under the COHIBA study from May 2010 to May 2011. This report is based on the SFA Medium chain chlorinated paraffins (EU) by Environment and Health Administration, City of Stockholm. The results are for Estonia. Many of the results are rough approximations that cannot be taken as exact results for Estonia, but more as a base to plan future studies.

1 Introduction

Chlorinated paraffins (CPs) are straight-chain hydrocarbons that have been chlorinated to different degrees. Chlorinated paraffins are classified according to their carbon-chain length and percentage of chlorination, with carbon-chain lengths generally ranging from C10 to C30 and chlorination from approximately 35% to greater than 70%, by weight. Chlorinated paraffins are made by chlorinating paraffin fractions obtained from petroleum distillation. The three most common commercial feedstock used are short-chain (C10-13), intermediate-chain (C14-17) and long-chain (C18-30). This SFA covers the medium chain chlorinated paraffins (MCCPs, C14-C17).

According to the EU risk assessment report (EU RAR 2005) around 40 CAS numbers have been used to describe the whole chlorinated paraffin family at one time or another. Some of these CAS numbers that might cover the MCCP group are listed in Table 1. The CAS number 85535-85-9, is taken to represent the commercial MCCPs used in Europe (EU RAR 2005).

Table 1. Substances that might contain medium-chain chlorinated paraffins (EU RAR 2005).

| Substance | CAS no. |
|--|------------|
| Alkanes, C6-18, chloro | 68920-70-7 |
| Alkanes, C10-21, chloro | 84082-38-2 |
| Alkanes, C10-26, chloro | 97659-46-6 |
| Alkanes, C10-32, chloro | 84776-06-7 |
| Paraffins (petroleum), normal C>10, chloro | 97553-43-0 |
| Alkanes, chloro | 61788-76-9 |

The following classification is proposed for environmental effects of MCCPs: N – Dangerous for the environment, R50/53 – Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. This proposal is based on the acute



toxicity seen with *Daphnia magna* (48-hour EC₅₀ = 0.0059 mg/l), a high fish bioconcentration factor of 1,087 and the lack of degradation expected in standard ready biodegradation tests. This proposal was agreed at the Environmental Classification and Labelling Expert Meeting in September 2004 (EU RAR 2005).

1.1 Physical chemical properties

MCCPs are, as described above, a complex mixture of closely related chemicals. They are thick yellowish oily liquids boiling at over 200 °C, in the process decomposing with the release of hydrogen chloride gas. They are virtually insoluble in water but dissolve fully in most non-polar organic solvents like paraffin oil. They are non-flammable and do not evaporate easily.

The chemical structure of an MCCP of chain length C15 is shown in Figure 1.

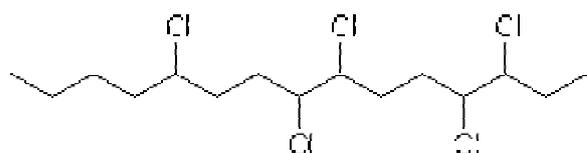


Figure 1. Chemical structure of a medium-chain chlorinated paraffin (C15).

The physicochemical properties of MCCP are to a large extent determined by their degree of chlorination, but also of their carbon chain length. Physical and chemical properties of some MCCPs are given in Table 2.

Table 2. Physical and chemical properties of some medium chained chlorinated paraffins, in relation to the degree of chlorination.

| Property | Chlorine content (%) | Value | Comments |
|--------------------------|----------------------|---|--|
| Physical state at npt | 40-63 | liquid | |
| Molecular weight (g/mol) | | 232.5-826.5 | Dependant on chain length and degree of chlorination |
| Melting point (°C) | | | Commercial mixtures have no distinct melting point |
| Vapour pressure (Pa) | 45 52 | 2.27x10 ⁻³ at 40 °C 1.3x10 ⁻⁴ at 20 °C | a value of 2.7x10 ⁻⁴ is used in the Environmental Assessment in the EU RAR (2005) |





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| | | | RAR (2005) |
|---|----------|------------------------|--|
| Log octanol-water partition coefficient (log K_{ow}) | 45 52 | 5.52-8.21 5.47-8.01 | a value of 7 is used in the Environmental Assessment in the EU RAR (2005) |
| Water solubility (mg/l) | 51 | 0.005-0.0027 | a value of 0.0027 is used in the Environmental Assessment in the EU RAR (2005) |

1.2 Regulatory status

We have no special regulation according to MCCP in Estonia.
The European regulations are valid also for Estonia and some of them is given below.

The Integrated Pollution Prevention and Control Directive (IPPC Directive, 2008/1/EC) concerns minimising pollution from various industrial sources throughout the EU. Operators of industrial installations covered by Annex I of the IPPC Directive are required to obtain an authorisation (environmental permit) from the authorities in the EU countries. A number of uses of MCCPs are covered under the IPPC directive.

MCCPs are classified as: R64 May cause harm to breastfed babies, R66 Repeated exposure may cause skin dryness or cracking and R50/53 Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment (ESIS 2009).

HELCOM Baltic Sea Action Plan also identifies MCCPs as substances of specific concern to the Baltic Sea.

1.3 Production

There is no registered production in Estonia according to Estonian Health Board.

1.4 Use

Estonia has a registered use of MCCP in polyurethane foams production. Further explanations in the production of polyurethane foams section 2.2 below.

The main uses of MCCPs are as secondary plasticisers in polyvinyl chloride (PVC) (60%), where a major use is in flooring (EU RAR 2005). MCCPs are also used as



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extreme pressure additives in metal working fluids (15%), as plasticisers and additives in paints, adhesives and sealants (15%), as flame retardant/ plasticisers in rubbers and other polymeric materials (7%), in fat liquors used in leather processing (3%) and in carbonless copy paper ($\ll 1\%$) (EU RAR 2005).

In addition to this it has been reported that some long-chain chlorinated paraffins based on a C18-20 carbon chain length may contain a substantial proportion (up to 17%) of C17 chlorinated paraffins (EU RAR 2005).

MCCPs are not used as flame retardant additives in their own right but as secondary plasticisers with flame retardant properties, often in conjunction with other plasticisers such as phosphate esters (EU RAR 2005).

The IPPC directive cover a number of uses of MCCPs; including (depending on the size of operation) production of MCCPs, metal working (only large companies in the ferrous and non-ferrous metals sectors), some PVC and plastics compounding/conversion sites and leather processing sites (larger sites only) (EU RAR 2005).

Due to high production volumes, a wide field of use, and their stability and persistency, chlorinated paraffins are globally in the environment distributed. Due to a ban of SCCP the use of SCCP decreased in EU-15. At the same time the use of MCCP increased due to substitutions of SCCP because of their similar use patterns. As a consequence MCCP concentrations in cod and flounder in the Baltic Sea were higher than estimated PNEC values in fish.

1.5 Environmental fate

MCCPs have a low vapour pressures and do not evaporate easily. The volatility in general decreases with increasing chlorine content. When the substance is released to air the releases to air are as hot gases and the possibility of condensation as the gas cools needs to be considered. This may lead to some of the releases initially to air entering other waste streams such as water (EU RAR 2005).

Water solubility of MCCPs is low. The actual measured $\log K_{ow}$ values vary between ~ 5.5 and 8.2 . Thus, when the substance is released to water, a substantial amount of the substance will be associated with sediment.





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When MCCPs are released to soil, they are predicted to remain mainly in the soil compartment, but a small amount may also be washed away to enter surface waters (EU RAR 2005).

No standard ready or inherent biodegradation test results are available for MCCPs. The potential for degradation of the chlorinated paraffin appears to increase with decreasing chlorination. Adsorption onto sludge is likely to be the major removal mechanism for MCCPs during waste water treatment processes. For the short-chain chlorinated paraffin, an equilibrium removal percentage of 93% by adsorption onto the sludge was determined. A similar degree of removal by adsorption onto the sludge as found for the short-chain chlorinated paraffins would also be expected for MCCPs.

In the EU RAR (2005) it is concluded that MCCPs meet the T-criterion and the screening criterion for P or vP. However, MCCPs do not meet the specific criteria for either B or vB laid down in the TGD (ECB 2003). However, there are uncertainties regarding both the persistence and bioaccumulation potential for MCCPs, and the available database of reliable laboratory studies and field monitoring data is fairly limited. Therefore further information would be needed in order to confirm whether the substance should be considered as a PBT substance or not (EU RAR 2005). MCCPs are currently under evaluation by the PBT Expert Working Group of the Technical Committee of New and Existing Chemicals (ESIS, 2010).

The main characteristics of medium-chain chlorinated paraffins relevant for the exposure assessment are that the substance is not expected to hydrolyse in water, is not readily or inherently biodegradable, has a high $\log K_{ow}$ value (~5.5-8.2), and has an estimated atmospheric half-life of 2 days. The high $\log K_{ow}$ indicates that medium-chain chlorinated paraffins will adsorb strongly onto sludge and sediments and are not expected to be mobile in soil. Bioconcentration factors up to 1,087 l/kg have been determined in rainbow trout. Uptake from food into fish and from soil into earthworms and plants has also been demonstrated. A bioconcentration factor of up to 5.6 has been determined for accumulation in worms from soil. The predicted fate of medium-chain chlorinated paraffins in waste water treatment plants is 93% adsorbed onto sludge and 7% released in water. Thus, when emitted to a water treatment plant the emissions from the plant will occur to water or to land via sewage sludge application (EU RAR 2005).



1.6 Environmental levels

There has been virtually no research on this substance in Estonia. The first data is from 2010 when it was studied in two European funded projects – BaltActHaz¹ and COHIBA. Therefore we mainly used data from these two projects for determining the possible sources of MCCPs.

In BaltActHaz, MCCP was measured from the effluents and sludge of several municipal WWTPs, waters and sediments of rivers and one point of coast, and sediments from two points of Narva River. The measured samples were below the NQS (2,5 µg/l and 2,5 mg/kg for water and sediments, respectively), except for one measurement from Tallinn WWTP sludge, where MCCPs were measured in concentration of 0,606 mg/kg dw.

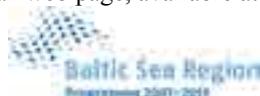
However, these results are in contrast with analyses done under COHIBA study, where MCCPs were found in concentrations over the LOQ from all the effluents and sludge samples, the concentrations from effluents varying from 2,95 to 1,62 µg/l (median 4,48 µg/l), and concentrations from sludge samples varying from 0,03 to 2,27 mg/kg. MCCP was found in concentrations over the LOQ in storm waters. In landfills, it was measured only once and the result was below the LOQ.

Table 3. MCCPs in landfills, storm waters, wastewaters and wastewater sewage sludge samples in Estonia 2009-2010 (Data from COHIBA WP3).

| Landfill | Stormwater | WWTP1 | | WWTP2 | WWTP3 | | WWTP4a | WWTP4b |
|----------|---------------|--------------|-------------------|-------------|--------------|-------------------|---------------|-------------|
| | | Water (µg/l) | Sludge (mg/kg dw) | | Water (µg/l) | Sludge (mg/kg dw) | | |
| < 0.2 | 1,11 and 2,91 | 0,44 – 1,71 | 10,58 | 1,11 – 4,84 | 1,00 – 3,01 | 0,03 and 2,27 | 2,22 and 5,86 | 0,96 – 8,40 |

It must be noted that three of the WWTPs overlapped in both projects, also the sampling times were roughly similar, and therefore we can suspect that the results of one project are not reliable as two different laboratories performed analyses for the projects. However, deciding, which of the results are more reliable, is out of the scope of this study.

¹ BaltActHaz web page, available at: <http://www.baltacthaz.bef.ee/>





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The uncertainties in the following emission strings are given with four letters, the first letter representing uncertainty for EF, the second for EFM, the third for division into compartments and the fourth for the yearly load. Uncertainty is classified according to the principles described in “Dealing with uncertainty in substance flow analysis within the COHIBA project”, a PM describing how data uncertainty is graded in WP4 of the COHIBA project.

If the Estonian yearly loads were scaled from the EU yearly load to Estonian population, the Estonian population was considered to be 0,3% of the EU population. This accuracy level was considered to be enough for given study; especially considering the very high uncertainty levels in other emission strings.

2 Sources of emissions of MCCPs in Estonia

2.1 Manufacture of rubber and plastic products

NACE: 22

There are several activities taking place in Estonia under that NACE according to Prodcom 2008. We don't know what kind of products they use and if the products might contain MCCP. Future studies based on the products are needed.

Spillage in raw material handling for use as plasticiser/flame retardant in other plastics and rubber

Yearly load - ? to WW

Uncertainty: N/A

MCCPs are liquids of low vapour pressure. Losses to the atmosphere are likely to be negligible when the substance is handled at ambient temperature. The liquid plasticisers are usually transported and handled in bulk, using enclosed storage systems and so minimal loss by spillage can occur. Estimated emission factor is of 0.01% to waste water.

Release from polymer/elastomer compounding in other plastics and rubber

Release from polymer conversion (processing) in other plastics and rubber

Yearly load - ? to WW, AO

Uncertainty: N/A





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The source of loss in this process is volatilisation to the atmosphere. It was assumed in the EU RAR (2005) that these air emissions will distribute 50:50 between air and water at the site as the gases cool. Estimated emission factor is 0.01% to air.

2.2 Manufacture of other chemical products

NACE: 20.5

Emissions from industrial applications from production of polyurethane foam

Yearly load - ? to WW

Uncertainty: N/A

Emissions during loading

Yearly load – 8 kg to IS

Uncertainty: C

Estonia was the third biggest producer of insulating foams in the world (after China and USA) in 2007. The production was 45 million bottles of foam in Estonia (60 million in China, 50 million in USA). It means that Estonia holds up to 29% from world market share of insulating foams (Ehitsuudised 11.10.2010²).

100% of MCCP is imported from Western Europe. MCCPs are used as fillers in the product, also acting marginally as plasticizer. Content of MCCPs is 5% to 15 % of overall canned product. 96% of foams are exported (70% to Russia), 3-4% are used in Estonian market (Ehitsuudised 11.10.2010).

The insulating foams are used in construction for mounting window- and doorframes, filling of cavities, sealing of openings in roof constructions and insulation materials, creating soundproof screens, filling of cavities around pipes, fixing and insulating of wall panels, roof tiles, etc.

1880 t of MCCP was used in Estonia in 2007, according to data from the web-page of Estonian Ministry of the Environment³ where 50 most common chemical substances in Estonia are given. This use is also registered in Chemicals Notification Centre (Estonian Health Board)⁴.

2 <http://www.ehitsuudised.ee/>

3 <http://www.envir.ee/964088>

4 <http://piksel.ee/kemikaalid/index.php?tid=sJfTXJ8iTThfYITkj7oHXglZU00aKZggJdIjUs8>





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Producers claim that there are no emissions of MCCPs to air during production. The amount of emissions to the wastewater is unknown at the moment. The amount of about 8 kg of spillage during loading is the producers' own estimation (taking into account the amount of substance used per year).

Further research is needed on that ES to calculate proper emission factors and hence calculate more accurate yearly loads to the environment.

2.3 Manufacture of paints, varnishes and similar coatings, printing ink and mastics

NACE: 20.3

Plasticiser in paints and varnishes: Formulation

Yearly load - ? to WW, AO

Uncertainty: N/A

MCCPs with chlorine contents around 50-60% are used as plasticisers in some paints, varnishes and other coatings. The main areas of application appear to be in corrosion or weather resistant coatings/paints for steel constructions, ships, industrial flooring, containers, swimming pools, facades and road markings (EU RAR 2005).

The MCCPs can be used as plasticisers in paints based on many resins, but are most commonly used in chlorinated rubber or vinyl copolymer-based paints. The chlorinated rubber-based paints are used in aggressive marine and industrial environments whereas the vinyl copolymer-based paints are used principally for the protection of exterior masonry.

The amount of MCCPs used in paints is unknown. Default emission factors from the TGD (ECB 2003) cited in the EU RAR (2005) are 0.1% to air and 0.3% to wastewater.

There are several paint producers in Estonia according to Prodcum 2008. As these companies are mainly sub-contractors for other EU producers, the information they are able to disseminate is limited and there is no proper information for calculating the yearly loads. Further research is needed.





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2.4 Construction of roads and motorways; Painting and glazing; Building of ships and boats; Treatment and coating of metals; machining

NACE: 42.11, 43.34, 30.1, 25.6, 49

Industrial use: Plasticiser in paints and varnishes: application

Yearly load - ? to WW

Uncertainty: N/A

MCCPs with chlorine contents around 50-60% are used as plasticisers in some paints, varnishes and other coatings. The main areas of application appear to be in corrosion or weather resistant coatings/paints for steel constructions, ships, industrial flooring, containers, swimming pools, facades and road markings (EU RAR 2005). Default emission factors from the TGD (ECB 2003) cited in the EU RAR (2005) are 0.1% to wastewater.

There are several activities taking place in Estonia under those NACE codes according to Prodcom 2008. We don't know what kind of products they use and if the products might contain MCCP. Further research is needed.

2.5 Manufacture of other chemical products n.e.c.; Forging, pressing, stamping and roll-forming of metal; powder metallurgy; Treatment and coating of metals; Machining

NACE: 20.59; 25.50; 25.61; 25.62; 24; 25; 28

Industrial use Extreme pressure additive in metal cutting/working fluids: formulation

Yearly load - ? to WW

Uncertainty: N/A

MCCPs are used in both oil-based and water-based (emulsion) metal cutting/working fluids. In most oil-based cutting fluids, the chlorinated paraffin content is around 5-10% (typically 5%), but can be up to 70% in some heavy drawing applications. In water-based metal cutting/working fluids, the chlorinated paraffin may be present typically at around 5% in the formulation. In use, this formulation is diluted (emulsified) in water to give the final metal cutting/working fluid. The typical dilution is around 1:20 with water. Thus if





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the chlorinated paraffin is present at 5% in the formulation, the concentration in the fluid in use is around 0.25%. Industry specific information (EU RAR, 2005) gives an emission factor of 0.25% to wastewater from formulation of metal cutting/working fluids.

There is reported use of this application in the Swedish Product register in 2007 (Swedish Chemicals Agency 2010) – as coolants and lubricants for metal forming and processing. There are several activities taking place in Estonia under those NACE codes according to Prodcom 2008. We don't know what kind of products they use and if the products might contain MCCP. However, we can assume the situation in Estonia to be similar to that in Sweden. Hence, if this application does take place in Estonia, the substances containing MCCPs are probably in use as well. Further research is needed.

Industrial use: Extreme pressure additive in metal cutting/working fluids: Use in oil based fluids

Yearly load - ? to WW

Uncertainty: N/A

The major losses of oil-based metal cutting/working fluids are associated with the swarf (chip and splinter). It is thought that the vast majority (90%) of swarf produced (and the adhering cutting fluid) is melted for re-use (EU RAR, 2005). Default emission factors from TGD (2003) cited in EU RAR (2005) are 18.5% to waste water, and 0.02% to air.

The release to the environment depends on the size of the facility and the presence of swarf reprocessing. The estimated emission factors are 4% for larger facilities with swarf reprocessing, and 18% for smaller facilities without swarf reprocessing.

There are several activities taking place in Estonia under those NACE codes according to Prodcom 2008. We don't know what kind of products they use and if the products might contain MCCP. Further research is needed.

Industrial use: Extreme pressure additive in metal cutting/working fluids: Use in emulsion based fluids

Yearly load - ? to WW

Uncertainty: N/A

Default emission factors from the TGD (ECB 2003), cited in the EU RAR (2005), are 31.6% to wastewater, and 0.02% to outdoor air. Industry specific information (EU RAR, 2005) indicates an emission factor of 50% to wastewater.





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There are several activities taking place in Estonia under those NACE codes according to Prodcom 2008. We don't know what kind of products they use and if the products might contain MCCP. Further research is needed.

2.6 *Manufacture of pulp*

NACE: 17.11

Release from recycling of carbonless copy paper

Yearly load – 4 kg to WW

Yearly load high – 100,04 kg to WW

Uncertainty: BBCC

MCCPs are used in carbonless copy paper (EU RAR, 2005). When this is recycled releases of MCCP can occur. Industry specific release estimation from the EU RAR (2005) gives an emission factor of 10%, *i.e.* fraction of the amount used that is released to wastewater. Figures on the actual recycling rate are unavailable.

The rate of paper recycling is many times lower in Estonia (17,5%) than in Western and Northern Europe. The majority of the waste paper collected in Estonia is exported (55,6%) (Maves 2008), 39% is used for making new paper, cardboard, insulation materials or packaging. 3000 tons of waste paper is used by Räpina Paper Mill a year (10% from collected paper).

Räpina Paper Mill is a paper production plant, which uses scrap paper collected in Estonia as a raw material. Räpina Paper Mill does not accept waste paper soiled with lubricant, freshed and waxed paper, carbonless (NCR) and carbon paper, parchment, glassine, and photo paper. But they use material from confidential documents that are disposed and can contain copy paper. The other paper mill does not recycle paper (information from their IPPC permit⁵). Therefore we can assume that some of the MCCPs can be recycled.

The yearly load was calculated as follows: 20 tons of copy paper is recycled in Estonia a year, 5% of it could contain MCCPs, the MCCP content of the paper being around 3-4% by weight then, and when recycled, 10% of the amount is released to wastewater

5 <http://www.ippc.envir.ee/english/index.htm>





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The yearly load high is the result derived from the EU SFA, using the Estonian population as a basis for scaling. We left it here for comparison and consider it to be very inaccurate.

2.7 Emission from (private) consumption; during lifetime use of articles, goods and chemical products and preparations

Release from use in PVCs over their service life through volatilisation, leaching, wear and tear

Yearly load – 0-70 kg to AO

Yearly load – 0-70 kg to WW

Uncertainty: ACCC

Although MCCPs are of low vapour pressure at ambient temperatures, the vapour pressure is not so low as to preclude the possibility of volatilisation from plastics and other polymers during their service life. This is particularly true of the MCCPs with lower chlorine contents.

MCCPs can also be emitted from leaching of plasticiser from PVC flooring during washing. The derived emission factor will also include contributions from loss of particulates, degradation etc. from the material due to weathering or erosion.

In the EU RAR (2005) an emission factor of 0.05% over the life time is given for volatilisation from PVC. An emission factor of 0.05% over life time is given for leaching.

The yearly load high is the result derived from the EU SFA, using the Estonian population as a basis for scaling. The results are given as a range as we do not have better data for Estonia.

Release from use in paints over their service life through volatilisation, leaching, wear and tear

Yearly load – 0-90 kg to AO

Yearly load – 0-33 kg to WW

Uncertainty: ACCC

Like for PVC above MCCPs can also volatilise from paints. An emission factor 0.4% (over 5-7 years life time) is given in the EU RAR (2005). An emission factor of 0.15% of the amount MCCPs used in paints is given in the EU RAR (2005) for release over their service life (5-7 years) through leaching.





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The yearly load high is the result derived from the EU SFA, using the Estonian population as a basis for scaling. The results are given as a range as we do not have better data for Estonia.

Release from use in sealants over their service life through volatilisation, leaching, wear and tear

Yearly load – 0 - 3,2 kg to AO

Yearly load – 100 – 290 kg to WW

Uncertainty: ACCC

MCCPs can also volatilise from sealants. An emission factor of 0.05% (over life time) volatilised of the amount MCCPs used in sealants is given in EU RAR (2005). An emission factor of 0.15% (over 10-30 year life time) for release from use in paints over their service life through leaching is given in the EU RAR (2005). In this case a service life of 10-30 years is estimated and taken into account.

The yearly load high is the result derived from the EU SFA, using the Estonian population as a basis for scaling. The results are given as a range as we do not have better data for Estonia.

Release from use in rubber/polymers over their service life through volatilization

Yearly load – 0 – 3 kg to AO

Uncertainty: ACCC

MCCPs can also volatilise from rubber. An emission factor of 0.05% volatilised (over the life time) of the amount MCCPs used in rubber is given in EU RAR (2005). For the applications in rubber and polymers other than PVC, the potential for exposure to water appears to be limited according to (EU RAR, 2005), and leaching was not considered for this application.

The yearly load high is the result derived from the EU SFA, using the Estonian population as a basis for scaling. The results are given as a range as we do not have better data for Estonia.

Waste remaining in the environment

Yearly load – 3 – 3,5 kg to AO

Yearly load – 740 – 880 kg to FSW

Yearly load – 270 – 450 kg to WW

Yearly load – 2230 – 2630 kg to FS





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Uncertainty: CCCC

MCCPs may also enter into the environment as a result of “waste” from the products themselves during their useful lifetime and disposal, for example by erosion/particulate losses of polymeric products, paints and sealants as a result of exposure to wind and rain or may occur as a result of their mode of use.

No agreed method is currently included in the TGD (ECB 2003) for addressing these potential sources of release. The yearly loads given below are estimated in the EU RAR (2005). They are based on calculations from DEHP and then fitted to the individual applications of MCCP, and the amounts used in the applications (EU RAR 2005).

Rough estimations of emission factors used in the EU SFA are given in Table 4 below. As these releases of MCCP are essentially bound within a polymer matrix, the actual bioavailability and environmental behaviour of the MCCP is unknown.

Table 4. Emission factors and yearly load for release of MCCPs from waste remaining in the environment (based on figures from 1997 (EU RAR, 2005)).

| Compartment | Emission factors |
|---------------|------------------|
| Air | 0.001%-0.002% |
| Surface water | 0.4%-0.5% |
| Waste water | 0.015%-0.025% |
| Soil | 1.2%-1.5% |

The yearly loads for Estonia are the results derived from the EU SFA, using the Estonian population as a basis for scaling.

2.8 Emission from historical activities, for example contaminated land

Leakage from municipal landfill

Yearly load – 0 – 54 kg to WW

Uncertainty: CCCC

Leakage of MCCPs from municipal landfills can occur from disposed material containing MCCPs. A figure for leakage on the European scale is given in EU RAR (2005). The figure is based on calculations for DEHP and fitted to the production volume of MCCPs within the EU (EU RAR 2005). The emissions could also go to surface water or to soil, depending on the techniques used for treating leakage at the landfills. Calculation from





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these figures gives an emission factor of 0.003%. The yearly load high is the result derived from the EU SFA, using the Estonian population as a basis for scaling. The results are given as a range as we do not have better data for Estonia.

2.9 Construction

NACE: F

Yearly load - ? to WW

Uncertainty: N/A

Reported use of MCCPs in Sweden (Swedish Chemicals Agency 2010) in 2008, from the construction industry, includes use as insulating materials and sealants. Further, for use as adhesives, impregnation agents for paper, putty, rust preventives, and filler materials. Reported use in Sweden in the Swedish Product register in 2008 (Swedish Chemicals Agency 2010) from transport and storage include the use of anti corrosive paint.

We can assume the situation in Estonia to be similar to that in Sweden. Hence, if these applications do take place in Estonia, the substances containing MCCPs are probably in use as well. Further research is needed.

2.10 Crop and animal production, hunting and related service activities

NACE: 01

Dispersion of sludge on farmland

Yearly load of this ES is considered in ES "MCCP in sewage sludge from municipal STPs".

When entering a WWTP MCCPs mainly adsorbs to sewage sludge. Spreading of sludge from WWTP that treat effluent that contains MCCPs can be a route of exposure to soil.

2.11 Worldwide activities outside the region, for example atmospheric deposition of long range transport

NACE: Y



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Atmospheric deposition

Yearly load - ? to FSW

Yearly load - ? to FS

Yearly load - ? to AS

Uncertainty: N/A

Atmospheric deposition is a possible source of MCCPs to the environment. Deposited MCCP could originate from sources outside as well as inside the EU as the substance is still in use within the union.

Few measurements of MCCPs in air are available, but a report on MCCPs measured in air cited in Friden et al (2007) gives concentrations of MCCPs in air in Lancaster, UK, of 3040 pg/m^3 . However, we don't consider this EF to be representative for Estonia, hence the yearly loads could not be calculated. However, for future references when there will be monitoring data, the division into the compartments was also made according to the data from Estonian Environment Information Centre (2010).

2.12 Sewerage

NACE: 37

Emissions of MCCP with effluent water from municipal STPs.

Yearly load – 51,79 – 59,16 kg to FSW

Yearly load – 22,19 – 25,35 kg to CSW

Uncertainty: CAAC

The calculations were done using the data from COHIBA WP3 and the preliminary results from the BaltActHaz project – that gave us the EF. The EF was considered to be the average result of all WWTP-s. For min scenario, the results under LOQ were considered to be 0; for max scenario, the results below LOQ were considered to be LOQ. The EF was then multiplied by the EFM, i.e. the amount of effluents produced per person a day – 125 litres (according to Statistics Estonia 2010), the number of inhabitants (1 340 021 according to Statistics Estonia 2010), and the number of days a year (365).

MCCP in sewage sludge from municipal STPs.

Yearly load – 2,45 – 4,61 kg to AS

Yearly load – 5,21 – 9,79 kg to FS

Uncertainty: CAAC





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In the statistical report by Wieland (2003) sludge disposal in the EU member states is described. According to this report 32 % of the sludge was used within agriculture, 13 % was composted, 25 % landfilled, 13 % incinerated and 17 % was disposed using other methods. The situation in the candidate countries at the time (CZ, HU, PL, SI and SK) was rather similar, the biggest difference being less incineration (1 %) and more landfilling (39 %).

As a calculation exercise the amount of MCCP disposed in the sewage sludge can be estimated. According to the EU statistics (Wieland 2003) the yearly production of sewage sludge is approximately 23 kg dry solid per capita. In the statistics from the year 2002 (Wieland 2003) 32 % of the sewage sludge is used within agriculture. When calculating the results, disposal on landfill, compost and other are designated to the compartment FS, incineration is assumed to achieve complete combustion.

The calculations for Estonian yearly load were done using the data from COHIBA WP3 and the preliminary results from BaltActHaz project that gave us the EF. The EF was considered to be the average result of all WWTP-s. The representability is highly uncertain due to limited data. The EFM is the one from European SFA-s, considered to be representative to Estonia by Mr Kõrgmaa, an expert of WWTPs and sewage sludge (personal communication). The yearly load was calculated by multiplying EF with EFM and number of inhabitants in Estonia.

2.13 Treatment and disposal of non-hazardous waste

NACE: 38.21; 38.22

MCCPs in landfill leachate

Yearly load – 0 – 0,00411 kg to FSW

Yearly load – 0 – 0,00411 kg to FS

Uncertainty: C

The calculations were done using the excel sheet provided by IVL. The data used was from the COHIBA WP3 results from the study of landfill leachate. However, this result is considered extremely inaccurate. There was only one result from landfill leachates for Estonia - and that was a nd result, hence we also used the Lithuanian max result for Estonia as we consider it to be similar enough (we also considered Finnish, Swedish, and Latvian max MCCP results, but these were a little lower) as it is based on two samples from one landfill. We assume the load to be higher, considering the high amounts of





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MCCPs used in different products and also the amount from leakage from landfills calculated in a previous ES.

We also think that the leachate from the hazardous wastes should be in a different ES. However, we didn't find it meaningful to create an additional ES as we have no data from the effluents of leachates of hazardous waste landfills.



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3 SFA diagram

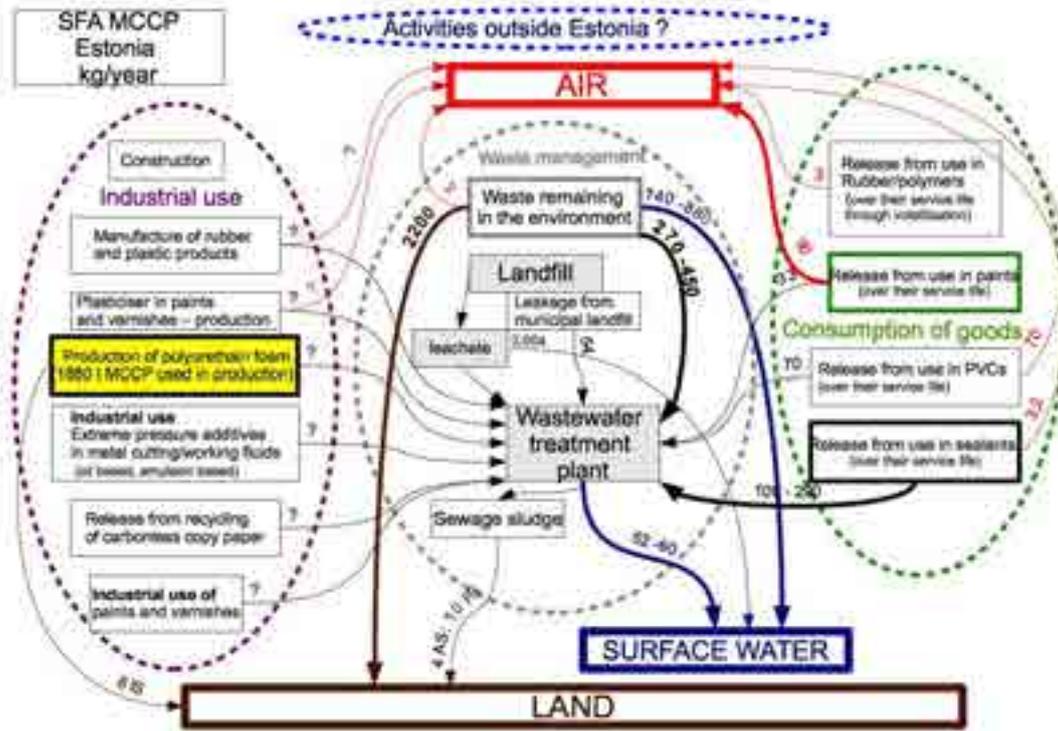


Figure 2. SFA diagram for MCCPs in Estonia.



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4 Conclusions

4.1 Quantitative estimation of the most relevant sources to each environmental compartment (Soil, water and air)

The most important source for MCCPs is the production of polyurethanes. The use of MCCPs in this application is registered in both Chemicals Notification Centre and Estonian Ministry of the Environment has listed MCCP as one of the 50 most common chemical substances in Estonia. This situation is in dark contrast with other hazardous substances that are generally not registered in Estonia due to small volume used. However, the releases from this application are mainly unknown, except the estimated 8 kg to IS.

One of the most important sources seems to be the waste remaining in the environment that give high emissions to all main compartments (3 kg AO, up to 880 kg to FSW, up to 450 kg WW, and up to 2630 kg FS a year).

Significant amounts of MCCP emissions are also coming from private consumption and construction in Estonia as the substances are present in many building materials, e.g. PVCs, paints, sealants, rubber and polymers etc. For example, besides the waste remaining in the environment, high emissions to come also from the use of sealants (up to 290 kg to WW), and use of paints over the service life (up to 90 kg to AO).

4.2 A qualitative estimation of time trends for future scenarios.

Risk reduction measures have been placed for the short-chain (C₁₀₋₁₃) chlorinated paraffins, for use in metal cutting/working fluids and leather fat liquors. The MCCPs have similar uses, and can be considered as replacements for the short-chain chlorinated paraffins in some of these applications. Any reduction in use of the short-chain chlorinated paraffins in these areas could lead to an increased use of MCCPs as a replacement. The effect of such substitutions is currently unknown, although an increasing trend in use in metal working/cutting fluids between 1994 and 1997 was shown in EU RAR (2005). More recent data on this was not found.





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Since the emission estimates mainly are based on data from 1997 it is likely that the situation has changed. Some of the sources mentioned here may not be relevant and some may be missing. The proportions between different uses may also have changed.

One of the companies in the Estonian main industrial application for MCCP has declared that they have already started the work to substitute the use with other less hazardous substances. We can assume that the uses in industrial part are decreasing.

To make qualitative estimations further studies are needed to map the current situation for Estonia.

In our opinion, the most relevant reduction possibilities are in the industrial sector, with the use of BAT and BEP. Also, raising the awareness of the general public and the industry managers is an important step to be taken. It has been our and our colleagues' experience that, quite often, the managers in the industry are not aware of their potential use of hazardous substances as the substances are often additives and may be often detected only by thorough research through the safety cards. This is also one reason why we didn't consider the information straight from the producers to be of A-type accuracy.

Also the proper treatment of wastewater would give a good effort to protect that the MCCPs would not end up in the environment.





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ANNEX L - Substances flow analysis for endosulfan in Estonia

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This study was carried out under the COHIBA study from May 2010 to May 2011. This report is based on the SFA Endosulfan (EU 27) by IVL Swedish Environmental Research Institute. The results are for Estonia. Many of the results are rough approximations that cannot be taken as exact results for Estonia, but more as a base to plan future studies. The results are for Estonia.

1 Introduction

Endosulfan is a chlorinated organic compound used as a pesticide against insects and spiders. Technical grade endosulfan is a mixture of the two isomers α -endosulfan and β -endosulfan, both biologically active. The main metabolite of endosulfan is endosulfan sulphate.

This substance flow analysis concerns α - and β -endosulfan. The fate of endosulfan sulphate is however also of importance due to the toxicity also of this metabolite.

Table 1: CAS numbers for endosulfan as listed in POPRC (2009)

| Substance name | CAS nr |
|--|------------|
| alpha (α) endosulfan | 959-98-8 |
| beta (β) endosulfan | 33213-65-9 |
| Technical endosulfan | 115-29-7 |
| Endosulfan sulphate* stereochemically unspecified | 1031-07-8 |

* Technical endosulfan is a 2:1 to 7:3 mixture of the α - and the β -isomer.

1.1 Physical chemical properties

The chemical structure of endosulfan is shown in **Figure 1** and the physical and chemical properties the endosulfan isomers and the degradation product endosulfan sulphate are listed in **Table 2**.

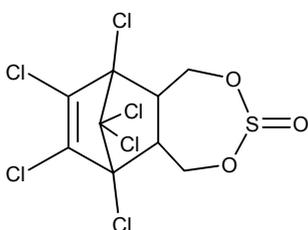


Figure 1: Chemical structure of endosulfan



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Table 2: Physical chemical properties of endosulfan (POPRC 2009 if not annotated)

| Property | α isomer | β isomer | Technical mixed isomers | endosulfan sulphate |
|--|--------------------------|--------------------------|---|--------------------------|
| Physical state at npt | | | Colourless crystals ^a | |
| Molecular weight (g/mol) | 406.96 | 406.96 | | 422.96 |
| Melting point (°C) | 109.2 | 213.3 | 70-124 | 181-201 |
| Vapour pressure (Pa, at 25°C) | 1.05E-03 | 1.38E-04 | 2.27E-05 – 1.3E-03, recommended value: 1.3E-03 | 2.3E-05 |
| Log octanol-water partition coefficient (log Kow, at pH 5.1) | 4.7 | 4.7 | 3.6 | 3.77 |
| Water solubility (mg/l at pH 5, 25°C) | 0.33 | 0.32 | 0.05-0.99, recommended value: 0.5 | 0.22 |
| Dissociation constant | n.a. (no acidic protons) | n.a. (no acidic protons) | n.a. (no acidic protons) | n.a. (no acidic protons) |
| Henry's Law Constant (Pa m ³ /mol, at 20°C) | 1.1 | 0.2 | 1.09-13.2, recommended value: 1.06 | |

a) Footprint PPBD

1.2 Regulatory status

Endosulfan has been used world wide since the 1950's. Estonia has never produced endosulfan and the import of the substance was banned with Estonian legislation in 1968¹. The regulation for storage and usage of residues was also regulated very precisely with this decree. Since 1991 the Estonian legislation has been brought to compliance with the European legislation. The Directive 79/117/EC (European Council 1978) was adapted in 1999. Estonia became a member of EU in May 2004. Endosulfan was excluded from Annex 1 of EU Directive 91/414 (Commission decision of 2 December 2005, 2005/865/EC). In directive 2008/105/EC, the daughter directive to the water framework directive (2000/60/EC), environmental quality standards (EQS) are set for endosulfan (AA-EQS: 0.005 and 0.0005 µg/l for inland surface waters and other surface waters, respectively).

¹ Kloororgaaniliste taimekaitsevahendite sisseveo keelustamine Eesti NSV Ministrite Nõukogu määrus, 21.10.1967 nr 414 aastast 1968; "The banning of importing the chloroorganic pesticides", the decree of Council of Ministers of Soviet Estonia, 21.10.1967, No 414, since 1968





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Endosulfan is also listed in Commission regulation 1451/2007 as an active substance “identified as existing” and thus included in the review programme under the biocide directive (98/8/EC).

Endosulfan is listed by the Chemical Review Committee (CRC) as a candidate substance for inclusion on Annex III of the Rotterdam Convention (Estonia consolidated the convention in March 2006). Endosulfan is also listed as a chemical for review under the Stockholm Convention on persistent organic pollutants (Estonia consolidated the convention in 2008).

The national monitoring for the residues of pesticides covers only foodstuffs and fodder for animals at this time in Estonia.

1.3 Production

Estonia has never produced endosulfan.

1.4 Use

Estonia has not used endosulfan since 1970-s and all the reserves have been removed.

1.5 Environmental fate

In the report of the Swedish screening of endosulfan, Palm Cousins *et al.* (2005) have made an assessment of the likely environmental fate, and partition behaviour, of endosulfan using the Equilibrium Criterion (EQS) model (Mackay *et al.* 1996). The results of this modelling exercise indicated that the mode of release, *i.e.* emission to air, water or soil, influences the partitioning of the substance to a high degree. The model predicted that releases to a certain medium would result in a predominant partitioning to the same medium.

The degradation of endosulfan generates several transformation products of which the main metabolite during aerobic microbial degradation is endosulfan sulphate, a substance with similar toxic properties as the mother compound. Other, more polar, degradation products of endosulfan includes endosulfan diol, endosulfan lactone and endosulfan ether. The degradation pattern of endosulfan differs in the different media. Abiotic degradation of endosulfan is believed to occur mainly by hydrolysis, a process relevant at high pH values, and oxidation by OH radicals in the atmosphere. (POPRC 2009)

Endosulfan and the main metabolite endosulfan sulphate are persistent compounds with degradation half-lives for the sum of the α - and β -isomers and endosulfan sulphate





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reported in POPRC (2009) ranging from 28-391 days in soil, 3.3-273 days in water-sediment systems (Jones 2002; Jones 2003; both quoted in POPRC 2009) and 2-27 days in the atmosphere (Buerkle 2003, quoted in POPRC 2009).

In the draft dossier on endosulfan by UNECE (2004) it was concluded that, based on data from a range of studies, endosulfan and endosulfan sulphate have potential for long range transport. Losses of endosulfan and endosulfan sulphate to air may be substantial after agricultural application, a process enhanced by increased temperatures and furthermore, the substances have been found in remote areas.

1.6 Environmental levels

Due to the persistence and long-range transport of endosulfan and endosulfan sulphate these substances can be found in the environment also in regions where endosulfan has been banned, *e.g.* in Sweden. We can assume that it is also relevant for Estonia. No monitoring data available for Estonia. Therefore we have put the chapter from EU SFA here to give some background information.

Palm Cousins *et al.* (2005) measured endosulfan in air, deposition, sediment and biota as well as in landfill and compost leachate and sludge from municipal sewage treatment plants (STP) in Sweden. Both endosulfan isomers and endosulfan sulphate were found in air and deposition. In sediment, biota and compost leachate samples, only the metabolite endosulfan sulphate was found in detectable levels. In the sludge and landfill leachate samples neither endosulfan nor its metabolite were found in detectable levels.

Selected results on environmental levels of endosulfan at European locations, as reported in the literature are listed in **Table 3**.



Table 3: Environmental levels on endosulfan at European locations, as reported in the literature.

| Location | α -isomer | β -isomer | endosulfan sulphate | References |
|--|--------------------|-------------------|-----------------------|---|
| <i>Air (pg/m³)</i> | | | | |
| Råö, Sweden background 2004, 2006 | 1.9-35 | 0.2-2.4 | 0.07-1.2 | Kaj <i>et al.</i> 2007; Palm Cousins <i>et al.</i> 2005 |
| Pallas, Finland background 2004, 2006 | 2.5-19 | <0.08-0.36 | <0.05-0.43 | Kaj <i>et al.</i> 2007; Palm Cousins <i>et al.</i> 2005 |
| Sweden, urban air | 9.9-28 | <2-2.8 | <0.4-0.79 | Palm Cousins <i>et al.</i> 2005 |
| Central Pyrenees 2000-2003 | 1.0-6.6 | 0.5-1.6 | - | Van Drooge <i>et al.</i> 2004 |
| High Tatra 2001-2002 | 1.4-42.8 | 0.7-7.5 | - | Van Drooge <i>et al.</i> 2004 |
| <i>Water (ng/l)</i> | | | | |
| Europe ^a | 7.3 \pm 24.2 | 5.3 \pm 7.3 | 6.9 \pm 3.3 | EC 1999 (Annex I) quoted in OSPAR 2004 |
| Germany ^b , 2002-2004 | 10.4/12.3/58 | 12.6/11.9/26.1 | | UBA 2005 |
| <i>Suspended Solids (μg/kg)</i> | | | | |
| Germany, Main 2000-2001 | 19 | | | BLfW 2002 |
| Germany, 2002 | 334.5 ^c | | | HLUG 2003 |
| <i>Sediment (ng/g DW)</i> | | | | |
| Background Sweden (n=5) | <DL ^d | <DL ^d | 0.09-0.15 | Palm Cousins <i>et al.</i> 2005 |
| Urban, Sweden (n=6) | <DL ^d | <DL ^d | <0.3-0.45 | Palm Cousins <i>et al.</i> 2005 |
| <i>Biota (ng/g lipid)</i> | | | | |
| Background Sweden (n=6) | <DL ^e | <DL ^e | <DL ^f -7.7 | Palm Cousins <i>et al.</i> 2005 |
| Baltic Sea (n=23) | <LOQ ^g | <LOQ ^g | <0.3-4.6 ^g | Lilja <i>et al.</i> 2009 |





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- a) Monitoring data included in the COMMPS procedure (combined monitoring- and modelling-based procedure for the prioritization of substances), monitoring stations with less than 10 % detection frequency have been discarded, and the data can thus be assumed to represent the situation in areas where endosulfan is under active use. Values are median values \pm SD.
- b) 6 single measurement are above EQN in the joint data pool of UBA and federal states: Oder 26.1 and 11.9, Havel: 10.4, 12.3 and 12.62 Vechte: 58
- c) Total endosulfan in suspended solids in wastewater of an industrial sewage plant
- d) DL varied between 0.5-7 ng/g dry weight
- e) Herring and Baltic herring, DL varied between 2-9 ng/g lipid
- f) DL varied between 1-46 ng/g lipid
- g) Herring, perch and flounder; LOQ varied between 3.8-49 ng/g lipid for the α - and β -isomer



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2 Sources of emissions of endosulfan

The uncertainties in the following emission strings are given with four letters, the first letter representing uncertainty for EF, the second for EFM, the third for division into compartments and the fourth for the yearly load. Uncertainty is classified according to the principles described in “Dealing with uncertainty in substance flow analysis within the COHIBA project”, a PM describing how data uncertainty is graded in WP4 of the COHIBA project.

If the Estonian yearly loads were scaled from the EU yearly load to Estonian population, the Estonian population was considered to be 0,3% of the EU population. This accuracy level was considered to be enough for given study; especially considering the very high uncertainty levels in other emission strings.

Emissions of endosulfan refer to the sum of the α - and β -isomer. For sources that could also emit endosulfan sulphate in considerable amounts also this substance has been included.

2.1 Growing of non-perennial crops; Growing of perennial crops

NACE codes: 01.1 Growing of non-perennial crops

01.2 Growing of perennial crops

Yearly load – 0 kg to AS, SW, OA

These strings are not relevant for Estonia as there has been no usage for the substance in agriculture for almost 40 years (See the regulatory status in this document.)

2.2 Manufacture of food products

Emissions of endosulfan during manufacture of food products

NACE codes: only relevant for primary produce treated with endosulfan during cultivation, e.g. various fruit, vegetables and cereals.

Yearly load – insignificant.

Uncertainty: C-C-

This source could be relevant for Estonia. There are manufacturers of food products in Estonia and the producers may import some of their raw materials from countries outside





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the EU that still could be using endosulfan. At the same time this hypothesis cannot be confirmed according to the data we have at the moment. There is no official statistical data about the import of foodstuffs that may contain endosulfan (according to Statistics Estonia). Hence we concluded this string to have “insignificant” yearly load for Estonia. Another reason for concluding this was because of the data how much Estonian people produce and consume self-cultivated products. For example – 80% of the potatoes were grown locally in 2007 (32% of these were grown by small farmers who don’t use any chemicals in Estonia).

For example the statistics for 2007 states that the amount of locally produced foodstuffs as such: 80% of potatoes (32% of them produced by small farmers), other vegetables 63% (29% of which is produced by small farmers or by residents). 29% of berries and 28% of juices were grown and made by residents². Small farmers and local residents do not use any chemicals.

2.3 Manufacture of pesticides and other agrochemical products

Production of endosulfan

NACE codes: 20.20 Manufacture of pesticides and other agrochemical products

Yearly load – 0 kg to OA, WW, FS

Uncertainty: AAB-

There has never been any production of endosulfan in Estonia.

2.4 Other – Private consumption

Endosulfan residues on foodstuffs

Yearly load – insignificant

Uncertainty: --CC

Reference source not found

² Elanike toitumisharjumused ja toidukaupade ostueelistused, 2007 Eesti konjunkturi instituudi läbiviidud uuring; The habits of nutrition and preferences of buying foodstuffs of Estonian population, Estonian Institute of Economic Research 2007, also available at: http://www.agri.ee/public/juurkataloog/UURINGUD/eki_tarbijauuringud/Elanike_toitumisharjumused_ja_toidukaupade_ostueelistused_2007.pdf.





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“Leaf crops” and “root crops” (hereafter called foodstuffs) with endosulfan residues (α -isomer, β -isomer and endosulfan sulphate) enter European households either as non processed or processed foodstuffs. See chapter 0 for more information on data and assumptions made.

Household consumption – foodstuffs

For our calculations we used the calculation form provided by Hanna Andersson (EY SFA excel). The Estonian population was 1 340 021 inhabitants in 01.01.2010. The yearly amount of endosulfan on foodstuffs used by households in Estonia could be estimated to be in the range 0.48-3.28 g.

There has been no usage of endosulfan in Estonia for at least 40 years. Also, according to Estonian statistics, of all the fruits and vegetables used by Estonians, 73% are produced nationally and small farmers that mostly do not use any chemicals at all produce 30% of that amount. Also, according to the recommendations 2006/88/EC and 2006/794/EC the member states should control and monitor the levels of dioxins and PCBs, including non-dioxin like PCBs, in food and feed. According to Estonian national monitoring programme of food 2008³, α -endosulfan, β -endosulfan, and endosulfan sulphate were not detected in analysed samples.

Therefore, we can conclude that the yearly load of endosulfan in Estonia from household foodstuff consumption is insignificant.

Losses from wood impregnated with preservatives containing endosulfan

Yearly load – 0 kg

Historical use of impregnated wood is a possible source of endosulfan, not further quantified in this study.

Endosulfan emission from cotton textiles

Yearly load - ?

The use of endosulfan as a pesticide on cotton crops could potentially lead to endosulfan residues on cotton textiles. This source has not been possible to verify.

³

http://www.terviseamet.ee/fileadmin/dok/Kasulikku/Laborid/Toidu_kvaliteet_ohutus_08.pdf





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2.5 Other – Worldwide activities outside Estonia

Atmospheric deposition of endosulfan in Estonia

Yearly load low 0,047 and high 1,77 kg to SW (6%).

Yearly load low 0,23 kg/y and high 8,9 kg to AS (30%).

Yearly load low 0,5 and high 18,9 kg to FS (64%).

The yearly load low and high for Estonia was calculated, scaling the EU yearly load low and high to Estonian territory (45227 km²). Data from the map of Estonia was used for designating the loads to compartments. The Estonian territory is divided as follows: 6% surface water, 30% agricultural soil and 64% forest soil⁴.

EU emission factors were used for calculation of atmospheric deposition 0,047 ng/m² day for low and 1,8 ng/m² day (Kaj L., Ekheden Y., Dusan B., Hansson K., Palm Cousins A., Remberger M., Brorström-Lundén E. and Schlabach M., (2007) "Screening 2004 - uppföljningsprojekt". IVL Rapport B 1745). During the COHIBA project new atmospheric deposition monitoring data from Sweden came available.

Deposition numbers from Swedish air database (summary made by IVL partners: Swedish Environmental Protection Agency: National Air Monitoring National Air Database, www.ivl.se) were used to calculate the yearly load. We used average value after discussion with our air monitoring specialist Erik Teinmaa. The Swedish monitoring stations are located on the similar latitude and we considered it comparable to Estonia. The average deposition per day on 2009 was 0,05 ng/m². No new calculations of yearly load were made. The yearly load low can be considered more accurate at the moment in our region.

2.6 Sewerage

NACE code: 37.00 Sewerage

Emissions from STPs - effluent water

Yearly load - insignificant

As all the results from the WWTPs were below the LOQ, and there are no other sources to suggest otherwise, we assume the EF and therefore the yearly load to be insignificant. We also assume there is no endosulfan in Estonia, so this number is 0.

⁴

Estonian forestry 2009 last entered 15.03.2011
<http://www.keskkonnainfo.ee/failid/forestry2009/EstonianForestry.swf>



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Emissions from STPs - sewage sludge

Uncertainty: CAA-

Yearly load - 0,0163 kg to AS

Yearly load - 0,0381 kg to FS

The EF was considered to be the average result of all WWTPs. The representability is highly uncertain due to a very limited amount of data. The EFM is the one from European SFAs, considered to be representative to Estonia by an expert. The yearly load was calculated when multiplying EF with EFM and number of inhabitants in Estonia.

The data for endosulfan in sewerage sludge is extremely scarce. The analyses of endosulfan in sewerage sludge performed under the Work Package 3 of the COHIBA project were practically the first ones to be done in Estonia. Therefore, further research is needed as we assume that if there are any residuals of endosulfan, most likely these will end up in sewage sludge of the wastewater treatment plants.

2.7 Manufacture of wood and of products of wood and cork, except furniture; manufacture of articles of straw and plaiting materials

Emissions from sites manufacturing impregnated wood

NACE codes: Only relevant for impregnation of wood

There is no data for usage of endosulfan on this field in Estonia.

2.8 Treatment and disposal of non-hazardous waste; Treatment and disposal of hazardous waste

Endosulfan sulphate in compost leachate

Yearly load - ?

This ES could be somewhat relevant for Estonia due to the possible load of endosulfan from foodstuffs originating from countries where endosulfan is still in use, however, there is no data available.

Endosulfan sulphate in landfill leachate

Yearly load - 0,0384 kg to FSW

Yearly load - 0,0384 kg to FS





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Uncertainty: ---C

COHIBA study (Work Package 3 analyses) indicated that neither the α - nor β -isomers of endosulfan were found from the leachate of a major old Estonian landfill. However, endosulfan sulphate, a metabolite of endosulfan was found in one of the two samples (38,4 ng/l) performed under the COHIBA study, significantly exceeding the AA-EQS (5 ng/l) and MAC-EQS (10 ng/l) for inland surface waters. The yearly load was calculated from that result, using the calculation sheet provided by IVL.

However, one must keep in mind that this data is extremely inaccurate as there were only two samples taken from one landfill in Work Package 3 and only one of them showed any results for any isomers over the limit of quantification (5 ng/l). Hence the probability factor C. Still, we assume this result to be more accurate for Estonia than the yearly load scaled down from the European SFAs.

However, it is obvious that further research is definitely needed for the endosulfan isomers in landfill effluents in Estonia. We assume that landfills may be an important source for endosulfan sulphate (but probably not for α - and β isomers) in Estonia. There has been no research done for endosulfan in compost in Estonia.

2.9 Manufacture of textiles and 14 manufacture of wearing apparel

Endosulfan emissions from cotton fabric

NACE codes: Only relevant for cotton textile

Yearly load - ?

Cotton harvested from crops treated with endosulfan could potentially contain endosulfan residues that will be washed out either during processing of the cotton in to textile fibres and/or during the manufacture of the textile or textile articles. This potential source has not been possible to verify.

2.10 Manufacture of chemicals and chemical products

Chemical industry

NACE codes: 20.14 Manufacture of other organic basic chemicals

Yearly load – 0 kg

Uncertainty: ---A, reference source not found





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There has never been any usage of endosulfan in the chemical industry in Estonia.

2.10 Other – Historic activities

Soil to air transfer from land areas contaminated from historic use of endosulfan as a pesticide. This source is however not possible to quantify within the scope of this study, but will be addressed in the modelling task within the COHIBA project.



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3 SFA diagram

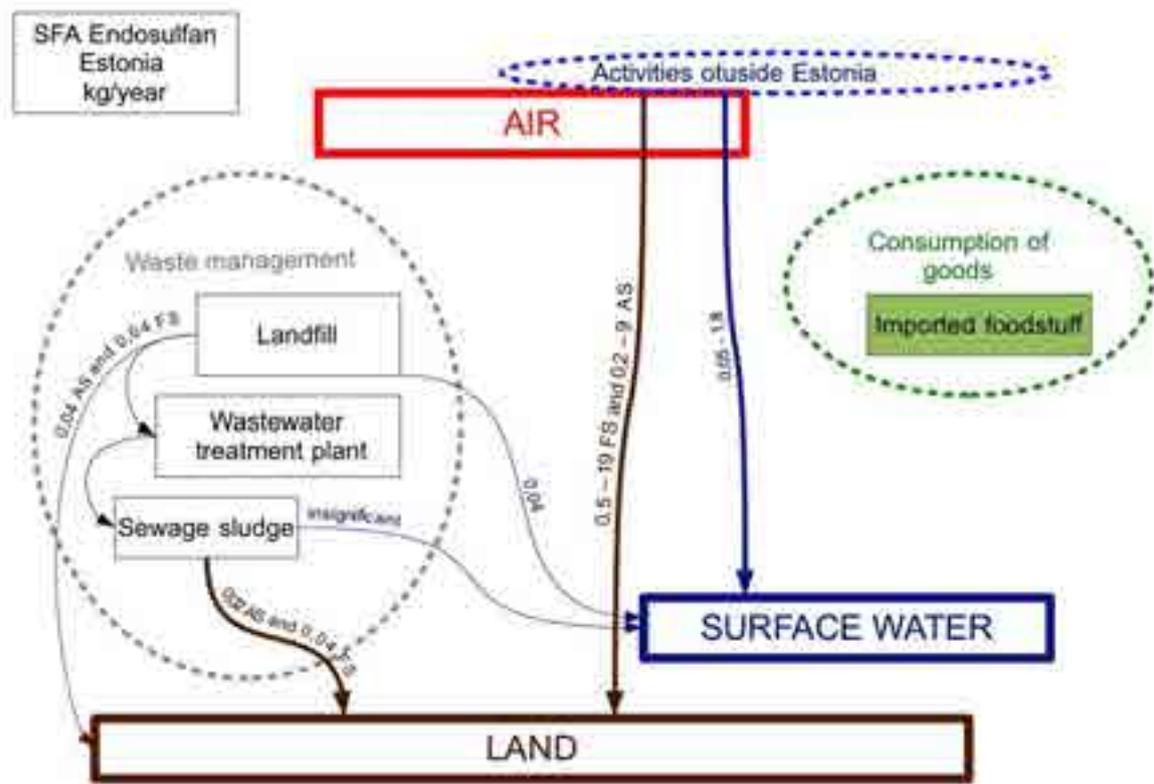


Figure 2. SFA diagram for endosulfan in Estonia.



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4 Conclusions

4.1 Quantitative estimation of the most relevant sources to each environmental compartment (soil, water and air).

As the major field of application for endosulfan, *i.e.* the use as a plant protection product, is now banned within EU agricultural use of the substance is not longer a source of the substance within EU27. Thus diffuse sources originating from activities outside EU have instead become more important. Long-range atmospheric transport of endosulfan and subsequent deposition on land and surface water and endosulfan on imported foodstuffs have been identified as two possible important sources. The yearly load of endosulfan from atmospheric deposition to surface water in Estonia was estimated to be 0.05-1,77 kg and 0.7-27 kg for the yearly load of endosulfan from atmosphere to land. The load to wastewater originating from endosulfan residues in foodstuffs was considered to be insignificant. The contribution of endosulfan via imported foodstuffs could thus be underestimated, the emissions from the WWTP overestimated or a source of endosulfan may be missing.

All of the estimations are associated with large uncertainties and the data presented should be interpreted with caution.

4.2 A qualitative estimation of time trends for future scenarios.

Recognition of the hazardousness of endosulfan, as well as its potential for long range transport in the atmosphere, will probably lead to further decreased emissions of the substance. The fact that active use of endosulfan should already have been discontinued within EU, does however mean that the rate and character of further decreased emissions are difficult to foresee.





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ANNEX M - Substance flow analysis for Hg in Estonia

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This study was carried out under the COHIBA study from May to December 2010. The results are for Estonia. The analysis does not refer to a specific year, but the most recent available data has been used. Many of the results are rough approximations that cannot be taken as exact results for Estonia, but more as a base to plan future studies.

1. Introduction

Mercury is a naturally occurring element, and is regulated by a number of European rules. Elemental mercury (Hg^0) is the only metal in liquid form at room temperature. Mercury is an extremely rare element in the earth's crust. It is found either as a native metal (rare) or in different minerals, with cinnabar (HgS) being the most common ore. The metal is extracted by heating cinnabar in a current of air and condensing the vapour. Mercury is used in various industries and in products commonly consumed. At present, several mercury applications are limited or forbidden. Mercury is emitted into the environment from a number of natural as well as anthropogenic sources. In contrast with the other heavy metals, mercury and many of its compounds behave exceptionally in the environment due to their volatility and capability for methylation. Mercury is outstanding among the global environmental pollutants of continuing concern. The most important sources of direct emissions to water are dental amalgam use, chlor-alkali and power plants, ferrous and non-ferrous industries along with waste disposal (SOCOPSE D3.1 Mercury).

Atmospheric deposition is of high importance when it comes to sources of mercury. The global emissions of anthropogenic mercury to air for 2005 were estimated to be 1921 tonnes. The main source category is combustion of fossil fuels in power plants and industrial boilers which contribute about 500 tonnes (26 per cent of the global emissions to air). An additional 380 tonnes of mercury (20 per cent) are associated with fossil fuel combustion for residential heating. Artisanal small scale gold mining contributes about 323 tonnes (17 per cent). Other important sectors are cement production (190 tonnes, 10 per cent), non-ferrous metal industries (excl. gold) (130 tonnes, 7 per cent) and large-scale gold production (110 tonnes, 6 per cent). The remaining 15 percent originate from iron and steel production, waste management, cremation, chlor-alkali industry and mercury production (UNEP, 2010).

Information on heavy metals including estimates of deposition loads related to the Baltic Sea catchment is available at the HELCOM website, for example HELCOM (2010), Bartnicki et al (2008), and Gusev (2009). In HELCOM (2010, page 24) the relative



importance of atmospheric deposition to the Baltic Sea is given: In 2006, 3.4 tonnes of mercury was deposited from the atmosphere directly to the Baltic Sea surface (Bartnicki et al. 2008) while waterborne loads from point and diffuse sources were 10.8 tonnes (Knuuttila, 2009).

Table 1. CAS numbers for mercury and selected compounds (with uses in the Swedish products register 2008).

| Substance | CAS# |
|--|------------|
| Mercury, Hg | 7439-97-6 |
| Mercury dichloride, HgCl ₂ | 747-94-7 |
| Mercury dinitrate, Hg(NO ₃) ₂ | 10045-94-0 |
| Dimethyl mercury, Hg(CH ₃) ₂ | 539-74-8 |
| Mercury, (neodecanoato-O)phenyl- | 26545-49-3 |
| Sulfuric acid, mercury(2+) salt (1:1) | 7783-35-9 |
| Mercury, chlorophenyl- | 100-56-1 |

Options for reducing mercury use in products and applications, and the fate of mercury already circulating in society can be found in European Commission (2008).

1.1 Physical chemical properties

Mercury is a heavy, silvery transition metal, liquid at room temperature and pressure. Mercury is an extremely rare element in the earth's crust, having an average crustal abundance by mass of only 0.08 parts per million. However, because it does not blend geochemically with those elements that comprise the majority of the crustal mass, mercury ores can be extraordinarily concentrated considering the element's abundance in ordinary rock. At 20°C, the vapour pressure of the metal is 0.17 Pa, and a saturated atmosphere at this temperature contains 36 g m⁻³ of mercury (Gavis & Ferguson, 1972).

Table 2. Physical and chemical properties of mercury (CAS: 7439-97-6) (Handbook of Chemistry and Physics, 1987).

| | |
|-------------------------------|-------------------|
| Property | |
| Physical state at npt | liquid |
| Density (g cm ⁻³) | 13.534 (liquid) |
| Atomic weight (g/mol) | 200.59 |
| Melting point (°C) | -38.83 (234.32K) |
| Boiling point (°C) | 356.73 (629.88K) |



| | |
|---|---------------------|
| Critical point | 1750K, 120.00MPa |
| Heat of fusion (kJ mol ⁻¹) | 2.29 |
| Heat of vaporisation (kJ mol ⁻¹) | 59.11 |
| Heat of capacity (J mol ⁻¹ K ⁻¹) (at 25°C) | 27.983 |

Mercury dissolves to form amalgam with gold, zinc and many metals. When heated, mercury also reacts with oxygen in air to form mercury oxide, which then can be decomposed by further heating to higher temperatures. Mercury does not react with most acids, such as dilute sulphuric acid, though oxidizing acids such as concentrated sulphuric acid and nitric acid or aqua regia dissolve it to give sulphate and nitrate and chloride. Similar to silver, mercury reacts with atmospheric hydrogen sulphide. Mercury even reacts with solid sulphur flakes, which are used in mercury spill kits to absorb mercury vapours (spill kits also use activated charcoal and powdered zinc) (Socopse 3.1).

1.2 Regulatory status

Estonia joined the EU in May 2004 and has reconciled all the EU directives and has also all the regulations need to observe them.

The Water Framework Directive (2000/60/EC), so-called WFD, identifies mercury as a priority substance. As a priority substance, mercury is subject to controls for the progressive reduction of discharges, emissions and losses (article 16.6 of WFD). Moreover, mercury is identified as a priority hazardous substance (annex X of WFD). Mercury is also included in the Environmental Quality Standards (EQSs) for surface waters Directive (2008/105/EC) (Table 3). In the case of metals the surface water EQSs refer to the dissolved contamination rather than the total. Inland surface waters encompass rivers and lakes and related artificial or heavily modified water bodies.

Table 3` Environmental Quality . tandards in surface waters for mercury in µg/l (From 2008/105/EC).

| Inland surface waters Annual average value (AA-EQS). It applies to the ... | Other surface waters Annual average value (AA-EQS). It applies to the ... | Inland surface waters Maximum allowable concentration (MAC-EQS). | Other surface waters Maximum allowable concentration (MAC-EQS). |
|--|---|---|--|
| | | | |





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| | | | |
|-------------------------------|-------------------------------|------|------|
| concentration of all isomers. | concentration of all isomers. | | |
| 0.05 | 0.05 | 0.07 | 0.07 |

The Commission has adopted a legislative proposal to introduce an environmental quality standard (EQS) for methyl mercury in biota and sediments. The EQS proposed for biota is 42 ng/g, i.e. a factor 47 below the GW criterion for human consumption of fish. The proposal is currently under debate in the European Parliament and the Council. As Estonian legislation is compliant to the EU legislation, Hg is also listed as a priority substance and has set water quality standards under the Estonian law (RT I 2010, 51, 318; RT I 2010, 65, 484).

In addition to the WFD, the Groundwater Directive (2006/118/EC) establishes a regime that sets groundwater quality standards with measures to prevent or limit inputs of pollutants into groundwater. This Directive concerns Mercury; compliance with the threshold values to be established by the member countries.

Mercury is taken into account in several Best Available Techniques Reference Documents (BREFs), associated with industrial activities, where Emission Limit Values (ELVs) are often found. ELVs are often associated with Best Available Techniques (BAT) described in the BREFs.

In Estonia, mercury is also regulated by Ambient Air Protection Act (RT I 2004, 43, 298) and its regulations – “Tselluloosi ja tsemendi tootmisel välisõhku eralduvate saasteainete heitkoguste määramismeetodid” (RTL 2004, 108, 1725) (methods for analysing emissions from cellulose and cement production to ambient air). According to this regulation, the load is calculated by either measuring the emissions or by calculations. If calculations are used, these must be corrected according to real measurements.

Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture.

Council Directive 79/117/EEC of 21 December 1978 prohibiting the placing on the market and use of plant protection products containing certain active substances

Directive 98/8/EC of the European Parliament and of the Council of 16 February 1998 concerning the placing of biocidal products on the market.

Directive 2000/53/EC on end of life vehicles, which regulate the content of mercury, lead, cadmium, and hexavalent chromium of materials and components in vehicles as from 200

Directive 94/62/EC on packaging and packaging waste, which limits the concentration of





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lead, mercury, cadmium and hexavalent chromium in packaging

1.3 Production

There is no production of mercury in Estonia

1.4 Use

In 2007, the use and sale of Mercury was reported to be 2 kg, waste and scrap 19 kg, and stocks in enterprises 12 kg in Estonia (Statistics Estonia, 2010).

One important part to keep in mind is that although the use of coal is minimal in Estonia, five thermal power plants use oil-shale for fuel. There is little data available on the content of Hg in oil-shale and even existing ones vary. From the literature the content of Mercury has been shown varying from 0,015 to 0,8 g/t. (Missing reference).

1.5 Environmental fate

Mercury is a toxic and persistent metal with significant adverse effects on the environment and human health. It is poisonous in soluble forms such as mercuric chloride or methyl mercury, but is less harmful in an insoluble form, such as mercuric sulphide (Socopse 3.1).

PEC/PNEC ratios ratio (the predicted environmental concentration (PEC) to the predicted no-effect concentration (PNEC) where PEC/PNEC ratios of greater than unity are indicators that there may be a risk of concern) for water, sediment, soil and (local) secondary poisoning (poisoning through the predatory food chain) has been given by for example European Commission (2002, page iii), as follows:

- for water, the PEC/PNEC ratios for inorganic and organic mercury were significantly less than unity;
- for sediment, the PEC/PNEC ratios were significantly less than unity for inorganic mercury whilst those for organic mercury were in the range 0.2 - 0.4;
- for soil, the PEC/PNEC ratios for inorganic mercury were about 0.2; and
- for secondary poisoning, the PEC/PNEC ratios were significantly less than unity for the terrestrial food chain (inorganic mercury) whilst those for the aquatic food chain (organic mercury) approached unity (0.9).

European commission (2002, page 66-67) gives:



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In the atmosphere, the main form present - and the majority of that emitted – is elemental mercury. Elemental mercury has a half-life in the atmosphere of several months to a year. Due to its relatively long lifetime in the atmosphere, elemental mercury in the vapour phase can be transported over large distances. Whilst monovalent mercury is not found in the atmosphere, bivalent mercury may be present in inorganic form (for example, mercuric chloride). Bivalent forms may be attached to particulate matter (especially in the sub-micron range) and may result from (slow) oxidation of elemental gaseous mercury. The bivalent forms have a much shorter half-life in the atmosphere (days) as they undergo both dry and wet deposition (Lee et al., 2001). Methyl mercury may constitute a few percent of the atmospheric mercury.

Elemental mercury is oxidised in water to Hg^{2+} in the presence of oxygen, a process enhanced by the presence of organic substances in the aquatic environment. Bivalent mercury can react in a number of ways in the aquatic environment, such as:

- formation of HgS in anaerobic conditions in the presence of hydrogen sulphide;
- reaction to form elemental mercury, which is then readily lost to the atmosphere,

thought to be a key process in natural loss to air through degassing; and

- reaction to form methyl mercury via biochemical processes.

Methyl mercury has a greater potential for entry into food chains and subsequent bioconcentration, as compared to elemental or inorganic mercury. It is also the most toxic form of mercury. Methyl mercury is formed naturally in the environment, mainly in the freshwater and marine sediments, although it may also be formed in the water column. Microorganisms, especially sulphate reducing bacteria, are capable of methylating mercury, including some soil organisms in addition to those in the aquatic environment. In the terrestrial environment, the majority of mercury present is in inorganic form with a lower fraction of organic mercury than in the aquatic environment.

In the aquatic environment, mercury is taken up readily by invertebrates and by fish, with accumulation in the former being greater than in the latter. Organic mercury and salts of bivalent mercury can be readily taken up by organisms in the aquatic and terrestrial environment. Generally, organic mercury is taken up more readily than inorganic mercury and is also released more slowly.





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1.6 Environmental levels

The hazardous substances (mainly the WFD 33 priority substances or substance groups) have been monitored in Estonia during the last years, but generally, the main focus has been on the concentrations of hazardous substances in biota (Baltic herring and perch from the estuaries and open seas). There haven't been so many water samplings.

Mercury in rivers

In the hydrochemical monitoring of North- and South-Eastern rivers (TUT 2010b), the heavy metals were measured in five rivers. The concentrations of Mercury didn't exceed the LOQ in any of the samples.

The general picture also holds true according to the data of TUT, the mercury pollution loads to the Baltic Sea via rivers is negligible. In the study where 15 rivers were screened, the whole pollution load of Mercury to the Baltic Sea (rivers, industrial and municipal WWTP-s) was estimated to be 0 t/y (TUT 2010a).

The study ordered by Estonian Ministry of Environment (conveyed by MAVES) was made on the priority hazardous substances of WFD and studied these substances in the coastal waters and surface waters. According to this study, mercury was not detected in any rivers, i.e. the results were always under the LOQ (0,1 µg/l).

Mercury in biota

In 2009, Mercury was measured in the Baltic herring and perch caught from the coastal sea. The average concentration in the muscles of Baltic herring (0,018 ± 0,002 mg/kg wet- and 0,071 ± 0,009 mg/kg dry weight) was lower than the concentration in the liver (0,033 ± 0,002 mg/kg wet- and 0,113 ± 0,005 mg/kg dry weight). In perch, however, the concentration of Mercury was higher in muscles (0,055 ± 0,014 mg/kg wet and 0,238 ± 0,067 mg/kg dry weight) than in livers (0,040 ± 0,001 mg/kg wet and 0,164 ± 0,008 mg/kg dry weight). The mercury concentration is generally higher in perches than in Baltic herring.

The concentration of mercury was generally lower in the livers of Baltic herrings caught from the Gulf of Riga than those caught from the mouth of Gulf of Finland or in the eastern part of Gulf of Finland. However, the concentration of mercury in the muscles of the Baltic herring caught in the Gulf of Riga was higher than those caught from the mouth of Gulf of Finland or the eastern part of Gulf of Finland. Then again, the concentrations of Mercury were very low in Baltic herrings and the differences are not statistically reliable.



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The concentrations of mercury in the fishes are generally the same as in the previous years.

Mercury in precipitation

Mercury has also been monitored in the precipitation. The concentration of heavy metals is generally quite low in the precipitation in Estonia. In 2009, Mercury was not detected in the Northern Estonian monitoring, and detected only twice over the LOQ (0,05 µg/l) in two samples in Southern Estonia (Alam-Pedja in September and Otepää in October) (Estonian Environment Information Centre 2010, Estonian Ministry of the Environment web-page¹).

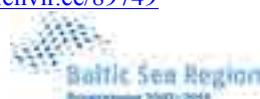
Mercury in COHIBA WP3 studies

The results from COHIBA WP3 show that some Mercury is led to the WWTPs as it is found from the sludge, but generally in low concentrations. Some Mercury is also emitted from the landfill to the environment.

Table 4. Hg in WWTP effluents and sludge, landfill and stormwaters (data from COHIBA WP3).

| WWTP1 | | WWTP2 | WWTP3 | | WWTP4a | WWTP4b | Landfill | Stormwater |
|--------------|----------------|--------------|--------------|----------------|--------------|--------------|-------------|------------|
| Water (µg/l) | Sludge (mg/kg) | Water (µg/l) | Water (µg/l) | Sludge (mg/kg) | Water (µg/l) | Water (µg/l) | (µg/l) | (µg/l) |
| <LOQ – 0,05 | 0,23 | <LOQ – 0,05 | <LOQ – 0,05 | 0,44 and 0,5 | <LOQ | <LOQ | <LOQ – 0,10 | <LOQ |

¹ <http://www.envir.ee/89749>





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2 Sources of emissions of Mercury in Estonia

The uncertainties in the following emission strings are given with four letters, the first letter representing uncertainty for EF, the second for EFM, the third for division into compartments and the fourth for the yearly load. Uncertainty is classified according to the principles described in “Dealing with uncertainty in substance flow analysis within the COHIBA project”, a PM describing how data uncertainty is graded in WP4 of the COHIBA project.

If the Estonian yearly loads were scaled from the EU yearly load to Estonian population, the Estonian population was considered to be 0,3% of the EU population. If the Estonian yearly loads were scaled from the EU yearly load to Estonian area, the Estonian area was considered to be 1% of the EU area. This accuracy level was considered to be enough for given study; especially considering the very high uncertainty levels in other emission strings.

2.1 Agriculture, forestry, and fishing - Crop and animal production, hunting and related service activities

NACE: A 01

Emission due to spreading of sewage sludge on agricultural land

Yearly load from this ES is included in ES “Hg in sewage sludge from municipal STPs.” (under “Sewerage”).

Part of the Hg in sludge will be due to uptake by crops and part of it will be leached to groundwater, with surface runoff to surface water, emitted to air by erosion or evaporation or just accumulated in the soil. This use is regulated by Directive 86/278/EEC and its revisions. Guideline for mercury content of sludge applied on land is 16-25 ppm (COM, 2005).

Emissions from agriculture and forestry

Yealy load - ? to AO

Uncertainty: N/A

Emissions from agriculture and forestry to atmosphere are mentioned as a source as



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mercury can be accumulated in these kinds of soils, and depending on fate, might be emitted to air, leached to groundwater and surface waters. Note that the use of mercury in biocides and pesticides is prohibited by Directives 79/117/EEC and 98/8/EEC. Category 2 according to Lecloux (2007). No data is available for this source.

2.2 Manufacture of veneer sheets and wood-based panels

NACE: 16.21

Manufacture of veneer sheets and wood-based panels

Yearly load – 20 kg to AO

This yearly load is based on only one company – Repo Vabrikud AS that states this load in E-PRTR. There are more companies in Estonia with similar productions but there is no emission data.

2.3 Manufacture of pulp & Manufacture of paper and paperboard

NACE: C 17.11; 17.12

Paper and pulp production processing - Production of pulp from timber or similar fibrous materials

Yearly load – 8,64 to AO

Yearly load – 6,35 to FSW

Yearly load – 1,13 to FS

Yearly load – 0,31 to WW

Uncertainty: CCAC

There is no data for that activity in Estonia in E-PRTR, which is rather typical as there is not much information about Estonia in E-PRTR whether or not the emissions actually exist. However, according to PRODCOM 2008 the production of pulp in Estonia is 9% from EU total. Hence, we took 9% as an EF. Then the total EU loads were taken from E-PRTR that gave us an EFM. The yearly loads for this activity are 9% of similar EU loads.

Total production volume in Estonia 136,8 thousand tons of pulp in 2009 (Statistics Estonia (2011). Horizon Pulp & Paper, Estonian Cell - these are the biggest companies in the sector. They do not use/emit Hg (personal communication; Jelena Lebedeva, June 2010).



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Emissions from pulp and paper industry

This source is assumed to be included in the following ESs.

Paper and wood production processing - Production of paper and board and other primary wood products

Yearly load – 9,3 kg to AO
Yearly load – 4,9 kg to FSW
Yearly load – 0,22 kg to FS
Yearly load – 2 kg to WW
Uncertainty: CCAC

There is no data for that activity in Estonia in E-PRTR, which is rather typical as there is not much information about Estonia in E-PRTR whether or not the emissions actually exist. However, according to PRODCOM 2008 the production of pulp in Estonia is 5,66% from EU total. Hence, we took 5,66% as an EF. Then the total EU loads were taken from E-PRTR that gave us an EFM. The yearly loads for this activity are 9% of similar EU loads. Uncertainties are high but our opinion is that it is still reasonable to add these loads. The division between compartments is the same as in the EU SFA.

2.4 Manufacture of industrial gases

NACE: C 20.11

Chemical industry - Industrial scale production of basic inorganic chemicals – Gases

Yearly load - ? to WW

There is no data for that activity in Estonia in E-PRTR, which is rather typical as there is not much information about Estonia in E-PRTR whether or not the emissions actually exist. However, this ES could be relevant for Estonia as according to Prodcum, 2008, there is some industry under that NACE, namely the production of: *Argon, Rare gases (excluding argon), Hydrogen, Nitrogen, Oxygen, Carbon dioxide, Nitrogen oxides, Inorganic oxygen compounds of non metals (excluding sulphur trioxide (sulphuric anhydride); diarsenic trioxide, nitrogen oxides, silicon dioxide, sulphur dioxide, carbon dioxide)*, but the data about this is confidential.



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2.5 Manufacture of other inorganic basic chemicals

NACE : C 20.13

Chemical industry - Industrial scale production of basic inorganic chemicals

Yearly load - ? to FSW, AO

Uncertainty: N/A

Chemical industry - Industrial scale production of basic inorganic chemicals -Non-metals, metal oxides or other inorganic compounds

Yearly load - ? to WW

Uncertainty: N/A

There is no data for that activity in Estonia in E-PRTR, which is rather typical as there is not much information about Estonia in E-PRTR whether or not the emissions actually exist. Personal communication also did not give data about using/emitting of Hg. Other researches (BEF 2007) report that use/emission of Hg is not found in chemical industry. Hence, we can assume this ES to be irrelevant for Estonia, but we cannot be sure. Further research is needed.

Chemical industry - Industrial scale production of basic inorganic chemicals – Unspecified

Yearly load - ? to WW

Uncertainty: N/A

There is no data for that activity in Estonia in E-PRTR, which is rather typical as there is not much information about Estonia in E-PRTR whether or not the emissions actually exist.

Under the NACE 20.13, the following activities are take place in Estonia, according to Prodcom, 2008:

Alkali or alkaline-earth metals; rare-earth metals, scandium and yttrium; mercury

Fluorides; fluorosilicates; fluoroaluminates and other complex fluorine salts

Sulphates of barium or aluminium

Sulphates (excluding those of aluminium and barium)

Sodium hydrogencarbonate (sodium bicarbonate)

Compounds of rare-earth metals, of yttrium or of scandium or mixtures of these metals

The data about these activities is confidential. We don't know the companies under these



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activities (although one of them is obviously AS Silmet, the producer of rare-earth metals) and we also don't know if they might use or emit Mercury.

Under the NACE 20.13, the activity „Silicates; commercial alkali metal silicates“ is also mentioned in Prodcom, 2008. In Estonia, the sold volume was 15 000 kg SiO₂ in 2008. We don't know the companies under these activities and we don't know if they might use or emit Mercury. Further research is needed.

2.6 Manufacture of other organic basic chemicals

NACE: C 20.14

There is no data for that activity in Estonia in E-PRTR, which is rather typical as there is not much information about Estonia in E-PRTR whether or not the emissions actually exist.

Under the NACE 20.14, the following activities are take place in Estonia, according to Prodcom, 2008:

Unsaturated acyclic hydrocarbons (excluding ethylene, propene, butene, buta-1.3-diene and isoprene)

m-Xylene and mixed xylene isomers

Propan-1-ol (propyl alcohol) and propan-2-ol (isopropyl alcohol)

Benzoic acid; its salts and esters (Velsicol!)

Citric acid and its salts and esters

Carboxylic acid with alcohol, phenol, aldehyde or ketone functions

Aldehyde-ethers, aldehyde-phenols and aldehydes with other oxygen function

Other organic compounds, n.e.c.

Rosin and resin acids; and derivatives; rosin spirit and oils; run gums

The data about these activities is confidential. We don't know the companies under these activities (although one of them is obviously Velsicol, the producer of benzoic acid) and we also don't know if they might use or emit Mercury.

Under the NACE 20.14, the following activities with the production values and volumes are also mentioned:

Acetic acid – value 22 000 EUR, sold volume 30 000 kg, total volume 7 121 000 kg

Methanal (formaldehyde) – value 137 000 EUR, sold volume 102 000 kg

Wood charcoal whether or not agglomerated (including shell or nut charcoal) – value



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2 524 000 EUR, sold volume 4 956 000 kg
Naphthalene and other aromatic hydrocarbon mixtures (excluding benzole, toluole, xylole) – value 2 957 000 EUR, sold volume 6 609 kg 000, total volume 6 609 000 kg
Phenols – value 984 000 EUR, sold volume 631 000 kg, total volume 663 000 kg
Undenatured ethyl alcohol of an alcoholic strength by volume $\geq 80\%$ - value 1 046 000 EUR, sold volume 1 841 000 l.

However, we don't know the concrete factories, we also don't know if they might use or emit Mercury. Therefore it's impossible to get any EF-s from this data. We can only be sure these activities are performed in Estonia. Further research is needed.

Chemical industry - Industrial scale production of basic organic chemicals

Yearly load - ? to AO, FSW

Uncertainty: N/A

Chemical industry - Industrial scale production of basic organic chemicals - Oxygen-containing hydrocarbons

Chemical industry - Industrial scale production of basic organic chemicals - Nitrogenous hydrocarbons

Chemical industry - Industrial scale production of basic organic chemicals - Halogenic hydrocarbons

Chemical industry - Industrial scale production of basic organic chemicals - Organometallic compounds

Chemical industry - Industrial scale production of basic organic chemicals - Unspecified

Yearly load - ? to WW

Uncertainty: N/A

Emissions due to manufacturing of basic organic chemicals

Yearly load - ? to FSW

Uncertainty: N/A

2.7 Manufacture of explosives

NACE: C 20.51

Chemical industry - Industrial scale production of explosives and pyrotechnic products



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Yearly load - ? to WW

Uncertainty: N/A

In Prodcom 2008, the activity “Prepared explosives (excluding propellant powders)” is mentioned under NACE 20.51. Also – we know for a fact that there is one producer of explosives for military in Estonia (Fortestar OÜ²). There were also public news in June 2011 about explosions in a warehouse³.

However, the data about the production of explosives is confidential. The activity “Matches (excluding Bengal matches and other pyrotechnic products)” is also mentioned with the value 105 000 EUR, and sold volume 11 000 kg.

There is no data for that activity in Estonia in E-PRTR, which is rather typical as there is not much information about Estonia in E-PRTR whether or not the emissions actually exist. In fact, there should be data about these activities in E-PRTR for Estonia as well, as it is written in Regulation (EC) No 166/2006/EC Annex I – Activities and Capacity threshold - Installations for the production on an industrial scale of explosives and pyrotechnic products no capacity threshold is applicable (i.e. all facilities are subject to reporting).

We can conclude that these kinds of activities take place in Estonia, but we don't know if the producers use or emit Mercury. Swedish Products register (2010) gives that there were Hg uses in Sweden in 2008 from this activity. Therefore we can assume this situation is rather similar in Estonia. Further research is needed.

2.8 Manufacture of other plastic products & Treatment and coating of metals

NACE: 22.29; 25.61

Production and processing of metals - surface treatment of metals and plastics using electrolytic or chemical processes

Yearly load - ? to FSW, WW

Uncertainty: N/A

² <http://www.fortestar.ee/>

³ <http://www.tallinnapostimees.ee/468570/mustamael-tehnopoli-hoones-kargatasid-plahvatused/>





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There is no data for that activity in Estonia in E-PRTR, which is rather typical as there is not much information about Estonia in E-PRTR whether or not the emissions actually exist.

Under the NACE 22.29 and 25.61 the following activities are listed:

Plastic articles of apparel and clothing accessories (including gloves, raincoats, aprons, belts and babies' bibs)

Self-adhesive strips of plastic with a coating consisting of unvulcanized natural or synthetic rubber, in rolls of a width ≤ 20 cm

Tableware and kitchenware of plastic

Plastic fittings for furniture, coachwork or the like

Statuettes and other ornamental articles of plastic (including photograph, picture and similar frames)

Plastic parts for apparatus of HS 85.25 to 85.28

Metallic coating by immersion in molten metals (zinc galvanizing or tin dipping)

Metallic coating in zinc by electrolysis

Heat treatment of metals (excluding metallic coating, plastic coating)

Anodizing of metals

The data about these activities is confidential. We don't know the companies under these activities and we also don't know if they might use or emit Mercury.

Under the NACE 22.29 and 25.61 the following activities with the production values and volumes are also mentioned:

Other toiletry and household articles of plastics n.e.c

Plastic parts for lamps, lighting fittings and illuminated signs and name-plates

Office or school supplies of plastic (including paperweights, paper-knives, blotting pads, pen-rests and book marks)

Perforated buckets and similar articles used to filter water at the entrance to drains, of plastic

Other articles made from sheet

Other articles of plastics or other materials

Plastic parts for machinery and mechanical appliances, excluding internal combustion piston engines, gas turbines

Plastic products, parts of apparatus of HS 85.35 to 85.37, and 85.42

Plastic parts and accessories for all land vehicles (excluding for locomotives or rolling stock)

Plastic parts for electrical machinery and equipment, sound recorders and reproducers, television image and sound recorders and reproducers



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Plastic parts for optical, photographic, cinematographic, measuring, checking, precision, medical or surgical instruments and apparatus

Metallic coating by electrolysis or chemical treatments of metals other than zinc (including nickel, copper, chromium, precious metals, etc)

Plastic coating of metals (including powder coating)

Other coatings (phosphating etc)

Wet painting and varnishing of metals

Other metallic surface treatments

However, from the data available from Prodcop, 2008, it's impossible to calculate a meaningful ES. We can only conclude that these kinds of activities take place in Estonia, but we don't know if the producers use or emit Mercury. Further research is needed.

2.9 Manufacture of other non-metallic mineral products

Emissions due to manufacture of mineral products

NACE: C 23

This ES is included in the other strings with NACE 23.

2.10 Manufacture of glass and glass products

Mineral industry - Manufacture of glass, including glass fibre

NACE – C 23.1

Yearly load - ? to AO, WW

Uncertainty: N/A

There is no data for that activity in E-PRTR for Estonia. Only big facilities have to report to E-PRTR (with a melting capacity of 20 tonnes per day). However, there should be some data in E-PRTR as at least one factory with IPPC permit fulfils the criteria of big facility (156 t per day). The plant produces glass containers for foodstuffs, liquors, beers, soft drinks, chemicals, and pharmaceuticals. Products are mainly exported and the production volume has been increasing in previous years. Plant produces approximately 57000 tonnes/year (in 2004). The melting capacity is 20 tonnes per day.

There are also several activities listed in Prodcop 2008 as taking place under that NACE in Estonia, such as:



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Non-wired sheets, of cast or rolled glass, whether or not with absorbent, reflecting or non-reflecting layer; but not otherwise worked;

Wired sheets or profiles, of cast or rolled glass, whether or not with absorbent, reflecting or non-reflecting layer; but not otherwise worked;

Non-wired sheets, of float, surface ground or polished glass, having a non reflecting layer;

Non-wired sheets, of float, surface ground or polished glass, having an absorbent or reflecting layer, not otherwise worked, of a thickness > 3.5 mm (excluding horticultural sheet glass);

Non-wired sheets, of float, surface ground or polished glass, coloured throughout the mass, opacified, flashed or merely surface ground (excluding horticultural sheet glass);

Other sheets of float/ground/polished glass, n.e.c.;

Other glass of HS 7003, 7004 or 7005, bent, edge-worked, engraved, etc;

Toughened (tempered) safety glass, of size and shape suitable for incorporation in motor vehicles, aircraft, spacecraft, vessels and other vehicles;

Toughened (tempered) safety glass, n.e.c.;

Laminated safety glass, of size and shape suitable for incorporation in motor vehicles, aircraft, spacecraft, vessels and other vehicles;

Laminated safety glass, n.e.c.;

Multiple-walled insulating units of glass;

Other glass mirrors, whether or not framed;

Glass preserving jars, stoppers, lids and other closures (including stoppers and closures of any material presented with the containers for which they are intended);

Bottles of colourless glass of a nominal capacity < 2.5 litres, for beverages and foodstuffs (excluding bottles covered with leather or composition leather, infant's feeding bottles);

Bottles of coloured glass of a nominal capacity < 2.5 litres, for beverages and foodstuffs (excluding bottles covered with leather or composition leather, infant's feeding bottles);

Other articles of glass fibre, of non-textile fibres, bulk, flocks, others;

Other articles of glass, n.e.c.

Hence, we can assume that the production certainly exists in Estonia, but we cannot be sure if they use or emit Mercury or not. Swedish Products register (2010) gives that there were Hg uses in Sweden in 2008 from this activity, we can assume this situation to be similar in Estonia. Further research is needed.

2.11 Manufacture of clay building materials & Manufacture of other porcelain and ceramic products

Mineral industry - Manufacture of ceramic products including tiles, bricks, stone



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where or porcelain

NACE : C 23.3; 23.4

Yearly load – ? to AO

Uncertainty: N/A

There is no data for that activity in Estonia in E-PRTR, which is rather typical as there is not much information about Estonia in E-PRTR whether or not the emissions actually exist. However, the production exists in Estonia according to Prodcum 2008:

Non-refractory clay building bricks (excluding of siliceous fossil meals or earths);

Non-refractory clay roofing tiles;

Ceramic tableware, other household articles;

Ceramic statuettes and other ornamental articles.

However, there is no information about specific emission factors and we cannot be sure if they use or emit Mercury or not. Further research is needed.

2.12 Manufacture of cement, lime and plaster

Mineral industry - Production of cement clinker or lime in rotary kilns or other furnaces

NACE: C 23.5

Yearly load – 4,16 – 5,2 kg to AO

Uncertainty: ABAC

Mercury emitted from cement production originates from coal and other fuels used and raw material such as limestone and other additives. Mercury concentrations are highly variable in fuels and raw materials (UNEP 2010).

The EF 0,004 g/t of clinker is taken from Estonian Informative Inventory Report, 2010. For EFM we used data from the company – the production was 1 040 000 t in 2008 (849 000 of tons of clinker 2006⁴).

2.13 Manufacture of basic precious and other non-ferrous metals;

⁴ <http://www.epl.ee/artikkel/387121>





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Casting of light metals; Casting of other non-ferrous metals

NACE: C 24.4; 24.53; 24.54

Production and processing of metals - Production of non-ferrous crude metals from ore, concentrates or secondary raw materials - Metallurgical, chemical or electrolytic production of non ferrous metals

Yearly load - ? to WW

Uncertainty: N/A

There is no data for that activity in Estonia in E-PRTR, which is rather typical as there is not much information about Estonia in E-PRTR whether or not the emissions actually exist. However, the production exists in Estonia, according to Prodcum, 2008:

Beryllium, chromium, germanium, vanadium, gallium, hafnium (celtium), indium, niobium (columbium), rhenium and thallium, and articles of these metals, n.e.c.; waste and scrap of these metals (excluding of beryllium, chromium and thallium)

Titanium and articles thereof (excluding waste and scrap), n.e.c.

Magnesium and articles thereof (excluding waste and scrap), n.e.c.

Copper and copper alloy tube/pipe fittings including couplings, elbows, sleeves, tees and joints excluding bolts and nuts used for as-sembling/fixing pipes/tubes, fittings with taps, cocks, valves

Unwrought lead (excluding lead powders or flakes, unwrought lead containing antimony, refined)

Refined unwrought lead (excluding lead powders or flakes)

Aluminum plates, sheets and strips > 0.2 mm thick

Unwrought aluminium alloys in secondary form (excluding aluminium powders and flakes)

The data for these industries is confidential and we cannot be sure if they use or emit Mercury or not. Further research is needed.

Production and processing of metals - Production of non-ferrous crude metals from ore, concentrates or secondary raw materials

Yearly load - ? to WW

Uncertainty: N/A

There is no data for that activity in Estonia in E-PRTR, which is rather typical as there is not much information about Estonia in E-PRTR whether or not the emissions actually exist. However, the production exists in Estonia, according to Prodcum, 2008: (24.53)



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„Light metal castings for land vehicles excluding for locomotives or rolling stock, construction industry vehicles“

The data for these industries is confidential and we cannot be sure if they use or emit Mercury or not. Further research is needed.

2.14 Casting of iron; Casting of steel

NACE: 24.51; 24.52

Production and processing of metals - Ferrous metal foundries

Yearly load - ? to AO

Uncertainty: N/A

Activities under that NACE for Estonia are:

Parts for other utilisation (malleable iron casting)

Grey iron castings for locomotives/rolling stock/parts, use other than in land vehicles, bearing housings, plain shaft bearings, piston engines, gearing, pulleys, clutches, machinery

Steel castings for machinery and mechanical appliances excluding piston engines, turbojets, turboprops, other gas turbines, lifting or handling equipment, construction industry machinery/vehicles.

The data for these industries is confidential and we cannot be sure if they use or emit Mercury or not. Further research is needed.

2.15 Manufacture of fabricated metal products, except machinery and equipment; Manufacture of other transport equipment; Manufacture of furniture; Other manufacturing

NACE: C 25; 30; 31; 32

Surface treatment of substances, objects or products using organic solvents

Yearly load - ? to WW

Uncertainty: N/A

There is no data for that activity in Estonia in E-PRTR, which is rather typical as there is



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not much information about Estonia in E-PRTR whether or not the emissions actually exist. However, the production exists in Estonia, according to Prodcum, 2008. The data for these industries is confidential and we cannot be sure if they use or emit Mercury or not. Further research is needed.

2.16 Electricity, gas, steam and air conditioning supply

NACE: D 35?

Energy sector - Thermal power stations and other combustion installations.

Yearly load – 500,9 kg to AO

Uncertainty: C

Yearly load - ? to WW, FSW

Uncertainty: N/A

The yearly load for AO is from the E-PRTR. There are 2 facilities involved in Estonia: Eesti Energia Narva Elektriijaamad AS, Balti Elektriijaam – 98.9 kg; Eesti Energia Narva Elektriijaamad AS, Eesti Elektriijaam – 402 kg.

There is no data for the mercury load to WW or FSW in E-PRTR and there hasn't been a chance to get the data by other means.

Energy sector - Coke ovens

Yearly load - ? to WW, AO

There is no data for that activity in Estonia in E-PRTR, which is rather typical as there is not much information about Estonia in E-PRTR whether or not the emissions actually exist. However, there are semi-coke ovens in the Northern Eastern Estonia, using oil shale that contains Mercury. Therefore we can assume that some Mercury emissions do exist, but we cannot calculate the yearly loads as there is no data.

2.17 Sewerage

NACE: 37

Waste and waste water management - Urban waste-water treatment plants

Yearly load – 0,027 – 0,471 kg to CSW



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Yearly load – 0,06 – 1,10 kg to FSW
Uncertainty: CAAC

There is no data for that activity in Estonia in E-PRTR, which is rather typical as there is not much information about Estonia in E-PRTR whether or not the emissions actually exist.

The Yearly load is calculated with the EF-s derived from the results of COHIBA WP3 and the preliminary results from BaltActHaz. Estonian population is considered to be 1340021 (Statistics Estonia 2010). The data from COHIBA and BaltActHaz preliminary results gave us the EF. The EF-s were considered to be the average result of all WWTP-s (for the EF low - the results under LOQ were considered to be 0 and for the EF high – the results under LOQ were considered to be LOQ). The EF was then multiplied by the EFM, i.e. the amount of effluents produced per person a day – 125 litres (according to Statistics Estonia 2010), the number of inhabitants (1 340 021 according to Statistics Estonia 2010), and the number of days a year (365).

Waste and waste water management - Independently operated industrial waste-water treatment plants serving a listed activity

The data is limited for specifically industrial WWTP-s. Because these (limited) results were very similar to the results from the municipal WWTP-s (i.e. mostly <LOQ or exactly on the level of LOQ), these few results were considered under the last string (urban waste-water treatment plants).

Hg in sewage sludge from municipal STPs.

Yearly load – 4,87 kg to AS
Yearly load – 10,36 kg to FS

The concentration of Mercury in sewage sludge is based on the measurements made in Estonia under COHIBA study and BaltActHaz preliminary results. The representability is highly uncertain as the data is extremely limited. Statistical data on sewage production and disposal is EU statistics, but it is considered to be representative for Estonia, according to Mr Kõrgmaa, an expert on sewage sludge. For estimation of Estonian emissions were used Estonian population data (1340021, Statistics Estonia 2010). Disposal on landfill and landscaping is designated to the compartment FS, use in agriculture (including spreading on the farmland) is designated for the compartment AS.

The data from COHIBA WP3 and the BaltActHaz preliminary results gave us the EF. The EF was considered to be the average result of all WWTP-s. The representability is highly





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uncertain due to limited data. The EFM is the one from European SFA-s, considered to be representative to Estonia by an expert. The yearly load was calculated by multiplying EF with EFM and number of inhabitants in Estonia.

2.18 Treatment and disposal of non-hazardous waste

NACE: E 38.21

There was 0,224 t of Hg waste in 2009 in Estonia (Estonian Environment Information Centre 2010⁵). 0,01 t of Mercury-containing batteries were landfilled in 2009. 2 tons of Mercury oxide elements and batteries were marketed in Estonia (Estonian Ministry of the Environment 2007⁶). There is only information about the price of different groups of goods in Statistics Estonia at this moment (June 2011).

Waste and waste water management - Landfills (excluding landfills closed before the 16.7.2001)

Emissions from landfills

The loads from these ESs are included in another string

Incineration of non-hazardous waste is included in Directive 2000/76/EC - waste incineration

Yearly load - ? to FSW, FS, AO

Uncertainty: N/A

No data for the incinerated waste, except for the EFM – 14 685 tons, which is the amount of recycled municipal waste in Estonia. The assumption is that all the waste is incinerated for getting electricity. Therefore this ES should be included in the thermal power station string?

Emissions from municipal waste incineration

The load from this ES was considered in the previous ES

Waste and waste water management - Disposal of non-hazardous waste (leachate)

Yearly load – 0,0001 kg to FSW

Yearly load – 0,0001 kg to FS

Uncertainty: C

⁵ http://www.keskkonnainfo.ee/failid/jaatmed/summary_hazard_2009.pdf

⁶ <http://www.envir.ee/108234>





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The calculations were done using the excel sheet provided by IVL. The data used was from the COHIBA WP3 results from the study of landfill leachate. However, this result is considered extremely inaccurate as it is based on two samples from one landfill.

Emissions from the treatment and disposal of non-hazardous waste

The yearly load from this ES was considered in the previous ES

2.19 Treatment and disposal of hazardous waste

NACE: E 38.22

Waste and waste water management - Disposal or recovery of hazardous waste

Yearly load - ? to AO, FSW, FS, WW

Uncertainty: N/A

The total load would be 0,224 t of Hg waste in 2009 (Estonian Environment Information Centre) – this would be the EFM. But there is no EF, it is impossible to calculate the yearly loads from hazardous waste. However, we assume this ES to be relevant for Estonia.

Emissions from the treatment and disposal of hazardous waste

Yearly load from this ES was included in the previous ES

2.20 Land transport and transport via pipelines

NACE: H 49

Emissions due to erosion of tiers

Yearly load – 0,0088 kg to FSW

Uncertainty: CBCC

We used the EU EF as there is no proper data to get a good EF for Estonia. EF – 0,001 g mercury released per 1,000,000 km driving. The road transport mileage in Estonia 8780,0 million km per 2008 year (Estonian Informative Inventory Report, 2010) – that gave us the EFM.

Emissions due to erosion of roads



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Yearly load – 0 – 26,34 kg to FSW

Uncertainty: B-

Tallinn University of Technology Department of Transportation (<http://www.ttu.ee/teedeinstituut>) has confirmed that the bitumen used in road building in Estonia does practically not contain Mercury because there is no Mercury in oil shale that is used for making bitumen in Estonia (Personal communication Ülle Leisk august 2011).

But for future scenarios this ES should be left here as relevant as we have an open market with EU and many big road construction public procurements have been done by other EU countries, so the origin of the bitumen is not always from Estonia any more. On that assumption we have put the yearly load high as the lowest value calculated with EU emission factors and the yearly load low as 0.

Emissions from transportation devices (land transport) running on distilled fuels (jet fuels, diesel fuels, heating oil, and kerosene)

Yearly load – 67,78 kg to AO

Uncertainty: CBBC

We used the EU EF as there is no proper data to get a good EF for Estonia. EF – 0,0001 g mercury released per litre fuel used. EFM – 677 799 000 litres

The road transport fuel + railway sector fuel + agriculture machinery + commercial and institutional sector (Military sector is also included) + household and gardening sector + industrial machinery sector consumption= 26000 t + 315770 t + 381630 t + 17070 t + 46000 t + 130 t + 13410 t + 4100 t + 960 t + 29000 t = 834 070 t per 2008 year (Estonian Informative Inventory Report, 2010)

Calculation: 26000 t of diesel used in railway sector * 0,84g/cm³(density) + 315770 t of gasoline used in road transport * 0,75g/cm³ (density) + 381630 t of diesel used in road transport * 0,84g/cm³ (density) + 17070 t used in agriculture machinery * 0,84g/cm³ (density) + 46000 t of light fuel oil * 0,97g/cm³ (density) + 130 t of gasoline used in commercial and institutional sector (Military sector is also included) * 0,75g/cm³ (density) + 13410 t of diesel used in commercial and institutional sector (Military sector is also included) * 0,84g/cm³ (density) + 4100 t gasoline used in household and gardening sector * 0,75g/cm³ (density) + 960 t diesel used in household and gardening sector * 0,84g/cm³ (density) + 29000 t of diesel used in industrial machinery * 0,84g/cm³ (density) = 677799000 Litres.



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Yearly load = EF*EFM.

It is assumed that all mercury present in fuel oils will be released into the atmosphere during the combustion process. Hg content of light fuels: 0,05g/ton. The release factor is a very rough estimation.

2.21 Water transport

NACE: H 50

Emissions from transportation devices (e.g. Ships) running on heavy fuels (residual fuels)

Yearly load – 1,97 kg to AO

Uncertainty: CBBC

It is assumed that all mercury present in fuel oils will be released into the atmosphere during the combustion process. Hg content of heavy fuel: 0,2 g/ton. The release factor is a very rough estimation.

EF – 0,0000085 g mercury released per liter fuel used

Calculation of EFM: 238000 t of bunker fuel oil * 089 g/cm³ (density) + 20000 t of marine diesel oil * 1,01 g/cm³(density) = 232020000 Liters. (EU EF and number of litres calculated from tons are used.)

International maritime navigation sector:

- EF for Marine diesel oil 0,05 g/t

- EF for Bunker fuel oil 0,02 g/t

238000 t of bunker fuel oil and 20000 t of marine diesel oil were used for 2008. National maritime navigation is excluded due it uses Light fuel oil (13000 t) and Diesel (7000 t). (Estonian Environment Information Centre 2010)

Calculation: 238000 t *0,02 g/t + 20000 t *0,05 g/t = 4760 g + 1000 g = 5,76 kg emission of Hg from navigation (shipping) per 2008

2.22 Dental practice activities

NACE – Q 86.23



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Emissions due to dentists working with (old) dental filling

Yearly load – 122 kg to WW

Uncertainty: BBBC

We used the EU EF as there is no proper data to get a good EF for Estonia. EF – 0,27 g per dentist per day if there is no amalgam separation, 5% of that value with amalgam separation. EFM - 92,3 number of dentists per 100000 inhabitants, according to Statistics Estonia (2010).

No data on number of dentists in EU 27 was found, but numbers for some EU countries, in Eurostat 2008c. In Poland the number of practising dentists per 100000 inhabitants was 34, and in Estonia 92, in 2008, which has been used to calculate the range, as these countries are the similar in this perspective. It has been estimated that approximately 19 tonnes of mercury per annum are used for amalgam in the UK. Some 20 percent of this is actually put into teeth, and the remainder may either be discharged to sewer, collected in an amalgam separator device attached to a dental chair, or enter a solid waste stream for either disposal or recycling [OSPAR, 2000].

According to the Flemish Environmental Agency, for new amalgam: 61% of the mercury is put in teeth, 14% is collected through a dedicated waste stream and 25% is discharged in the wastewater. Amalgam separators recover 95% of the discharged mercury and are obliged in Flanders from 2003. This brings the final emission factor to 5% of 25% of the purchased mercury (which is lowering due to replacement by synthetic products).

2.23 Funeral and related activities

NACE: S 96.03

Emissions from crematoria

Yearly load – 4,2 – 4,6 kg to AO

Uncertainty: BBBC

Swedish Products register (2010) gives that there were Hg uses in Sweden in 2008 from this activity. We can assume this situation to be similar in Estonia. We used the EU EF as there is no proper data to get a good EF for Estonia. EF – 0,000934 g per cremated



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corpse⁷, if no filters are installed. EF high – 1 g per cremated corpse, if no filters are installed. EFM – 4600 number of corpses cremated/yr (personal communication with all crematoriums in Estonia, Nov 2010).

The amount of mercury in the mouth of a person with fillings was on average 2.5 grams according to a Swiss study. A Japanese study estimated mercury emissions from a small crematorium there as 26 grams per day. In Reindl (2002), it was concluded that data vary greatly and that 1 g per corpse is a good average release factor. If this number is used and the number of deaths in 2007 (according to Lanzieri (2008) assuming all dead corps were cremated - which is a huge overestimation, an emission can be calculated. From European Commission (2008b, page 8): “The European Environmental Bureau has published a detailed mass balance analysis of mercury used in dental applications. This report has examined – in a quantitative manner and across the EU-27 - all sources of amalgam Hg and the pathways by which it can enter the environment.” The authors state that most of this will ‘likely’ end up in various environmental media: i.e. in soil, in the atmosphere, in surface water, and in ground water. It is unclear where the crematoria are to be shown in relation to these numbers.

2.24 Activities of households

NACE: X

Emissions due to food handling and consumption

Yearly load – 0 - 1,72 kg to WW

Uncertainty: BABC

The estimation is given as min and max scenarios. Minimum is put to 0, according to an expert opinion (Keddy Paasrand, EERC). For yearly load high we the EU number was scaled down from the EU yearly load, basing the calculation on population. Månsson & Bergbäck gives an emission of 1 kg/year in 2002 for Stockholm, with ca 780000 inhabitants. Using this number would give an emission factor of 1.28E-06 kg/person and year.

⁷ <http://www.eea.europa.eu/publications/emep-eea-emission-inventory-guidebook-2009/part-b-sectoral-guidance-chapters/6-waste/6-c/6-c-d-cremation-tfeip-endorsed-draft.pdf>





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2.25 Emission Strings Added by COHIBA

Emissions from wood burning stoves

Yearly load – 168,04 kg to AO

Uncertainty: BCBC

It was calculated total wood and wood products/wastes used for primary production of energy for 2009 in tonnes was: 1245000 t + 1343000 t + 1230000 t + 383000 t = 4201000 tonnes of dry wood (Statistics Estonia 2010). We used the EU EF as there is no proper data to get a good EF for Estonia.

There can be another way of calculation of estimation of that particular string used. If EF (1 mg/GJ) is used for wood (for area energy sources) that is used in Estonian Informative Inventory Report, 2010 and average calorific value for woods 18,9 MJ/kg (<http://deepzone2.ttu.ee/soojus/loengud/paist/mse006102.pdf>), and 4201000 tonnes of wood and wood product/wastes used for 2009.

Then calculation will be as follows:

$1 \text{ mg/GJ} * 18,9 \text{ MJ/kg} * 4201000 \text{ t} = 79,4 \text{ kg}$ of Hg emission from burning of wood in stoves.

EF – 0,04 g mercury released per ton dry wood burned

EFM – 4 201 000 tons/year

Measuring equipment (medical thermometers, other mercury in glass thermometers, thermometers with dial, manometers, barometers, sphygmomanometers, hygrometers, tensiometers, gyrocompasses, reference electrodes, hanging drop electrodes and other similar uses) - Emissions due to use of this equipment

Yearly load – 0,0021 – 0,0051 kg to AO

Uncertainty: CBCC

We assume this ES to be important for Estonia, but we couldn't find proper Estonian-specific EF-s or EFM-s to this ES.

However, in the EU SFA it was stated that 2.8% of the overall use of mercury in EU27 (in 2007) was attributed to measuring equipment. Voluntary initiatives and regulations have resulted in replacing mercury depending equipment with others. In laboratories and households such equipments still exist, but is not seen as an important source of emissions, but rather as a societal stock. An assumption is that 0.01% of the Hg from this use is emitted to air.



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Our assumption was that the rough level of miscellaneous use (percentage-wise) might be similar to the overall EU use, we therefore scaled the EU yearly load to Estonian population (0,3% of EU population), i.e. we assumed the yearly load of this ES to be 0,3% of the EU yearly load. However, one must keep in mind that this assumption is a very rough one and this ES surely needs reconsidering after further research is done on the topic.

Light sources (fluorescent tubes, compact fluorescent tubes, HID lamps and other lamps) - Emissions due to the use of these products

Yearly load - ? to waste

Uncertainty: N/A

3.1% of the overall use of mercury in EU27 (in 2007) was attributed to light sources. These products should be handled as hazardous waste, be due to material recycling or unintentionally end up in the non-hazardous waste, why they should be included in other emission strings. These products are also important as a societal stock. It is possible that the emission string above related to electrical equipment and lightening is covering this use.

Miscellaneous uses (porosimetry and pycnometry, conductors in seam welding machines - mainly maintainance, mercury slip rings, maintenance of lighthouses, maintenance of bearings, illegal gold production, other applications) -Emissions due to the use of these appliances etc

Yearly load– 0,045 – 0,342 kg to AO

Uncertainty: C-BC

We assume this ES to be important for Estonia, but we couldn't find proper Estonian-specific EFs or EFM to this ES. However, in the EU SFA it was stated that 15.2% of the overall use of mercury in EU27 (in 2007) was attributed to miscellaneous uses. These appliances should be handled as hazardous waste or be due to material recycling, why they should be included in other emission strings. These products are also a part of the societal stock. Here is assumed that 0.1% of this use is emitted to air and is not included in other emission strings.

Our assumption was that the rough level of miscellaneous use (percentage-wise) might be similar to the overall EU use, we therefore scaled the EU yearly load to Estonian population (0,3% of EU population), i.e. we assumed the yearly load of this ES to be 0,3% of the EU yearly load. However, one must keep in mind that this assumption is a





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very rough one and this ES surely needs reconsidering after further research is done on the topic.

Chemicals (chemical intermediate and catalyst - excl PU, catalyst in polyurethane (PU) production, laboratories and pharmaceutical industry, preservatives in vaccines and cosmetics, preservatives in paints, disinfectant, other applications as chemical) - Emissions due to the use of products related to this chemicals use

Yearly load – 0,0084 – 0,0177 kg to AO

Uncertainty: C-BC

This source is assumed to be of negligible importance, although 10.2% of the overall use of mercury in EU27 (in 2007) was attributed to chemicals. The major use in EU was as a catalyst, primarily for PU production, where part of mercury might be reused, or emitted at the industrial site and as such included in the emission strings related to production. Part of the mercury might be included in products used (PU, paints, vaccines, cosmetics and disinfectants) and should be emitted to air, water or soil either directly or through the waste stream. An assumption is that 0.01% of the Hg from this use is emitted to air.

Our assumption was that the rough level of miscellaneous use (percentage-wise) might be similar to the overall EU use, we therefore scaled the EU yearly load to Estonian population (0,3% of EU population), i.e. we assumed the yearly load of this ES to be 0,3% of the EU yearly load. However, one must keep in mind that this assumption is a very rough one and this ES surely needs reconsidering after further research is done on the topic.

Atmospheric deposition

Yearly load – 26,14 kg to FSW

Yearly load – 130,7 kg to AS

Yearly load – 64 kg to FS

Uncertainty: BBAC

The yearly loads are calculated from EU yearly load (99 000 kg) on area basis, considering Estonian area to be about 1% of the EU area. The total load from atmospheric deposition was calculated to be 435,6 kg and this was divided in between the compartments according to the Estonian landscape (Estonian Environment Information Centre 2010).

For comparison – the official data from EMEP shows total load to be 400 kg and also



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gives the main sources.

MSC-E gives Estonian data as following:

The total anthropogenic emissions – 0,6 t/y for 2008 and 0,4 t/y for 2009.

Annual depositions to Estonia – 32,7 kg

Mercury depositions to Estonia from national and external sources for 2008: min: 7,9 g/km²/y, max: 42 g/km²/y. For 2009: 6,7 g/km²/y, max: 36 g/km²/y.

Mercury total depositions to the country in 2008 amounts to 0.5 t/y. Contribution of global, natural, and historical emission sources to total depositions accounts for 75 %.

From official data it is obvious the fluxes are decreasing.

Annual depositions to Estonia

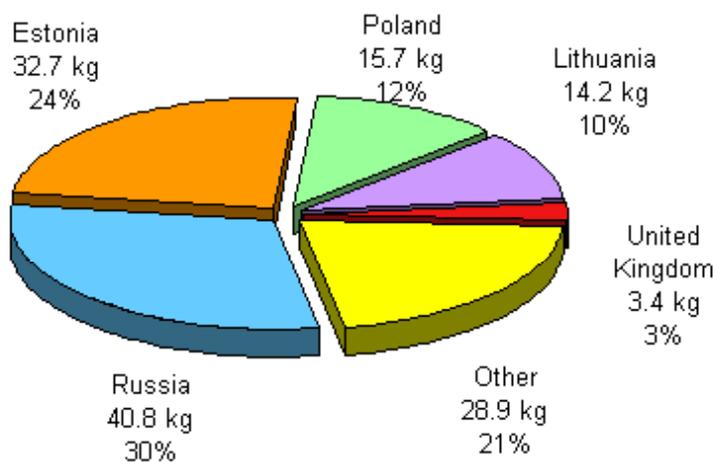


Figure 1. Depositions and transboundary fluxes.

Contaminated soil

Yearly load - ? to FSW

Discharges to surface waters by point sources can be expected due to concentrated mercury contaminated soil. It is difficult to do estimation for these point sources for the





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whole region – no data was found in literature.



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3 Emission Strings with no load

There were several emission strings that could be assumed to have some load in Estonia but we have confirmed them to be negligible the most.

3.1 Processing and preserving of meat & Processing and preserving of poultry meat

NACE: C 01.63; 10; 10.11; 10.12; 10.51; 10.86; 10.89; 11

Animal and vegetable products from the food and beverage sector – Slaughterhouses
Treatment and processing of animal and vegetable materials in food and drink production - Vegetable raw materials
Treatment and processing of milk

Controls and analyses have never shown any problems with Hg in the food, no sample has contained Hg. The data is from 2004 (Estonian Veterinary and Food Laboratory (VAFL)⁸). On expert level we can consider this not important source for Estonia.

For illustration purposes, we also scaled the EU total load for Estonian population (0,3% of the EU population):

Vegetable raw materials: Yearly load 0,009 FSW; 0,006 WW; 0,04 FS.

Slaughterhouses: Yearly load 0,013 to FS; 0,005 WW.

Milk: Yearly load 0,005 WW

Those are industrial activities so the scaling with population is unreliable.

3.2 Manufacture of coke and refined petroleum products

Energy sector - Manufacture of coal products and solid smokeless fuel

While Estonia does not use coal that much, the same processes are done with the oil shale that contains mercury in negligible amounts. There is no emission data in E-PRTR as

⁸ www.vetlab.ee/?a=attach&id=42f0a527a3bd9952b2a16





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Estonia does not report to E-PRTR about coal products and solid smokeless fuel.

So right now we consider this ES to be negligible for Estonia due are country uses coal in a very little amount (74 000 t in industry sector + household 7000 t + 5000 t for electric energy production= total (86000t per 2009) (Statistics Estonia 2010⁹).

3.3 Manufacture of batteries and accumulators

Emissions due to manufacture of primary batteries and electrical control and switching equipment

NACE – C 27.20

There is only one relevant activity under that NACE code in Prodcom 2008 (Primary cells and primary batteries) and this source is not quantified by the EU. It was possible to calculate that the amount Estonia is producing is 0,005 % of total EU load. We consider that negligible at the moment for Estonia.

About switching equipment and electrical control> Lamps and lighting fittings, 1 539.1 thousand units (statistics of Estonia for 2009), but the data on lamps and lighting fittings for 2009 have been revised on 22.12.2010. So can be different.

There is also no data in E-PRTR. Further research is needed, but we assume this source to be negligible for Estonia.

3.4 Activities of households

NACE: X

Emissions in human excrements (due to amalgam fillings)

The load from this ES is included in another string

Amalgam fillings are practically not used any more in Estonia (only rarely to fix old fillings). The average person, with dental amalgam fillings, excretes mercury through body waste (urine and faeces). The average amalgam filling has more than 0.5 gram of mercury.

⁹ Tahkekütuste bilanss



4 SFA diagram

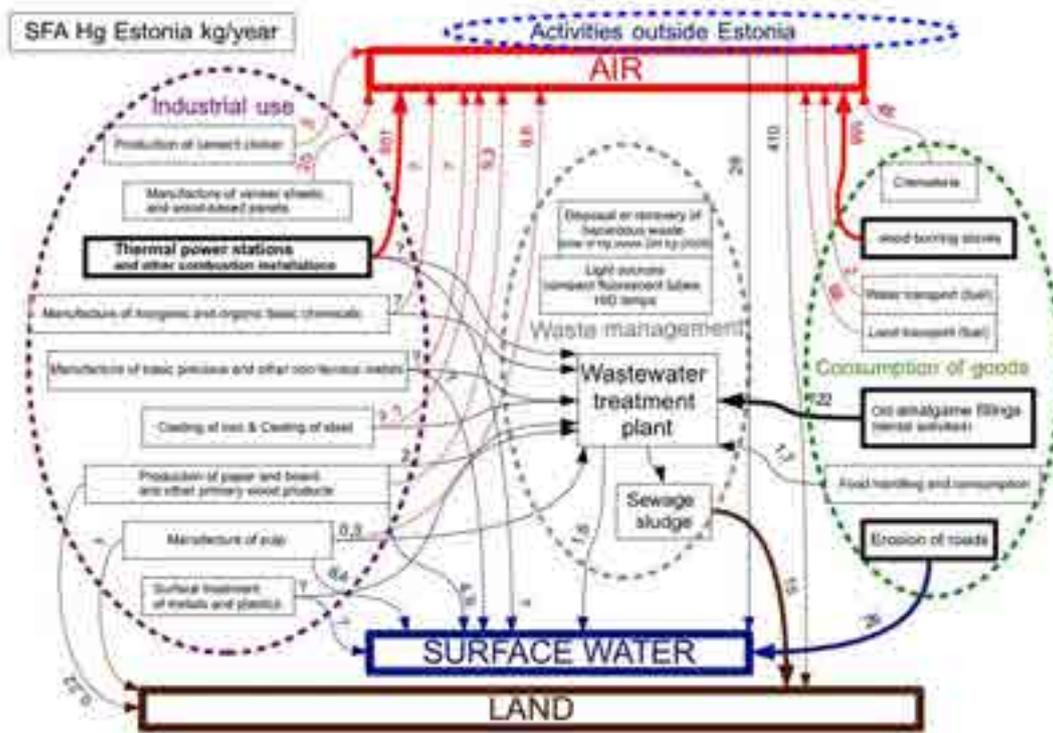


Figure 2. SFA diagram for Hg in Estonia.



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5 Conclusions

5.1 Quantitative estimation of the most relevant sources to each environmental compartment (Soil, water and air)

The most relevant source to air is thermal power installations (501 kg). Wood burning stoves are also an important source in Estonia as many people use wood for heating their houses. This source gives 168 kg of Hg a year to air.

Even though amalgam is mostly no longer used as a dental filling (only for fixing old fillings), many people still have old fillings and this together gives a significant load of 122 kg to wastewater.

Main loads to surface waters are not that obvious as many of the potential sources could not be quantified. At the moment it seems like the most important load to FSW comes from erosion of roads (26 kg), but production of paper and board and other primary wood products also give a load to FSW (4,9 kg), as does the load from wastewater treatment plants (1,6 kg). Wastewater treatment plants seem to be generally a significant point to monitor as sludge from wastewater treatment plants also gives a significant load (15 kg) to soil.

Atmospheric deposition of Hg is also high and gives a load of 410 kg a year to land and 26 kg to water a year.

5.2 A qualitative estimation of time trends for future scenarios.

Due to global efforts to decrease the mercury uses and emissions, a future scenario is that these should be lower. Dental use of Hg amalgam fillings is decreasing, as is the content of Mercury in consumer products, which will affect the concentration in wastewater. Emissions to air by point sources, especially power plants, will be decreased, which will also affect atmospheric deposition.

It is quite clear that wastewater treatment plants are an important secondary source of Hg, which means that monitoring the effluents and sludge and restricting the use of sludge is an important step that helps to reduce the amount of Hg circling in the environment. Innovative technologies that help to increase the efficiency of removing hazardous substances could also be used.





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ANNEX N - Substance flow analysis for Cadmium in Estonia

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This study was carried out under the COHIBA study from May to December 2010. The results are for Estonia. The analysis does not refer to a specific year, but the most recent available data has been used. Many of the results are rough approximations that cannot be taken as exact results for Estonia, but as a base to plan future studies.

1 Introduction

Cadmium is naturally occurring as one of the metallic components in the earth's crust and oceans, and is present everywhere in our environment. Cadmium is a heavy metal with a high toxicity. Cadmium is toxic at very low exposure levels and has acute and chronic effects on health and environment. Cadmium, being a natural element, will not degrade in nature and will thus, once released to the environment, stay. The mobility will depend on the adsorption to particles and subsequent sedimentation, though. New releases add to the already existing deposits of cadmium in the environment. Cadmium and cadmium compounds are, compared to many other heavy metals, relatively water soluble. They are therefore also more mobile in e.g. soil, generally more bioavailable and tend to bioaccumulate (COWI, 2003). Cadmium is known to cause cancer (especially lung-cancer for workers exposed to cadmium dust), osteoporosis and other skeleton problems, kidney malfunctions, and there are also indications of hormonal effects.

Cadmium metal is produced as a by-product from the extraction, smelting and refining of the non-ferrous metals zinc, lead and copper. It is further processed into other compounds including cadmium oxide. Cadmium occurs naturally in the environment from the gradual process of weathering, erosion and abrasion of rocks and soils, and from singular events such as forest fires and volcanic eruptions. Cadmium is thus naturally released to the atmosphere, aquatic environment, and terrestrial environment. Production of iron and steel, non-ferrous metals, particularly zinc, phosphate fertilisers and fossil fuel combustion plants seem to be the major anthropogenic sources of cadmium measured in the environment (SOCOPSE D.3.1, 2009).

There are several CAS numbers relevant for Cd and Cd compounds, of which some are listed in Table 1. These are those listed in the extract from the products register used in the COHIBA project¹.

¹ Cohiba SPR_4oct10_nonCOnf.xls





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Table 1. CAS numbers for cadmium

| Substance | CAS# |
|--|-------------|
| Cadmium oxide | 1306-19-0 |
| Dodecanoic acid, cadmium salt | 2605-44-9 |
| Cadmium | 7440-43-9 |
| Cadmium zinc sulfide yellow | 8048-07-5 |
| Cadmium sulfate | 10124-36-4 |
| Cadmium sulfoselenide orange | 12656-57-4 |
| Cadmium fluoborate | 14486-19-2 |
| Cadmium sulfoselenide red | 58339-34-7 |
| Silicic acid, zirconium salt, cadmium pigment-enca | 102184-95-2 |

1.1 Physical chemical properties

Cadmium is a relatively rare, soft, bluish-white, transition metal.

Table 2. Physical and chemical properties of cadmium (CAS: 7440-43-9)

| Property | |
|--------------------------|--------|
| Physical state at npt | solid |
| Molecular weight (g/mol) | 112.42 |
| Molecular formula | Cd |
| Melting point (°C) | 321.07 |

Cadmium is produced in two physical forms as non-pyrophoric and pyrophoric. Pyrophoric cadmium is highly flammable (SOCOPSE D.3.1, 2009).

1.2 Production

No production in Estonia

1.3 Use

In 2007, the use and sale of cadmium was reported to be 13 kg, waste and scrap 5 kg, stocks in enterprises 20 kg (Statistics Estonia, 2010).



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1.4 Regulatory status

Estonia joined the EU in May 2004 and has reconciled all the EU directives and has also all the regulations need to observe them.

The Water Framework Directive (2000/60/EC), so-called WFD, identifies cadmium as a priority substance, which means this substance has been shown to be of major concern for European waters. As a priority substance, cadmium is subject to controls for the progressive reduction of discharges, emissions and losses (article 16.6 of WFD). Moreover cadmium is identified as a priority hazardous substance (annex X of WFD).

Cadmium is also included in the Environmental Quality Standards (EQSs) for surface waters Directive (2008/105/EC). In the case of metals the surface water EQSs refer to the dissolved contamination rather than the total. For cadmium and its compounds the EQS values vary depending on the hardness of the water as specified in five class categories (see Table 3). Inland surface waters encompass rivers and lakes and related artificial or heavily modified water bodies.

Table 3. Environmental Quality Standards for cadmium in µg/l (From 2008/105/EC).

| Water classes | hardness | Inland surface waters Annual average value (AA-EQS). It applies to the total concentration of all isomers. | Other surface waters Annual average value (AA-EQS). It applies to the total concentration of all isomers. | Inland surface waters Maximum allowable concentration (MAC-EQS). | Other surface waters Maximum allowable concentration (MAC-EQS). |
|---|----------|---|--|---|--|
| Class 1: < 40 mg CaCO ₃ /l | | 0,01 (Class 1) | 0,2 | 0,01 (Class 1) | 0,01 (Class 1) |
| Class 2: 40 to < 50 mg CaCO ₃ /l | | 0,08 (Class 2) | | 0,45 (Class 2) | 0,45 (Class 2) |
| Class 3: 50 to < 100 mg CaCO ₃ /l | | 0,09 (Class 3) | | 0,6 (Class 3) | 0,6 (Class 3) |
| Class 4: 100 to < 200 mg CaCO ₃ /l | | 0,15 (Class 4) | | 0,9 (Class 4) | 0,9 (Class 4) |
| Class 5: > 200 mg CaCO ₃ /l | | 0,25 (Class 5) | | 1,5 (Class 5) | 1,5 (Class 5) |





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As Estonian legislation is compliant to the EU legislation, Cd is also listed as a priority substance and has set water quality standards under the Estonian law (RT I 2010, 51, 318; RT I 2010, 65, 484).

In addition to the WFD, the Groundwater Directive (2006/118/EC) establishes a regime that sets groundwater quality standards with measures to prevent or limit inputs of pollutants into groundwater. Cadmium is concerned by this Directive; compliance with the threshold values to be established by the member countries.

Cadmium is taken into account in several Best Available Techniques Reference Documents (BREFs), associated with industrial activities, where Emission Limit Values (ELVs) are often found. ELVs are often associated with Best Available Techniques (BAT) described in the BREFs. Examples, where Cd is included, are BREFS for TiO₂ production, production of Large Volume Inorganics, Surface Treatment of Metals and Plastics, Metal dye, Pigment, and for Contamination in zinc. <http://eippcb.jrc.es/reference/> Mina paneks selle viite.

Regulations to reduce cadmium use at the source have now been amended in the REACH regulation. Commission Regulation EC 466/2001, which sets maximum levels for certain contaminants in foodstuffs, Directive 2000/53/EC on end of life vehicles, which regulate the content of mercury, lead, cadmium, and hexavalent chromium of materials and components in vehicles as from 200, Directive 94/62/EC on packaging and packaging waste, which limits the concentration of lead, mercury, cadmium and hexavalent chromium in packaging, and Directive 91/338/EEC, related to Cd plating, to mention some. Directive 2006/66/EC of the European parliament and of the council, of 6 September 2006, on batteries and accumulators and waste batteries and accumulators and repealing Directive 91/157/EEC is still the regulation when it comes to this use.

A number of international agreements have been established already in order to manage and control release of cadmium to the environment and limit human and environmental exposure to cadmium. Estonia has joined with the following agreements and instruments are addresses cadmium and its compounds in releases, products, waste and etc:

- The 1998 Aarhus Protocol on Heavy Metals under the UNECE Convention on Long-Range Transboundary Air Pollution (LRTAP);
- The Helsinki Convention on the Protection of the Marine Environment of the Baltic Sea Area;





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- The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal.

1.5 Environmental fate

Cadmium is released to the atmosphere, aquatic environment, and terrestrial environment. The assessment of atmospheric emissions is more advanced and accurate than the assessment of discharges to the two other compartments of the environment. Major portion of atmospheric emissions of Cd in Europe is deposited with wet and dry deposition to aquatic and terrestrial surfaces in Europe (SOCOPSE Deliverable 2.1, 2009).

Production of non-ferrous metals, particularly zinc, disposal of wastes and combustion of fuels to produce electricity and heat seemed to be the major sources of cadmium according to SOCOPSE Deliverable 2.1.

1.6 Environmental Levels of Cadmium in Estonia

The emissions to air have been reduced by Estonia and the European Union (Figure 1).

Data about the emissions from the point sources and diffuse sources has been compiled, calculated, and analysed by the Estonian Environment Information Centre. In 2008, the total air emission of cadmium was 618 kg in Estonia: point sources - 559.5 kg of which came from the point sources (and 501,2 kg, or 81% of these coming from the Narva Power Plants emissions).



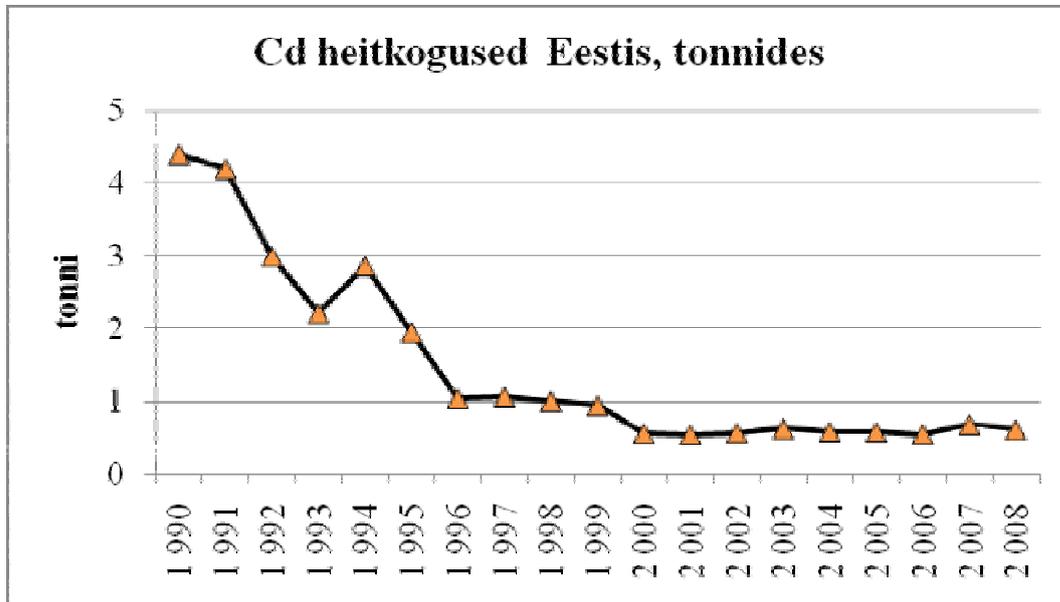


Figure 1. Cadmium emissions to Air in Estonia, in tons (Tallinn University of Technology, 2010).

1.6.1 Cadmium content in moss

Over the past five years (2004-2009) the minimum and median level of heavy metals in Kohtla-Järve, Pärnu, Viljandi and Tartu has declined or remained unchanged (Tallinn University of Technology, 2010). The average cadmium content was higher in 2004 than in 2009 in the same monitoring areas (Figure 2 and Table 4).



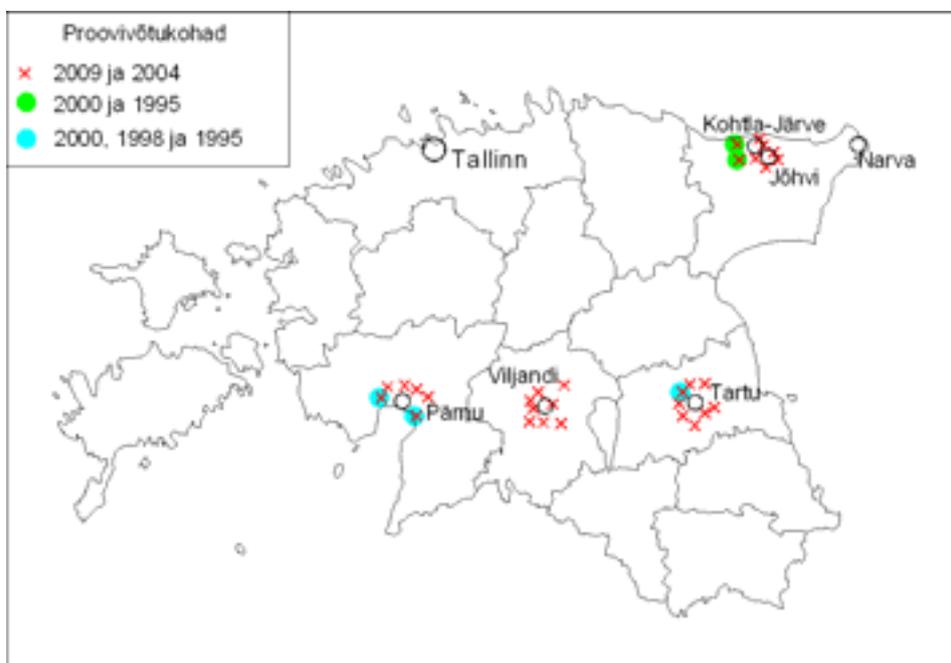


Figure 2. Moss monitoring points

Table 4. Moss Monitoring Results

| Area | 2004 | 2009 |
|--------------|----------------|------|
| | Microgram/gram | |
| Kohtla-Järve | 0,22 | 0.13 |
| Pärnu | 0,25 | 0.19 |
| Viljandi | 0,22 | 0.15 |
| Tartu | 0,20 | 0.15 |



1.6.2 Cadmium content in precipitation

From the precipitation monitoring results of Estonian national monitoring program it can be concluded that the emission loads have decreased in Estonia. The highest annual average concentration of 2009 was measured from the Vilsandi station (0,15 µg/l). The precipitation from the Harku station was the cleanest (0,03 µg/l). The highest monthly average was measured from the Lääne-Nigula station (0,33 µg/l). The results were under the LOQ (0,02 µg/l) in quite a few months in several stations.

1.6.3 Cadmium in marine organisms

The results from the monitoring of hazardous substances in marine organisms indicate that the content of heavy metals (cadmium, mercury, lead, zinc, and copper) tends to be generally somewhat higher in the organisms of Gulf of Finland than in the organisms of Gulf of Riga or Baltic Proper. Almost all the heavy metal concentrations that have been studied in organisms in the years 2001 - 2005 are lower than those in the 1990s (Figure 3).

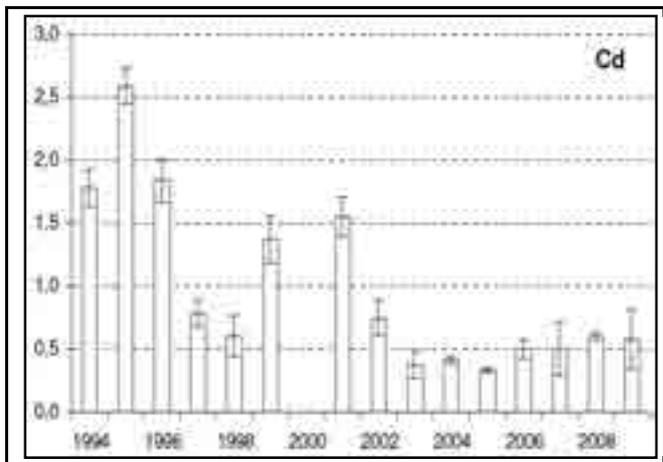


Figure 3. The Cd content (mg / kg dw) in the liver of herring in the coastal waters of Estonia 1994-2009 (Tallinn University of Technology, 2010).

1.6.4 Cadmium content in groundwater and rivers

According to the 2009 monitoring results in rivers the Cd levels were below the LOQ (0,1 mg/l) The yearly load of cadmium from the rivers to the Baltic Sea was 50 kg in





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Estonia (this number is representative for the whole Estonia with both diffuse and point sources) (TUT 2010).

We added the monitoring results from the previous years because the number of samplings was limited in 2009 due to the economic recession. Also – as the number of samplings had been higher in the previous years, the results were more accurate.

The pollution load of Cd from the rivers to the Baltic Sea was virtually non-existent in 2008. Small amount of load was from Valgejõgi, and Keila and Vihterpalu rivers (0,001 – 0,022 t/y). The load from rivers to the Baltic Sea was 0,238 t/y in 2008 (from industrial and municipal sources and rivers) (Tallinn University of Technology, 2009).

According to the Estonian legislation, the limit value and target value of cadmium in groundwater are 10 µg/l and 1 µg/l, respectively². In the groundwater samples taken in 2008 and 2009 (ca 90 samples), the Cd content was under the LOQ (0,2 µg/l).

1.6.5 Cadmium content in soil

According to the data from the project GEMAS (Geochemical mapping of agricultural and grazing land soil in Europe) by the expert group of geochemists there are 18 monitoring points for agricultural soils and 18 for pastures (or uncultivated lands) in the Estonian Support Network. The samples were collected from July to September in 2008.

Analytical results of soluble fractions of Support Network samples in royal water: Cd content in 18 agricultural soils (soluble in royal water) varied in the range from 0,055 to 0,365 mg/kg. Cd content in 18 samples from pastures (uncultivated lands) (soluble in royal water) varied in the range from 0,048 to 1,487 mg/kg. The Cd content of soluble fraction in royal water can be up to 30% of the total content.

1.6.6 Cadmium content in air

Emissions of heavy metals have dropped significantly. Total emissions of Cd to air have dropped from 4,40 t/y in 1990 to 0,62 t/y in 2008, giving a decrease of 85,99% (Estonian Environmental Information Centre 2010³).

² The regulation of the Minister of Estonia no 39, 11.august 2010 „The limit values of hazardous substances in the groundwater“ (<https://www.riigiteataja.ee/akt/13349010>)

³ Estonian Inf. Rep. 2009





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2 Sources of emissions of Cadmium Estonia

The uncertainties in the following emission strings are given with four letters, the first letter representing uncertainty for EF, the second for EFM, the third for division into compartments and the fourth for the yearly load. Uncertainty is classified according to the principles described in “Dealing with uncertainty in substance flow analysis within the COHIBA project”, a PM describing how data uncertainty is graded in WP4 of the COHIBA project.

If the Estonian yearly loads were scaled from the EU yearly load to Estonian population, the Estonian population was considered to be 0,3% of the EU population. If the Estonian yearly loads were scaled from the EU yearly load to Estonian area, the Estonian area was considered to be 1% of the EU area. This accuracy level was considered to be enough for given study; especially considering the very high uncertainty levels in other emission strings.

2.1 Crop and animal production, hunting and related service activities

NACE: A 01

Emissions from agriculture, application of phosphorous fertilizers on agricultural soil.

Yearly load – 5,53 kg to AS

Uncertainty: BAAC

Calculation of yearly load of Cd caused by the phosphorus fertilizer: **931776 ha * 23 kg/ha * 0,258 mg/kg = 5,53 kg**

The quantity of cadmium contained in a phosphate fertilizer depends on the source of the rock from which it was made. With current processes, much of the cadmium in the rock passes into the phosphate fertilizers produced from it (IFA, 2010).

The Estonian EF (0,258 mg Cd/kg P₂O₅ in fertilizer) was used. The area of AS was 931 776 ha in 2008 in Estonia and there were 23 kg/ha(as oxide) of phosphorus fertilizers used. The data from 2009 is not yet available (Tallinn University of Technology, 2010).





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In average, the amount of phosphorus fertilizers used in Estonia in 2008 was 23 kg/ha. Phosphorous fertilizers were delivered to Estonia from Finland, Russia, Lithuania, and, to a lesser extent, from Latvia. Lithuania and Latvia prepare/pack the phosphorous fertilizer deposits using the raw materials or finished products apparently from Russia. Both Finnish and Russian Cd content from phosphorite deposits is low, remaining below 0.1 mg/kg.

Agricultural Research Centre of Residues and Contaminants laboratory tests on ammonium phosphate for Cd phosphorus fertilizers in the years 2004, 2007, 2008, show that the Cd content ranged from <0.15 to 0.35. DAP, in average 0.258 mg/kg.

2.2 Mining of oil shale

NACE: 06.10

Mineral industry - Underground mining and related operations

Mineral industry - Opencast mining and quarrying

Yearly load - ? to SW

Uncertainty: N/A

There are two underground mines and six opencast mines registered in E-PRTR but there is no Cd data. All the facilities are subject to reporting (according to the Regulation (EC) No 166/2006), but there is no data in E-PRTR.

We have no data on the Cd emissions to water from the mining activities but we assume it to be an important source as there is some Cd in the oil shale (TUT, 1994).

There were 12 605 tons of oil shale mined in Estonia in 2009 (Statistics Estonia, 2010). At the same time 8300 t is estimated number for opencast mining in Estonia and nearly 7000 t can be annually mined in deep-level mines (Väli et al. 2008).

2.3 Manufacture of pulp, paper and paperboard

NACE: 17.11, 17.12

Paper and wood production processing - production of pulp from timber or similar fibrous materials

Yearly load ? to AO, WW, FSW, and FS



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Uncertainty: N/A

According to Prodcom 2008, there is some pulp production in Estonia. However, there is no monitoring data available and it is not possible to calculate the yearly load from the EU load as the releases from the different plants vary highly.

The data from the Prodcom tables:

Manufacture of pulp - Chemical wood pulp, soda or sulphate, other than dissolving grades - 60 486 thousand kg 90% std (EU Prodcom 2009) (0,3% of EU total production calculated from EU Prodcom data 2009)

Mechanical wood pulp; semi-chemical wood pulp; pulps of fibrous cellulosic material other than wood – 138 577 thousand kg 90% std (1% of EU total production calculated from the EU Prodcom data 2009)

Estonian Cell AS, an aspen pulp factory in Kunda (launched in 2006), is the largest pulp producer in Estonia. There is no data about the possible Cd emissions from the manufacturing process or about the uses of Cd in the process. There should be data in E-PRTR about the Cd emissions, as there is no threshold and all facilities are subjects to reporting, according to the Regulation (EC) No 166/2006. However, there is no data.

Paper and wood production processing - Production of paper and board and other primary wood products

Yearly load ? to FSW, FS, WW

Uncertainty: N/A

Yearly load 20-? kg to AO (data from one plant - Repo Vabrikud AS)

Uncertainty: C

In E-PRTR, the data is only from the big facilities, with a production capacity of 20 tons per day. There are four facilities reporting to the E-PRTR register. The emission data for Cd exists only for one plant – AS Repo Vabrikud – that states the emissions of Cd to AO.

There were 595 000 tons of paper and board produced in Estonia in 2008 (Statistics Estonia, 2010).

Horizon Tselluloosi ja Paberi AS, the largest paper and cardboard producer in Estonia (according to Economic Survey of Estonia 2009 (OECD, 2010)) has stated that they do not use or emit Cd (personal communication with Triin Rospel, environmental manager, October 2010).





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Further research is needed on that topic.

2.4 Energy sector

NACE: 19

Energy sector - mineral oil and gas refineries and thermal power stations and other combustion installations

Yearly load 569,8 kg to AO

Yearly load 22 kg to WW

Yearly load 0,56 kg to FSW

Uncertainty: C

The load to AO is based on the national monitoring data (Estonian Environment Information Centre, 2010c).

The load to WW is from E-PRTR. Estonia reported to E-PRTR for 2008 that Eesti Energia Narva Elektriijaamad AS, Balti Elektriijaam released 22,0 kg of Cd to the WW (E-PRTR, 2010).

Yearly load to FSW is based on national monitoring data (Estonian Environment Information Centre, 2010c). This number includes the load of leachates from the fields of oil shale wastes, i.e. this number is valid for the whole load from the energy sector.

2.5 Manufacture of dyes and pigments; Manufacture of paints, varnishes and similar coatings, printing ink and mastics

NACE: 20.30

Production of artist paint and pigments for other applications

Yearly load - ? to OA

Uncertainty: N/A

According to Prodcom 2008 several activities take place under NACE 20.30, but there is no information about potential uses of Cd. This was included as a potential source in Pan et al. (2009) but data is missing.



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2.6 Manufacture of other organic basic chemicals

NACE: 20.14

Chemical industry - Industrial scale production of basic organic chemicals

Yearly load - ? to OA, FS, FSW

Uncertainty: N/A

According to the Prodcum 2008, there are several activities listed for Estonia under NACE 20.14:

Unsaturated acyclic hydrocarbons (excluding ethylene, propene, butene, buta-1.3-diene and isoprene);

m-Xylene and mixed xylene isomers;

Propylene glycol (propane-1.2-diol);

Citric acid and its salts and esters;

Benzoic acid; its salts and esters;

Carboxylic acid with alcohol, phenol, aldehyde or ketone functions;

Enzymes and other organic compounds n.e.c.;

Production volumes for those activities are classified and we have also no data if Cd might be used under those activities.

Production volumes are given for following activities that take place in Estonia under NACE 20.14 (Prodcum 2008):

Acetic acid 32 000 kg a year.

Methanal (formaldehyde) 1042 000 kg/Y

Oils and other products of the distillation of high temperature coal tar, and similar products; Phenols 1088 000 kg/y

Other oils and oil products, n.e.c. 27 000 kg

It is not known, however, if Cd is used or emitted in this production.

There are also two facilities registered in E-PRTR:

Genovique Specialities Corporation – the Estonian facility was originally built in the 1940s. With the addition of the Benzoic acid unit in 1986 and the Ester unit which was added in 2002, the plant now occupies approximately 66 acres. This ISO 9002 certified state-of-the-art facility manufactures Genovique™ Benzoic Acid, Benzoflex® Benzoate Ester Plasticizers and Probenz® Sodium Benzoate in powder and granular forms⁴).

⁴ http://www.eastman.com/Company/Worldwide/our_sites/Pages/KohtlaJarve_Estonia.aspx





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Production volume of Benzoic acid is 35,860 tons according to E-PRTR, 2010. But there is no data about pollutant releases.

ES Sadolin AS, Rapla production unit (Akzo Nobel Coatings Oy partner company)⁵ produces paints, varnishes, and other materials and printing colours and mastics – 17 092 tons (E-PRTR, 2010). No data about pollutants.

2.7 Manufacture of explosives

NACE: 20.51

Chemical industry - Industrial scale production of explosives and pyrotechnic products

Yearly load ? to WW

Uncertainty: N/A

In Prodcom 2008, the activity “Prepared explosives (excluding propellant powders)” is mentioned under NACE 20.51. Also – we know for a fact that there is one producer of explosives for military in Estonia (Fortestar OÜ⁶). There were also public news in June 2011 about explosions in a warehouse⁷.

However, the data about the production of explosives is confidential. The activity “Matches (excluding Bengal matches and other pyrotechnic products)” is also mentioned with the value 105 000 EUR, and sold volume 11 000 kg.

There is no data for that activity in Estonia in E-PRTR, which is rather typical as there is not much information about Estonia in E-PRTR whether or not the emissions actually exist. In fact, there should be data about these activities in E-PRTR for Estonia as well, as it is written in Regulation (EC) No 166/2006/EC Annex I – Activities and Capacity threshold - Installations for the production on an industrial scale of explosives and pyrotechnic products no capacity threshold is applicable (i.e. all facilities are subject to reporting).

We can conclude that these kinds of activities take place in Estonia, but we don't know if the producers use or emit Mercury. Swedish Products register (2010) gives that there

⁵ <http://www.varvimaailm.ee/>

⁶ <http://www.fortestar.ee/>

⁷ <http://www.tallinnapostimees.ee/468570/mustamael-tehnopoli-hoones-kargatasid-plahvatused/>





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were Hg uses in Sweden in 2008 from this activity. Therefore we can assume this situation is rather similar in Estonia. Further research is needed.

2.8 Manufacture of glass and glass products

NACE: 23.1

Mineral industry - Manufacture of glass, including glass fibre

Yearly load ? to AO

Uncertainty: N/A

There is no monitoring data available.

In Estonia, there is one plant with an IPPC permit that produces glass containers for foodstuffs, liquors, beers, soft drinks, chemicals, and pharmaceuticals. The products are mainly exported and the production volume has been increasing in previous years. Plant produced approximately 57 000 tonnes of glass a year (in 2004).

Only big facilities (with a melting capacity of 20 tonnes per day) have to report to the E-PRTR. The Estonian factory fulfils the criteria of a big facility (156 t per day) but there is still no data in the E-PRTR 2008 about glass production in Estonia.

2.9 Manufacture of clay building materials; Manufacture of other porcelain and ceramic products; Manufacture of refractory products

NACE: 23.3; 23.20; 23.4

Mineral industry - Manufacture of ceramic products including tiles, bricks, stoneware or porcelain

Yearly load ? to AO

Uncertainty: N/A

There were 162,2 mln of bricks produced as a wall material, 14,6 mln of bricks produced as building bricks, and 593,0 m2 of roof bricks produced in 2008 (Statistics Estonia,





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2010). Wienerberger AS, the biggest producer in Estonia, produces 50 millions of bricks a year⁸. There is no data in Prodcum statistical level (Prodcum, 2008).

2.10 Manufacture of cement, lime and plaster; Manufacture of concrete products for construction purposes

NACE: 23.5; 23.61

Mineral industry - Production of cement clinker or lime in rotary kilns or other furnaces

Yearly load 33,96 kg to AO

Yearly load high 52 kg to AO

Yearly load – BBAC

The EF is from the Estonian Informative Inventory Report (Estonian Environment Information Centre, 2010) – 0,04 g/t Cd. The EFM is from the Kunda Nordic Cement AS 2006 data (Kallas, 2007). The yearly loads were calculated as the EF * EFM. The yearly load high was calculated, using the prognosis of the maximum production volume (1 040 000 t in 2008) of the plant (Kallas, 2007) as EFM high.

The statistical data about the clinker production is underestimated. Statistics Estonia, 2010 states only 324 000 t for 2008 and Prodcum, 2008 (the EU level) states the production for 2009 as 448 500 t. The differences are probably caused by the differences in the methods of data collection. This comment is for showing the general reliability for statistical data.

2.11 Manufacture of basic iron and steel and of ferro-alloys

NACE: 24.10

Production and processing of metals - Production of pig iron or steel including continuous casting

Yearly load - ? to OA, WW; FSW

Uncertainty: N/A

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http://www.wienerberger.ee/servlet/Satellite?pagename=Wienerberger/Page/Start05&sl=wb_ee_home_et



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Production and processing of metals - Production of pig iron or steel including continuous casting - Iron (pig iron) casting 1,2 t/y and steel casting 0,5 t/y Estonian statistics (Statistics Estonia, 2010). No production according to Prodcom 2008.

2.12 Manufacture of basic precious and other non-ferrous metals; Manufacture of fabricated metal products, except machinery and equipment)

NACE: 24.4; 24.44

Production and processing of metals - Production of non-ferrous crude metals from ore, concentrates or secondary raw materials

Yearly load - ? to AO, FSW, WW

Uncertainty: N/A

There is no emission data about Estonia in E-PRTR. Under this NACE, the following activity is listed in Prodcom, 2008: “Aluminium production; Unwrought aluminium alloys in secondary form (excluding aluminium powders and flakes)”. The production volume is classified in Prodcom, 2008.

Emission from zinc, copper and lead industry - melting of non-ferrous metal ores (i.e. sulphides)

Yearly load - ? to OA

Uncertainty: N/A

Several activities under NACE 24.4 No emission data. This source was included in Pan et al. (2009) but data is missing.

Use in metal alloys

Yearly load ? to OA

Uncertainty: N/A

In Prodcom, 2008, the activity listed under NACE 24.44 is “Copper and copper alloy tube/pipe fittings including couplings, elbows, sleeves, tees and joints excluding bolts and nuts used for as- sembling/fixing pipes/tubes, fittings with taps, cocks, valves” and the yearly production is stated as 477 000kg/y (Prodcom, 2008). This source was included in Pan et al. (2009) but data is missing.





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Use in corrosion protection

Yearly load ?

Uncertainty: N/A

Prodcom, 2008 lists the following activity taking place in Estonia under this NACE: “Copper and copper alloy tube/pipe fittings including couplings, elbows, sleeves, tees and joints excluding bolts and nuts used for as-sembling/fixing pipes/tubes, fittings with taps, cocks, valves”. According to Prodcom, 2008, the production volume under this activity is 477 t/y that we marked as an additional EF. This source was included in Pan et al. (2009) but data is missing.

2.13 Lead, zinc and tin production; Copper production

NACE 24.43

Primary non-ferrous metal production (smelters or hydrological technology)

The yearly load ? to FS, OA

Uncertainty: N/A

The Prodcom gave a few different activities under these NACEs. However, the data about production volumes under both descriptions was classified in Prodcom, 2008.

The emissions from “Lead, zinc and tin production; Refined unwrought lead (excluding lead powders or flakes)” (that was stated under NACE 24.43) would go to FSW.

The emissions from “Unwrought lead (excluding lead powders or flakes, unwrought lead containing antimony, refined)” would go to AO.

According to the SOCOPSE Deliverable 2.1 non ferrous metal production was responsible for a total emission of 52 tonnes of Cd per year to the atmosphere and 100 tonnes of Cd per year to water in Europe in year 2000. Hence, this is a potential source in Estonia as well.

2.14 Casting of iron; Casting of steel

NACE 24.51, 24.52





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Steel castings for machinery and mechanical appliances excluding piston engines, turbojets, turboprops, other gas turbines, lifting or handling equipment, construction industry machinery/vehicles

Production and processing of metals - Ferrous metal foundries Parts for other utilisation (malleable iron casting)

Production and processing of metals - Ferrous metal

Yearly load - ?

Uncertainty: N/A

2008 Prodcom data; no distribution in between compartments is made.

Under NACE 24.51 “Grey iron castings for locomotives/rolling stock/parts, use other than in land vehicles, bearing housings, plain shaft bearings, piston engines, gearing, pulleys, clutches, machinery”, the production volumes were stated as 1 914 000 EUR (Prodcom, 2008). Emissions from this source would go to AO.

Under NACE 24.52 “Steel castings for machinery and mechanical appliances excluding piston engines, turbojets, turboprops, other gas turbines, lifting or handling equipment, construction industry machinery/vehicles”, the production volumes were stated as 2 852 000 EUR (Prodcom, 2008).

Under NACE 24.51 “Parts for other utilisation (malleable iron casting)” the production volumes were classified (Prodcom, 2008). Emissions from this source would go to FSW.

2.15 Treatment and coating of metals

NACE 25.61

Production and processing of metals - Surface treatment of metals and plastics using electrolytic or chemical processes

Yearly load ? to WW, AO, FSW.

Uncertainty: N/A

In Prodcom, 2008, information for these ES-s could be under:

Metallic coating by immersion in molten metals (zinc galvanizing or tin dipping)

Metallic coating in zinc by electrolysis

Heat treatment of metals (excluding metallic coating, plastic coating)

Anodizing of metals





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Data for production volumes under these descriptions is classified in Prodcom, 2008.

In Prodcom, 2008, information for these ES-s could also be under:

Metallic coating by electrolysis or chemical treatments of metals other than zinc including nickel, copper, chromium, precious metals, etc)

Plastic coating of metals (including powder coating)

Other coatings (phosphating etc)

Wet painting and varnishing of metals

Other metallic surface treatments

The data about production volumes is only given in financial terms and we didn't use these numbers here at the moment.

We also have contacted some of the largest metal processing companies in Estonia. ArcelorMittal, the largest metal processing company in Estonia confirmed that they do not use or emit Cd (Personal communication with the quality manager, Oliver Viikson, June 2010). AS Norma, Tarkon AS, VG Holding AS, Vemo PK OÜ and Vasar Ltd do not use Cd or Cd compounds (Proposals for measures and actions for the reduction of pollution from hazardous substances for the Baltic Sea Action Plan, 2007).

2.16 Manufacture of fabricated metal products, except machinery and equipment; Manufacture of other transport equipment; Manufacture of furniture; Other manufacturing

NACE: 25; 30; 31; 32

Surface treatment of substances, objects or products using organic solvents

Yearly load ? to OA

Uncertainty: N/A

There are activities under those NACE codes in Estonia (Prodcom 2008), but the potential use of cadmium is not known. Further research is needed on that topic.

2.17 Manufacture of batteries and accumulators

NACE 27.20



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Manufacture of accumulators, primary cells and primary batteries

Yearly load - 0,003

Uncertainty: AB-C

No distribution in between compartments is made. The calculation was done as follows: The yearly production value for EU manufacture of accumulators etc was 668869,886; Estonian was 35, which is 0,0052%, therefore it can be considered that the amount of emissions is about the same percentage

2.18 Building of ships and floating structures & Repair and maintenance of ships and boats

NACE: 30.11; 33.15

Building of, painting or removal of paint from ships

Yearly load ? to CSW

Uncertainty: N/A

Estonia has a big repairing company, but there is no information about emissions.

Prodcom, 2008 gives several descriptions under these NACEs.

In Prodcom, 2008, the activities taking place under NACE 30.11 in Estonia are described as:

Offshore vessels

Other floating structures (including rafts, tanks, coffer-dams, landing stages, buoys and beacons)

Conversion and reconstruction of ships, floating platforms and structures

Sailboats (except inflatable) for pleasure or sports, with or without auxiliary motor

NACE 33.15 is described as:

Repairing of ships, boats and floating structures (excluding yachts, other pleasure or sports vessels, rowing boats and canoes)

The production volume under these descriptions is stated as 81 721 000 EUR.





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Under “Maintenance, repair, reconstruction, fitting out services of pleasure and sporting boats Maintenance, repair, reconstruction, fitting out services of pleasure and sporting boats” the production volumes are stated as 22 000 EUR (Prodcom, 2008).

2.19 Sewerage

NACE: 37

Waste and waste water management - Urban wastewater treatment plants

Yearly load – 68,46 kg to FSW

Yearly load – 29,34 kg to CSW

Uncertainty: B

(For comparison):

Yearly load – 0,87 – 2,10 kg to FSW

Yearly load – 0,37 – 0,90 kg to CSW

Uncertainty: C

The Yearly load is from the reported monitoring data from E-PRTR, 2010.

For comparison, we calculated the yearly load low, with the EF derived from the results of COHIBA WP3 and the preliminary results from BaltActHaz. Estonian population is considered to be 1340021 (Statistics Estonia 2010). The data from COHIBA and BaltActHaz preliminary results gave us the EF. The EF was considered to be the average result of all WWTP-s (for min scenario, the results under LOQ were considered to be 0, for max scenario, the results under LOQ were considered to be LOQ). The EF was then multiplied by the EFM, i.e. the amount of effluents produced per person a day – 125 litres (according to Statistics Estonia 2010), the number of inhabitants (1 340 021 according to Statistics Estonia 2010), and the number of days a year (365).

Waste and waste water management - Independently operated industrial wastewater treatment plants serving a listed activity

Yearly load - ? to FSW

Uncertainty: N/A

There is no data industrial WWTPs. Most of Estonian industries are using the municipal WWTPs, i.e. the WWTPs are mixed and there are no special industrial WWTPs in Estonia. The industrial effluents are included in “urban wastewater treatment plants” ES.





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Cd in sewage sludge from municipal STPs

Yearly load – 11,75 – 16,17 kg to AS

Yearly load – 24,97 – 34,36 kg to FS

Uncertainty: CBBC

The calculations were done using the data from COHIBA WP3 and the preliminary results from BaltActHaz project that gave us the EF. The EF was considered to be the average result of all WWTP-s. The representability is highly uncertain due to limited data. The EFM is the one from European SFA-s (Wieland, 2003), considered to be representative to Estonia by Mr Kõrgmaa, an expert of WWTPs and sewage sludge (personal communication). The yearly load was calculated by multiplying EF with EFM and number of inhabitants in Estonia. Disposal on landfill and landscaping is designated to the compartment FS, use in agriculture (including spreading on the farmland) is designated for the compartment AS.

2.20 Waste treatment and disposal

NACE: 38.2

Waste treatment and disposal. Emissions from landfilling of municipal solid waste (operational landfills only).

Yearly loads 0 – 0,00002 kg to SW

Yearly loads 0 – 0,00002 kg to FS

Uncertainty: C

The calculations were done using the excel sheet provided by IVL. The data used was from the COHIBA WP3 results from the study of landfill leachate. However, this result is considered extremely inaccurate as it is based on two samples from one landfill.

2.21 Treatment and disposal of hazardous waste; Recovery of sorted materials

NACE: 38.22; 38.32

Waste and waste water management - Disposal or recovery of hazardous waste

Yearly load – 0,014 kg to WW

Yearly load – 0,100 kg to OA





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Yearly load – 0,056 kg to FSW
Uncertainty: BBAC

WW in this case should be industrial waste water, and not municipal.

No relevant data for Estonia. However, we assumed that the amount of hazardous wastes is roughly correlated to the population, therefore we calculated the yearly load from the EU yearly load, using the population (0,03% of EU population) as a basis for scaling.

Pollutant transfers to waste water according to E-PRTR (2008), which is a register showing pollutant release reported for separate sector-facility.
<http://prtr.ec.europa.eu/PollutantTransfers.aspx>

2.22 Waste collection, treatment and disposal activities; materials recovery

NACE: 38.3

Emissions from materials recovery; Recycling of NiCd batteries

Yearly load – ? to FSW
Uncertainty: N/A

According to available data the batteries in Estonia have only been collected during the last few years, i.e. only deposited, probably until some bigger amount is collected. In 2009, 7 331 t of Ni-Cd batteries were collected in Estonia (in the beginning of the year, there were 49,861 t already collected). According to the data from Estonian Environment Information Centre, the batteries were only collected, not disposed, not recovered, not even recycled (Estonian Environment Information Centre, 2010b).

The NiCd batteries are a growing part in the production of batteries. These are used in laptops, mobile phones etc. They last for 4-5 years. About 50 t of NiCd batteries were released on the market in 2005 (plus 60 tons of batteries of the same type in products)⁹.

⁹ AS EcoPro, 2006, Uuring Eestisse sissetoodavate ning turustatavate patareide ja akude koguste, patarei- ja akujäätmete käitlemise kohta, Tallinn,
<http://www.envir.ee/orb.aw/class=file/action=preview/id=404432/Patareide+uuring+%282006%29.pdf>





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2.23 Construction of buildings & Civil engineering & Specialised construction activities

NACE: 41; 42; 43

Pollutant in Zn. Emission of Cd from the use of Zn in construction materials, due to corrosion.

Yearly load – 0,0174 – 17,42 kg to IS

Uncertainty: BABC

No relevant data for Estonia. However, we assumed that the amount of construction materials is very roughly correlated to the population, therefore we calculated the yearly load from the EU yearly load, using the population (0,03% of EU population) as a basis for scaling.

2.24 Other – passenger land transport

NACE: 49.3

Emissions from transport, storage and transportation; Car washing and degreasing

Yearly load – 13,4 kg to WW

Uncertainty: BABC

The yearly load is calculated from the EU yearly load, using the population (0,03% of EU population) as a basis for scaling.

2.25 Other - Losses from (private) consumption; during lifetime use (including tear and wear) of articles, goods and chemical products and preparations.

Release when washing & cleaning with detergents (probably phosphate based).

Yearly load – 3,62 kg to WW

Uncertainty: BAAC

The yearly load is calculated from the EU yearly load, using the population (0,03% of EU population) as a basis for scaling.





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This ES considers the phosphate-based detergents and includes washing of clothes and textiles, dishwashing by hand or machine. Cd content in detergents should diminish due to new legislations.

Release during use of artist paint.

Yearly load – 7 kg to WW

Uncertainty: BABC

The yearly load is calculated from the EU yearly load, using the population (0,03% of EU population) as a basis for scaling.

Emissions from consumption of food. Seeds (about 45%), potatoes (about 20%), dairy products (about 15%), vegetables, seafood, meat and fruit (about 25% altogether)

Yearly load – 0 kg to WW

Uncertainty: B

According to Veterinary and Food Board¹⁰ there have been no findings of Cd in food control programs in Estonia over the years. Hence we assume this ES to be irrelevant for Estonia.

For comparison we also calculated potential loads according to EU SFA data:

Yearly load – 2,95 – 5,5 kg to WW

Uncertainty: BAAC

Calculation of the yearly loads was based on the Stockholm data (estimated to be 1,7 – 3,2 kg/yr), using the population of Estonia (1 340 021 inhabitants) as a basis for scaling.

*Calculation for Stockholm: 0,0022g/inh. * 762 000 inh. in Stockholm = ca 1,7 kg/year
0,0041 g/inh. * 762 000 inh. in Stockholm = ca 3,2 kg/year*

*Calculation for Estonia: 0,0022g/inh. * 1340021 inh. in Estonia = ca 2,95 kg/year
0,0041 g/inh. * 1340021 inh. in Estonia = ca 5,5 kg/year.*

Emissions from smoking

Yearly load - ?

¹⁰ <http://www.vet.agri.ee/?op=body&id=680>





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Uncertainty: N/A

Smoking is a source to human intake of Cd. Tobacco has a content of Cd due to the uptake of Cd by the tobacco plant (Pan et al., 2009, for example). Quantities related to emissions from this source to air and waste water are not known, though.

2.26 Worldwide activities outside the region, for example atmospheric deposition of long range transport

Atmospheric deposition – wet+dry

Yearly load – 150,55 kg to FSW

Yearly load – 1605,89 kg to FS

Yearly load – 752,76 kg to AS

Uncertainty: BABC

Both wet and dry depositions are considered in this string. The yearly load is calculated from the EU yearly load, using the area (1% of EU area) as a basis for scaling. European deposition calculated from SOCPSE D2.1. The division into the compartments was also changed, according to the data from Estonian Environment Information Centre.

For comparison, MSC-E gives Estonian data as following:

Total anthropogenic sources for 2009 – 0,5 t/y. Contribution of external anthropogenic sources to Cd depositions in Estonia is considered to be very high, with only the thermal power plants in North-Eastern Estonia giving some load (Figure 4). For the same reason, North-Eastern Estonia is the place where most of the Cd is deposited (Figure 5)



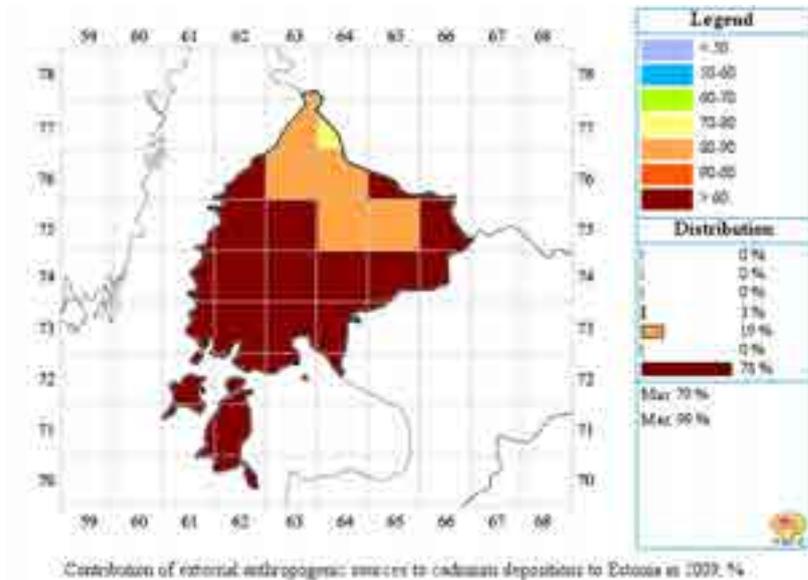


Figure 4. Contribution of external anthropogenic sources to Cd depositions to Estonia in 2009 (MSC-E 2011).

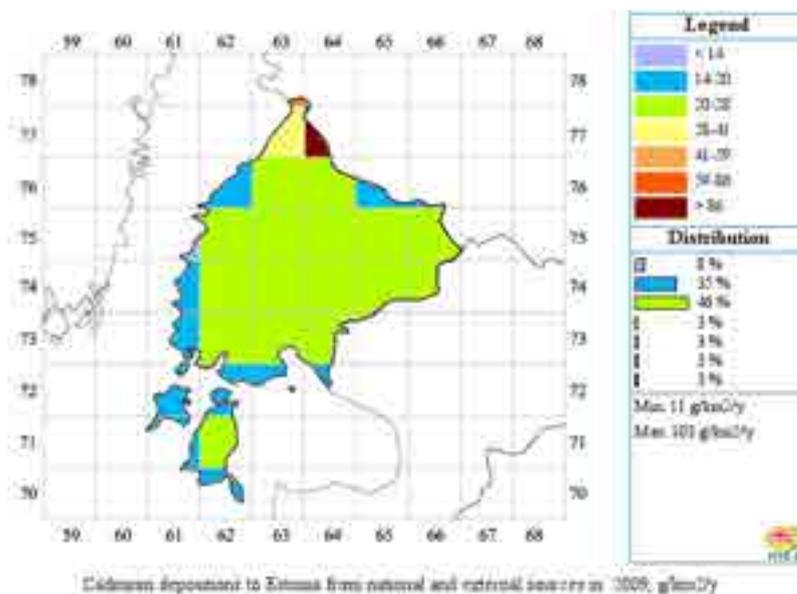


Figure 5. Cd depositions to Estonia from national and external sources in 2009 (MSC-E 2011).

Annual depositions from Estonia are 62 kg altogether (Figure 6), the same number as annual depositions to Estonia (Figure 7).

Annual total depositions from Estonia

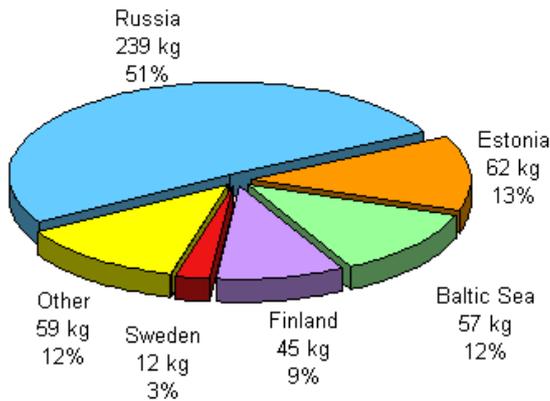


Figure 6. Annual Cd depositions from Estonia in 2009 (MSC-E 2011).

Annual depositions to Estonia

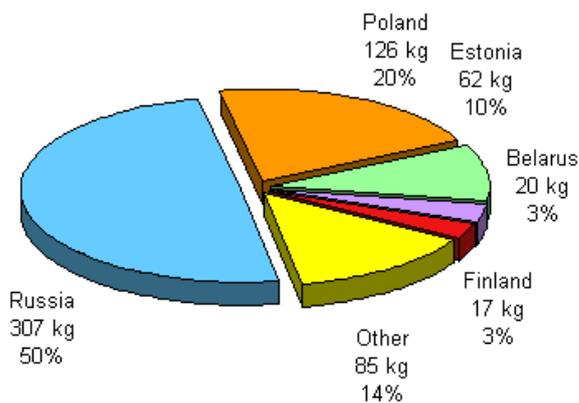


Figure 7. Annual Cd depositions to Estonia in 2009 (MSC-E 2011).





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According to HELCOM (2009) the deposition decreased with 46% if data from 1990 and 2007 are compared. About half of this decrease could be attributed to the period 2000 to 2007. Data from MSC-E also indicates decreasing atmospheric depositions.

2.27 Emission from historical activities

Losses from historically contaminated soils, Historical pollution of contaminated land

Yearly load - ? to FS, FSW

Uncertainty: N/A

No quantitative data about the historical contaminated land in Estonia. But the source is potentially relevant for Estonia.



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3 Emission Strings with no load

There were several emission strings that could be assumed to have some load in Estonia but we have confirmed them to be negligible the most.

3.1 Manufacture of fertilisers and nitrogen compounds

NACE 20.15

Chemical industry - Industrial scale production of phosphorous, nitrogen or potassium based fertilizers

Yearly load 0 to AO, FSW

There is no production of this type of fertilizes any more in Estonia. The production volume for fertilizers containing nitrogen, phosphorus and potassium (> 10% nitrogen) was 5000 t in 2008, but in 2009 the factory stopped the production of fertilizers (Prodcom, 2008). Since 2009, the P and N based fertilizers are 100% imported. In the last years there is a trend to import fertilizers with a low level content of Cd (Tallinn University of Technology, 2010).

Other nitrogen compounds: There is only 1 plant (Nitrofert AS), and that one has applied for IPPC permit. Nitrofert AS processes natural gas into ammonia and prilled urea. The company discharges wastewater into the municipal sewage system (Proposals for measures and actions for the reduction of pollution from hazardous substances for the Baltic Sea Action Plan, 2007).

The products are:

Anhydrous ammonia

Urea containing > 45% by weight of nitrogen on the dry anhydrous product (excluding in tablets or similar forms or in packages of a weight of <= 10 kg)

Ammonium nitrate (excluding in tablets or similar forms or in packages of a weight of <= 10 kg) (Prodcom, 2008).

Urea and ammonia are produced from natural gas so the Cd is not relevant for those productions. For ammonium nitrate the raw material is unknown at the moment.





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3.2 Manufacture of plastics in primary forms

NACE 20.16

Stabiliser in PVC

Yearly load 0

There is no production with a PVC use under the NACE 20.16 (Prodcom, 2008).

Baltplast is the biggest factory in Estonia that produces constructing materials. The factory was launched in 1984. Since 1994 the factory has been working under name Baltplast.

Today the range of products are following:

- paintable wallpaper «Seineks» also known as «structural» wallpaper. «Seineks» is constructed by application of PVC materials on paper surface. With this technology you can create a lot of wallpaper designs.
- floor cover «Bristlex» . This carpet is done of polyethylene material. It can be produced in all colors by the costumer needs.
- plastic construction profile and elevations.
- basketball ball of rubber for outside activity.
- all sorts of rubber goods¹¹.

BaltPlast OÜ has confirmed that Cd is not in use in the production and that the enterprise does not emit Cd/Cd compounds.

The main activity of Plasto AS has been the production and sales of plastic windows and doors and other wall elements. Since June 2007, AS Plasto uses the world's leading technology for the production of PVC windows. A fully automated CNC-managed window production line from the German company SCHIRMER has been installed in AS Plasto. The introduction of modern production technology enables to manufacture up to 600 windows a day. By today Plasto has become a leading manufacturer of plastic windows in Estonia and in the Baltic countries¹².

¹¹ http://www.baltplast.ee/uus_leht.html

¹² <http://www.plasto.ee/index.php?page=133&>





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3.3 Treatment and disposal of non-hazardous waste

NACE 38.21

Waste and waste water management - Incineration of non-hazardous waste included in Directive 2000/76/EC - waste incineration

Yearly load 0 to WW, AO, FS, FSW

There is no waste incineration in Estonia 2011. However, the incineration system is under development in Estonia and might be relevant in the future.

3.4 Other - Losses from (private) consumption; during lifetime use (including tear and wear) of articles, goods and chemical products and preparations.

Emissions from tap water.

Yearly load 0 kg to WW

According to personal communication with Ms Paasrand (EERC) who is an expert on heavy metals, there has been no findings of Cd in any tap water analyses for past 10 years in Estonia.



3 SFA diagram

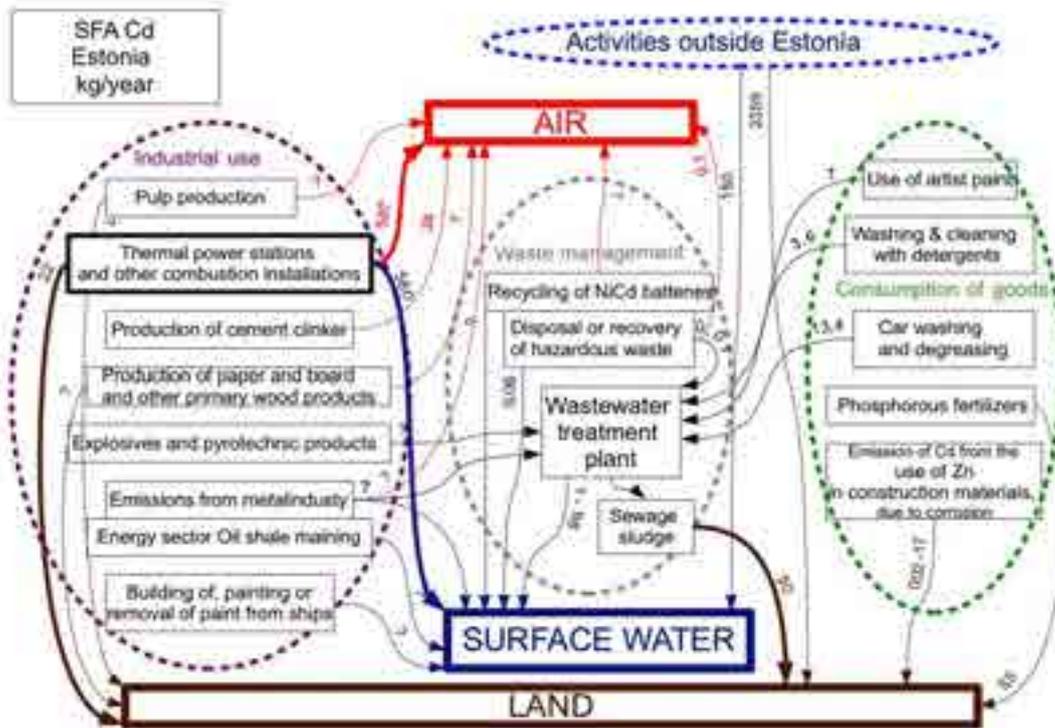


Figure 8. SFA diagram for Cd in Estonia.



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4 Conclusions

4.1 Quantitative estimation of the most relevant sources to each environmental compartment (Soil, water and air)

In E-PRTR, four facilities reported Cd releases to the register in 2008, 3 facilities releasing to air, 2 to water and 0 to soil.

The main source of Cd emissions in Estonia is definitely the thermal power stations and other combustion installations that altogether give emissions of 597 kg to air, 22 kg to soil and 560 kg to surface water, making this source the biggest emitter to air and surface water.

Great emissions to air also come from the production of cement clinker that emits 34 kg of Cd to air. It should be kept in mind that most of the emissions to air are not quantified; however, it is safe to say that the thermal power stations and other combustion installations are the main source.

The sources to wastewater are probably diffuse and mainly not quantified. According to available data, the biggest source is car washing and degreasing that emits 13,4 kg to WW, but this is unlikely to be the most important source altogether as several sources can be expected to be of the same order of magnitude.

The main source of Cd to soil originates from sludge from the WWTPs (50 kg a year) as Cd is a heavy metal and tends to settle in the sludge. A range of 1 to 98 kg Cd a year goes from wastewater treatment plants to surface water.

Besides those sources, atmospheric deposition is also a significant source, giving 2359 kg a year to soil and 150 kg to surface water.

4.2 A qualitative estimation of time trends for future scenarios

Decreasing emissions to air (worldwide) would be an important measure as atmospheric deposition is such an important source of Cd. When it comes to point sources, such as thermal power stations, better treatment, BAT, more monitoring and regulations should be managed.





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Better treatment processes for WWTPs and regulations on sludge use are important measures to be taken as well. As with all hazardous substances, general raising of awareness is also needed to reduce the emissions from diffuse sources.



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ANNEX O – List of abbreviations used in the study

| | |
|------------|---|
| AS | agricultural soil; a receiving compartment used in the SFA |
| BDE | bromodiphenylethers; listed as one of the 11 hazardous substances or substance groups by HELCOM BSAP |
| BSAP | HELCOM Baltic Sea Action Plan |
| CAS number | unique numerical identifiers assigned by the Chemical Abstracts Service to every chemical described in the open scientific literature |
| COHIBA | Control of Hazardous substances In the BAltic Sea region; The current project |
| CSW | coastal surface water; a receiving compartment used in the SFA |
| EF | emission factor; The emission factor is the estimated average emission rate of a given pollutant for a given source, relative to the units of activity |
| EFM | emission factor multiplier - usually used/produced amount; EF was multiplied with EFM to achieve a yearly load from given source |
| EMEP | European Monitoring and Evaluation Programme |
| EQS | Environmental Quality Standard |
| AA-EQS | Annual Average EQS; limit values for pollutants |
| MAC-EQS | Maximum Allowable Concentration EQS |
| E-PRTR | The European Pollutant Release and Transfer Register |
| ES | emission string; one possible pathway of a substance |
| EU | European Union |
| FS | forest soil; a receiving compartment used in the SFA |
| FSW | fresh surface water; a receiving compartment used in the SFA |
| HBCDD | hexabromocyclododecane; listed as one of the 11 hazardous substances or substance groups by HELCOM BSAP |
| HELCOM | Helsinki Commission; Governing body for 1992 convention signed by all the countries bordering on the Baltic Sea and by the European Economic Community |
| IA | indoor air; a receiving compartment used in the SFA |

| | |
|-------|---|
| IS | industrial soil; a receiving compartment used in the SFA |
| LOQ | limit of quantification |
| MSC-E | Meteorological Synthesizing Centre - East |
| MCCP | Medium-chained chlorinated paraffins or chloroalkanes C14-17; listed as one of the 11 hazardous substances or substance groups by HELCOM BSAP |
| NACE | A code for statistical classification of economic activities in the European Community |
| NP | nonylphenols; listed as one of the 11 hazardous substances or substance groups by HELCOM BSAP |
| NPE | nonylphenol ethoxylates; listed as one of the 11 hazardous substances or substance groups by HELCOM BSAP |
| OA | outside air; a receiving compartment used in the SFA |
| OP | octylphenols; listed as one of the 11 hazardous substances or substance groups by HELCOM BSAP |
| OPE | octylphenol ethoxylates; listed as one of the 11 hazardous substances or substance groups by HELCOM BSAP |
| PBT | PBT pollutants are chemicals that are toxic, persist in the environment and bioaccumulate in food chains and, thus, pose risks to human health and ecosystems |
| PFOA | perfluorooctane sulfonate, a perfluorinated substance; listed as one of the 11 hazardous substances or substance groups by HELCOM BSAP |
| PFOS | perfluorooctanoic acid, a perfluorinated substance; listed as one of the 11 hazardous substances or substance groups by HELCOM BSAP |
| PNEC | predicted no effect concentration |
| SFA | substance flow analysis; traces the flows of a substance or substance group through a system defined in time and space by mapping of how the substance enters the system, the pathways within the system and identification of the receiving compartment in the environment. |
| SCCP | short-chained chlorinated paraffins or chloroalkanes C10-13; listed as one of the 11 hazardous substances or substance groups by HELCOM BSAP |
| STP | see WWTP |

| | |
|------|--|
| TBT | tributyltin compounds; listed as one of the 11 hazardous substances or substance groups by HELCOM BSAP |
| TPhT | triphenyltin compounds; listed as one of the 11 hazardous substances or substance groups by HELCOM BSAP |
| TGD | technical guidance document |
| WP | work package; The project consist of six work packages: WP1 - management, WP2 - Communication and Information, WP3 - Innovative approaches to chemical controls of hazardous substances, WP4 - Identification of sources and estimation of inputs/impacts on the Baltic Sea, WP5 - Cost effective management options to reduce discharges, emissions and losses of hazardous substances, WP6 - Capacity building and knowledge transfer |
| WWTP | wastewater treatment plant; the same as STP - sewage treatment plant |

This is the report of Estonian results of COHIBA project Work Package 4. The goal of this study was to assess sources and pathways of 11 hazardous substances of specific concern to the Baltic Sea. The aim was also to quantify the inputs of the selected hazardous substances to the Baltic Sea by assessing and using models.

In the long term this will facilitate the understanding of the link between the sources and releases of the selected substances to the effects in the marine environment enhancing the ecosystem approach to the management of human activities also with regard to hazardous substances.

This report summarises the results from the substance flow analyses (SFA) conducted for Estonia. These results will be used in WP4 to make a joint assessment of the most important sources of hazardous substances in the Baltic Sea region.



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Baltic Sea Region
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