COHIBA

CONTROL OF HAZARDOUS SUBSTANCES
IN THE BALTIC SEA REGION

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Major Sources and Flows of the Baltic Sea Action Plan Hazardous Substances

WP4 FINAL REPORT

COHIBA Project Consortium

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WP4 FINAL REPORT

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Foreword

The project, Control of hazardous substances in the Baltic Sea region (COHIBA), was initiated to address the situation in the Baltic Sea as regards hazardous substances:

Pollution caused by hazardous substances still 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.' (www.helcom.fi)

The COHIBA Project set out to identify the sources and inputs of 11 hazardous substances of special concern, as detailed in the Baltic Sea Action Plan (BSAP), and to develop measures to reduce emissions of these substances. The overall objective was to support the implementation of the BSAP with regard to hazardous substances, by developing joint actions to reach the goal of the programme. The COHIBA Project aimed 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, and
- contribute to the development of national implementation programmes.

The Project ran for three years (2009-2012) and was co-financed by the European Union within the Baltic Sea Region Programme 2007-2013. The Project was led by Finnish Environment Institute (SYKE), and had 22 partners from 8 countries and several associated organisations involved in it.

The present report is the final report of work package (WP) 4: Identification of sources and estimation of inputs/impacts on the Baltic Sea (led by IVL Swedish Environmental Research Institute). The results of WP4 were developed as a joint effort from all partners involved in the WP; Table 1 lists the partners who gave substantial input, especially to the work with the substance flow analyses (SFA).

Table 1: In principle all COHIBA partners were involved in the WP4. In this table are listed the partner organisations involved in, and contributing substantially to, the work in WP4.

Country	**Partner organisation**
Finland	Finnish Environment Institute
Denmark	DHI
Estonia	Baltic Environmental Forum Estonia
	Estonian Environmental Research Centre
	Tallinn University of Technology
Germany	Federal Environment Agency of Germany
	Fraunhofer ISI
Latvia	Baltic Environmental Forum Latvia
Lithuania	Baltic Environmental Forum Lithuania
Poland	Institute for Ecology of Industrial Areas
Sweden	IVL Swedish Environmental Research Institute
	Swedish Chemicals Agency
	City of Stockholm, Environment and Health Administration

Glossary

APE	Alkylphenol ethoxylates
AP	Alkylphenols
BAT	Best available technique
BSAP	Baltic Sea Action Plan
BSR	Baltic Sea region
Cd	Cadmium
COHIBA	Control of hazardous substances in the Baltic Sea region
CSO	Combined sewer overflows
decaBDE	Decabromodiphenyl ether
dl-PCB	Dioxin like polychlorinated biphenyls
EMEP	European Monitoring and Evaluation Programme
EPA	Environmental Protection Agency
EPS	Expanded polystyrene
EQS	Environmental Quality Standard
EU	European Union
HBCDD	Hexabromocyclododecane
HELCOM	Helsinki Commission
Hg	Mercury
HIPS	High impact polystyrene
IMO	International Maritime Organisation
I-WWTP	Industrial wastewater treatment plant
MCCP	Medium-chain chlorinated paraffins
MVC	Mono vinyl chloride
M-WWTP	Municipal wastewater treatment plants
NP	Nonylphenols
NPE	Nonyphenol ethoxylates
octaBDE	Octabromodiphenyl ether
OP	Octylphenols
OPE	Octylphenol ethoxylates
OSPAR	The Convention for the Protection of the marine Environment of the North-East Atlantic

PBDE	Polybrominated diphenyl ethers
PCB	Polychlorinated biphenyls
PCDD	Polychlorinated dibenzodioxins
PCDF	Polychlorinated dibenzofurans
pentaBDE	Pentabromodiphenyl ether
PFC	Perfluorinated compounds
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
PLC4	Pollution Load Compilation 4
PNEC	Predicted No Effect Concentration
POP	Persistent Organic Pollutants
PVC	Polyvinyl chloride
REACH	Registration, Evaluation, Authorisation and Restriction of Chemical substances (EU 850/2004)
SCCP	Short-chain chlorinated paraffins
SFA	Substance flow analysis
SVHC	Substances of very high concern
TBT	Tributyltin
TEQ	TCDD toxic equivalents
TPhT	Triphenyltin
UN	United Nations
UNEP	United Nations Environment Programme
WFD	Water Framework Directive (2000/60/EC)
WP	Work package
WWTP	Wastewater treatment plant
XPS	Extruded polystyrene

Summary and key messages

A summary of the results and conclusions in WP4 and the content of this report are given in Chapter 5, Issues of concern. The results of WP4 can also be described with the use of the key messages:

1. By conducting substance flow analyses (SFA) in almost all Baltic Sea countries participating in the Project, we have created a unique dataset of emission estimates for substances listed in the Baltic Sea Action Plan (BSAP-substances).

2. The work in identification of the major sources and flows of the BSAP-substances has led to an increased awareness in the region, of the importance and complexity of source tracking.

3. Use and emission patterns show regional differences as well as differences between the substance groups; Southern Baltic Proper and Gulf of Finland are the regions indicated as receiving the highest loads of the BSAP-substances.

4. Locally increased levels of several BSAP-substances were identified in and around urban areas.

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

6. 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.

7. Long-range atmospheric transport is an important pathway into the region for several of the substances.

8. There is a need for measured data concerning both environmental levels and emission factors. These data gaps create numerous uncertainties in the results.

9. There is a need for chemical product registers and emission registers covering the BSAP-substances.

10. Coastal emissions to water are of particular importance but emissions to all environmental media and within the whole Baltic Sea region are important for the input to the Baltic Sea.

1 Introduction

1.1 WP 4: Identification of sources and estimation of inputs/impacts on the Baltic Sea

The objective of WP4 in the COHIBA Project was to assess the release patterns and pathways into the Baltic Sea marine environment of the substances of concern (Table 2). 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 and the effects that these have on the marine environment. This could enhance the ecosystem approach to the management of human activities, with particular regard to hazardous substances. The results of this work package also provided crucial input to the assessment of management options of reducing discharges, emissions and losses of hazardous substances, which was the focus in work package 5 (WP5) of the COHIBA Project.

Sources and pathways of the selected hazardous substances, within the Baltic Sea catchment area, were assessed mainly by substance flow analysis (SFA) and chemical fate modelling. To further add to the picture, two additional tasks were performed. The loads to surface waters and land areas due to atmospheric deposition was estimated with the use of monitoring data and the input from contaminated soils and sediments were (qualitatively) assessed, mainly with the use of literature studies.

The methodologies used and how they were applied in the present project are further described by Andersson *et al.* (2012) in the WP4 background paper.

Table 2: 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), nonyphenol 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

1.1.1 Substance flow analysis

To identify the major sources and pathways of the selected hazardous substances the methodology of SFA was applied. The basic idea of an SFA is to make industrial, service-life and waste related as well as environmental flows of a substance visible and comparable, and to facilitate identification of the major sources. The SFA should contain flows and emissions of a substance from manufacture to use and finally, to end-of-life; provided that they occur within the system borders.

SFAs were conducted in accordance to the common WP4 approach (see the WP4 background paper, Andersson *et al.* 2012) in Sweden, Finland, Estonia, Latvia, Lithuania, Poland and Germany and the results were reported in national summary reports for each country (available on www.cohiba-project.net). In these countries, emissions of the selected hazardous substances to air, land and water within the catchment of the Baltic Sea were estimated. The receiving compartments, *i.e.* to which an emission could be directed, were defined and chosen so that the estimated loads could be used as input for the Baltic chemical fate model, POPCYCLING-Baltic, and the local model SMURF (Table 3). Emissions to surface water (fresh surface water, coastal surface water and surface water, unspecified), land (agricultural soil, forest soil or impervious surfaces) and air were regarded as emissions to environmental compartments. Emissions to wastewater and indoor air were regarded as indirect emissions and were evaluated in detail in order to find upstream sources to municipal wastewater treatment plants (M-WWTPs) or sources of indoor emissions. The data and bar charts describing emissions do not include atmospheric deposition, which was assessed separately (see Chapter 3.1). In the substance specific SFA diagrams the estimated loads from atmospheric deposition is included as flows between air and land/water.

Table 3: Receiving compartments

Compartment	**Abbreviation**
Fresh surface water	FSW
Coastal surface water	CSW
Wastewater	WW
Agricultural soil	AS
Forest soil	FS
Impervious surface	IS
Air outdoor	AO
Air indoor	AI

Where possible the emissions from a specific source were quantified with a “low” and “high” emission estimate - aggregated these created a low and high emission scenario. The low and high emission scenarios give, only to some extent, an indication of the uncertainty of the data. As a range of emission factors were not always available, the estimated yearly loads were often not given as ranges (*i.e.* the same value was used in both the low and high scenario). This does not, however, mean that the given value does not have an uncertainty range. As a result there are cases where the difference between the low and high emission scenario is small. This is not to be interpreted as though the uncertainty is small.

The estimated emissions were placed in one of the six categories defined within COHIBA WP4 (Table 4). This was used as a working tool and in some cases it was difficult to categorise the sources, therefore the results of total loads being emitted in the respective categories should be interpreted with care.

The resulting emission estimates were included in a common spreadsheet, which was the basis for the assessment of data on emissions in the present report.

Table 4: The source categories used in COHIBA

Industry	Production, formulation and processing
Service life	Use of consumer goods (incl. buildings)
M-WWTP	Municipal wastewater treatment plants, emissions with effluent and sludge
Waste and sewerage	Materials recovery, recycling, landfilling, incineration
Other	Including *e.g.* agriculture, accidental fires, construction activities and energy production (not industrial)
Historic contamination	Contaminated soils and sediments

1.1.2 Chemical fate modelling

In WP4, models were used to assess the fate of a substance in the environment after emission. The model served to synthesise data on emissions, flows and occurrence – to achieve an ‘overall picture’, as well as to highlight the most important flows for the occurrence of a certain chemical in the environment.

The POPCYCLING-Baltic model was applied to provide a link between the estimated emissions of selected substances within the catchment of the Baltic Sea and the inputs to the Sea. The model was further used to study spatial patterns of the contamination in the marine environment and to investigate the effect of changing scenarios. The selected substances for this modelling exercise were PBDE (congeners 47, 99 and 209), HBCDD, NP/NPE and endosulfan.

The local model SMURF was applied to predict the concentrations and distribution of selected substances in the urban area of Stockholm and to identify and quantify the main input sources to the Baltic Sea ecosystem from such an area. A specific focus of the Stockholm study was also to address the role of the indoor environment as a sink or source of chemical transport to the urban area overall, and thus the role it plays in mediating chemical transport from the urban area to the Baltic Sea. The selected substances for this modelling exercise were PBDE (congeners 47, 99 and 209), HBCDD and NP/NPE.

1.1.3 Case studies

In addition to the case study conducted for the Stockholm area, case studies were performed in Russia and Denmark; the Baltic Sea coastal countries not taking part in the common WP4 approach. The Danish case study focused on the Copenhagen catchment area and the discharges to the Copenhagen Harbour and the Sound (Øresund). Measurement campaigns conducted within WP3 and hydrodynamic modelling were used to identify and prioritise sources of the selected substances. The Russian case studies however used the common methodology of WP4 to estimate emissions of the selected hazardous substances in the St Petersburg and Kaliningrad areas.

1.1.4 Deliverables in WP4

In addition to, and providing the basis for this final report of WP4, the following deliverables were produced:

- WP4 Background paper
  Identification of sources and estimation of inputs to the Baltic Sea
- National summary reports (Sweden, Finland, Estonia, Latvia, Lithuania, Poland and Germany)

- WP4 - Hydrodynamic fate modelling of hazardous substances in Copenhagen Harbour Modelling of discharges from land based point sources
  Danish WP4 report
- Stockholm case study report
- Substance flow analysis case study report of St.Petersburg city and Leningrad region (Russia)
- Case study report on potential emission sources of HELCOM priority substances from Kaliningrad region (Russia)
- Modelling the fate of selected organic contaminants in the Baltic Sea – application of the POPCYCLING Baltic model

The reports contain detailed descriptions of both methodologies and results presented in the WP4 final report and they are all available on the COHIBA website (www.cohiba-project.net).

2 Most important sources as found in the substance flow analyses

The dataset obtained from the SFAs was used to assess which are the major sources and flows for the BSAP substance groups. Furthermore, the dataset was used to assess which substance groups were particularly relevant for the source categories M-WWTP, industry, service life, waste and recycling, agriculture and energy. This dataset was derived from the SFAs conducted nationally, as described above, and all underlying data including references of these data can be found in the national summary reports available on www.cohiba-project.net.

2.1 By substance

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

Introduction

Chlorinated dioxins and dioxin-like compounds are a class of structurally and chemically related polyhalogenated aromatic hydrocarbons which includes polychlorinated dibenzo-p-dioxins (PCDDs or dioxins), dibenzofurans (PCDFs or furans) and the 'dioxin-like' biphenyls (PCBs). The PCDD/Fs are substances formed unintentionally in combustion processes; the most important factor in forming dioxin-like compounds is the temperature of the combustion gases. PCBs have on the other hand been intentionally produced and used in *e.g.* hydraulic fluids, coolant-insulation fluids in transformers and plasticisers in paint (Walker *et al.* 2006). The co-planar PCBs, *i.e.* only certain congeners of the 209 possible, are dioxin-like. The mode of action is the same for PCDD/Fs and the dioxin-like PCBs, which is why amounts are often reported in aggregated form in the unit of toxic equivalent quantities (TEQ). In the present report all different kinds of TEQ have been regarded as comparable.

Important regulations in this context include for example the Stockholm Convention on Persistent Organic Pollutants (POPs), the Convention on Long-range Transboundary Air Pollution and the PCB Directive No 96/59/EC on the controlled elimination of polychlorinated biphenyls and terphenyls (PCB/PCT).

Results

As evident in Figure 1, the majority of emissions to environmental compartments were categorised as 'other'; with the largest share of emissions within the Baltic Sea Region (BSR) seemingly originating from Poland. The most important sources in this category were residential combustion, accidental fires and heat and power production. Polish emissions from residential combustion contributed to more than 70% of the total load from this source within the BSR. Industrial sources were mainly combustion related. Historic contamination as a source was, in the majority of cases, not possible to quantify, which means that the contribution from this source is most probably larger than indicated in the figure below (see also Chapter 3.2).

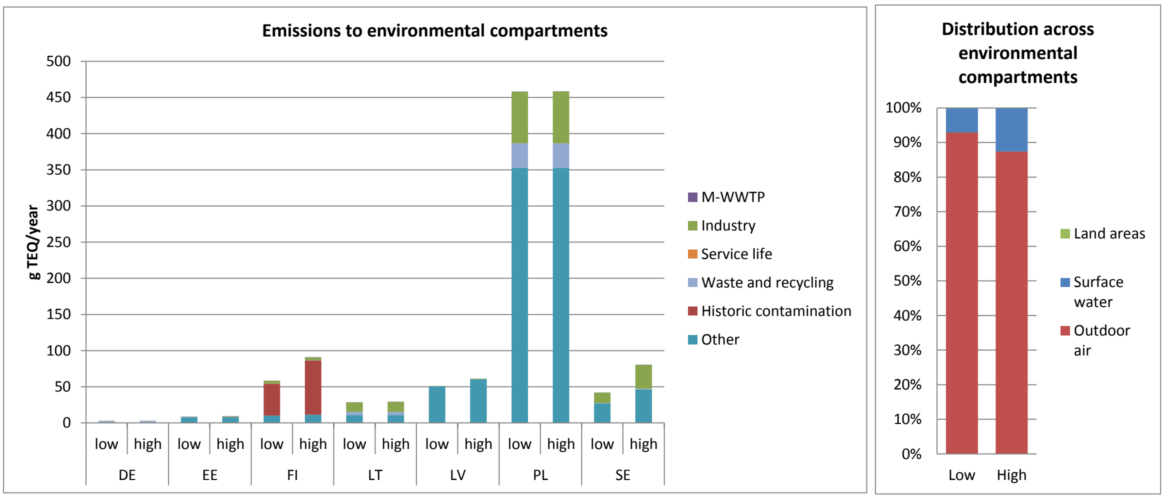

Figure 1: Total load of dioxins, furans and dioxin-like PCBs per country, to environmental compartments; air, land and surface water (left). The distribution of emissions across environmental compartments is shown in the figure to the right. There were large data gaps for the dl-PCBs, meaning that these figures mainly show emission of the PCDD/Fs.

Emissions to air dominate the environmental releases (Figure 1). Estimations of atmospheric deposition within the region (Figure 2) were in the same order of magnitude as estimated air emissions. Emissions to air are thus indicated to be an important source of the loads to land and waters, possibly also with input from outside the region.

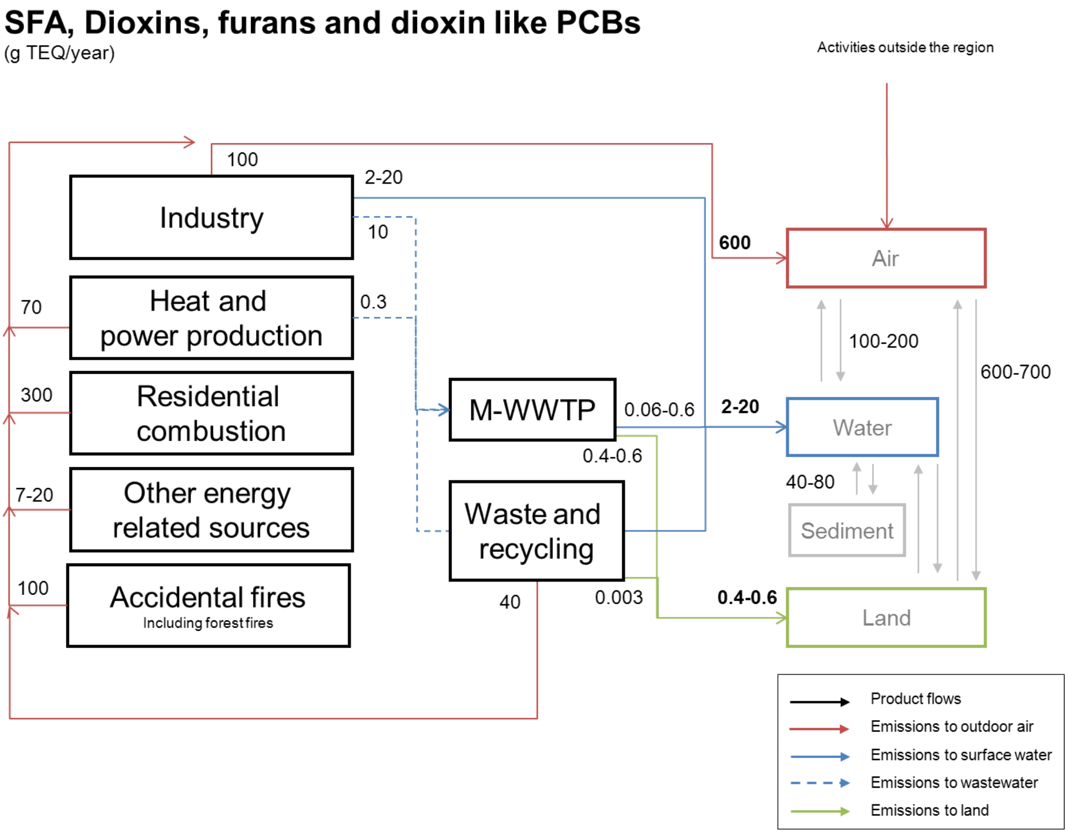

Figure 2: Simplified substance flow analysis (SFA) for dioxins, furans and dioxin-like PCBs in the Baltic Sea Region (c. 2008- c.2011). There were large data gaps for the dl-PCBs, meaning that these figures mainly show emission of the PCDD/Fs. Numbers are rounded to one significant digit.

Discussion and conclusions

Unabated air emissions such as residential combustion and accidental fires are the major sources of dioxins and dioxin-like substances. Poland was identified as the country with the largest emissions. Looking at the total emissions on a per capita basis, Finland and Latvia seem to have similar or higher emissions.

As the many of the emission estimates for the dioxins are based on EMEP emission data (www.emep.int), they were regarded as reliable data and thus the overall dataset for this substance group was also assessed to have a comparatively low level of uncertainty. Emissions from accidental fires and historically contaminated sites are, however, important exceptions and there are large data gaps with regard to data on emissions of dl-PCBs. Furthermore, as transfers to waste and transfers within the waste sector were not in focus in the present study, we have not identified the major flows with waste and there may be relevant data gaps concerning emissions from waste handling.

The awareness of the hazardousness of these substances, in addition to an effective inventory of emissions, lead to the conclusion that emissions will be further reduced. As these substances are unintentionally produced, a complete reduction of emissions was judged impossible to achieve.

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

Introduction

Tri-substituted organotins have mainly been used as biocides. For tributyltin (TBT) the dominant application has been the use as a biocide in antifouling paints and wood preservatives. It has also been used as a biocide in other applications such as insoles for shoes and non-allergic pillows, and as a pesticide. Mono- and di-butyltin compounds are still used as stabilising agents in PVC plastics and TBT is commonly found in these products as an impurity. Triphenyltin compounds (TPhT) have been used as biocides in antifouling products but also as fungicides on several types of crops.
The use of tri-substituted organotins in antifouling paints became prohibited in EU in 2003 (Directive 2002/62/EC, Regulation 782/2003/EC) and the International Maritime Organisation (IMO) created an international ban in 2008 (IMO 2010). Furthermore, biocidal use of organotin compounds was banned in EU 2006 (Directive 98/8/EC). TBT is also included on the list of priority substances in the Water Framework Directive (WFD, Directive 2000/60/EC). However, TBT and TPhT have been incorporated into products with long lifetimes in the use or waste stage, and may thus continue to be released into the environment also after the introduction of bans.

Results

No emission data were found for TPhT and it was therefore not possible to quantify the emissions of TPhT to the Baltic environment. However, in the Swedish SFA for organotin compounds potential emission sources are identified and described (Swedish WP4 Summary report).

There is a considerable uncertainty in the SFA data for TBT. About 26% of the emission estimates made in this study for TBT are given a question mark (?) for the yearly load, meaning that it is a possible source of emissions but it was not possible to calculate the load due to lack of data. For sources categorised as historic contamination there are no loads reported at all, although it is known that there are emissions from contaminated sediments in for example harbour areas (see Chapter 3.2). One must therefore keep in mind that the sources identified in this study as most important for TBT emissions into the Baltic environment may not be the dominating ones if the estimations are performed with an improved data set.

According to this study the emissions of TBT into the Baltic environment are mainly distributed to land and air (Figure 3, right) and are dominated by emissions from service life sources (Figure 3, left). The indication that emissions to air appear to be more important than emissions to water is, however, most likely due to lack of data as the volatility of most organotin compounds is low. The main source in the service life category is use of timber treated with TBT as a biocide. This is estimated to be a source in Estonia, Poland and Sweden, but only Sweden has reported emission loads. Hence the total emission from this source to the Baltic environment may be underestimated. The use of products containing organotin compounds as catalysts are also reported to be a rather important source, dominated by two types of products; on the one hand products in which TBT has been used for esterification and powder coating (used in heating and air condition systems, office furniture and household appliances such as washing machines and refrigerators, etc.), and on the other polyurethanes (used in upholstered furniture, mattress fillings, car seats, etc.). These are reported as potential sources in Germany, Estonia, Poland and Sweden, but as only Estonia and Poland have reported emission loads the total emission to the Baltic environment may be underestimated.

In some countries industrial sources may also be of importance for TBT emissions into the Baltic environment (Figure 3, left). The main industrial source is the use of TBT compounds as intermediates in the production of other compounds, for example as a reducing agent for the conversion of alkyl halides to hydrocarbons and for desulfurisation of organic sulfides. This activity is reported to be present in Germany, Estonia and Poland but only Germany has quantified the loads. Emissions of TBT from product manufacture involving organotin compounds as catalysts, mainly in the esterification and powder coating of plasticisers for PVC, is also identified as a possible industrial source in Germany and Poland. This is however a rather uncertain source as only Poland has been able to report loads and the low and high scenario differs by a magnitude of 100.

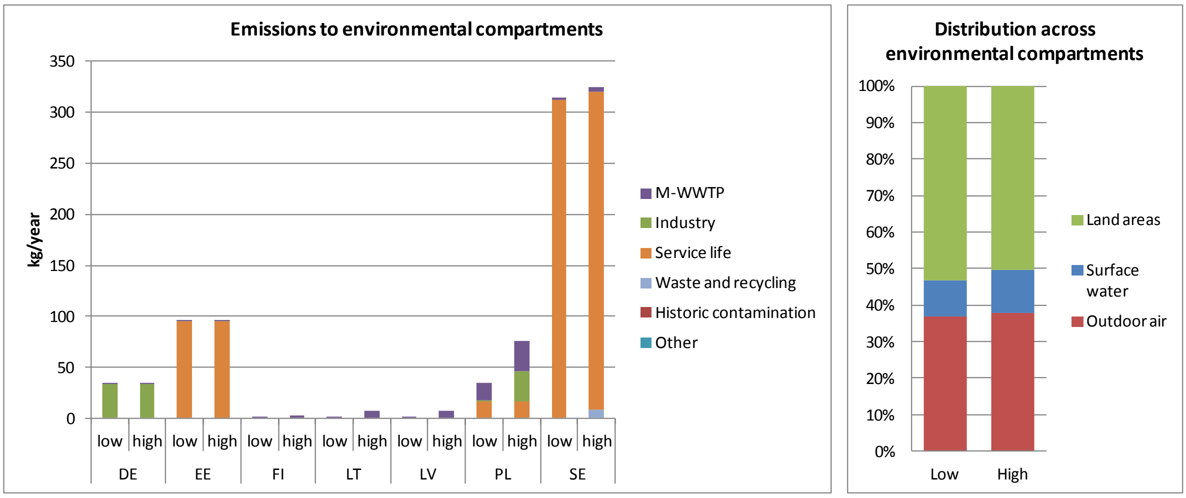

Figure 3: Total load of TBT per country to environmental compartments; air, land and surface water (left). The distribution of emissions across environmental compartments is shown in the figure to the right. These data are associated with uncertainties and a number of data gaps were reported by almost all countries (up to 60% of the identified sources were not possible to quantify in some countries).

Emissions from municipal M-WWTPs are also of importance for TBT in some of the Baltic countries (Figure 3, left). The emissions of TBT to wastewater primarily come from service life sources, mainly from the use of products containing catalysts but to some extent also from the use of rigid and flexible PVC products. PVC products are estimated to be emission sources in Germany, Estonia, Finland, Poland and Sweden but none of these countries have been able to quantify emission loads, hence the emissions may be underestimated. As mentioned before, it is important to consider the high level of uncertainty in the data for TBT. Thus, there may be other important sources of emissions of TBT to wastewater in addition to those identified in this study.

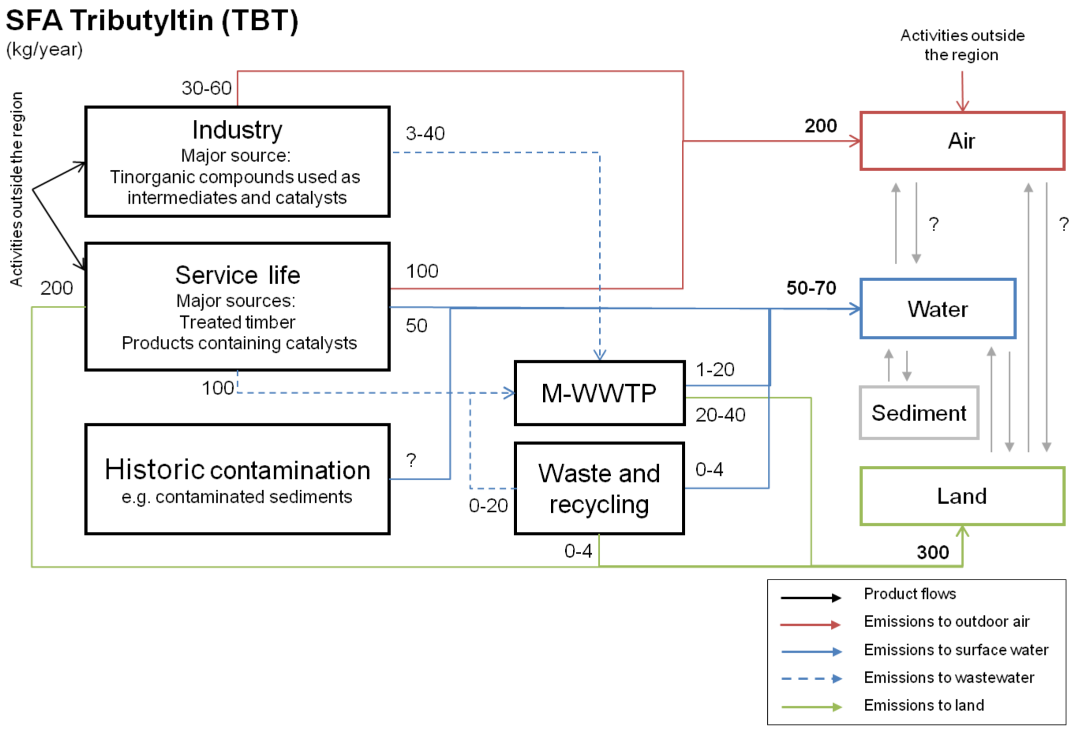

Figure 4: Simplified substance flow analysis (SFA) for TBT in the Baltic Sea Region (c. 2008- c.2011). Numbers are rounded to one significant digit.

Discussion and conclusions

Among the quantified sources emissions from service life sources directed to land areas are of most importance for releases of TBT into the Baltic environment. It is, however, well known that, for example emissions from contaminated soils and sediments in harbour areas are of importance for the release of TBT to surface waters, although the yearly load is yet to be quantified. Furthermore, butyltin compounds are commonly found in stormwater in urban areas. Responsible emission sources may for example be the use of sealants containing organotin compounds in tunnels and buildings. The influence of urban runoff on the local aquatic environment is, however, depending on whether stormwater is treated in M-WWTPs or is directly discharged to the recipients.

As mentioned before there is a considerable element of uncertainty in the data for TBT. A large part of the identified emission sources could not be quantified in this study due to a lack of data on emission factors and use. Hence, the sources identified in this study as most important for TBT emissions into the Baltic environment may not be the dominant ones if the analysis were performed with an improved data set. Thus, there is a need for new data regarding environmental levels and emission factors, and more information about former and present use.

2.1.2. Pentabromodiphenyl ether (pentaBDE), octabromodiphenyl ether (octaBDE), decabromodiphenyl ether (decaBDE)

Introduction

Polybrominated diphenyl ethers are brominated flame retardants (BFRs) which have been used since the early ‘70s in plastics, electronics, some textiles and upholstered furniture. Tetra- and pentabrominated diphenyl ethers belong to the nine ‘new’ persistent organic pollutants listed on the Stockholm Convention and are thus subject to a global ban. The use in the EU is strictly regulated, and only decaBDE is now allowed to be used, in products other than electronics. Furthermore, pentaBDE is also included on the list of priority substances in the WFD. On the global scale, no restrictions around decaBDE exist in Asia and the global demand of BFRs is expected to rise due to increasing requirements on fire security in developing countries. Furthermore, the substances have been incorporated into products with long lifetimes in the use or waste stage and may thus continue to be released into the environment even after the introduction of bans.

Results

The highest PBDE emissions in the Baltic Sea region are estimated to originate from Finland, Sweden and Poland. The order between the three depends on the emission scenario (Figure 5, left). On a per capita basis, the largest emissions are estimated to derive from Estonia, Finland and Sweden. Emissions into the environment are mainly to land areas, followed by outdoor air (Figure 5, right). Emissions of pentabrominated PBDEs are still estimated to be of a similar order of magnitude as those of decaBDE, particularly if releases indoors are taken into account.

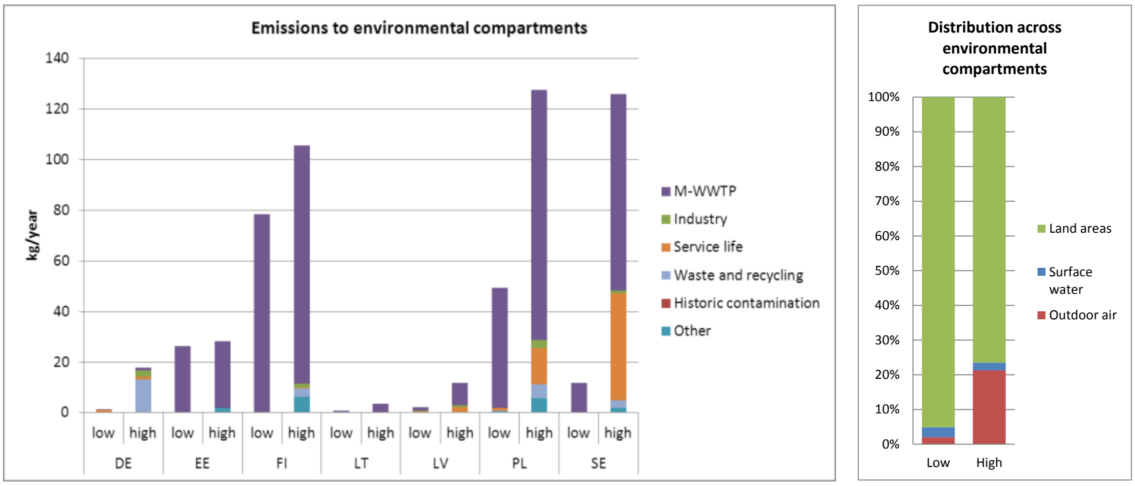

Figure 5: Total load to environmental compartments; air, land and surface water (left) of PBDE (penta+deca) per country for different source categories (left) and distribution of emissions across environmental compartments (right).

The emissions of PBDEs to environmental compartments within the Baltic Sea region as estimated in the COHIBA Project tend to originate mainly from the application of contaminated sewage sludge, followed by emissions during service life of flame retarded products in the form of release from the indoor environment. The main sources of emissions to outdoor air are estimated to be the indoor environment, steel industry and the accidental fires of waste.

The emissions to the indoor environment (300-900 kg/year) are estimated to be of a similar order of magnitude as the total emissions to the outdoor environment. The amount reaching the environmental compartments, however, is lower (3-60 kg), possibly as an effect of dust removal indoors (see Chapter 4.3). This could also be a result of missing data, as the Swedish study showed the opposite, an underestimation of emissions to indoor air. A substantial amount of the PBDEs released diffusively appear to end up in the sludge of municipal treatment plants, where it may be re-released into the environment via application of sludge as a soil improver. However, the pathways out from the indoor environment were difficult to assess for many countries, thus the figures presented should not be regarded as complete. A recent Swedish study indicated that indoor air may contribute as much as 86% of the total releases to outdoor air (see Chapter 3.2). The modelling study (Chapter 4) indicates low potential for transport of chemicals from inland soil to the Baltic, but it is possible that certain extreme conditions (*e.g.* flooding, erosion etc.), not considered in the model scenarios, could lead to such release. Empirical studies could help to explore this possibility further.

The estimated emissions to air (4-100 kg) are about a factor of 10-20 lower than the estimated atmospheric deposition in the area (approximately 100-700 kg/year for ΣBDEs 47, 99, 100, 209), indicating that long-range transport followed by deposition is likely to be important for these substances.

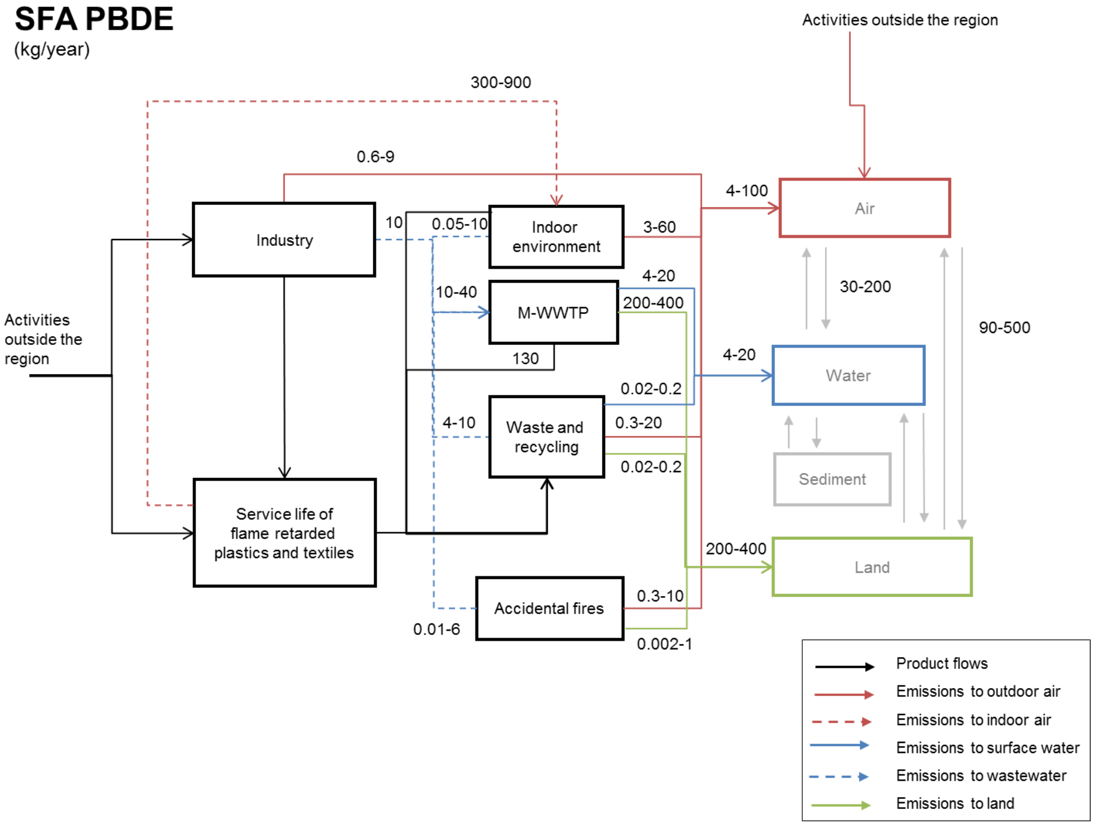

Figure 6: Simplified substance flow analysis (SFA) for PBDE in the Baltic Sea Region (c. 2008-c. 2011).

Discussion and conclusions

The use of PBDE has decreased to a minimum within the European Union during the last decade but sources of release to the environment are still present. In total we have estimated present emissions of 200-500 kg per year to environmental compartments within the Baltic Sea region. In addition, atmospheric deposition contributes to large loads on land and water, to a larger extent than can be explained by emissions to air within the region. This is an indication that sources outside the region contribute to the total load.

Diffuse emissions during the service life of flame retarded products are expected to occur predominantly in the indoor environment, and these have a potential to reach the outdoor environment. The extent to which this occurs is, however, still unclear, but recent studies indicate that this may be substantial. The extensive global regulation of PBDEs speaks for declining use and emissions in the future. Nevertheless, as no regulation for decaBDE exists in for example Asia, and the demand in developing countries increases, it is likely that PBDEs will remain in the global and Baltic environment for many years to come. To further reduce the risk of large emissions in the future it is important that global political acts are agreed upon. From a regional perspective it seems that emissions are best regulated by strict control over imported products, efficient removal and destruction of dust indoors and further treatment of contaminated sludge to remove harmful substances.

2.1.3. Perfluorooctane sulfonate (PFOS), Perfluorooctanoic acid (PFOA)

Introduction

PFOS and PFOA are, as the names imply, perfluorinated substances. This means that each hydrogen on the compound’s alkyl chain has been exchanged with a fluorine atom. PFOS can be used as salts or higher derivatives of the molecule or it can be incorporated into polymers[1]. PFOA occurs as a number of salts. Both substances are the final degradation products of a number of precursors, such as polymers (PFOS) or fluorotelomer alcohols (PFOA) and are extremely persistent, virtually non-degrading substances. Due to their surface-active properties these substances have been widely used both in industrial processes and in consumer articles.

The use of PFOS within the EU was restricted under REACH (Regulation (EC) No 1907/2006) and is now restricted under the EU POPs regulation (EU 850/2004). PFOA is less regulated but there are voluntary industrial actions to reduce emissions (the PFOA Stewardship programme (www.epa.gov)).

Results

The largest emissions were estimated to originate from Finland and Germany (depending on scenario, (Figure 7)). These are also the countries with the highest estimated emissions on a per capita basis.

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[1] In the present report emissions of PFOS-salts and higher derivatives such as xFOSAs and xFOSEs (see Andersson *et al.* 2012 for further details) have been included and aggregated. Emissions of PFOS incorporated in

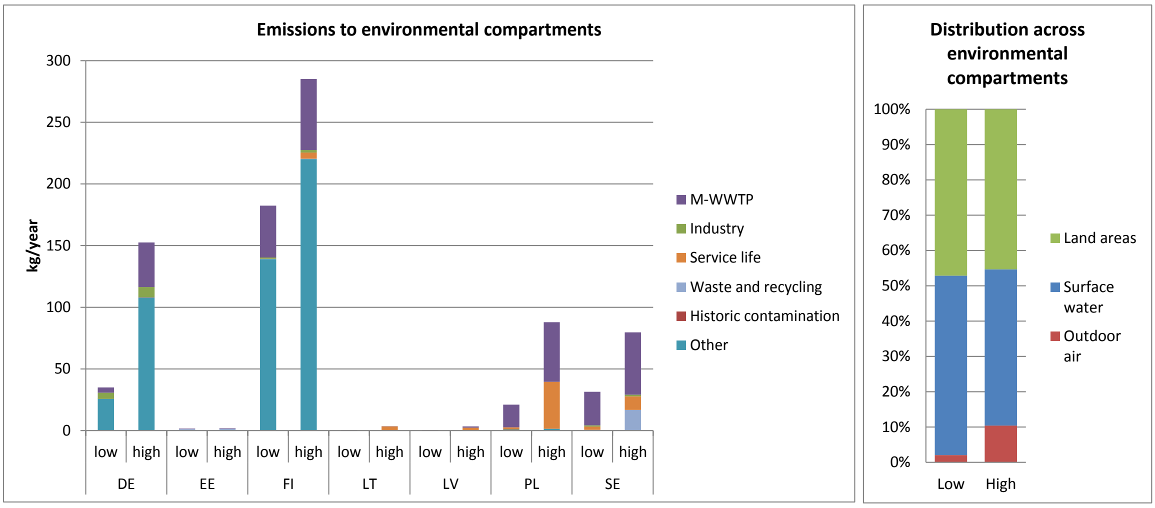

Figure 7: Total load of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) per country, to environmental compartments; air, land and surface water (left). The distribution of emissions across environmental compartments is shown in the figure to the right. These data are associated with uncertainties and a number of data gaps were reported by almost all countries (about 10% of the identified sources were impossible to quantify).

The main sources of PFOA to environmental compartments were M-WWTPs, release due to the transformation of fluorotelomer raw material (categorised as service life emissions) and the use of PFOS containing fire fighting foam, in which PFOA may be an impurity, (category ‘other’) with approximately 40%, 30% and 20% of the total of the high emission scenario, respectively. For PFOS the principal sources were the use of PFOS containing fire fighting foam (category ‘other’) and M-WWTPs with approximately 70% and 30% of the total. Important upstream sources to the M-WWTPs were for PFOS the metal plating industry, which was the major industrial source, and service life emissions from products and materials containing PFOS, and for PFOA the major upstream source was landfill leachate. Cleaning activities as a source of PFOS was only identified in Sweden, whether this is due to data gaps in the other countries is not known. The use of PFOS containing fire fighting foams was banned in June 2011, the estimated emissions in the present study are from before that ban.

Products and materials containing PFOS, for example impregnated carpets and apparel, were impregnated with polymeric materials containing PFOS (Brooke *et al.* 2004). Wear and tear of the material generates emissions, and in COHIBA emissions of impurities in the form of salts of PFOS, as well as lower derivatives were estimated. Wear and tear should also cause emissions of the polymers (containing PFOS), which could constitute a stock of PFOS-containing materials in the environment from which emissions were not quantified in the present study.

Emissions to air were assessed as less important than emissions to land and surface water (Figure 7). Long-range transport in the atmosphere or in the oceans may also contribute to the loads in the Baltic Sea but this was not possible to quantify in the present study (Figure 8).

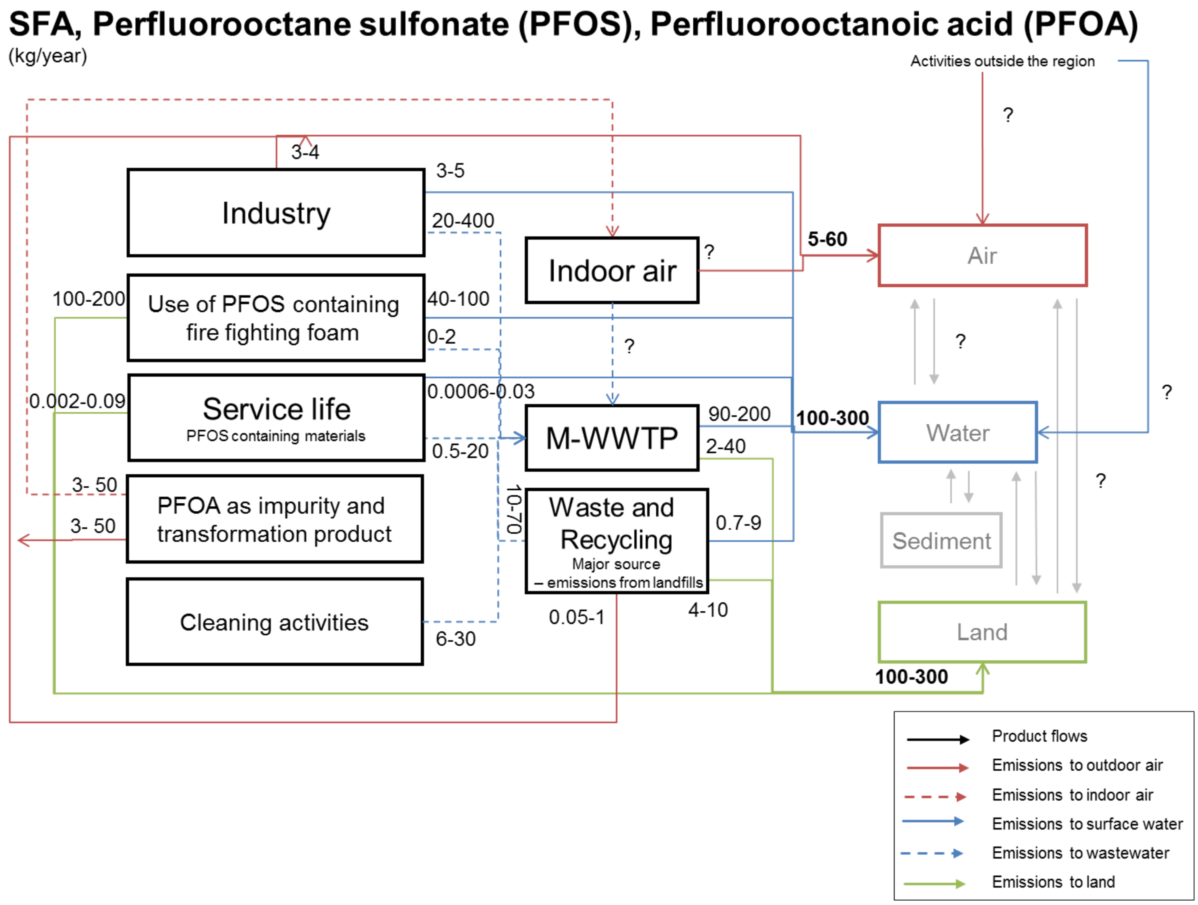

Figure 8: Simplified substance flow analysis (SFA) for perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in the Baltic Sea Region (c. 2008- c.2011). Numbers are rounded to one significant digit and include only emissions of PFOA-salt and PFOS-substances; PFOS-polymers have been excluded. There may also be import with products and articles.

Discussion and conclusions

Despite strict regulation of PFOS, emissions still seem to occur. Furthermore activities outside the EU may generate inflow to the BSR. Emissions of PFOA seem to originate, to a large part, from degradation of precursors such as fluorotelomer alcohols.

These emission estimates are associated with uncertainties, due to both data gaps and to the fact that some of the estimates were obtained by scaling from EU or even global data.

With the ban on the use of PFOS containing fire fighting foams coming into force in 2011, emissions of both PFOS and PFOA will decrease substantially based on the emission scenarios presented here. Emissions from the use phase of PFOS containing articles can be expected to decrease too as the stock accumulated in society decreases.

2.1.4. Hexabromocyclododecane (HBCDD)

Introduction

HBCDD is a brominated flame retardant used predominantly within the polymer and textile industry. The main use in plastics is in polystyrene insulation boards (XPS and EPS), used in buildings and under roads and similar constructions. Certain kinds of textiles are back coated with

HBCDD; *e.g.* curtains and mattresses. HBCDD is now regulated under REACH by inclusions on the list of authorisation (Commission Regulation (EU) No 143/2011).

Results

In many countries the use of HBCDD has decreased during the last decade. The largest emissions in the Baltic Sea region as identified in the present project come from Poland, followed by Finland and Germany (Figure 9). Poland and Finland were also the countries in which industrial activities were still identified to emit HBCDD in relatively high loads.

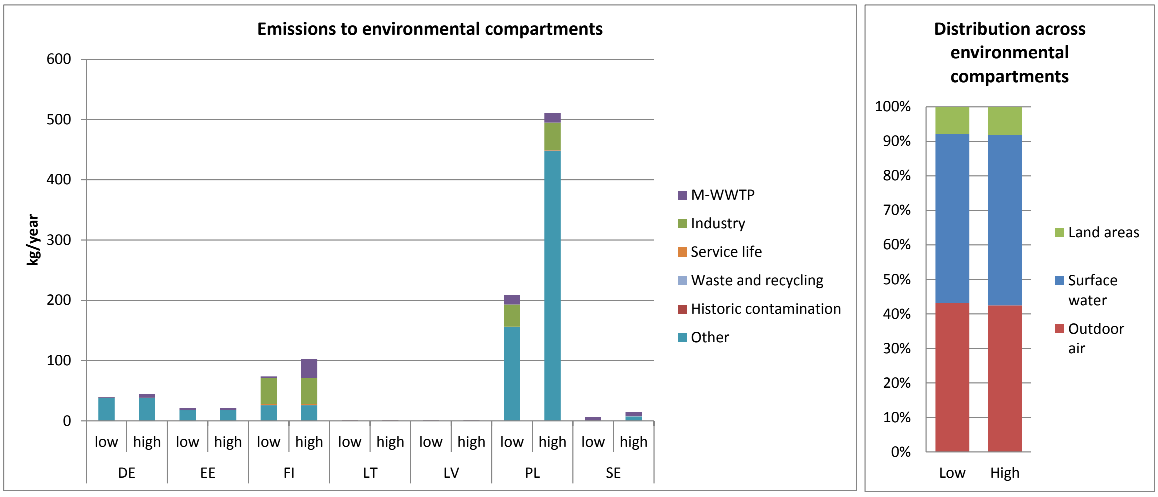

Figure 9: Total load of Hexabromocyclododecane (HBCDD) per country, to environmental compartments; air, land and surface water (left). The distribution of emissions across environmental compartments is shown in the figure to the right. These data are associated with uncertainties and a number of data gaps were reported by almost all countries (up to 25% of the identified sources were impossible to quantify in some countries).

The major sources of HBCDD to environmental compartments are construction and demolition of buildings (category ‘other’) and manufacturing of flame retarded products. Manufacture of HBCDD does not occur with the BSR. The estimated emissions from the demolition of buildings may be a future scenario as many buildings with HBCDD containing insulation material are not yet being demolished. Moreover, HBCDD is also emitted during the service life, albeit in smaller quantities. It was estimated that part of the service life emissions would end up in wastewater; in the WWTP HBCDD is removed from the water phase by partitioning to sludge. As part of this sludge is used as a soil improver, the substance does still enter the environment.

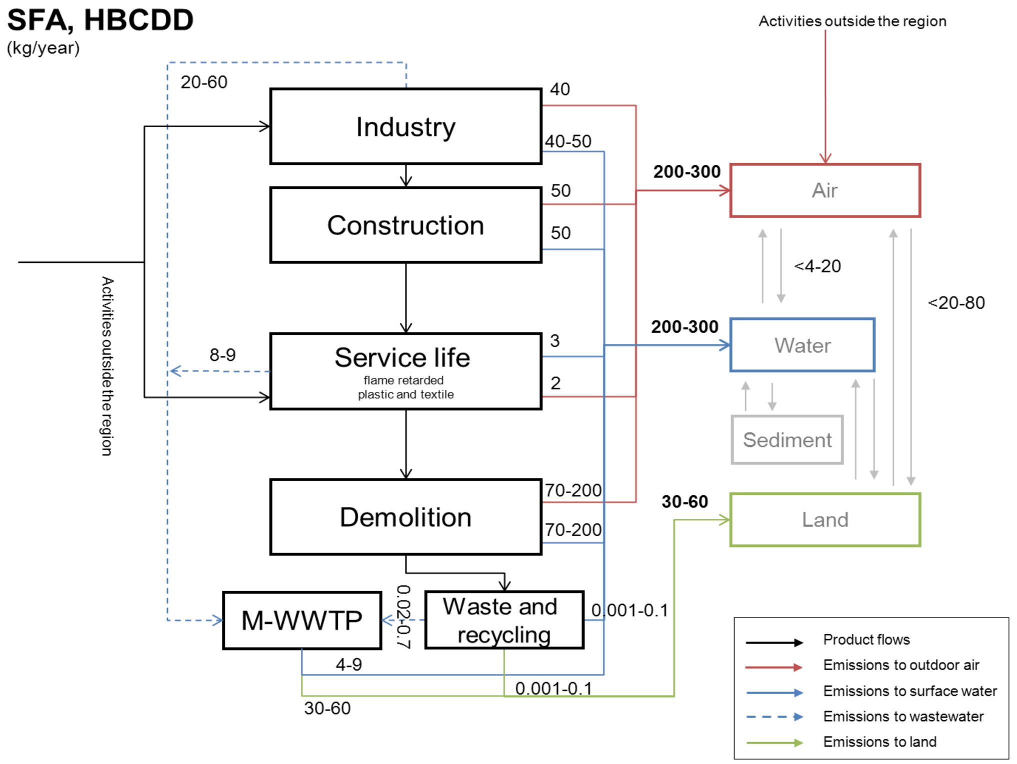

Figure 10: Simplified substance flow analysis (SFA) for Hexabromocyclododecane (HBCDD) in the Baltic Sea Region (c. 2008- c.2011). Numbers are rounded to one significant digit.

Discussion and conclusions

Even though the use of HBCDD has decreased during the last decade, we could still identify total emissions of 400-700 kg per year within the BSR. These loads are, however, associated with a number of uncertainties, particularly the estimated emissions from construction and demolition activities, and there are substantial data gaps in some countries.

The inclusion of HBCDD on the list of substances for which an authorisation is needed under REACH may, however, lead to even greater decreases in the use of this substance, and thus also to decreased emissions. To further reduce the risk of large emissions in the future it is important to find demolition techniques which reduce emissions of hazardous substances. From a regional perspective, it seems that implementation of emissions reduction measures should be focussed on Poland. However, on a per capita basis emissions were higher in Finland, Estonia and Germany.

2.1.5. Nonylphenols (NP), nonyphenol ethoxylates (NPE)

Introduction

Nonylphenol (NP) is an organic compound that belongs to a broad family, the alkylphenols (AP), and more specifically to the group of long-chain APs. The name nonylphenol can be applied to a number of isomer substances that have a phenol ring structure and an alkyl chain of C_9H_{19}. Nonylphenol ethoxylates (NPE) belongs to the class of chemicals called alkylphenol ethoxylates (APE). Degradation of NPEs in WWTPs or in the environment generates the more persistent NP. Thus NPE sources are also possible sources of NP.

NP is a breakdown product of NPE, but is also used as itself, as for example, a stabiliser in rubbers and plastics. NPEs are predominantly used as industrial and domestic detergents and cleaning agents. Depending on the number of ethoxy groups NPEs possesses different properties. NPEs can be used as surfactants and detergents (<10 ethoxy groups), emulsifiers (10-30 ethoxy groups) or dispersants (up to 80 ethoxy groups). Products containing NPEs have also been for example, textile processing, pulp and paper processing, oil and gas recovery, steel manufacturing, resins and protective coatings, paints, pharmaceuticals and pesticides. Moreover, NPEs have been used in a wide range of consumer products, including personal care products, cosmetics and paints.

Because of their high aquatic toxicity, a number of countries have had voluntary agreements with industry not to use NP or NPEs in domestic detergents since 1976. Under the OSPAR Convention, it was recommended that NPEs should be phased out from cleaning agents for domestic use in 1995 and for industrial use in 2000.

NP is included on the list of priority substances in the WFD. Furthermore, the use of NP and NPEs has been restricted within the EU since 2006 the REACH regulation (1907/2006/EC).

Often when information is given on the content of NP and NPE in products and articles it fails to distinguish between the two compounds. This renders it difficult to differentiate between the emissions of NP and NPE. Furthermore, the ethoxylates are easily degraded to phenols in WWTPs and in the environment. Therefore, measured concentrations in, for example, wastewater effluents, stormwater or surface water do not always mirror the emitted amount of the same compound. This is why reported emissions in this study are a combination of the sum of NP and NPE and NP-equivalents (NPeq).

Results

According to this study the majority of the emissions of NP and NPE to the Baltic environment are distributed to surface waters (Figure 11, right). The yearly loads differ a lot between countries (Figure 11, left), but not as much if put in relation to the population (Lithuanian and Polish industrial sources excluded).

The NP and NPE emissions into the Baltic environment mainly come from industrial sources in Lithuania and Poland, whereas in the other countries M-WWTPs are the dominant source (Figure 12) (Figure 11, left). In Lithuania the industrial emissions are dominated by emissions from the use of NPE as an auxiliary in the leather processing industry (50-60% of total industrial emissions depending on scenario). This is followed by the use of NPE as an auxiliary in the pulp and paper industry and the use of NPE in metal extraction, refining and processing industries. In Poland the industrial emissions are dominated by the formulation of NPE mixtures (1-10% of total industrial emissions depending on scenario) followed by the use of NPE as auxiliary in the leather processing industry.

In the category ‘other’, Finland has reported significant emissions to land from car washes. Furthermore, Sweden and Poland have reported emissions originating in agriculture from the use of pesticides containing NPE. The use of NPE in pesticides is regulated under REACH (Regulation (EC) No 1907/2006), but this does not cancel existing national authorisations of pesticides containing NPE which were granted before 2003.

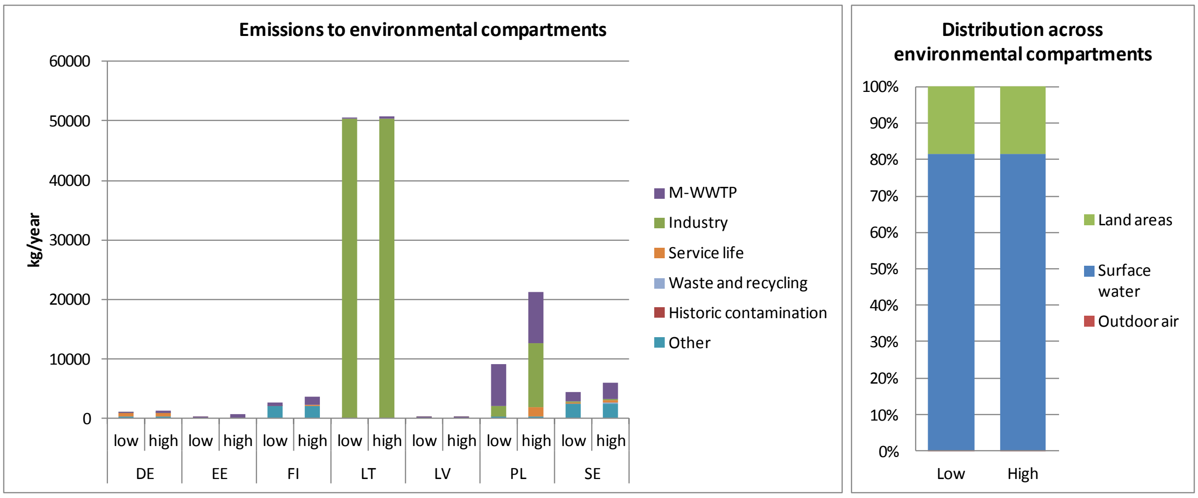

Figure 11: Total load of NP and NPE per country to environmental compartments; air, land and surface water (left). The distribution of emissions across environmental compartments is shown in the figure to the right. Numbers are rounded to one significant digit. These data are associated with uncertainties and a number of data gaps were reported by almost all countries (up to 30% of the identified sources were not possible to quantify in some countries).

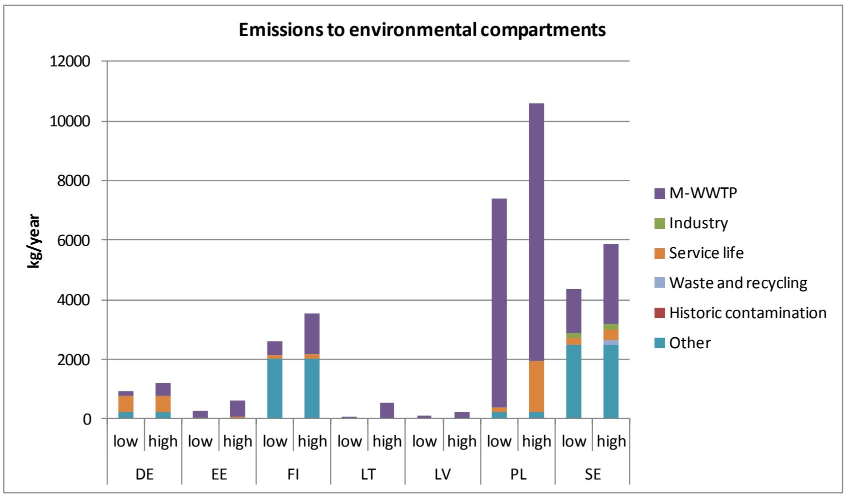

Figure 12: Total load of NP and NPE per country to environmental compartments; air, land and surface water with the Lithuanian and Polish industrial sources excluded.

The upstream sources of NP and NPE to the M-WWTPs are mainly in the service life category and are dominated by emissions from washing of textiles containing NPE (about 40% of total emissions to wastewater). This is followed by the use of NPE in industrial and institutional cleaning (about 15-30% of total emissions to wastewater depending on scenario), which was not expected to be a large source at present as the use of NP and NPE in this application is restricted under REACH (Regulation (EC) No 1907/2006). Other important sources of emissions to wastewater are emissions from car washes and emissions due to private use of detergents.

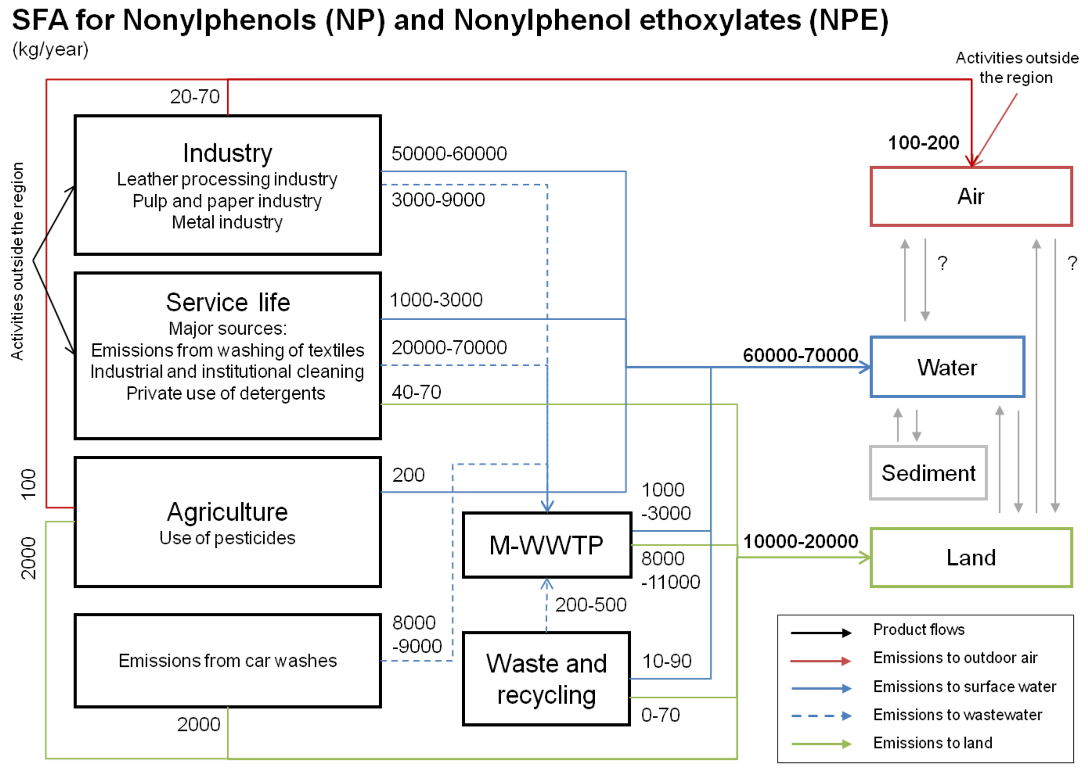

Figure 13: Simplified substance flow analysis (SFA) for NP and NPE in the Baltic Sea Region (c. 2008-c.2011). Numbers are rounded to one significant digit.

Discussion and conclusions

Apart from industry, M-WWTPs are the dominating source of emissions of NP and NPE to the Baltic environment followed by emissions from the category ‘other’ (*e.g.* agriculture and car washes). Large quantities of NP and NPE are annually released into the surface waters and land areas in the Baltic Sea catchment.

Due to the fact that the use of NP and NPE has been restricted for many applications a reduction can be expected. Nevertheless, industrial sources are still potential emitters of large quantities. Furthermore, one important emission source is textiles imported from outside the EU. Hence, reduction off this source depends on restrictions either for import of products and articles containing NP and/or NPE or for the use of NP and NPE in such products and articles in non-EU countries too.

2.1.6. Octylphenols (OP), octylphenol ethoxylates (OPE)

Introduction

Octylphenol (OP) and octylphenol ethoxylates (OPE) are high production-volume substances of the wider family alkylphenols. The 4-tert-OP has two main uses, the production of phenol-formaldehyde resins and the production of OPE. The resins are mainly used in rubber formulation, but are also used in printing inks and paints. OPEs have a wider area of usage than OP, including emulsion polymerisation, water-based paint production, textile processing, and pesticide and veterinary medicine formulation.

OP is included on the list of priority substances in the WFD, and has been listed as 'high concern' on the EU endocrine disrupter priority list (European Commission, 2007). It has also been added to the Candidate List in REACH for inclusion in Annex XIV, the Authorisation List of REACH.

As for NP and NPE, the information given on the content of OP and OPE in products and articles often fails to distinguish between the two compounds, which renders it difficult to differentiate between the emissions of OP and OPE. And similar to NPEs, OPEs are easily degraded to phenols in WWTPs and in the environment and measured concentrations in, for example, wastewater effluents, stormwater or surface water do not always mirror the emitted amount of the same compound. This is why reported emissions in this study are a combination of the sum of OP and OPE and OP-equivalents (OPeq).

Results

According to this study a small part of the emissions of OP and OPE in the Baltic area are distributed to air and the main part is rather evenly distributed to surface waters and land areas (Figure 14, right). The yearly loads differ a lot between countries (Figure 14, left), also on a per capita basis. This is probably not due to lack of data, as the dataset for OP and OPE has a relatively low proportion of data gaps compared to the other BSAP-substances, but is rather an effect of different use pattern in the countries. The largest emissions were estimated to origin from Finland, Poland and Sweden, also on a per capita basis.

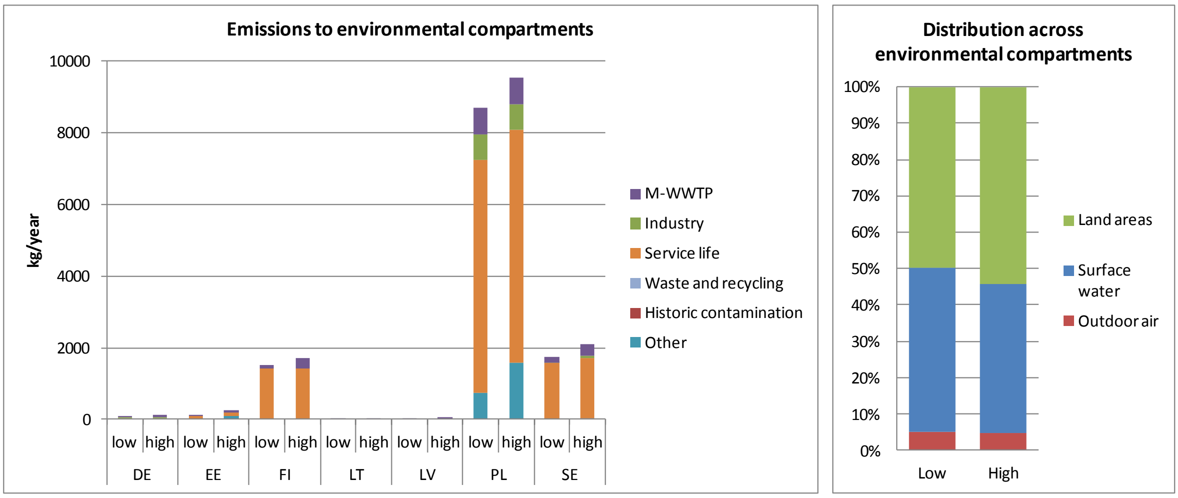

Figure 14: Total load of octylphenols (OP) and octylphenol ethoxylates (OPE) per country to environmental compartments; air, land and surface water (left). The distribution of emissions across environmental compartments is shown in the figure to the right. Numbers are rounded to one significant digit. These data are associated with uncertainties and a number of data gaps were reported by almost all countries (up to 3% of the identified sources were not possible to quantify in some countries).

The emissions were dominated by releases of OP from the service life category (Figure 14, left), where the main source was emissions from abrasion from tyres, which represents almost 100% of the reported emissions in this category. Emissions from impurities in commercial NP products may be a service life source but no loads have been reported and therefore the size was difficult to estimate. In Poland and Estonia there are possibly releases of OP and OPE in agriculture, from use of pesticides containing OPE, but only Poland has quantified the loads for this source.

Industrial sources include the use of OP-based resins in insulation varnishes (about 50% of the industrial emissions) in Poland and Germany and the manufacture of OP-based resins (about 10% of the industrial emissions) in Poland and maybe Estonia.

Emissions from M-WWTP were of some relevance for OP and OPE in all of the Baltic countries (Figure 14, left). The emissions to wastewater primarily come from private washing of textiles containing OPE, which represents 30-50% of the total emissions to wastewater.

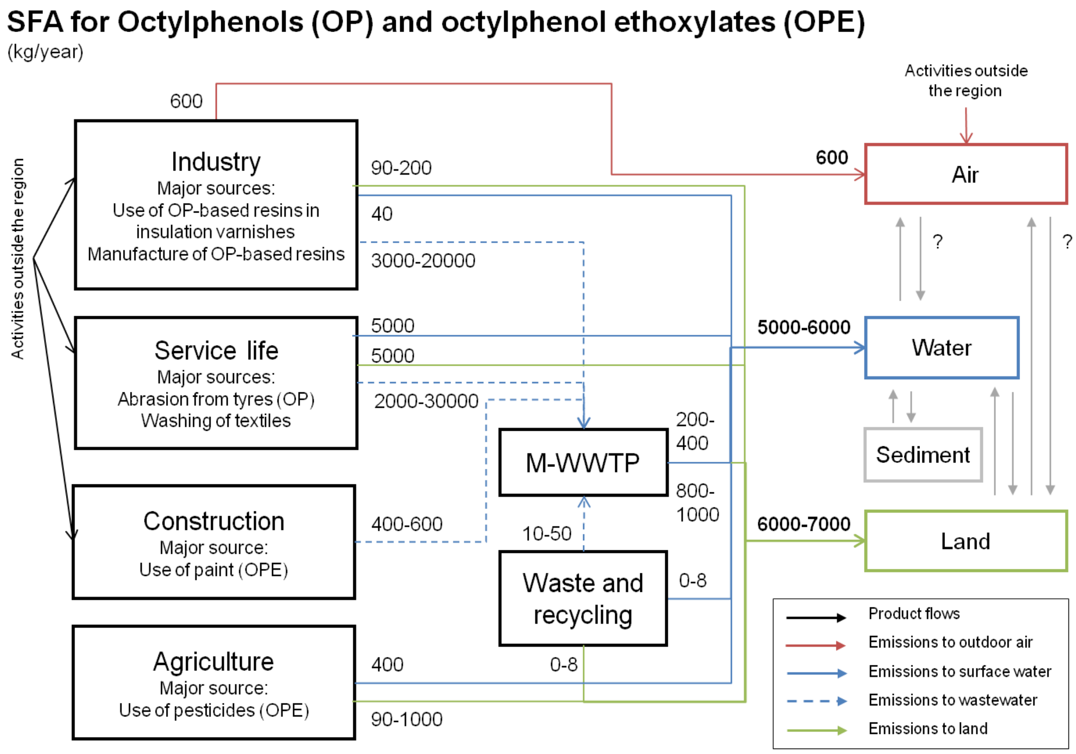

Figure 15: Simplified substance flow analysis (SFA) for octylphenols (OP) and octylphenol ethoxylates (OPE) in the Baltic Sea Region (c. 2008- c.2011). Numbers are rounded to one significant digit.

Discussion and conclusions

Even though the dataset for OP and OP has a low proportion of data gaps (about 6%), the data are associated with uncertainties. OP and OPEs are less studied than other substances like NP and NPEs and several of the emission factors are very uncertain, such as the emission factor for washing of textiles. The largest part of the emissions of OP and OPE is directed to wastewater but emissions to land and surface water are of importance as well. For emissions to wastewater washing of textiles is the dominant source, whereas the emissions to land and surface water mainly come from abrasion of tyres.

The decreased use of NP and NPE due to the restrictions applied on these substances could lead to a replacement of NP and NPE with OP and OPE. Thus there is a risk of increasing loads of OP and OPE reaching the environment in the future. On the other hand, as OP is included on the Candidate List in REACH, the use and subsequent emissions of OP may also decrease.

2.1.7. Short-chain chlorinated paraffins (SCCP), medium-chain chlorinated paraffins (MCCP)

Introduction

The main uses of short-chain chlorinated paraffins (SCCP) in the EU are as flame retardants in rubbers and textiles, and as plasticisers in paints and coatings. A major application for SCCPs has been in metal cutting/working fluids, but this use is now restricted in the EU. The principal uses of medium-chain chlorinated paraffins (MCCP) in the EU are as secondary plasticisers in PVC, mainly in flooring. MCCPs are also used as for example extreme pressure additives in metal working fluids, as plasticisers and additives in paints, adhesives and sealants and in fat liquors used in leather processing.

SCCPs are included on the list of priority substances in the WFD. Additionally, a risk profile is currently being prepared for SCCPs under the Stockholm Convention on POPs. Under the REACH-regulation (1907/2006), SCCPs is added to the Candidate List of substances subjected to authorisation.

Results

According to this study the emissions of SCCP and MCCP in the Baltic area are mainly distributed to land areas (Figure 16, right), and the distribution between environmental compartments does not differ very much between the low and high emission scenarios.

The emissions of MCCP are about ten times higher than the emissions of SCCP and the number of sources identified for MCCP is almost twice as many as those identified for SCCP.

For both SCCP and MCCP the emissions into the Baltic environment mainly come from service life sources (Figure 16, left), but for MCCP industrial sources were also still important in some countries. In the service life category emissions from waste remaining in the environment (*e.g.* particulates of polymeric products, paints and sealants containing chlorinated paraffins) were the absolutely dominant source, both for SCCP and MCCP, in all countries. The second largest source was release from lifetime use of paints and PVC (volatilisation, leaching, wear and tear), which was also a source in all countries. Industrial sources were only reported for MCCP. The dominating source was use of MCCP as plasticiser in the manufacture of PVC in Poland and Germany, with most emissions coming from Poland. This was also reported to be a possible source in Finland. Latvia reported industrial emissions from use of MCCP as plasticiser in formulation of paints and varnishes. This may also be a source in Germany and Estonia.

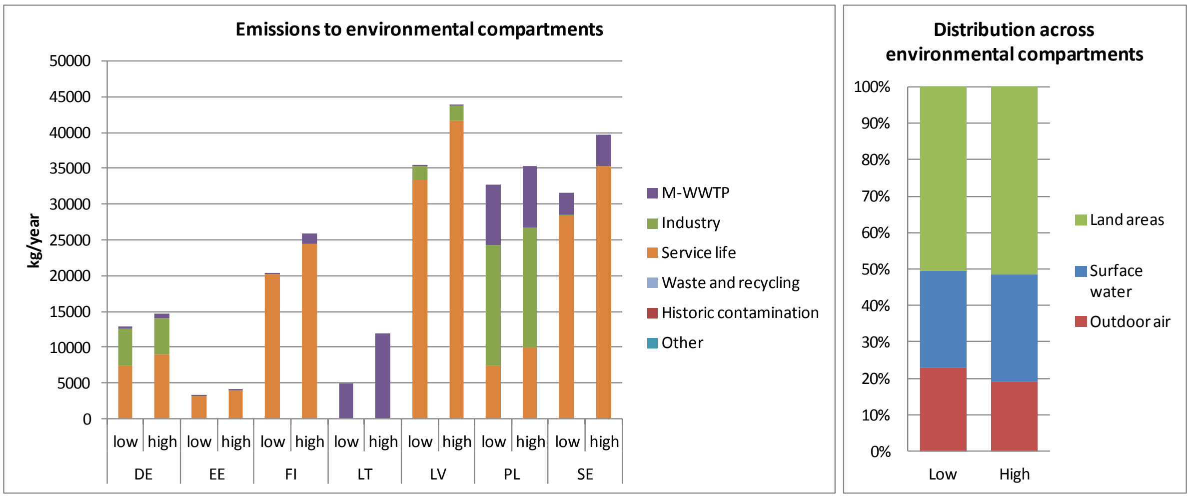

Figure 16: Total load of Short-chain chlorinated paraffins (SCCP) and medium-chain chlorinated paraffins (MCCP) per country to environmental compartments; air, land and surface water (left). The distribution of emissions across environmental compartments is shown in the figure to the right. Numbers are rounded to one significant digit. These data are associated with uncertainties and a number of data gaps were reported by almost all countries (up to 20% of the identified sources were not possible to quantify in some countries).

Emissions from M-WWTP were of importance for SCCP and MCCP in some of the Baltic countries (Figure 16, left). The emissions of MCCP to wastewater primarily come from industrial sources, mainly from the use of MCCP as an additive in metal cutting/working fluids. This source has been quantified in Finland, Poland and Sweden, and identified as a possible source also in Estonia. In the service life category volatile and leaching loss over lifetime use of products containing SCCPs and MCCPs was the main source of emissions to wastewater, but only accounted for less than 10% of the total emissions to wastewater.

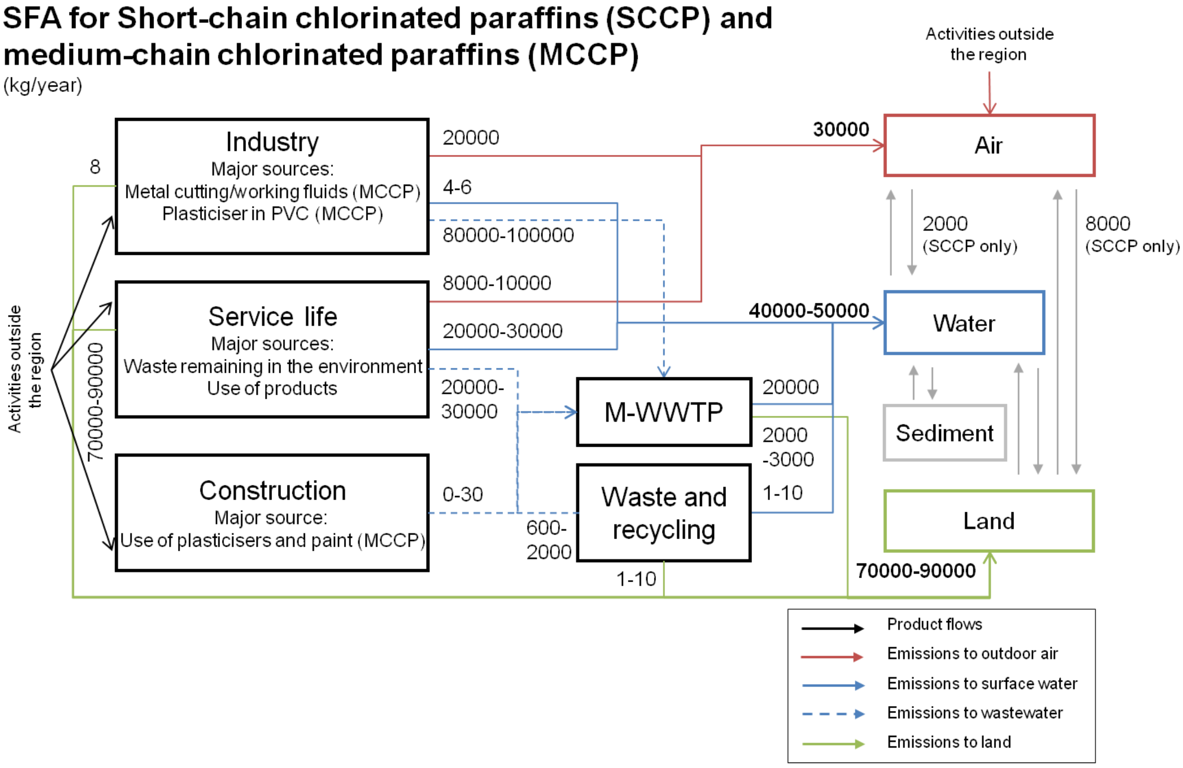

Figure 17: Simplified substance flow analysis (SFA) for short-chain chlorinated paraffins (SCCP) and medium-chain chlorinated paraffins (MCCP) in the Baltic Sea Region (c. 2008- c.2011). Numbers are rounded to one significant digit.

Discussion and conclusions

The total yearly load to the Baltic Sea catchment is higher for SCCP and MCCP than for any of the other BSAP substance groups. The annual emissions of SCCP and MCCP are about 140 000-180 000 kg. The use of SCCPs has decreased since the 1990s and due to the fact that SCCP is added to the Candidate List in REACH, a further reduction of SCCP use can be expected. However, as the main sources of emissions are sources that can sometimes have a long service-life, there will be a delay in the effect of reduced use on the yearly releases to the environment. Risk reduction measures have been put in place for the use of SCCPs in metal working fluids and leather fat liquors. As the MCCPs have similar uses, and can be considered as replacements for the SCCPs in some of these applications, a reduction in the use of SCCPs in these areas could lead to an increased use of MCCPs. However, at least in Sweden also the use of MCCPs has decreased since 1996 (See statistics on the use of chlorinated paraffins in Sweden according to the Swedish Product Register, SPR 2011).

It is well worth noting that the uncertainty of some of the estimations for SCCP and MCCP emissions are large. The most significant sources such as use of products and waste remaining in the environment are based on very rough estimations. The amount of for example waste remaining in the environment is very difficult to estimate.

2.1.3 Endosulfan

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 are biologically active. The main metabolite of endosulfan is endosulfan sulfate which was also included in this SFA. Endosulfan has been used since the 1950s but is now banned within the EU (Commission decision of 2 December 2005, 2005/865/EC). From 2012 endosulfan will also be included in the Stockholm Convention on POPs. It is also identified as a priority hazardous substance under the WFD.

Results

Due to the ban and previous phase-out of endosulfan by many Baltic Sea coastal countries (some of which have never used the substance), direct emission sources are, in principle, absent. Some releases may occur as a result of human consumption of imported foodstuffs (theoretically generating emissions to wastewater from food industry and households), making M-WWTPs important sources to surface water and land (Figure 18). Endosulfan may also enter the region via long-range transport and deposition on land and water contributed largely to the total loads (Figure 19). Relatively small amounts were estimated to still be used within agriculture (illegally). The largest emissions were estimated to come from Poland although the highest emissions on a per capita basis were from Latvia and Germany.

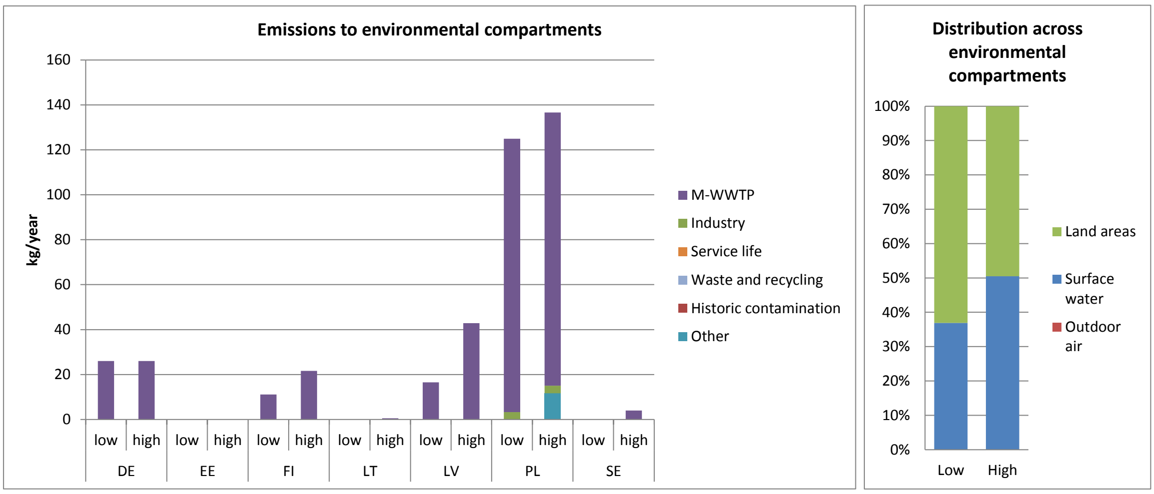

Figure 18: Total load of endosulfan per country, to environmental compartments; air, land and surface water (left). The distribution of emissions across environmental compartments is shown in the figure to the right. These data are associated with uncertainties and a number of data gaps were reported by almost all countries (up to 10% of the identified sources were impossible to quantify in some countries).

The estimated input to the M-WWTPs was approximately one order of magnitude smaller than the estimated output (based on measured concentrations, see Andersson *et al.* 2012 and Nakari *et al.* 2011). Both estimates are uncertain but they show that emissions of endosulfan still occur within the BSR despite the ban and that the input to the M-WWTPs via residues on foodstuffs may be underestimated. Atmospheric deposition may also contribute to the load to the M-WWTPs and there may be additional sources not identified in the present study.

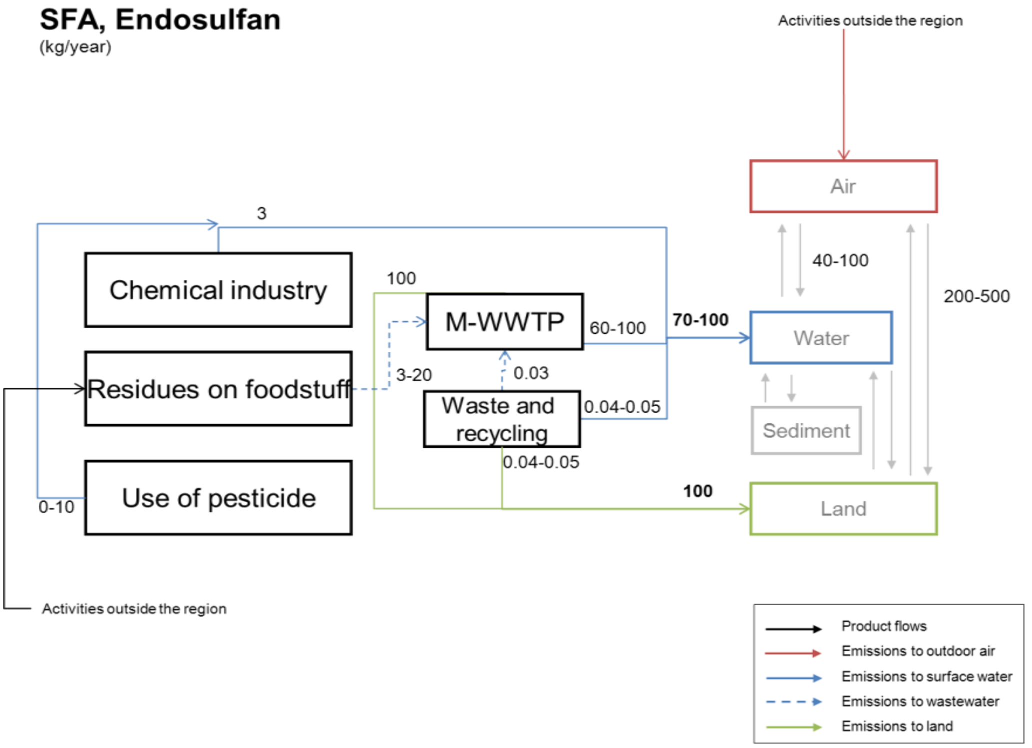

Figure 19: Simplified substance flow analysis (SFA) for endosulfan in the Baltic Sea Region (c. 2008-c. 2011). Numbers are rounded to one significant digit.

Discussion and conclusions

Despite the ban there still seem to be emissions of endosulfan within the region. Furthermore, additional quantities enter via atmospheric long-range transport.

The emissions to wastewater due to residues on foodstuffs should, however, be seen more as a calculation example as the figure is based on a number of assumptions that have not been possible to validate.

2.1.4 Mercury

Introduction

Too high a concentration of mercury in fish has been found to be a problem in most countries in northern Europe. Mercury is found in trace quantities in most non-ferrous ores. For many years the largest producer of by-product mercury in the EU-25 was Finland, from refining of zinc and copper ores, including those imported from Sweden. European and national regulations have a predominant influence on whether by-product mercury is recovered, released to the environment or disposed of. All mercury use is carefully regulated, especially in Sweden. Omitted from the national bans are uses that are regulated in harmonising European legislation, such as use in batteries and energy saving bulbs. Mercury has historically been used in a large number of products and industrial processes that are now regulated or banned. Its main sources to the environment today are releases from processes in which mercury is present as a contaminant, *i.e.* in fuels and industrial raw materials. The stock in society is also still emitting from sources such as dental amalgam fillings, which predate the regulation of this use. This mercury is emitted through waste water, excreted from bodies and from dental medical waste, and released into the air from the cremation of corpses. Another stock is mercury accumulated in forest soils due to atmospheric deposition. This mercury is emitted with runoff, especially as a result of groundwater level fluctuations, and could be an important source to surface waters.

Results

The categories ‘other’ and ‘industry’ were found to totally dominate over other categories for all countries (Figure 20, left, Figure 21). In the case of mercury, ‘other’, was predominantly energy–related. The category, ‘industry’, was also heavily related to energy sources (cement production or coal industry; together with zinc production). Poland, with both a large industry and use of coal in the energy sector, was found to dominate among the countries. The source dental amalgam (divided into category ‘other’ if emitted from dental practices and ‘service life’ if emitted from everyday use), resulted in yearly emissions of 400-600 kg for the reporting countries, which is small in relation to other sources, but is the most important source to M-WWTPs. Historic contamination did not emerge as an important source category. This could be due to lack of data, as there are several locations where mercury concentrations in sediments are found to be high, and there are also several reports on releases of mercury from deposits that have accumulated in forest soil due to atmospheric deposition.

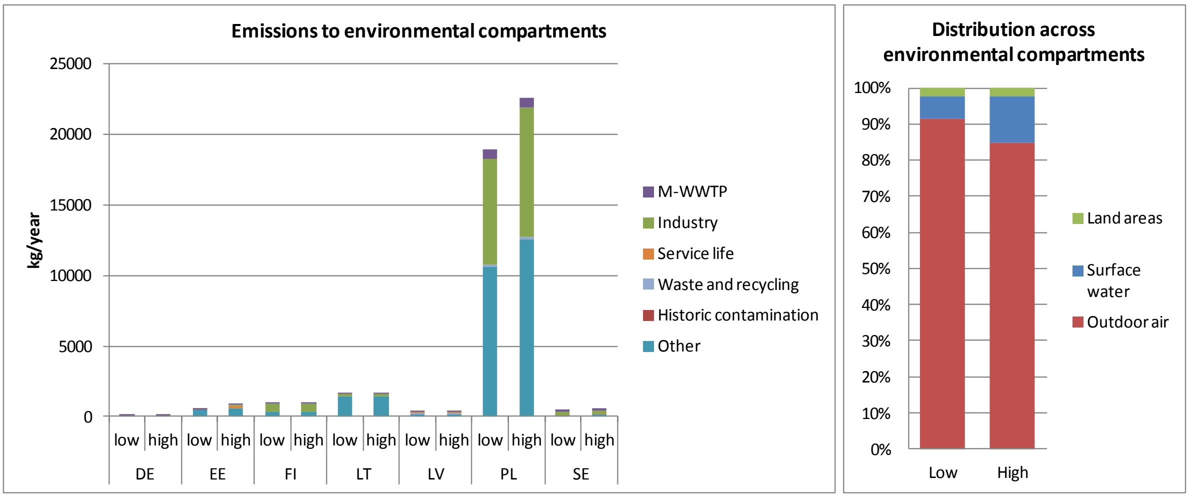

Figure 20: Total load to environmental compartments; air, land and surface water of mercury per country for different source categories (left) and distribution of emissions across environmental compartments (right).

The emissions of mercury were mainly distributed to air in both the low and high scenarios (Figure 20, right).

According to the calculations of atmospheric deposition (Chapter 3.1.1), 30 000 kg of mercury is deposited on the Baltic Sea and its catchment area every year, while the calculated emission to air is about the same amount, 20 000-30 000 kg/year (Figure 21).

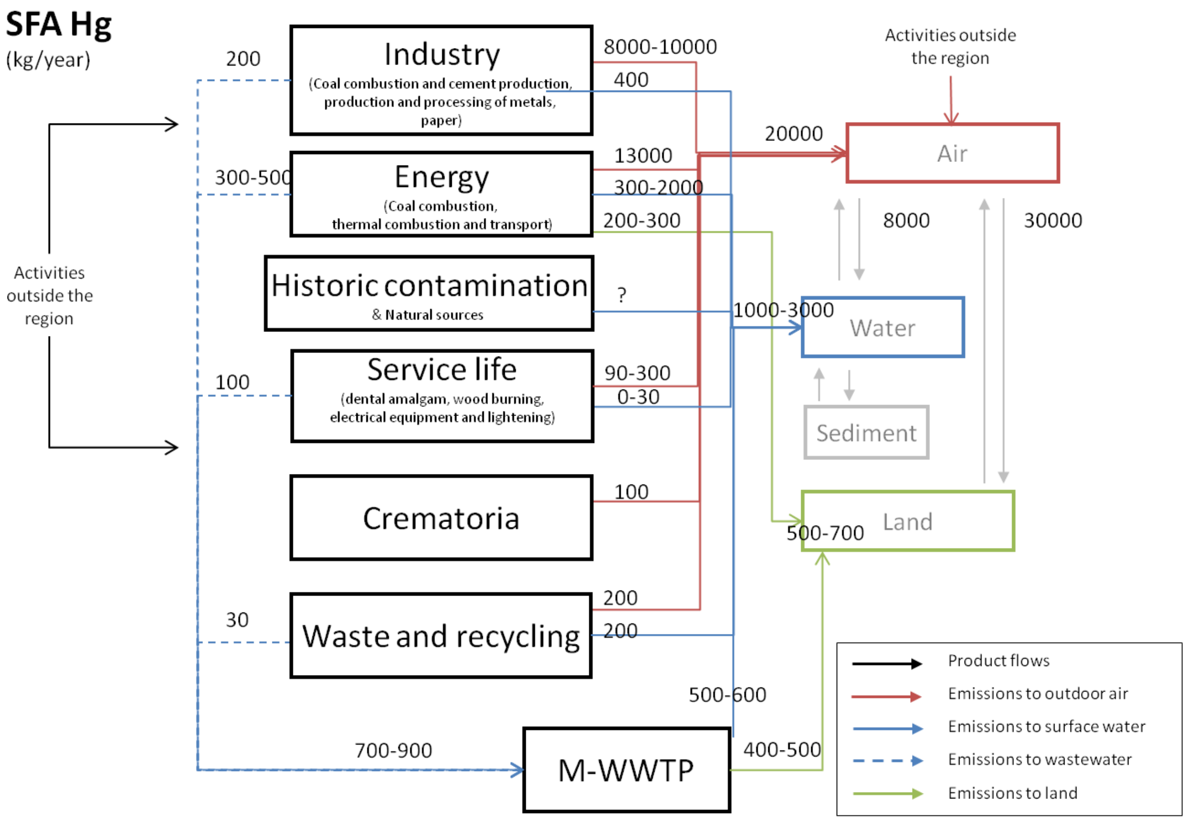

Figure 21: Simplified substance flow analysis (SFA) for mercury in the Baltic Sea Region (c. 2008-c. 2011). Numbers are rounded to one significant digit.

Discussion and conclusions

The use of mercury has decreased which is the reason why stock in society (service life) and historic contamination could be assumed to be of a relatively greater importance today. For these categories there were data gaps from all countries. The critical issue, moreover, should be energy-related industrial sources. Although there are uncertainties, the metals are more studied and monitored than most other hazardous substances. Emission trends should be decreasing due to mercury bans and restrictions and other activities related to the mercury strategy implemented by the EU and the global instrument on mercury developed by UNEP.

2.1.5 Cadmium

Introduction

Cadmium occurs naturally in the environment and is released from the gradual process of weathering, erosion and abrasion of rocks and soils, and from singular events such as forest fires and volcanic eruptions. Fossil fuel combustion, phosphate fertilisers and production of metals seem to be the major anthropogenic sources of cadmium found in the environment. Old mining tailings also release cadmium. Cadmium metal is produced as a by-product from non-ferrous metal production and the metals and their compounds are used as pigments, stabilisers, coatings, specialty alloys, electronic compounds and in rechargeable nickel-cadmium batteries. There are several EU directives and regulations on cadmium, in addition to international agreements.

Acid sulfate soils and sediments contain iron sulfides, for example pyrite. When exposed to air, due to drainage or disturbance, these soils produce sulfuric acid; often releasing for example cadmium. Finland and Sweden have the largest areas of these kinds of soils in Europe. Due to a more flat topography and a larger land area exposed to postglacial land uplift, the environmental impact seems to be greater in Finland, where higher quantities of cadmium are discharged from acid sulfate soils than by the entire industry (Sundström and Åström 2006). Artificial draining of soils for agricultural purposes, especially during the 20th century, has accelerated the leaching. Leaching contributes significantly to the total riverine emissions of cadmium into the Baltic Sea. Through the rivers located on the western coast of Finland, emissions are estimated to be some 1.8 tonnes/year (Finnish WP4 National summary report), compared to the total riverine inputs to the Baltic Sea of around 3.3 tonnes/year (HELCOM 2011). After entering the brackish sea water most of the heavy metals precipitate and deposit in the river estuaries and bays but are exposed to sediment re-suspension and transport to open sea area.

Results

Polish industry was found to dominate the emissions. Finland reported historical sources, which included the acid sulfate soils described above. No other country reported this source due to lack of data (Figure 22, left). The category ‘other’ was important for cadmium, and included thermal power stations and other combustion installations (including combustion in households) as well as traffic. The emissions of cadmium were mainly distributed to air (Figure 22, right), due to combustion being a very important source. The category ‘other’ also included agriculture, which was related to the use of mineral fertilisers and sewage sludge. For Sweden, emissions from agricultural activities included the use of lime, with a quantity of the same order of magnitude as mineral fertiliser. No other country reported lime as a cadmium source. As Sweden has had lower cadmium content in used mineral fertilizer, compared to most other countries, lime might be relatively more important as a source in Sweden.

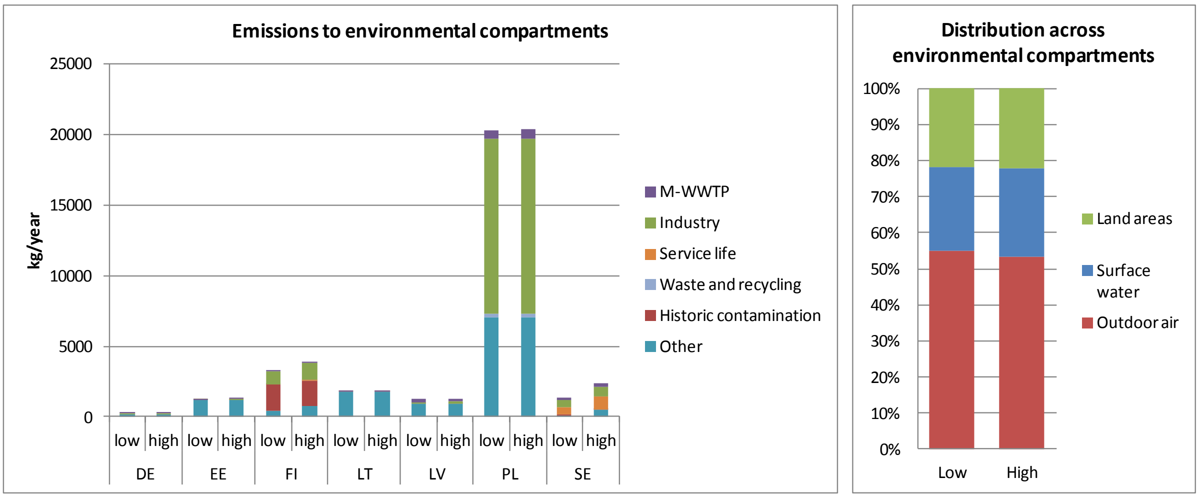

Figure 22: Total load to environmental compartments; air, land and surface water of cadmium per country for different source categories (left) and distribution of emissions across environmental compartments (right).

Emissions to air were found to be 20 000 kg (Figure 23), which could be compared to the atmospheric deposition onto the Baltic Sea and its catchment area of 60 000 kg (Chapter 3.1.1). Upstream sources to M-WWTPs comprised service life activities, mainly the use of artist paint, car washing, washing with detergents and consumption of food (Figure 23).

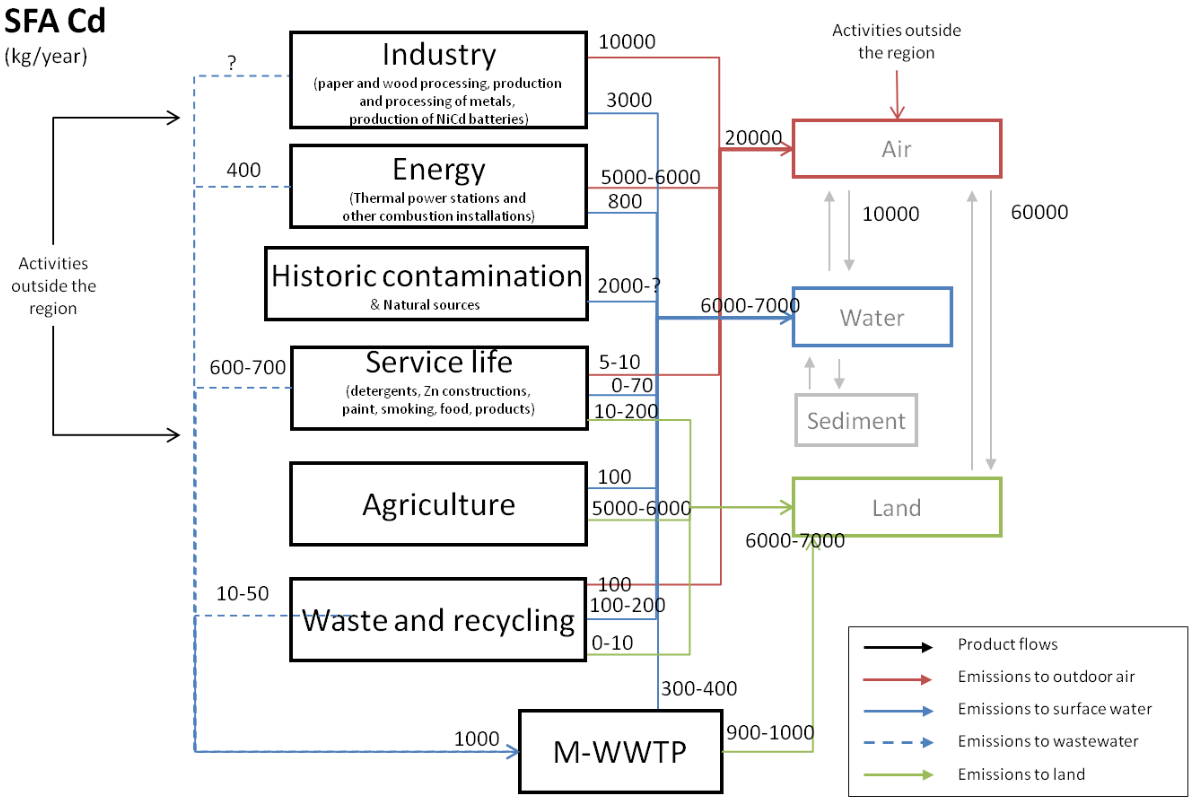

Figure 23: Simplified substance flow analysis (SFA) for cadmium in the Baltic Sea Region (c. 2008- c. 2011). Numbers are rounded to one significant digit.

Discussion and conclusions

A critical issue concerning cadmium, might be the contamination of soils and sediments, but on this source there were data gaps for most countries. The agricultural sources relating to both mineral fertiliser and sewage sludge (and maybe also to the use of lime) needs more attention. The emissions from industry and energy use could be further controlled, which together with use regulations would lead to a decreasing trend. Even though there are uncertainties, these should be minor compared to those of other hazardous substances.

2.2 By source category

2.2.1 M-WWTP

Municipal wastewater treatment plants (M-WWTP) are mainly constructed to receive and treat wastewater from households. The main pollutants that are targeted for removal in an M-WWTP are particulate matters, easily degradable organic material as well as nutrients such as phosphorous and nitrogen (Swedish EPA 2008). The primary purpose of the treatment plants is not to remove hazardous substances from the wastewater.

There are different types of M-WWTPs. In an M-WWTP with primary treatment, the wastewater is treated mechanically. During the mechanical treatment, the wastewater is passed through bar screens and filters followed by sedimentation which allows large solid pollutants to be separated from the wastewater (Swedish EPA 2008). In a secondary M-WWTP, in addition to the mechanical treatment, biological and chemical treatments are also performed (Lehr *et al.* 2005). Examples of biological treatment steps are active sludge treatment and membrane bioreactors. Tertiary treatment could involve further biological treatment or advanced treatment steps such as ozonation or passing the wastewater through constructed wetlands to achieve an even further reduction of pollutants. Besides water treatment, sludge treatment can also be included in an M-WWTP. After separation of the sludge, the sludge can be dewatered and digested. The main purpose of digesting sludge is to reduce the amounts of sludge, but it has been shown that digestion can also degrade pollutants within the sludge. The design of the WWTP has a considerable influence on how much reduction of the load of hazardous substances can be achieved.

The Urban Waste Water Directive (91/271/EEC) is the EU legislation aiming to protect surface waters from pollution by wastewater. According to this directive, secondary treatment of wastewater is required for all discharges from normal areas and tertiary treatment is required in sensitive areas (*e.g.* the whole of Sweden). For the newer member states, all of the deadlines in the directive have yet to expire. Within HELCOM there are two recommendations that are especially relevant in this context; 28E/5 on municipal wastewater treatment and 28E/6 on on-site wastewater treatment of single family homes, small businesses and settlements up to 300 person equivalents (p.e.).Table 5 show connection rates to M-WWTPs in the BSR countries in (EC 2011).

Table 5: Per cent (%) of generated load collected in collecting systems and treated by secondary treatment; secondary treatment in place/monitoring results comply with secondary treatment (EC 2011)

Country	**Collected in collecting systems (%)**	**Share treated by secondary treatment (%)**
Denmark	100	100/99
Germany	98	97/97
Estonia	90	82/69
Latvia	80	79/77
Lithuania	94	82/82
Poland	85	81/76
Finland	99	99/99
Sweden	100	100/99

In COHIBA the importance of M-WTTPs as an emission source of the BSAP hazardous substances to surface water (via the effluent) and to land areas (via sludge use in agriculture or landscaping) was investigated using statistics from the PLC4 inventory (Helcom 2004, www.helcom.fi), EU statistics on sludge generation (www.eurostat.eu) and the screening executed within the Project (the methodology is described by Andersson *et al.* 2012). Figure 24 is based on these data.

In Figure 24 it can be seen that the emissions via M-WWTPs were predicted to be particularly important for endosulfan, PBDEs and the perfluorinated compounds (PFOS, PFOA). For the metals, the dioxins, TBT, HBCDD, OP, OPE, SCCP and MCPP, on the other hand, less than 10% of the total load to environmental compartments was predicted to come from M-WWTPs.

From looking at a mass balance of estimated loads in to and out from the M-WWTPs it was seen that for all substances except PBDEs, endosulfan and HBCDD, the loads were reduced in the M-WWTPs. This reduction was not necessarily due to degradation as in this context the incineration and landfilling of sludge were also regarded as a reduction of the environmental load. The larger output than input for the PBDEs was interpreted as a lack of data on emissions to wastewater, *i.e.* the M-WWTPs are not adding to the PBDE load but rather there is a lack of data on the upstream sources. The same interpretation was made for HBCDD. For endosulfan the mass balance was positive for the low emission scenario. This was interpreted as the input to the M-WWTPs in the low scenario having been underestimated, or there being more upstream sources to the M-WWTPs that have not been identified. It is also possible that the output load was overestimated as it was based on few measurements. For the perfluorinated substances such a mass balance is difficult to make as precursors may degrade in the M-WWTP and thus generate increased levels in the outgoing waters (see *e.g.* Schultz *et al.* 2006).

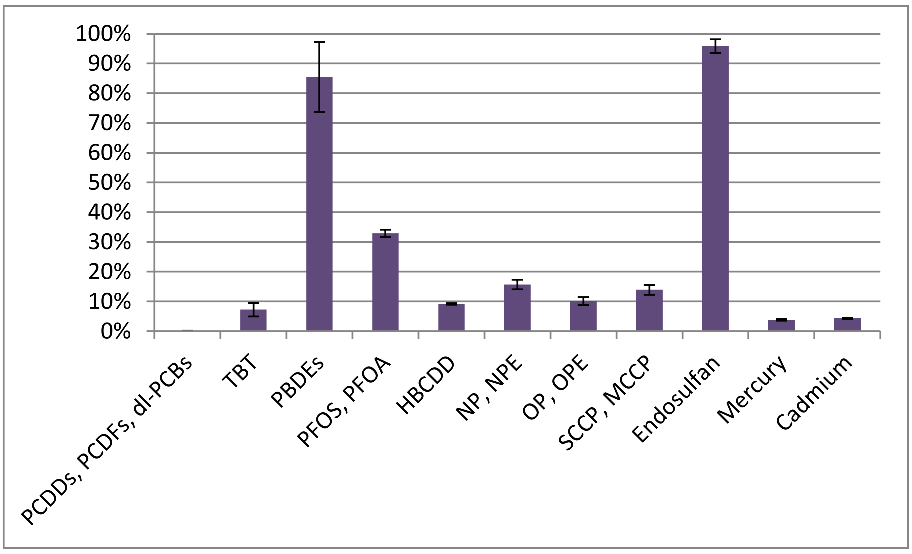

Figure 24: Importance of M-WWTP as a transport pathway (total load with effluent water and sludge), average emission with low high as error bars.

With the exception of the perfluorinated substances and the chlorinated paraffins (SCCP, MCCP), all substances were assessed to have more than 50% of the load from M-WWTPs transferred to the environment via sludge.

To conclude, the M-WWTPs do in general work as efficient barriers of emissions to the environment. Most of the BSAP-substances are, however, rather persistent and the use of sludge in agriculture or landscaping may move the substances of concern to land areas. The M-WWTPs were assessed to be a particularly important pathway to the environment for endosulfan, PBDEs and the perfluorinated substances.

2.2.2 Industry

Industrial emissions are related to intentional use of the substances as agents in production processes or as ingredients in products or, to unintentional emissions in technological processes (Table 6). In recent years industry emissions of hazardous substances have decreased in importance as the use of these substances is restricted or/and the control measures are more efficient.

Table 6: Substance emissions relevant for industrial processes to receiving compartments. The waste flows have not been in focus in the COHIBA Project and there might thus be relevant data gaps in this category.

Industry	**Water**	**Air**	**Wastes**
Ferrous and non-ferrous metal	Hg, Cd	PCDD/Fs, Hg, Cd	PCDD/Fs, Hg, Cd
Metal and machinery	MCCP, Cd, OPE, NPE	-	MCCP, Cd
Chemical and plastics industry	HBCDD, MCCP, OPE	HBCDD	-
Mining sector	OPE, Cd, Hg	-	-
Other (leather, paper)	NP, NPE, OPE, Cd	-	-

Industry emissions are potentially important in relation to intentional use of MCCP, HBCDD, NP, NPE, OPE and unintentional emissions are important for dioxins, furans and dioxin like PCBs, mercury and cadmium (Figure 25).

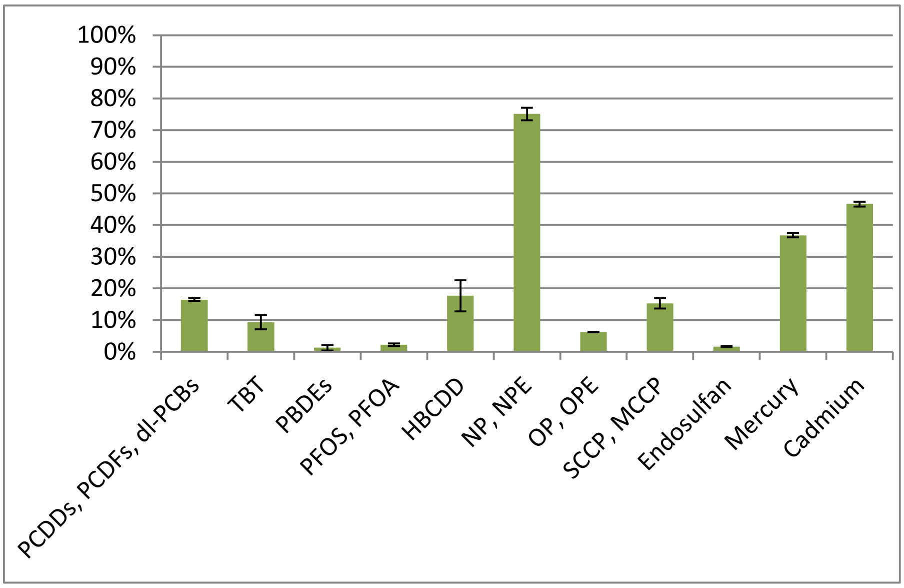

Figure 25: Relative industrial source emission share in the total load of hazardous substances to the environment, average emission with low high as error bars.

In ferrous and non-ferrous primary and secondary metal production, air emissions of mercury (11% share of the total load) and PCDD/F (9%) are especially important. Emission to surface water is less important – reported only for mercury in ferrous metals production in Finland (<5%). Cleaning and degreasing in metal plating cause emissions to wastewater appropriately: OP and OPE use in Sweden (50% share of wastewater load), and NP and NPE in Poland and Latvia (13% share). Metal moulding is an important source of MCCP emission to wastewater (65% share), mainly in Poland, as well as MCCP use in metal cutting/working fluids (less than 10%). Metal plating is also a minor PFOS emission source with the largest emissions coming from Sweden (high emission scenario), followed by Germany, Finland and Poland. Less important sources include, for cadmium, metal plating in restricted applications (aircraft), reported for Finland and Poland, and for deca and pentaBDE processing of metal scraps.

The mining sector is an important source of direct emissions of cadmium, mercury and PCDD/F to surface water, particularly in Poland. Mining of nonferrous ores causes cadmium emission to surface water (5% of the total load). Mercury emissions are important, mainly in hard coal mining, with emissions to air around 9% and to surface water with 1% share of the total load. There are relatively low emissions to wastewater and surface water, reported chiefly for the manufacture of NPE, NP in Poland, use of TBT as intermediates in production of other compounds, only in Germany, and minor mercury emission from the chlor-alkali industry.

Paper and pulp production is likely to be a minor source of cadmium and mercury with emissions of both reported for Finland, Sweden and Estonia. Emission to surface water of NP due to NPE and NP use as auxiliaries in pulp and paper industry is reported only for Lithuania with 14% of the total load. Substance usage in production of plastic and textile materials is an important source of emission, especially to wastewater. A major HBCDD emission source (20% share in the total) is the manufacture of flame retarded EPS (Poland and Finland), followed by XPS boards (Poland). NP and NPE emission to wastewater from leather processing is reported mostly in Lithuania (45% share). This estimation is highly uncertain. MCCP use as a plasticiser in PVC and also in paints and varnishes, is reported for Poland, Latvia, Germany and Sweden with emissions to wastewater (10% share), and to air (17% of the total load). Other sources of emission to wastewater include; OPE use in plastic and rubber production, PVC recycling and the textile industry (cadmium), NP use in paints and resins and textile manufacture (decaBDE).

Professional use of hazardous substances in special applications can be a source of emissions to wastewater *e.g.* NPE, NP, OP, OPE use in industrial cleaning (5% share), OPE emission in photography in Sweden and Poland to wastewater (12% share), use of OPE, NP, NPE in paints, adhesives and other products in industry. In energy-related processes, *e.g.* cement production, cadmium emission to the air is reported (around 10% of the total load). Production of goods is a minor emission source for PFOS, decaBDE, cadmium, mercury, and NPE.

Conclusions

Industry is an important source mainly for OPE, NP, NPE in metal, plastics and leather industries, HBCDD in plastic industry, MCCP in metal production and unintentional emissions of cadmium, mercury and dioxins, furans and dioxin-like PCBs. It is of minor importance for emissions of TBT, PBDEs, endosulfan and PFOS/PFOA as these substances are not allowed to be used in products and their use in production is highly restricted and controlled.

Use of OPE, NP and NPE in metal industry is important for Poland and Sweden. Highest emissions of MCCP are in the metal industry in Poland. Use of NP in leather industry is specific only for Lithuania. HBCDD use in plastic industry is specific in Finland and Poland. The unintentional emissions are predominantly occurring in Poland in the mining and metal industries.

The industrial emissions are mainly emitted into the air and through wastewater discharges. The contaminants are then essentially removed with the exception for PFOS and PFOA in M-WWTP or I-WWTP. Relatively low loads, with the exception of NP, HBCDD, cadmium and mercury, are reported for surface and coastal waters and soils.

The estimations of hazardous substance loads are a good indication of the current applications and emission pathways in the Baltic Sea Region industries. The calculations show discrepancies between countries and applications suggesting that over and underestimations are very likely to occur in the reported results. High emissions for certain applications are reported only for some countries. Furthermore, the industrial technological processes are under strict BAT requirements and for some substances legal restrictions are imposed. Because of the declining use of MCCP in metalwork the emissions could currently be lower than estimated in COHIBA.

2.2.3 Service life of consumer articles and materials

Introduction

As was pointed out in the chapter on industrial sources (Chapter 2.2.2), in many areas the importance of industrial point sources has declined and emissions have shifted to diffuse consumption-related sources, including construction materials, traffic, personal care products and commodities such as textiles and electronics (Bergbäck 1991; Sörme *et al.* 2001; Jonsson *et al.* 2008).

Whereas the releases from industries can be relatively easily monitored, regulated and reduced, the diffuse sources related to consumption cannot. Their diffuse character makes it difficult to identify or monitor them, or to apply treatment technology in an efficient way. In addition, unlike for industrial sources, it is sometimes difficult to assign who is responsible for a consumption-related release (Sörme *et al.* 2003). Is it the owner of the commodity, the supplier or the manufacturer? Thus, whereas the introduction of environmental regulatory institutions has been successful in reducing the emissions from many industrial sources, the shift described above is a challenge that may have to be handled in other ways.

This section will give examples of substances for which the service life of consumer articles and construction materials has been found to be important for their releases to the Baltic Sea environment, as described in the substance chapters in Chapter 2.1. Where M-WWTPs have been identified as an important source to the Baltic Sea (see Chapter 2.2.1), the origins of the releases to these utilities has been investigated further, and where it has been found that the service life of articles and materials is important, such origins of release are also included here.

Results

Service life releases to the Baltic Sea environment

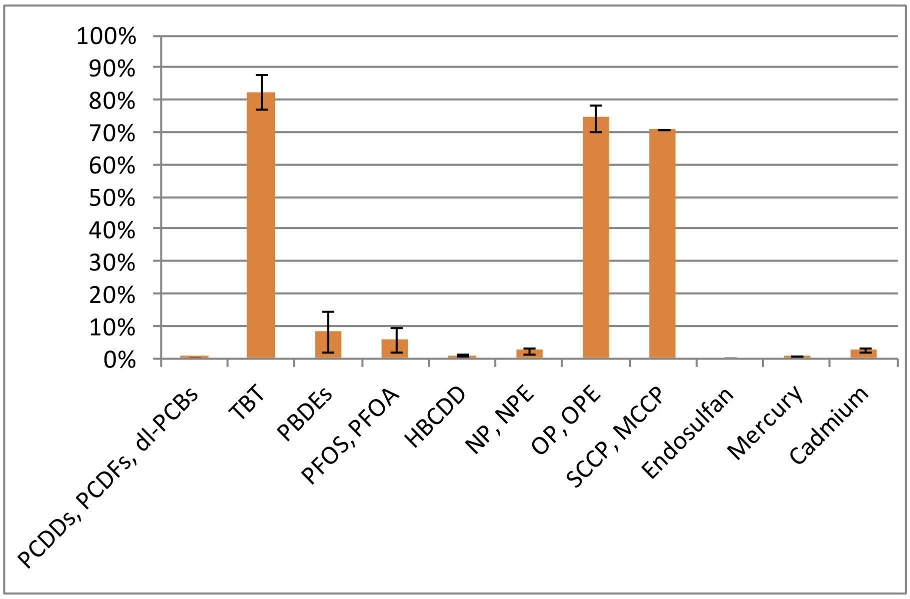

Figure 26: Relative importance of service life sources for total emissions of BSAP priority substances to the Baltic environment.

Figure 26 shows the percentages of emissions of BSAP priority substances into the Baltic environment that originate from service life sources according to the substance flow analyses summarised in Chapter 2.1. These seem to be dominant for three substance groups; TBT, OP/OPE, and SCCPs and MCCPs.

According to the substance flow analysis for TBT (see Chapter 2.1.2) the predominant source to the Baltic environment is TBT biocides from the use of treated timber, with contributions also coming from the use of products containing catalysts, powder coated products and polyurethane products. It should be noted that these releases could not be quantified in all countries, so the releases could in fact be even larger.

For OP and OPE**,** releases of abrasion particles from tyres are the dominant source to the environment (see Chapter 2.1.6).

According to the SFAs for chlorinated paraffins (Chapter 2.1.7), sources in the service life category are especially important for the medium-chained but also for the short-chainedcompounds. For both compounds, the source *waste remaining in the environment* is responsible for approximately 90% of the service life releases. In the EU risk assessment report for MCCP (ECB, 2005); this source is defined as erosion/particulate losses of polymeric products, paints and sealants during the use or waste handling of products and articles. It should be noted that the uncertainties are greater for the SCCP data than for MCCP, especially regarding industrial releases.

If the receiving compartment indoor air is included, PBDEs are also among the substances for which service life sources are important. Releases from flexible polyurethane and electronic appliances are the dominant sources. The importance of the indoor air compartment is discussed further in Chapter 2.1.2.

Service life releases via wastewater

For the substances for which releases from M-WWTPs were identified as an important source to the Baltic environment (see Chapter 2.2.1), the origins of the emissions from the treatment plants were investigated further. Service life was found to be a significant source category, at least potentially, for two substance groups: PBDE and nonylphenol/nonylphenol ethoxilates (NP/NPE). Figure 27 shows from which sources the load of these pollutants to the M-WWTPs originates.

For the PBDEs, the indoor environment is a significant source to the M-WWTPs according to the high emission scenario. The big difference between the scenarios illustrates the difficulties in predicting the fate of pollutants released into the indoor environment.

For NP/NPE, the load to the treatment plants comes mainly from washing of textiles containing NP and NPE. In the high emission scenario a significant contribution also comes from industrial and institutional cleaning.

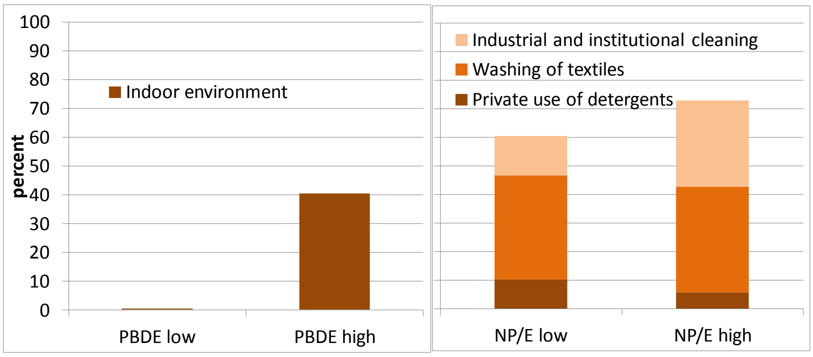

Figure 27: The relative contributions to the M-WWTP loads of PBDE and nonylphenol/nonylphenol ethoxylates from different sources according to the low and high emission scenario respectively.

Discussion and conclusion

The results of the SFA work in this project confirm that release via service life is important for several of the substances in the Baltic Sea region. The examples presented in this section also illustrate several important characteristics of service life releases of hazardous substances:

- Releases often come from goods or materials with long lives, such as building materials (*e.g.* TBT in timber). This means that even as regulations on the use of the substances are enforced, they only slowly reduce the load on the environment.
- Many uses of products cause releases of particles to the environment through wear and tear (*e.g.* MCCP and SCCP). These can remain in the environment for a long time and cause a continued release of their contents of hazardous substances. Again, this is a release that is hard to control in the short run by applying new regulations on the use of the substances.
- Releases often come from the use of articles in households (*e.g.* NP/NPE in textiles, TBT and PBDE in polyurethane). Because of their diffuse character such releases are difficult to identify, quantify, monitor and regulate. It is also more difficult to assign who is responsible, compared to, for example, industrial point sources.
- Releases into the environment from M-WWTPs are sometimes important, but the treatment plants themselves should not be seen as the emitter, as the releases in fact take place up-stream from the plants (*e.g.* NP/NPE from textiles). The treatment plant is more of a conveyor of these releases. Some treatment plants have extensive work to reduce these up-stream releases, but their direct possibilities of influencing the incoming load is often limited (Sörme *et al.* 2003).

As the service life releases are often associated with the use of consumer articles, traffic and building materials, they are of special interest in areas where there is a concentration of these activities – *i.e.* in population centres. In-depth studies were performed in two Baltic case cities: Stockholm and Copenhagen (see Chapter 4.3 and separate reports).

2.2.4 Waste and recycling

Solid waste that is not reused or recycled may be incinerated or placed in landfills. Incineration is a process that generally reduces or eliminates hazardous substances if these are contained in the waste. It may, however, generate new contaminants such as halogenated dioxins and furans. In a landfill some degradation may occur but there may also be losses of hazardous substances due to evaporation and leaching. The design of the landfill has a large effect on the character and size of emissions. Recycling generally includes shredding processes which may generate air emissions of hazardous substances in both gaseous and particulate form.

The EU Waste Framework Directive (2008/98/EC) is an important part of the EU legislation on waste. HELCOM recommendations relevant in this context are for example 31E/4 proper handling of waste/landfilling, and, 27/1 limitation of emissions into atmosphere and discharges into water from incineration of waste.

In COHIBA estimations of emissions via landfill leachate were made based on the data from the screening performed within the Project (see Andersson *et al.* 2012). Estimations of emissions from for example incineration or recycling have been made on a case by case basis and did not follow a common methodology.

Activities in the category waste and recycling do sometimes generate emissions to wastewater (not shown in figure). Emissions from these sources to wastewater, in relation to total emissions to wastewater, contribute to less than 10% for all substances. For TBT, PFOS, PFOA and cadmium, landfills via leachate, were estimated to be an important source to wastewater. Furthermore, for the PBDEs recycling as an emission source was predicted to be important.

Figure 28 shows estimated emissions from the category waste and recycling to air, land and surface waters, in relation to total emissions to the same compartments. Emissions from this category contributed to less than 10% of total emissions for all substances. For the dioxins, mercury and cadmium emissions from waste incineration account for a major part of the estimated emissions from waste and recycling to environmental compartments. For TBT, PFOS and PFOA landfill leachate was estimated to be a relatively important source, while the dismantling of electronics was estimated to be an important source of PBDEs (high emission scenario).

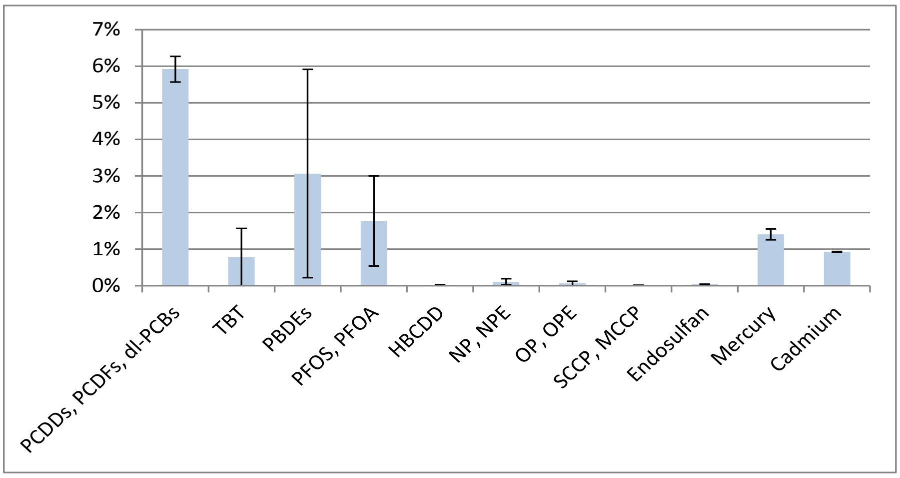

Figure 28: Emissions from the waste and recycling category to total emissions to environmental compartments, land, air and surface water, in relation to total emissions to the same compartments. The bars show the mean value of the low and high scenario and the error bars show the low and high scenario, respectively.

Focus in the COHIBA report has not centred on the end-of-life section of the life cycles of the substances. Therefore the results shown here; that sources within waste and recycling are not of particularly high importance, may not be entirely correct as there are several data gaps for these kind of sources. The results do, however, indicate for which substances the end-of-life may be particularly important from an emissions perspective.

2.2.5 Other

Emission sources that did not fit in any of the four categories described above (M-WWTP, Industry, Service life and Waste and recycling) were placed in the category 'other'. In this chapter two of the main sub-categories are described; agriculture and energy. Emissions from sources categorised as 'other', in relation to total emissions, are shown in Figure 29.

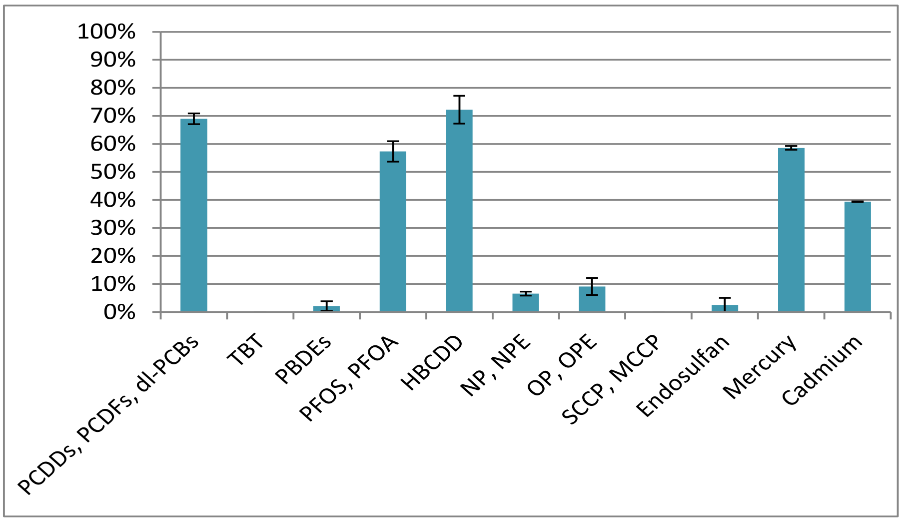

Figure 29: Emissions to air, land and surface water categorised as 'other', in relation to total emissions to the same compartments. The bars show the mean value of the low and high scenario and the error bars show the low and high scenario, respectively.

2.2.5.1 Agriculture

According to the information gathered during the project, BSAP hazardous substances can enter the Baltic Sea due to the pollution of soil, surface water and groundwater, predominantly from the following plant cultivation activities:

- use of pesticides, biocides and disinfectants (as ingredients in pesticides and as formulation additives - NP, NPE, OP, OPE);
- application of phosphorous fertilisers on fields and liming of agricultural soils (cadmium);
- spreading of sewage sludge from MWWTPs on agricultural land (full set of BSAP hazardous substances).

Due to legal permits on polluting activities that were handed out by local authorities before 2005 and are due to expire soon, limited emissions of NP/NPE on soil from use of pesticides were found. In its turn, use of phosphorous fertilisers generated a significant load of cadmium on farmland. Sewage sludge has been used in agriculture over a long time and is generally the re-used material that carries the highest load of organic contaminants among used fertilisers. It has, nevertheless, valuable agronomic properties. The utilisation of sewage sludge is subject to provisions stipulated in the EU Directive 86/278/EEC on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. Moreover, the Urban Waste Water Treatment Directive (91/271/EEC) and Waste Framework Directive (2008/98/EC) prescribe that sludge arising from waste water treatment should be managed in an appropriate way.

Generalisation of emission data about project target substances from plant cultivation activities demonstrated that the total load of all those hazardous substances on agricultural land reaches about 15-18 tonnes/year; hereof contribution of pesticides/biocides application on fields was 2.3-3.1 tonnes/year. The application of phosphorus fertilisers on fields was the biggest source of cadmium pollution in soil, 5.4-5.7 tonnes/year: application of sewage sludge was 6.9-8.9 tonnes/year (Table 6). Due to the data gaps on liming of acidic agricultural soils cadmium emission from this activity was not estimated.

Table 6: Emissions of BSAP-substances from main plant cultivation activities, kg

Agricultural activity	**Cd**	**NP**	**NPE**	**OP**	**OPE**	**Other target substances**	**Total emission**
Application of phosphorus fertilisers	5000-6000	-	-	-	-	-	5000-6000
Use of pesticides, biocides and disinfectants	-	50	2000	-	90-900	-	2000-3000
Use of sewage sludge	500-500	4000-5000	700-1000	100	40-100	2000	7000-9000
Total emission	6000	4000-5000	3000	100	100-1000	2000	10000-20000

About 249 000 tonnes of sewage sludge is used yearly for agricultural purposes in BSR countries with the biggest share coming from Poland - 50% (Polish WP4 National summary report). Use of sewage sludge as fertiliser was a significant source of all target substances on agricultural land (50% of emissions by mass from all BSAP hazardous substances), followed by application of phosphorous fertilisers (30%) and use of pesticides, biocides and disinfectants (20%). Due to application of sewage sludge on land agriculture was a substantial source of releases of endosulfan, cadmium and PBDEs into the environment in relation to the total emissions.

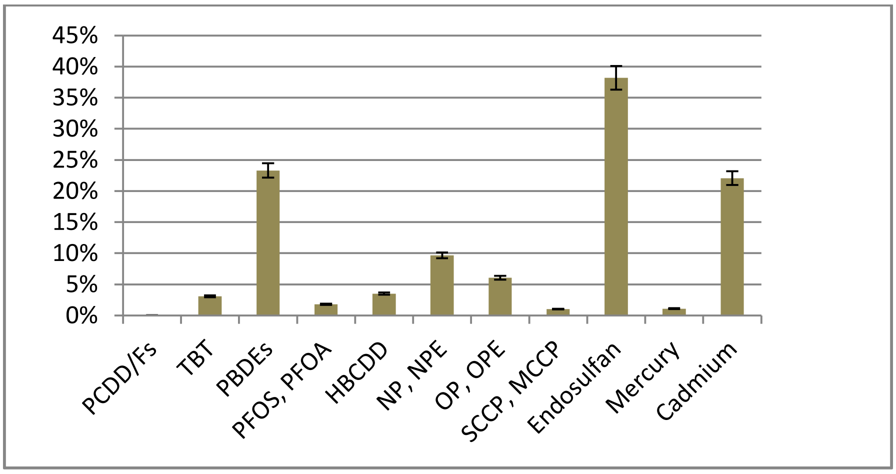

Figure 31. Emission share of BSAP hazardous substances from agriculture in relation to total emissions into the environment. The bars show the mean value of the low and high scenario and the error bars show the low and high scenario, respectively.

Concluding remarks

With respect to contamination of soil by dispersion of sewage sludge on farmland and possible leakages to surface water and groundwater, cadmium, NP/NPE, OP/OPE as well as SCCP/MCCP are rising concerns because of their quantity and their toxicity to humans and aquatic organisms.

There are large uncertainties in the emission estimations, particularly for organic contaminants SCCP/MCCP, PFOS/PFOA, PBDEs, PCDD/Fs and OP/OPE due to limited monitoring data on composition and quality of sewage sludge.

Sewage sludge addition to the total land area used in plant cultivation is a considerable source of soil contamination. Precautionary provisions are of importance in locations where use of sewage sludge as fertiliser is practised on a regular basis; with regard, inter alia, also to the input of cadmium. Risk reducing measures for cadmium have long been an important issue in *e.g.* Sweden (KEMI 2011).

2.2.5.2 Energy

Energy production is predominantly the source of unintentional emissions of three groups of HELCOM hazardous substances; dioxins, furans and dioxin-like PCBs, mercury and cadmium). For other HELCOM hazardous substances the emissions are negligible.

The emission is a result of thermal processes during fuel burning and it is determined by the technology applied and the occurrence of impurities in fuels. The main sources within the energy sector are: individual heating systems, power plants, electricity transformations, and use of products containing cadmium batteries. Products containing these substances make up a marginal source as there are restrictions and/or a high level of control imposed on their use such as: use of mineral oil (containing PCBs) in energy transformation and high rate of recycling for Ni-Cd industrial batteries.

The main release pathway for PCDD/F, cadmium and mercury is air emission; with much smaller input coming from discharges to surface water and deposition of wastes onto land. Municipal heating facilities, heating systems at enterprises and in individual buildings are important sources of air emissions, especially for PCDD/F and less for cadmium, mercury (Figure 30),

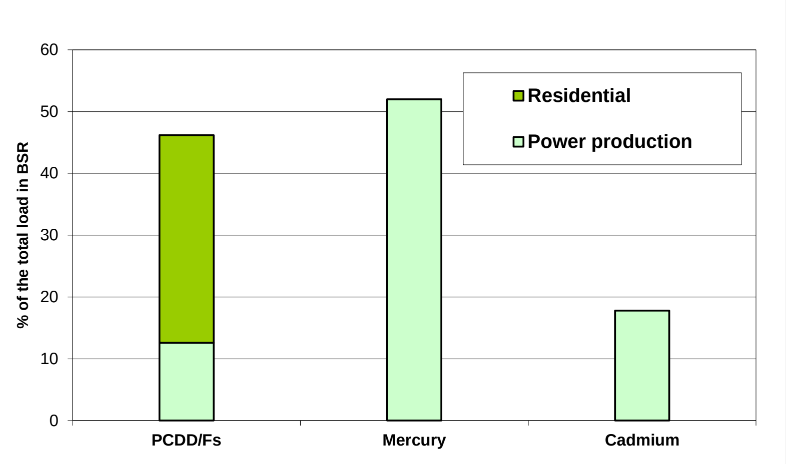

Figure 30: Share of cadmium, mercury and PCDD/F emissions from energy related activities in the total load in the Baltic Sea catchment

PCCD/F emissions to the air from power plants are around 10% of the total load to the environment. The energy sector is a minor source of PCDD/Fs emissions to the surface water and wastewater (around 3% of the total load). The major air emissions come from individual installations and small-scale municipal combustion plants, amounting to 34% of the total load.

Energy production is the main source of mercury (>50% of emissions in the total load) in almost all countries, and Poland is the major emitter. The emission share for Poland in the energy sector is respectively 70% for PCDD/F, 90% for mercury and 88% for cadmium. Air emission is the main release pathway for these substances.

Combustion processes in fuel transformations, mostly coal and coke production, are relevant only for Poland. Energy production is a source of cadmium emission to the air (~16%) and to surface water (3% of the total load) in almost all countries, with Poland as the major emitter.

Discussion and conclusions

The energy sector is an important source of emissions, predominantly into the air, of dioxins, furans, mercury and cadmium. In case of dioxins, the residential sector is the main source of emissions in the Baltic Sea region. This is mainly relevant for Poland. Mercury emissions can be attributed to large and medium power plants as it is emitted in gaseous phase giving an input to long range transport. Cadmium and dioxins emissions are more likely to be emitted by small installations as they are bound to particles.

The main uncertainty of the assessment is related to residential heating as the inventories are based on general assumptions. For power production the uncertainty is relatively low as the facilities have to report the emissions according to legal requirements.

The energy sector is the most important in Poland, taking into account both the residential heating systems, power plants and energy transformations. To conclude; sources of air emissions for cadmium, mercury and dioxins cause subsequent air deposition in the Baltic Sea catchment and as they such constitute essential input to the environment in the Baltic Sea catchment.

3 Important pathways

3.1 Long range atmospheric transport and atmospheric deposition

Substance flow analyses have identified air as a major receiving compartment for emissions of several BSAP-substances and for these substances, atmospheric transport and deposition may constitute an important pathway into the Baltic Sea and its catchment area. In addition, several of the BSAP-substances are persistent and they may enter the Baltic Sea region via atmospheric long range transport (UNEP Stockholm convention on POPs and UNECE-LRTAP).

Air and deposition measurements, which include several of the BSAP-substances, are carried out in the Baltic Sea region (EMEP’s database Co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe, Swedish monitoring program for air pollutants, www.ivl.se). Measurement data have been used to assess the importance of atmospheric transport and to estimate the atmospheric input of hazardous substances to the Baltic Sea region. Adopting the estimated annual deposition fluxes and assuming that the measured deposition fluxes are relevant for the entire Baltic sea (Baltic Sea surface area 415 266 km^2) and its catchment (Baltic Sea catchment surface area ; 1720 270 km^2), the total annual input of the selected substances via atmospheric deposition has been estimated. Methods for estimation of deposition fluxes are described in the WP4 background document where the uncertainty is also shown.

3.1.1 Deposition fluxes of the BSAP-substances in the Baltic Sea region

The estimated annual input of the selected BSAP-substances via atmospheric deposition to the Baltic Sea and its catchment area is given in Table 7, where the total emissions into the region to all compartments from the different source categories are also shown. The total emission estimates for the different substances are based on data found in Chapter 2. Below, the estimated annual deposition is compared to the summed emissions to air, surface water and land.

Table 7: The estimated annual deposition to the Baltic Sea and to the Baltic Sea and its catchment;and the total emissions to environmental compartments in the Baltic Sea region, both low and high scenarios, for different BSAP-substances.

	Annual deposition		**Total annual emissions to environmental compartments**	
Substance groups	*Baltic Sea area*	*Baltic Sea catchment area*	*Baltic Sea and its catchment area* low	*Baltic Sea and its catchment area* high
Dioxins (PCDD) and furans (PCDF), Dioxin-like polychlorinated biphenyls (PCBs)	100 g TEQ	600 g TEQ	600 g TEQ	700 g TEQ
Pentabromodiphenyl ether (pentaBDE), Octabromodiphenyl ether (octaBDE) Decabromodiphenyl ether (decaBDE)	80 kg	400 kg	200 kg	500 kg
Hexabromocyclododecane (HBCDD)	20 kg	70 kg	350 kg	700 kg
*Short-chain chlorinated paraffins (SCCP) Medium-chain chlorinated paraffins (MCCP)	*2000 kg (SCCP)	*8000 kg (SCCP)	140000 kg	160000 kg
Endosulfan	100 kg	400 kg	180 kg	350 kg
Mercury	8000 kg	30000 kg	20000 kg	25000 kg
Cadmium	10000 kg	60000 kg	25000 kg	30000 kg

*MCCP not included in the deposition fluxes

The estimated annual deposition of PCDDs/ PCDFs is in the same order of magnitude as the total emissions to environmental compartments in the region. This indicates that the atmospheric pathway is important for the occurrence of these substances in the Baltic Sea and its catchment area.

Atmospheric deposition seems to be an important pathway into the Baltic Sea for brominated diphenyl ethers too. Deca-BDE contributes a large share to the estimated amounts, 60 kg/year to the Baltic Sea and 300 kg/year to whole of the Baltic Sea catchment.

The atmosphere is an important pathway for HBCDD and an input to the Baltic Sea via deposition has been identified; however, direct emissions to the environmental compartments in the region seem to be quantitatively more important.

Both SCCPs and MCCPs are transported in the atmosphere thus deposition will be a possible pathway to the Baltic Sea for these substances also (Fridén 2011; www.ivl.se). The deposition estimates, which are only available for SCCPs, show that the amounts of SCCP deposited into the Baltic Sea are significantly greater compared to the other organic substances; although the emissions of SCCP are only one tenth the amount of the emissions of MCCP. However, air is not the main receiving compartment of these chemicals and the deposition seems be to minor compared to the estimated emissions to the environmental compartments for the Baltic Sea region.

Endosulfan is not used in the region so atmospheric long range transport and deposition are important for the presence of this substance in the Baltic Sea region. The estimated annual deposition into the Baltic Sea and its catchment is in the same order of magnitude as the total emissions to environmental compartments in the regions.

Atmospheric transport and deposition is an important pathway for both mercury and cadmium to the Baltic Sea. The estimated annual deposition of the metals into the Baltic Sea is greater compared to the estimated emissions to environmental compartments in the region, especially for cadmium, which indicate that long range transport into the region could also be important.

Both measurements and models have shown that PFOS and PFOA are transported in the atmosphere over long distances and that they have also been found in ecosystems in remote areas (Armitage 2009). Measurement of PFOS and PFOA in air and precipitation at the Swedish west coast also indicate that atmospheric deposition is an important pathway for these substances. However, deposition estimates for the Baltic Sea region based on this data are impossible to perform (www.ivl.se).

The SFAs have shown that air emissions of nonylphenols /nonyphenol ethoxylates and octylphenols /octylphenol ethoxylates are of minor importance compared to other emission sources and these substances have not been detected in air at background sites in Sweden either. No data from deposition measurement in background areas of these substances is available.

Atmospheric transport is not the main pathway for tributyltin/ triphenyltin compounds into aquatic environments and data on concentrations in air and amounts in precipitation have not been found.

According to the results of the modelling study (Chapter 4.1) the atmosphere was predicted to be the main input pathway, to the open sea, of the substances included in the modelling study; PBDEs (congeners 47, 99 and 209), HBCDD, and endosulfan. In addition, the model predicted that there could also be a deposition of NP to the Baltic Sea. Moreover, using only within-region estimated emissions resulted in substantial underpredicted deposition rates and concentrations in sediment, indicating that additional sources not taken into account are also important. One of these is likely to be atmospheric deposition due to long-range transport.

In conclusion, atmospheric transport and deposition seems to be important for the occurrence of several of the BSAP-substances in the Baltic Sea and in the Baltic Sea catchment area. Furthermore, atmospheric transport is an important pathway for several of the substances into the region.

3.2 Contaminated soil and sediments

Along the coastal areas of the Baltic Sea, sediments are often contaminated with hazardous substances due to industrial or other activities. Examples of hazardous substances in contaminated sediments are metals such as mercury and cadmium, and many organic compounds; PCBs, TBT, PAHs etc. How to handle contaminated sediments is a major problem. Alternatives are few, costly and require complicated methods (www.smocs.eu). Sediments act as a sink for hazardous substances as long as they are not disturbed physically (*e.g.*, by dredging or hydrographic changes), by biophysical disturbances (bioturbation by organisms), through benthic organisms feeding on sediment particles, or by microorganisms (*e.g.* methylation of mercury). Disturbance of contaminated sediments may result in the resuspension of hazardous substances and increase their availability for chemical and biological processes. An important criterion for evaluating the significance and risks of hazardous substances at contaminated sediments is their present or future potential for mobility (SedNet 2004, Weber *et al.* 2009).

Many water and port managers face the continuous effort of dredging in order to maintain the required water depth. Europe-wide, the volume of dredged material is very roughly estimated at 200 million cubic meters per year (SedNet 2004). In Finland, for example, the estimate for the amount of contaminated dredged spoils during 2008-2018 is about 1.2 million m^3 (Finnish Ministry of Environment 2007). There are three types of dredging: capital, maintenance and remediation dredging. Capital dredging is used, for example, for land reclamation, deepening fairways, etc. Maintenance dredging is mainly to keep waterways at a defined depth to ensure safe navigation, and remediation dredging is to solve environmental problems of contaminated sediments. Contamination mainly leads to problems in maintenance dredging because given standards or regulations do not allow the free disposal of heavily contaminated materials into the aquatic system. There is a lot of information on the different options of dredged-material management available (*e.g.* http://www.sednet.org). In the following, examples of those substances and cases with major present importance within the Baltic Sea region are briefly discussed.

3.2.1 TBT, TPhT

Most TBT and TPhT leach into Baltic Sea water from maritime sources such as antifouling paints on ship hulls and TBT-contaminated harbour sediments. Consequently, coastal areas, especially those located near shipyards and ports, contain large amounts of TBT. Elevated levels can also be found in narrow shipping lanes and in marinas. The marina areas are commonly used as service areas for small boats where the scraping of old antifouling paint and repainting have occurred. Because of the adverse effects of TBT on marine invertebrates, such use has been widely banned for small boats (<25 m) within the EU since the late 1980s. Despite this, a recent Swedish study of small-vessel marinas found TBT concentrations comparable to those in large harbours (Eklund *et al.* 2008).

3.2.2 Dioxins and furans

The highest historical PCDD/F and dioxin-like polychlorinated biphenyl (PCB) contamination burdens have arisen as a result of the production of chlorine and of chlorinated organic chemicals. In particular, the production, use, storage and negligent disposal of chlorinated pesticides, and PCBs have led to historical releases into soils and sediments.

A major PCDD/F contaminated sediment site within the Baltic Sea region is the River Kymijoki and its estuary, in the Gulf of Finland, because of emissions from the production of chlorphenol wood preservative in the upper reach of the river from the 1940s to 1984. Significant amounts of PCDD/Fs have been transported to the Gulf of Finland since then. The total historical sum (from 1940 to 1984) that ended up in the water and sediments was approximately 29 kg (I-TEQ) of which (12.4 kg as WHO-TEQ) was transported to the Gulf of Finland; the rest is situated in river sediments (Salo *et al.* 2008). The annual PCDD/F flux to coming into the Gulf of Finland from the erosion of river sediments varied from 44 -75 g/year I-TEQ during 2000-2006 (Verta *et al.* 2009). This is equal to the present annual atmospheric deposition to the whole of the Baltic Sea (Bartnicki *et al.* 2009). It is estimated that the impacted sedimentary area stretches a distance of 75 km out from the coast (Isosaari *et al.* 2002).

More local hotspots, *e.g.* close to old pulp bleaching and mono vinyl chloride (MVC) production plants, have also been observed in several other locations on the Swedish and Finnish coasts (Verta *et al.* 2007, Sundqvist *et al.* 2009). The importance of these hotspots as a dioxin source to Baltic marine biota still remains open and, in general, the atmospheric source is believed to contribute the major fraction of PCDD/Fs found in Baltic Sea fish.

3.2.3 Heavy metals (mercury and cadmium)

Based on HELCOM 2010 assessment, mercury and cadmium show, in general, high concentrations in Baltic Sea surface sediments. They have somewhat different distribution patterns, as mercury shows more local anomalies located closer to the sources, while cadmium, as a more mobile element, seems to have occupied the bottoms of larger sea areas.

High sediment mercury concentrations were found in several estuaries and particularly in the western Bothnian Bay, eastern Gulf of Finland, off south-eastern Sweden and in the Sound, although local contaminated areas were not included (HELCOM 2010). Local contamination of mercury has been identified in several locations; *e.g.* close to many old pulp and paper mills (former mercury use as slimicide) and former chlor-alkali plants (mercury cell electrolysis method), and large cities such as Stockholm and Copenhagen (*e.g.* Cato and Apler 2011).

According to HELCOM 2010 assessment, cadmium concentrations were particularly high in sediments in the Bothnian Bay, eastern Gulf of Finland, Northern Baltic Proper, Western and Eastern Gotland Basins and the Pomeranian Bay. The extent to which geogenic sources such as acid sulfate soils (see Chapter 2.1.5), affect the background concentrations for cadmium in sediments in the different basins is uncertain. However, it can be estimated that the surface sediment concentrations in large areas of the Baltic Sea exceed the threshold values given by OSPAR and Swedish EPA, especially for cadmium, for good environmental status (HELCOM 2010).

4 Regional differences and scenario assessment

4.1 Regional differences in Baltic Sea

A modified version of the chemical fate model POPCYCLING-Baltic (Mattila & Verta, 2008) was used to assess the fate of a selection of the target chemicals (PBDE (congeners 47, 99 and 209), NP/NPE, HBCDD and endosulfan). Emissions as estimated in the substance flow analyses (chapter 2) were used to extrapolate emissions from countries in the drainage area that were not partners within the COHIBA Project. Together with physical-chemical properties of the substances (see Palm Cousins 2012), these emissions were used as input to the model and steady state concentrations in various matrices were recorded. For each chemical both the low and the high emission scenario was modelled. The following assumptions were made:

- The emissions estimated within COHIBA have been constant over the modelled time period;
- The environment is considered to be at steady state – *i.e.* there is no change in concentrations or net flows over time;
- There is no net transport of chemical into, or out from, the Baltic region, *i.e.* the inflow from outside equals the outflow from inside;

The results from the modelling exercises indicated the following:

- The concentrations in air of PBDEs and HBCDD, NP and endosulfan in the Baltic Sea region as a result of the emissions in the region are predicted to be evenly distributed over the area. The different emission scenarios result in concentrations differing by one order of magnitude for PBDEs whereas for the other substances, the predicted levels were similar, regardless of emission scenario.
- Surface water concentrations for all the modelled substances are predicted to be highest in the Neva region in the Gulf of Finland, for both emission scenarios. For PBDEs, the concentrations are predicted to be more evenly distributed between coastal and marine areas, than NP and endosulfan, which show significantly higher concentrations in coastal regions. This is likely to be an effect of the slower degradation rates in combination with higher estimated emissions to air of PBDEs compared to the other substances (with the exception of HBCDD, which also has higher emissions to air), as the main input pathway to the open sea is predicted to be via the atmosphere.
- The concentrations in sediment are predicted to vary by a factor of 30 to 5 000 between different model regions, depending on substance. Neva is again indicated to be a key area in terms of high concentrations, but for PBDEs, the high emission scenario instead highlights South Baltic Proper and Swedish Baltic Proper as showing the highest levels.

The model was also used to predict the key input pathways to different model regions. Overall, between 0.4% and 16% of the total within-region emissions of the target substances are predicted to reach the Baltic Sea, depending on the substance and scenario. This appears to be entirely governed by the direct emissions on the coastline. Less than 1% of the total emissions inland (to air, freshwater and soil) are predicted to reach the Baltic Sea via riverine input and atmospheric deposition, long-range transport not considered (see Figure 31).

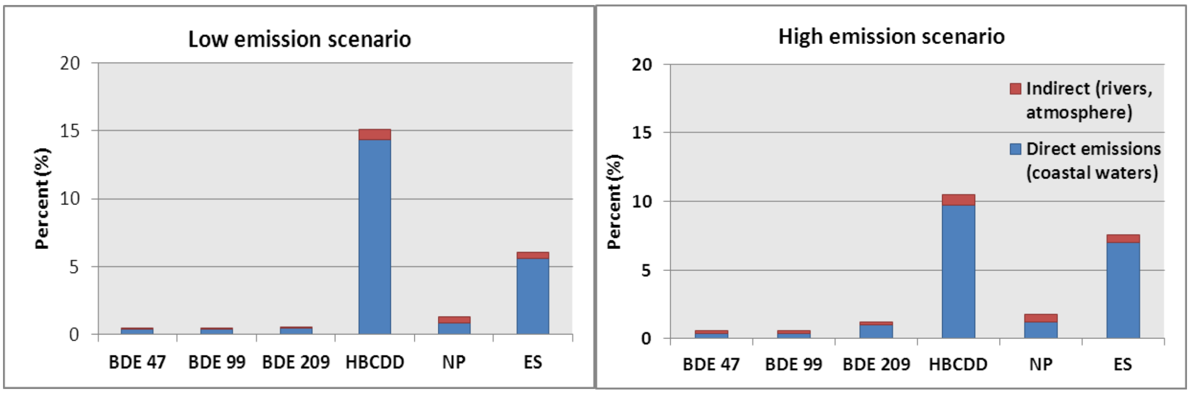

Figure 31: Percentage of total emissions predicted to reach the Baltic Sea via direct emissions (to coastal waters), riverine input and net atmospheric deposition (*i.e.* deposition minus volatilisation). Predicted percentages representing the two emission scenarios assessed are presented.

A comparison between modelled and measured concentrations revealed in most cases underpredicted model concentrations, indicating potential importance also of other sources, such as long range atmospheric transport. Underpredicted levels in sediment could also be a result of higher emissions in the past. Some inconsistencies in model/measured ratios made the model evaluation difficult. This was particularly true for PBDEs, for which air concentrations were generally close to agreement or even overpredicted by the model, whereas deposition rates were underpredicted. In many cases, the monitoring data used for evaluation were below the detection limit, which hinders model comparison A larger dataset of measured concentrations of the target compounds in several matrices in the Baltic Sea could improve the model evaluation.

4.2 Case studies: St Petersburg and Kaliningrad region

In addition to substance flow analysis, which was carried out in each of the Project partner countries, a supplementary study and SFA was also done in St Petersburg and the Leningrad region surrounding it. Added to that was an overall situation assessment of potential hazardous substances emission sources from the Kaliningrad region. Thus filling the gaps and obtaining information on all coastal regions around the Baltic Sea.

The gathering and analysis of information from Russian regions were done based on the same principles as for the EU countries. For almost all of the substance groups the main emission sources turned out to be consumption and use of ready products and articles, followed by long-range transport and deposition of pollutants. Industrial sources were identified as sources in only few cases, mostly for substances which are well-known and have been used for a long time, such as the heavy metals.

These typical trends showed up in both regions and should be evaluated with caution. The main reason for this is that there are very big uncertainties and data gaps, especially when considering emission and production volume information from the industrial sector. There are two main particularities behind this. Firstly, quite a few of the HELCOM BSAP priority hazardous substances are not regulated in Russia, quite the opposite, in fact, as there is no ban on their total emissions. Either way, no official emissions data are being collected due to the assumption that either the substances are not there, or because they are not considered to pose a particular threat to the environment. Secondly, information on used (and not emitted) substances, raw and auxiliary materials is considered to be a commercial secret so no information is available on this. That only leaves statistical information gathering from official yearbooks and bureaux of statistics on the amount of production produced from industrial sectors which are likely users and/or producers of the substances in question.

At the same time, judging from industrial enterprises present in St Petersburg and Kaliningrad, industry is a potentially important source of emissions. For example, it is certain that such enterprises are present:

- Leather tanning and finishing;
- Chemicals production (including polymers, cleaning agents and fertilisers);
- Metal works and plating;
- Production of components for electrical and electronic equipment;

Another important issue is the differentiated status of wastewater treatment in Russian regions s on the Baltic Sea coast. While in St Petersburg waste water treatment system is quite sophisticated, with constant improvements ongoing and almost all sludge being incinerated in designated facilities, in Kaliningrad the situation is not so advanced. At the moment, 20 WWTPs are working in the Kaliningrad region (both municipal and industrial), out of which 13 employ only mechanical treatment. Furthermore, approximately 20% of overall generated waste water effluents are being completely untreated. Naturally, this is likely to be a source of emissions of hazardous substances; however, due to the lack of measurements, quantification is not possible at the moment.

When comparing the EU and Russian side of the BSR, it becomes visible that uncertainties and data gaps are found in similar places but to different extents; especially when comparing the Eastern Baltic Sea region countries (the Baltic States and Poland) with Russia. For example, emission data from industrial enterprises are lacking complete information, but in EU countries, at least some information on used raw materials and products is available from environmental permits, not the case in Russia, allowing for more precise emission estimates. Furthermore, analytical measurement data are more common in EU countries than in Russia, mostly because of the gap between these regions created by different legal frameworks towards classification and management of hazardous substances. Emissions from imported goods seem to be similarly difficult to assess in all countries and regions around the Baltic Sea.

Future trends for emissions from the St Petersburg and Kaliningrad regions will most probably be dependent on possible changes in the legal frame of regulations of these substances. Trends over the last 20 years have already shown that for substances which are strictly regulated, used and emitted amounts are steadily decreasing. For example, total mercury consumption in the Russian Federation has decreased 2.5 – 3 times over the past 20 years, *e.g.* amount of mercury applied in dental amalgam fillings manufacture was reduced from 6 tonnes in 1991 to 0.8 tonnes in 2001. Input of cadmium into water bodies of St-Petersburg in 1990 was 2 337 tonnes, in 2008 – 2009 emissions were reduced to nearly zero.

Further information on the results of the Russian case studies can be found in the case study reports available on www.cohiba-project.net.

4.3 Urban areas

Europe is one of the most densely populated continents and today about 75 % of the European population resides in urban areas. This is estimated to increase to 80% by the year 2020 (EEA, 2010). At the same time, human consumption of articles is increasing, which leads to an accumulation of chemical-containing articles and goods in urban areas. Urban areas differ from the general environment in many ways, a large fraction of the land is made-up by impervious surfaces, which creates a barrier for chemicals depositing via the air. Thus, instead of migrating into a soil compartment, where they, depending on the physical-chemical properties would remain more or less immobile, chemicals in urban areas will temporarily adsorb to organic layers built up on the hard surfaces (and made up of other pollutants) and then be rinsed of with rain water and enter storm water systems. Depending on the infrastructure in the city this may then be further transported to surface waters or treatment plants. In addition, because of the high population density, urban areas contain large volumes of indoor air, where many articles containing hazardous chemicals are primarily used. In the indoor environment, these substances may be released during the service life of the articles and partition to surfaces, dust or air, from where they can be transported further via ventilations streams or to municipal waste systems. In conclusion, because of the high population density and therefore also potential high density of article-related chemicals, together with the special characteristics of the urban environment, these areas were given special focus in the COHIBA project by two separate case studies, one in the municipality of Stockholm, and one in the harbour of Copenhagen.

4.3.1 The Stockholm case study

Introduction

The aim of the Stockholm case study was to predict the distribution and transport pathways of selected substances in an urban area and to identify and quantify the main input sources to the Baltic Sea from such an area. A specific focus of the Stockholm study was also to address the role of the indoor environment as a sink, or source, of chemical transport to the urban area overall. This would, in turn, facilitate the investigation of the role it plays in mediating chemical transport from the urban area to the Baltic Sea.

Local-scale SFAs for Stockholm were performed for PBDE, HBCDD and the group of NP and NPE. The quantified emissions were used as input to a local-scale urban model, and were, together with physical-chemical property data of the substances, the driving parameters for the model, which then predicted concentrations, intermedia transport and total residence times in the system.

Results of the local scale SFAs

The direct emission sources of PBDEs to the Stockholm environment are limited. Since many of the potential emission sources are located outside the region (such as plastics manufacturing plants, steel production plants and recycling facilities of electronic goods), and potentially contaminated municipal sewage sludge also is transported for treatment or application elsewhere, the single most important source in Stockholm appears to be the indoor environment. From there, PBDEs may be transported to outdoor air via ventilation outlets or transferred to municipal waste or local sewage systems (via vacuuming bags and/or wet mopping).

The estimated emissions to air are higher than the estimated atmospheric deposition in the area, implying that Stockholm may act as a source of PBDEs to neighbouring regions, including the Baltic Sea.

Demolition of buildings is indicated as the most important source of emissions of HBCDD both to surface water and air (high scenario), although this is most probably a future scenario, when buildings from the nineties are being demolished. In the service life category the dominating sources are emissions of HBCDD to air from flame retarded HIPS plastic and particulate emissions of HBCDD from flame retarded textiles. However, atmospheric deposition only corresponds to a minor load of HBCDD to surface water compared to the other sources, but is the only source of emissions of HBCDD to land in the Stockholm area.

Effluent water from M-WWTPs was shown to be an important source of emission for HBCDD, NP and NPE into the Stockholm environment. However, even though the substances partition to sludge, emissions to land from application of sludge is not relevant for this area as all municipal sewage produced within Stockholm is used outside the region.

Most of the emissions of NP and NPE are directed to the M-WWTPs. The major sources for emissions directed to wastewater are washing of textiles, industrial and institutional cleaning and cleaning with products from outside EU. This is in agreement with the SFA results on a Swedish scale (Swedish WP4 summary report). Leaching of NP from concrete is also estimated to be a considerably large source in Stockholm with emissions mainly directed to impervious surfaces and then further transported by stormwater to surface waters and the wastewater system.

Stockholm Multimedia URban Fate model (SMURF)

To allow for assessment of the urban fate of chemicals released indoors an indoor-inclusive multimedia fugacity model of Stockholm (SMURF) was used for the modelling exercise (Palm Cousins in prep.) A simplifying assumption made in the model is that runoff from impervious surfaces is transported directly to surface water. In reality, about 50% of the stormwater in Stockholm is treated in M-WWTPs. Relative to other transport routes, the amounts transported from urban surfaces are predicted to be low; thus this simplification is not expected to have a large impact on the overall results. The role of storm water and sewage system, including combined sewer overflows in transporting chemicals from urban areas to the sea is addressed in more detail in the Copenhagen case study (Chapter 4.3.2).

The results from the Stockholm modelling study shows that the PBDEs and HBCDD are predicted to mainly partition to indoor surfaces in the low emission scenario, a consequence of their use in building and consumer products indoors (leading to relatively high estimated emissions to indoor air), and their low estimated emissions to surface water in the low emission scenario. NP is predicted to mainly partition to soils and sediment, due to the estimated releases to soil and surface water. NP is also predicted to have the highest steady state amounts and the longest residence times in the urban environment.

In the high emission scenario, larger fractions of the decaBDE and HBCDD are predicted to partition to sediment. This increases the predicted steady state amount, but reduces their environmental residence time, because of the fairly fast burial rates in the Stockholm sediments, compared to the estimated dust removal rate, which was the main removal pathway in the low emission scenario.

To assess the potential of the Stockholm environment to act as a source area of chemical transport to the Baltic Sea, the SMURF model was used to determine the percentage of the total annual emissions of different chemicals that would be transported out of the region with air and water for the different emission scenarios. Transport with water implies transport directly out to the Swedish Coast, whereas transport out with air may take different directions depending on the wind. The potential for further transport out from the Stockholm area appears to be related to the primary receiving compartment. For chemicals mainly emitted to indoor or outdoor air, such as BDEs 47, 99 and also BDE 209 and HBCDD in the low scenarios – a large percentage (30-70%) of the emitted amounts are predicted to leave the Stockholm environment with air. When emissions are mainly to soil and/or surface water, such as for NP and HBCDD and BDE 209 in the high emission scenario, a lower percentage (2-20 %) of the emitted amounts are predicted to leave the system, and still mainly with air. About 2% of the emitted NP is expected to be transported out of Stockholm, mainly with water. This corresponds to in total 2.7 kg/year, which is still a lot more than the estimated transport with air of HBCDD (0.15 -0.18 kg/year), BDE 209 (0.01-0.02 kg/year) or the penta components BDE 47 (0.5 kg/year) or BDE 99 (0.1 kg/year). And as opposed to the transport with air, the releases via the waterways are directed to the Baltic Sea directly.

Discussion and conclusions

Compared to the whole of Sweden, the source profiles are different for Stockholm for all three substance groups but there are also similarities (Swedish WP4 National summary report; Stockholm case study report). For PBDE the single most important source in Stockholm, as well as in Sweden, appears to be the indoor environment, due to release from articles during their service life. Furthermore, the dominating emission sources in the service life category are possibly the concrete for NP and NPE, the flame retarded HIPS plastic and textiles for HBCDD both in Stockholm and in Sweden. However, there are rather large emissions of NP and NPE reported in Sweden from agricultural use of pesticides containing NPE, but as there is no agriculture in Stockholm this is not a relevant source there.

Is Stockholm, then, a representative urban area? For both HBCDD and NP/NPE, M-WWTPs were the dominating sources of emissions to the environment of Stockholm, but only via effluent water (according to the SFA work). Even though these substances partition mainly to sludge, emissions to land from application of sewage sludge are not relevant for this area as all sewage sludge generated at the Stockholm M-WWTPs is transported outside the region. However, this may not be a typical situation for urban areas. Neither is the fact that there are no industrial emissions for these substances in Stockholm typical for urban areas. In Stockholm there are no industries using PBDEs (such as plastics manufacturing plants, steel production plants and recycling facilities of electronic goods), NP and NPEs (*e.g.* formulation of NPE mixtures) or HBCDD (*e.g.* manufacture of EPS), but this may vary between regions. Demolition of buildings was shown as a future contribution to releases of HBCDD to the Stockholm environment and these emissions will be concentrated to urban areas in general.

The modelling study indicates that air will be the main chemical transport pathway out from the city. This is in agreement with previous modelling studies in urban areas which have shown that advective transport with air is the main removal pathway for many organic pollutants (*e.g.* Diamond and Thibodeaux 2010). For NP, with no estimated emissions to air, advective transport with water becomes the main pathway to the Baltic Sea area, but the percentage of the emitted amounts predicted to be released via this route are small. Instead the dominant removal process for NP in Stockholm is predicted to be sediment burial followed by reaction in soils and sediments. Thus the importance of transport of NP to the Baltic Sea depends on the size of the emissions. In absolute terms, the Stockholm environment may still contribute by larger amounts of NP to the Baltic Sea than PBDEs and HBCDD, also because water is a more direct pathway than air, for which the final end-point depends on the wind direction.

4.3.2 Modelling of hazardous substances in the urban area of Copenhagen

The Danish COHIBA activities have focused on the Copenhagen catchment area and the discharges to the Copenhagen Harbour and the Sound (Øresund). The objectives were to identify and prioritise the sources through a combination of measuring campaigns, load estimations and hydrodynamic fate modelling.

Methodology

Measuring campaigns have been carried out for the 14 different land-based point sources. The following categories of point sources were identified in the Copenhagen Harbour area: Large wastewater treatment facilities (both treated water and by-pass water), combined sewer overflows (CSO), urban run-off, waste deposits, and industrial facilities. Measurements have been carried out for the 11 BSAP hazardous substances and the same has been done for bisphenol A, which is part of the same chemical analysis standard as nonyl-/octylphenols. All measuring results are reported in (Nielsen *et al.* WP3 2011).

The specific point sources are illustrated in Figure 32. All sources were screened to determine the concentrations of all the BSAP-substances. The results of chemical analyses and flow measurement were used to prepare load estimations for all substances. Example findings describing load estimates for PFC are included in Figure 32. Load estimations for other substances can be found in (Nielsen *et al.* WP5 2011).

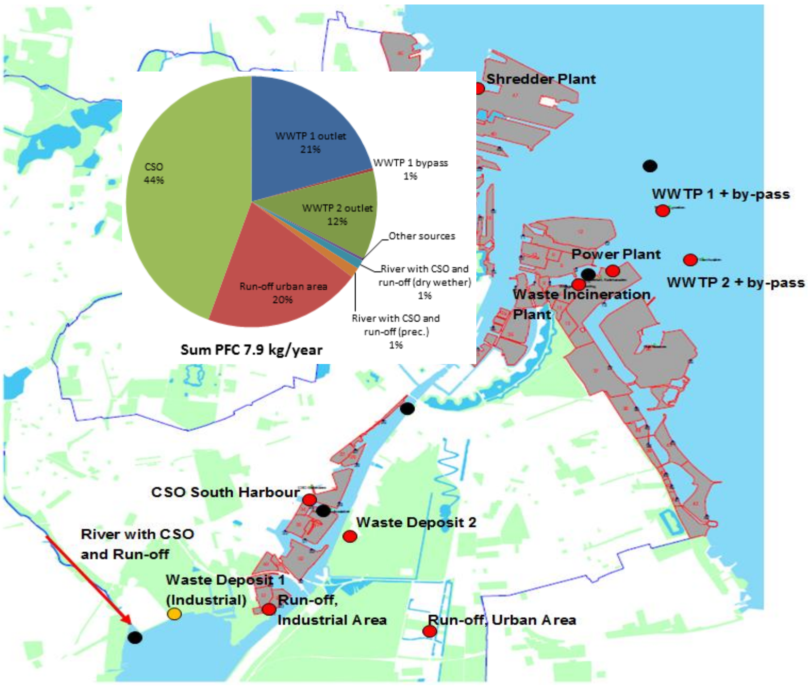

Figure 32 Monitoring points in the Danish case study in Copenhagen and a pie chart illustrating PFC load estimates for these point sources.

In the next phase of the project, hydrodynamic marine fate modelling (MIKE 3 and ECOlab) was carried out for selected substances. PFC and bisphenol A were found to be present in the sources in concentrations that justified such modelling. The model takes substance specific fate data (biodegradation, photolysis and hydrolysis) and adsorption to suspended solids into account. Figure 33 shows an example of the fate modelling of PFC. The modelling activities are reported in (Nielsen *et al.* WP4 2011).

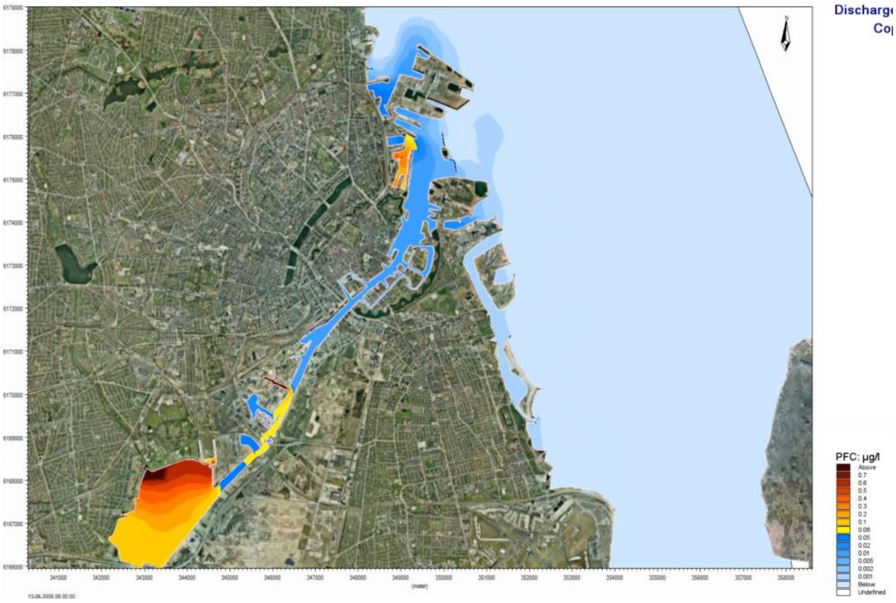

Figure 33: Hydrodynamic fate modelling of PFC in Copenhagen Harbour. The map illustrates the predicted situation after heavy rain in June 2009. This is a picture from the video animation, which can be viewed at www.cohiba-project.net.

Results

The monitoring, load estimation and modelling activities have enabled the prioritisation of actions addressing point sources of BSAP-substances in Copenhagen. The results of the methodology are illustrated for PFC in Figure 32 and Figure 33. The pie chart in Figure 32 illustrates that the combined sewer overflows and urban run-off account for 64% of total point source discharges of PCF into Copenhagen Harbour (7.9 kg/year). Large urban wastewater treatment plants contribute a further 33%. As shown in Figure 33, marine fate modelling predicts that concentrations will exceed environmental quality standard-EQS (0.08 µg/L, see Nielsen *et al.* WP4 2011) in periods after heavy rain. Although the EQS is exceeded in shorter periods after heavy rain it should be noted that the yearly average concentration of PFC never exceeds the EQS at any point in the harbour area.

Conclusions

Through a combination of measuring campaigns, load estimations and hydrodynamic modelling, the Danish case study has made it possible to determine whether or not point sources are important in emissions of the hazardous substances listed in the Baltic Sea Action Plan. The study shows that out of the 11 BSAP-substances, land-based point sources are important for:

- Perfluorinated compounds (PFC)
- Nonylphenol ethoxylates (NPE)
- Bisphenol A (not a BSAP-substance itself, but analysed using the same method as NPE)
- Mercury

The most important point sources for these four prioritised substances can be condensed to the main source categories showed in Table 8. It is clear that no single source category is responsible for all four substances.

Table 8: Main sources categories for the Danish prioritised substances

Substance	**Source category**
PFC	Urban run-off and Combined Sewer Overflows (CSO)
NP+NPE	Industrial zone, River (CSO + run-off) and Urban WWTP
Bisphenol A	Waste Incineration, Urban WWTP (plus WWTP By pass)
Mercury	Urban WWTP

Measures can now be focussed on the relevant point sources of the prioritised substances. In future, as the numbers of emerging pollutants increase (including WFD Prioritised Substances), the same methodology can be used to decide whether actions targeting point sources are necessary and beneficial. For further information see the three Danish COHIBA reports: (Nielsen *et al* WP3, 2011), (Nielsen *et al.* WP4 2011) and (Nielsen *et al.* WP5 2011).

4.4 Scenario assessment

To address the impact of emission reductions on the concentrations of target chemicals in the Baltic Sea, the POPCYCLING-Baltic model was used to simulate a scenario where all emissions cease at a certain point in time. The time for the different chemicals to reduce their initial concentrations by 50% and 90% ($T_{50\%}$, $T_{90\%}$) were recorded for water and sediment in the two key areas of interest; South Baltic Proper and the Neva Region. A general finding was that the higher the initial concentration, the faster the response time. Also, the time for reduction of concentrations was much shorter in the Neva Region than in the South Baltic proper, due to quick outflow with water to the Gulf of Finland and the remaining Baltic Sea. The order of reduction time was for the South Baltic Proper:

- In water:

$T_{50\%}$: HBCDD=NP<endosulfan<BDE209<BDE47<BDE99;
$T_{90\%}$: NP<endosulfan <HBCDD<BDE47<BDE99=BDE209

With $T_{50\%}$ ranging from about two months for HBCDD to seven months for BDE 99 and $T_{90\%}$ varying from 4 months for nonylphenol to 40 months for BDE 99 and BDE 209

- In sediment:

$T_{50\%}$: HBCDD=NP<endosulfan <BDE209<BDE47<BDE99;
$T_{90\%}$: HBCDD<NP<endosulfan <<BDE47<BDE99=BDE209

With $T_{50\%}$ ranging from 6 months for HBCDD and NP to 20 months for BDE 99 and $T_{90\%}$ varying from 12 months for HBCDD to 54 months for BDE 99 and BDE 209.

The corresponding response times for the Neva Region were

- In water:

$T_{50\%}$: about 1 month for all substances;
$T_{90\%}$: HBCDD<NP<endosulfan <BDE 209<BDE47=BDE99

With $T_{90\%}$ varying from 2 months for HBCDD to 18 months for BDE 47 and BDE 99.

- And in sediment:

$T_{50\%}$: HBCDD=NP=endosulfan =BDE209<BDE47=BDE99;
$T_{90\%}$: endosulfan <HBCDD=NP<BDE209<BDE47<BDE99

With $T_{50\%}$ ranging from 2 to 3 months and $T_{90\%}$ varying from 5 months for endosulfan to 24 months for BDE 99.

Thus, reducing the emissions of the target chemicals will result in a fairly quick response in concentration within the Neva Region and/or Gulf of Finland whereas the South Baltic Proper will take longer time to recover from the pollution. The PBDEs are likely to remain longest in the aquatic environment if emissions cease.

5 Issues of concern

This chapter aims at highlighting the important messages from the earlier chapters by discussing different kinds of issues of concern and/or hotspots that could be of importance for risk managers. Hotspot can in this sense relate to, major sources giving rise to emissions of the BSAP-substances, geographical areas with high emissions, areas in the Baltic Sea with high concentrations of the substances but also substances of high concern for the region based on emitted amounts and inherent properties.

5.1 Emission patterns (sources and pathways)

The emission patterns were analysed using emission factors from literature (except emission factors from M-WWTP which were based on measurements within the project), and the emission patterns were condensed into a number of main source categories (including point sources as well as diffuse sources). The emissions from the sources were directed towards the receiving environmental compartments air, land and surface water.

Major sources

The emissions reaching the environment (air, surface water and land) from major source categories for the 11 substances (groups) are summarised in Table 9.

Table 9: Total emissions and emissions shares from main source categories for the 11 substance groups. (Emitted volumes: a= < 1 tonne, b= 1- 100 tonnes, c >100 tonnes, Share of emissions: xxx> 50%, xx 10-50%, x 1- 10%, ,empty cells mean < 1% or no estimates)

Substance (group)	**Total emissions**	**Sources**					
		Historic contami-nation	**Industry**	**Service life**	**Waste and recycling**	**M-WWTP**	**Other**
PCDD/PCDF/ dioxin-like PCBs	a[*]	xx	xx		x		xxx[1,2]
TBT	a	xx?	x	xxx		x	
PBDE	a		x	?	x	xxx	x?[2]
PFOS/PFOA	a		x	x	x	xx	xxx[3]
HBCDD	a		xx	x		x	xxx[4]
NP/NPE	b		xxx	x		xx	x[5]
OP/OPE	b		x	xxx		x	xx?[5]
MCCP/SCCP	c		xx	xxx		xx	
Endosulfan	a		x			xxx	x[5]
Mercury	b	?	xx	x	x	x	xxx[1]
Cadmium	b	x	xxx	x	x	x	xx[1,6]

[*] Expressed as toxic equivalent (TEQ)

[1-5] Main sources in category 'other': [1]combustion, [2]accidental fires, [3]use of fire fighting foam, [4]construction and demolition, [5]use of pesticides [6]use of contaminated fertilisers.

Total emission are highest for the MCCP/SCCP (about 140 000-175 000 kg per year) and lowest for endosulfan (170-200 kg per year) and PCDD/PCDF/dioxin-like- PCBs (650-700 g TEQ per year). Industrial point sources are still relevant for most compounds and are, according to the SFAs, the main sources, directly to the environmental compartments, for NP/NPE (mainly leather industry) and cadmium (paper and wood processing, production and processing of metals). Direct

emissions during service life are the main sources for TBT (biocide treated timber, products containing tinorganic compounds as catalysts), OP/OPE (abrasion from tyres) and SCCP/MCCP (waste in the environment, *e.g.* particulates of polymeric products, paints and sealants containing chlorinated paraffins). Industry and service life also contribute to a large extent with emissions into (and out of) M-WWTP. The M-WWTPs do in general work as efficient barriers of emissions to the environment but most of the BSAP-substances are rather persistent and adsorb into the sludge. Hence, the use of sludge in agriculture or landscaping transports the substances of concern from waste water to land areas. M-WWTPs constitute the main emission pathway for PBDEs (originating mainly from the indoor environment, adsorbed to dust) and endosulfan (residues on foodstuff) into the environment, respectively. It is also an important pathway for PFOS /PFOA emissions originating mainly from metal plating industry, service life and waste/recycling.
The Danish modelling work (chapter 4.3) showed that urban run-off and sewage overflow were important sources in urban areas for emissions, especially of PFOS/PFOA. In the category 'other', combustion (energy sector: individual heating systems, power plants, electricity transformations) and accidental fires are the main sources for PCDD/PCDF/PCBs and for mercury (Chapter 2.2.5). Use of fire fighting foam was the main emission source for PFOS to the environment (this use is now banned and will not be a major source in the future) while construction and demolition (of building material) is the main source for HBCDD. Agriculture can be a relevant direct source for OP/OPE (pesticides) and cadmium (mineral fertilisers). According to the SFAs direct emissions from waste, recycling and historical contamination are not main sources for any of the substance groups, but they contribute for most substances and there are big question marks regarding the estimated emissions from these sources (*e.g.* TBT, dioxins, cadmium, mercury coming from historic contamination, Chapter 3.2). In addition, emissions from waste and recycling contributes to the load to M-WWTPs for most substances, *e.g.* 50% of the mercury emissions to waste water originating from waste and recycling .

Distribution of emissions between compartments

According to the SFAs, different substances end up in different compartments. In order to take the best decisions on where measures should be applied it is important to know to which compartment the substances are emitted.

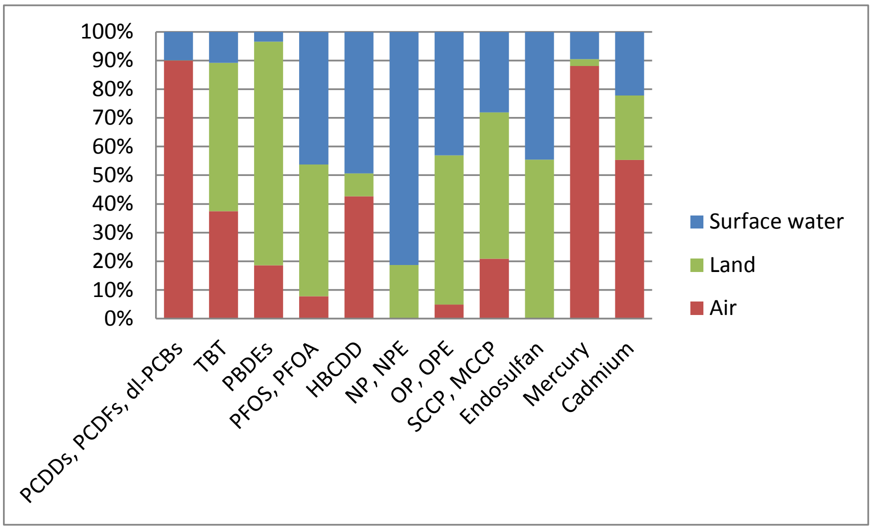

Figure 34: The relative distribution to different environmental compartment for the emissions of the different substances (mean for high and low scenario).

Figure 34 presents an overview of the receiving compartments, surface water, land and air, for the different substances. Emissions to waste water treatment plants are not shown here, but the resulting emissions from the treatment plants are included in the figure. Dioxins and the metals are mainly emitted to air (from combustion) while NP/NPE are mainly emitted to surface water, directly from service life and via M-WWTP (originating from service life and industry). PBDEs, organotins and MCCP/SCCP are mainly emitted to land via sludge, while the emissions of PFOS/PFOA, OP/OPE and endosulfan are emitted in about equal amounts to surface water and land. Emissions to air can result in long range transport of the substance which may result in deposition *e.g.* on the Baltic Sea, while emissions to surface water and land probably have a more local impact. Emissions to land can give delayed emissions to surface water (and air).

Point sources and diffuse sources

Direct measures towards sources are easiest for point sources such as industry or if the substance is used mainly in a few products with a short life-cycle. However, the importance of industrial point sources is declining and diffuse sources, such as articles with long life cycles (service life releases) and residential heating systems, play a bigger role for the emissions. Service life releases often come from consumer articles and such releases are difficult to identify, quantify, monitor and to assign to a responsible person. Articles with long lives (and waste from these), such as building materials, can remain in the society and the environment for a long time, even after restrictions, which implies slow reduction of the load on the environment after restrictions have come into force. Service life releases are of special interest in densely populated areas. M-WWTPs are conveyors of service life releases and some treatment plants have carried out extensive and successful work to reduce up-stream releases. Developed treatment techniques are other measures to decrease the emissions from M-WWTPs.

Conclusions

Although the emission data in the SFAs are associated with high levels of uncertainty, the substance flow analysis has proven to be a useful tool for finding the most important sources for emissions of substances into the environment, a tool that can be recommended when considering measures for the BSAP-substances as well as other substances. (One must, however, be aware that the outcome of the SFAs is totally dependent of the quality/relevance of the underlying emission estimates). The SFA results from this work package (WP4) of the COHIBA Project constitute a unique data material for the Baltic Sea Region, which has been used as input for WP5; dealing with management measures (Mathan *et al.* 2012).

Industrial sources remain relevant within the region, but diffuse sources (including emissions during the service life of consumer articles) are becoming increasingly important. It is difficult to make specific measures to reduce emissions from diffuse sources, especially for substances in many uses and in articles with long life, other than increased restrictions (including imported articles). M-WWTPs are important conveyors of emissions and it is therefore important to track upstream sources and perform necessary risk reduction measures there (*e.g.* substitution, pre-treatment of wastewater), as well as developed treatment techniques, to decrease the emissions from M-WWTP. It is also important to find demolition techniques which reduce emissions of hazardous substances in *e.g.* building material. Combustion facilities for energy/heating (especially residential) and to some extent waste are important sources for which measures should be proposed in order to decrease emissions to air.

5.2 Hotspot areas

Use and emission patterns show regional differences (different kinds of hotspot areas).

Countries

There was imbalance among main sources between the countries, for some of the substances. For instance there are still major industrial sources for NP/and NPE in Lithuania and Poland, and the leather industry in Lithuania contributes with about half of the total emissions of these substances in the region, according to the SFAs. Finland and Germany had the highest emissions of PFOS/PFOA, mainly due to use of fire fighting foam, while this use was not registered at all in *e.g.* Sweden (anymore). In general the estimated yearly loads differed a lot between countries, but not as much if presented as emissions per capita. The SFAs showed that Poland generally had the highest total emission, but Poland also has most habitants in, and a large areal part of, the catchment area of the Baltic Sea. The pattern therefore became different when emissions were calculated per capita. For endosulfan, dioxins and HBCDD, the largest total emissions were estimated to come from Poland but on a per capita basis the highest emissions for endosulfan were from Latvia and Germany, for dioxins Finland and Latvia had similar or higher emissions as Poland and for HBCDD emissions were higher in Finland, Estonia and Germany. The highest PBDE emissions in the Baltic Sea region originated in Finland, Sweden and Poland, while on a per capita basis, the largest emissions were estimated to derive from Estonia, Finland and Sweden. The yearly loads of OP/OPE differ a lot between countries, with the highest amounts released in Poland, and still so if presented as emissions per capita.

Data gaps on use and emissions of a substance in a country were treated differently between the countries. Countries that had available data to report (or tried to make expert judgments of emissions) seemed to end up with higher emissions compared to countries that used question marks or left blank when the emissions were not known. For instance the use of timber treated with TBT as a biocide was indicated to be a source in Estonia, Poland and Sweden, but only Sweden reported emission loads and accordingly had the highest emissions.

In the St Petersburg and Kaliningrad region the main emission sources for almost all substance groups turned out to be consumption and use of ready products and articles, followed by long-range transport and deposition (Chater 4.2). However, there are large data gaps for these SFAs and two reasons are i) Russian authorities lack information and legal frame to gather data on HELCOM substances or the substances have been totally banned for emissions, thus assuming that no emissions exist and ii) the use patterns (and not emissions) of chemicals in individual enterprises is considered as a commercial secret in Russia.

Local areas with high emissions

There are some local industrial areas, especially in Poland, with intentional as well as unintentional (*e.g.* as result of combustion), uses of the substances, resulting in locally high emissions of the substances.

Densely populated areas such as bigger cities have higher emissions of substances especially from diffuse sources and the emission patterns are expected to be similar between such areas, which means that these emissions/sources are suitable for common measure strategies between areas. According to the case studies (Chapter 4.3), Stockholm appeared to be a source for NP/NPE (originating from washing of textiles and concrete), PBDEs (from indoor air) and HBCDD (demolition of buildings) to the Baltic Sea. Large amounts of the substances emitted to wastewater in Stockholm are transported with the sludge to other areas in Sweden. The Danish modelling work indicated that out of the 11 BSAP-substances, land-based point sources were important for PFOS/PFOA, NPE and mercury in the Copenhagen area. The main sources were urban run-off and Combined Sewer Overflows (CSO), industrial zone, rivers and urban WWTPs.

Hotspot areas in the Baltic Sea According to the fate modelling (Chapter 4.1)

The highest concentrations in surface water for all modelled substances (PBDEs, HBCDD, NP/NPE, endosulfan) were predicted to be found in Neva Bay (easternmost part of Gulf of Finland), followed by the South Baltic Proper. Also for sediments, modelled concentrations were highest in Neva Bay for HBCDD, NP/NPE and endosulfan. The second most important area was the coastal South Baltic Proper followed by the entire Gulf of Finland and in the case of nonylphenol also the Skagerrak area. The ‘low scenario’ for PBDEs showed also highest concentrations in Neva Bay, for BDE 209 slightly higher in the coastal South Baltic Proper. In the high scenario for the PBDEs, the coastal areas of South Baltic Proper and Swedish Baltic Proper stood out as the key areas of interest, but relatively high levels were also predicted in the entire Gulf of Finland and in the Skagerrak area.

However, the modelled results showed inconsistencies with available data on measured concentrations in the different compartments. Reasons for this could be underestimated deposition rates by the model (*i.e.* scavenging ratio too low) or unrepresentativeness in the monitoring data used for comparison. On some occasions, in particular for BDE 209, the chemical was not detected in air, and half the detection limit was used to derive a median measured concentration. This may lead to an overestimation of the true median value. Judging from the air concentrations only, modelled and measured concentrations are in similar order of magnitude for PBDEs, which contradicts the theory of long-range transport being an important input pathway for these substances. However, considering the strict regulation of PBDEs in the region, it seems unlikely that there would be no influence from outside the Baltic Sea region.

Comparison with available monitoring data for biota summarised by HELCOM (2010) showed that the highest concentrations of BDE-47 (scattered data, no data for Neva Bay) was found in the South Baltic Proper and second highest were coastal waters in The Danish Straits, Western Gotland Basin, Bothnian Sea and Bothnian Bay. Coastal waters in Gulfs of Finland and Riga showed lowest concentrations. Similar patterns were found for HBCDD. NP/NPE was below detection limits in most biota samples while sediment concentrations were highest in The Danish Straits (very few data available for Gulf of Finland and the South Baltic Proper).

Conclusions

To obtain more homogenous data for all countries there is a need for national chemical product registers and emission registers. For some substances there is imbalance between countries regarding main emissions sources. How different countries have dealt with data gaps is one reason for differences in emissions from the different countries. Poland has the highest total emissions, but this is mainly due to its relatively higher share of the drainage area. Some industrial areas and densely populated areas, like big cities, are hotspots for emissions. According to the modelling exercises the Baltic Proper (south) and Gulf of Finland are potential ‘hotspot areas’ regarding concentrations of the (modelled) substances in the Baltic Sea.

5.3 Inland sources compared to coastal sources

The fate modelling exercise indicates that direct sources contribute more to the regional input of PBDEs (three congeners were modelled), HBCDD, NP/NPE and endosulfan into the Baltic Sea than do indirect releases via rivers and the atmosphere (Chapter 4.1). It should, however, be noted that this assessment did not take into account atmospheric deposition due to long-range transport from outside the Baltic Sea region. The modelling study also indicated that for the marine areas in the open Baltic Sea, the *atmosphere was the main input pathway*, but these flows were small in comparison to the direct releases on the coast. Southern Baltic Proper and Gulf of Finland were the regions indicated to receive the highest loads of selected BSAP-substances. For pentaBDE, atmospheric deposition was predicted to give a high contribution to the input in the Baltic Proper, especially in the high scenario. Overall, it appeared that in-land emissions had little impact on the regional input of the six modelled contaminants in the Baltic Sea. A model/measurement comparison did, however, indicate that other, external sources are likely to contribute to the concentrations found (or alternatively, that current emission are underestimated or have been higher in the past), for which the atmosphere is likely to be the main carrier. The percentage of regional inland emissions actually reaching the Baltic Sea (on an annual flow basis) was calculated to be rather small. However, in some cases the small contribution from inland emissions, in absolute terms, may correspond to similar or even higher amounts than the total amount of coastal emissions that end up in the Baltic Sea. Thus it is important to also consider the total emission strength of the emissions when prioritizing the reduction measures. It should also be mentioned that this picture was valid for the Baltic overall. In certain sub-areas such as the South Baltic Proper, also indirect releases via *e.g.* rivers were important, in particular for nonylphenol.

Conclusion

Direct coastal emissions to the Baltic Sea appear most important for ‘within-region’ sources according to the modelling. This indicates that locally high inland emissions in individual countries do not necessarily have a large influence on the Baltic Sea as a whole, in particular not if these are directed to soil. For the state of the Baltic Sea, efforts should thus primarily be made to reduce coastal emissions and long-range atmospheric transport and deposition. If coastal emissions are limited, then in-land measures such as reduction at sources releasing to freshwaters should be the next priority. It is not known if these conclusions also apply to the metals, but they are likely to apply also to other hydrophobic organic substances with a $\log K_{ow} > 5$.

5.4 Importance of sources outside the region

Emissions to air can cause long-range transboundary transport. The SFAs showed that air was the most important receiving compartment of emissions for PCDD/PCDF/dioxin-like PCBs, mercury and cadmium. Measurements in deposition showed that atmospheric deposition was important for the load of several of the BSAP-substances in the Baltic Sea and the Baltic Sea catchment (Chapter 3.1). Measured deposition and estimated emissions were in the same order of magnitude for PCDD/PCDF/dioxin-like PCBs indicating that there was balance between output and input in the region. For cadmium, mercury and endosulfan on the other hand, there appears to be a net transport into the region since the deposition was higher than the total sum of estimated emissions in the region. (Underestimation of emissions from sources within the region could be another reason for this imbalance). For endosulfan, there was no emission to air expected for the Baltic Sea Region according to the SFAs, but the measured deposition was in the same order of magnitude as estimated emission to water and land in the region. According to literature, there is also long-range transport of PFOS/PFOA but the relative importance of this could not be estimated within this project. Also for PBDE there was also a gap between emissions to air according to the SFA and measured deposition indicating transboundary influence. Parts of this gap could possibly be explained by underestimation of the releases from indoor air to outdoor air. Judging from the air concentrations only, modelled and measured concentrations are in similar order of magnitude for PBDEs, which contradicts the theory of long-range transport being an important input pathway for these substances. However, considering the strict regulation of

PBDEs in the region, it seems unlikely that there would be no influence from outside the Baltic Sea region.

Conclusion

According to measured deposition in comparison with emission estimates, sources outside the region can be of relatively high importance for endosulfan mercury and cadmium (possibly PBDE). Hence, measures/actions on a global level are needed for these substances.

5.5 Can prioritisation be made within the group of BSAP-substances?

The substances that have been studied within the COHIBA Project are prioritised because of their inherent hazardous properties, but are all 11 substance groups still relevant as issues of concern in the Baltic Sea Region? Among the 11 substance groups the total estimated emissions in the region (high scenario) ranged between 200 kg[2] (endosulfan) and 175 000 kg (MCCP+SCCP). Could it then be argued that *e.g.* endosulfan could be deleted from the priority list, since the emissions are 1000 times less than for MCCP+SCCP and it is also banned for use in the region? However, according to the environmental quality standards (EQS) listed in the daughter directive on priority substances (2008/105/EC) to the WFD, endosulfan (EQS = 0.0005 µg/l) is about 1 000 times more toxic than the chlorinated paraffins (EQS for SCCP is 0.4 µg/l, the predicted no effect concentration (PNEC) for MCCP is1µg/l, ECB 2005) and it is despite the ban still found in *e.g.* waste water samples. Also PBDEs and TBT which are emitted at a similar magnitude as endosulfan are extremely toxic according to their EQS values (0.0002µg/l).

The substances that are emitted in intermediate amounts (alkylphenols, mercury and cadmium) are also intermediately toxic according to their EQS values (0.01- 0.3µg/l). HBCD is emitted at lower amounts with an intermediate toxicity according to the EQS value (0.03 µg/l). There is no EQS value set for PFOS/PFOA but according to available information (*e.g.* summarised in KemI, 2004) they appear less toxic to aquatic organisms (PNEC > 1 µg/l) compared to the other substances emitted at similar amounts. On the other hand, PFOS is extremely persistent and found to accumulate in mammals and seabirds in very remote areas which may lead to effects in the long run and a low EQS will probably also be proposed for this substance. PCDD/PCDF/ dioxin-like PCBs are also emitted at relatively low amounts but are considered extremely toxic to humans exposed via food (*e.g.* fish).

In an integrated assessment HELCOM (2010) listed, in decreasing order, observations of the hazardous substances with the highest concentrations in biota in the Baltic Sea in relation to the target level (*i.e.* the contamination ratio). Of the included BASP substances they appeared in the following order on that list; mercury (3rd place), TBT (6th), cadmium (8th), PCDD/PCDF/ dioxin-like PCBs (9th), NP (10th), OP (17th) and PBDE (18th).

Conclusion

It has not been the aim of this project to evaluate the present status regarding the levels and effects of the BSAP-substances in the Baltic Sea but it can be concluded that it is not possible to prioritise measures between these substances based only on emitted amounts in the region.

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[2] The total yearly emissions for PCDD/PCDF/dioxin-like PCBs was about 700 g TEQ. This amount cannot be directly compared with the amounts for the other substances.

5.6 Time trends and effects of regulations

Most of the BSAP-substances are more or less regulated, which has resulted in reduced emissions, and new regulations are in the pipeline which will affect emission and concentrations in the Baltic Sea.

Observed/expected trends due to regulations

Emissions of dioxins and furans have decreased in all European countries, except Latvia, during the last two decades according to European Environment Agency (EEA website, 2012 a). The awareness of the hazardousness of the PCDD/PCDF/ dioxin-like PCBs, as well as an effective inventory of emissions, lead to the conclusion that emissions will be further reduced. However, since these substances are unintentionally produced complete reduction of emissions will be impossible to achieve. Data on concentrations in biota in the Baltic Sea indicate that the concentrations have levelled during the last decade (HELCOM, 2010).

Given that the use of triorganotins in antifouling paints has been banned internationally since 2008, the occurrence in the Baltic Sea is expected to decrease. However, emissions from contaminated soil and sediments in harbour areas are still of importance for the release of TBT to surface waters. Furthermore, biocidal use of organotin compounds was banned in the EU in 2006, but since these substances have been incorporated in articles with long life cycle, they may continue to be released into the environment for several years. According to HELCOM (2010), TBT and TPhT levels in biota in the Baltic Sea have consistently decreased since the ban in the EU (2003), but the concentrations are still of concern.

The use of HBCDD has decreased during the last decades. The inclusion of HBCDD on the list of substances for which an authorisation is needed (from 2015 for HBCDD) under REACH (Annex XIV), may lead to even further decreases in the use of this substance. But since HBCDD is used in articles with long life cycles, the reduction in emissions will be delayed. Hence, to reduce the risk of large emissions in the future it is important to find demolition techniques which reduce emissions for *e.g.* building material. Time series from monitoring sites along the Swedish coasts show a decreasing trend for HDCDD in herring muscle during the last years in the Southern Baltic Sea, whereas a significant increasing trend (3% per year) was found in guillemot eggs collected at Stora Karlsö. However, there are indications that the concentrations in the eggs have started to level out during the last years (Bignert *et al.* 2011, Havsmiljöinstitutet, 2011)

With the ban of use of PFOS in fire fighting foams coming into force in 2011, emissions of both PFOS and PFOA will decrease substantially based on the emission scenarios presented here. Also, emissions from the service life of articles can be expected to decrease as the stock of PFOS accumulated in society decreases. According to the Swedish Environmental Protection Agency's national monitoring programme, concentrations of PFOS in guillemot eggs have shown a distinct rise since the end of the 1960s but there is a possible levelling out in concentrations during the last years (Havsmiljöinstitutet, 2011).

Tetra- and pentaBDEs belongs to the nine ‘new’ persistent organic pollutants listed on the Stockholm Convention and are thus subject to a global ban. Their use in the EU is strictly regulated, and only decaBDE is now allowed to be used, in articles other than electronics. Time series of pentaBDE (BDE-47) concentrations in herring (muscle) from the Bothnian Sea, the Baltic Proper and the Kattegatt also show significant decreasing trends (HELCOM, 2010). On the global scale, no restrictions around decaBDE exist in Asia. The extensive global regulation of PBDEs speaks for declining use and emissions in the future. However, as no regulation for decaBDE exists in Asia, and the demand in developing countries increases, due to increasing requirements on fire security in these countries, it is likely that PBDEs will remain in the global and Baltic environment for many years to come. To further reduce the risk of large emissions in the future it is important that global political acts are agreed upon.

SCCPs are added to the Candidate List of substances subjected to authorisation under the REACH-regulation), and it has also been proposed that they are included in the Stockholm Convention on Persistent Organic Pollutants. For this reason, a further reduction in SCCP use can be expected. However, as the main sources of emissions are articles with sometimes long service-life, there will be a delay in the reduction of emissions to the environment. As the MCCPs have similar uses, and can be considered as replacements for the SCCPs in some of their applications, the reduction in use of SCCPs in these areas could have led to an increased use of MCCPs. However, in Sweden also the use of MCCPs has decreased since 1996.

According to the modelling exercise, NP and endosulfan concentrations in the Baltic Sea respond especially quickly to changing emissions (Palm Cousins 2012). Due to the fact that the use of NP and NPE has been restricted for many applications (see statistics from SPR, 2011, on use in Sweden of NPE) a reduction in the concentrations in the Baltic Sea can be expected. The restrictions applied to NP and NPE could lead to a replacement of NP and NPE with OP and OPE and a risk for increasing loads of these substances reaching the environment in the future. On the other hand, as OP is included in the Candidate List for inclusion in Annex XIV in REACH (Authorisation List) as well as in the WFD the use and subsequent emissions of OP may also decrease.

Endosulfan was banned within the EU in 2005. A global ban on the manufacture and use of endosulfan was negotiated under the Stockholm Convention in April 2011. The ban will take effect in mid-2012, with certain uses exempted for 5 additional years. Many countries had already banned the use of endosulfan or announced phase outs by the time the Stockholm Convention ban was agreed upon, but it is still used in about 30 countries, extensively in *e.g.* South America, China and India (UNEP; Stockholm Convention website). Since endosulfan is transported long-range in the atmosphere it can therefore be expected that the occurrence in Baltic Sea will decrease with the implementation of the global ban.

Emissions of mercury and cadmium have decreased significantly during the last decades (EEA web site, 2012b) mainly due to reduction of emissions from industrial and energy sectors. Deposition of cadmium and mercury has also decreased. Mercury should be expected to decrease further due to mercury bans and restrictions and other activities related to the EU strategy and the UN global treaty on mercury. Also in the Russian Federation total mercury consumption was decreased (2.5 – 3 times *e.g.* due to considerable reduced use of mercury in dental amalgam fillings) over the past 20 years, as well as emissions of cadmium into water bodies of St Petersburg (Chapter 4.2). However, both for cadmium and mercury, historical contamination could be of major importance for emissions in the future. According to HELCOM (2010), only a few of the locations where mercury and cadmium concentrations in biota have been studied in the Baltic Sea show decreasing temporal trends, and some even showed increasing trends. Upward trends were observed in the Sound area for mercury, in the Kattegatt for both metals, and in Åland, Finland for cadmium. Concentrations in biota relative to target levels are also high according to the HELCOM (2010) contamination ratio.

Conclusions

For many of the substances, emissions are decreasing due to restrictions and voluntary actions, and concentrations in the environment are decreasing or expected to decrease. However, for some of the well-known contaminants (dioxins/furans, mercury, cadmium) there are indications that concentrations in the Baltic Sea have levelled out, at levels that are still of concern. Other substances, like PFOS, are still increasing (or just levelling).

5.7 Overall uncertainties

The input data to the SFAs originate from a multitude of sources (literature as well as measurements conducted in the project) and have varying inherent uncertainty and relevance for the region. There are differences in availability of national data between the countries. For instance only Sweden, Denmark and Finland have national product registers. The status of emission registers also varies between the countries and they do not cover all of the BSAP-substances. The countries report large uncertainties regarding emissions during service life and for the waste sector, *e.g.* chemical composition of solid waste/leachates as well as number and areas of landfills. Some countries have made expert judgments when national information on a possible source was missing, while other countries have indicated a data gap or zero emission. Extrapolations from the EU SFAs have, to a large extent, been the basis for national emission estimates. Uncertainty is added when data are extrapolated and there are very few analytical data available for verification of estimates. Data on emissions from historically contaminated sites are almost completely lacking.

The low and high emission scenarios do only to some extent give an indication of the uncertainty of the data. As a range of emission factors were not always available the estimated yearly loads were often not given as ranges (*i.e.* the same value was used in both the low and high emission estimate), but this does not mean that the given value does not have an uncertainty range. As a result there are cases where the difference between the low and high emission scenario is small. This is not to be interpreted as if the uncertainty is small.

Modelled concentrations in the Baltic Sea showed inconsistencies with measured concentrations. Reason for this could be boundaries set for the model, unrealistic input data from the SFAs but also bad/incomplete monitoring data. There have not been enough resources within the project to make comprehensive sensitivity analysis to test the outputs from the model.

Conclusion

The quality of the input data to the SFAs varies considerably. Differences in estimated emissions between the countries when the data are aggregated could thus be due to actual differences but also to a large extent to differences in handling of data gaps.

Product registers and emission registers in all countries would improve the SFAs considerably.

To verify the modelling results, there is a need for more harmonised monitoring data (and chemical analysis with lower detection limits).

6 Implications for further work

The work with identification of the major sources and flows of the BSAP-substances in the Baltic Sea region has significantly improved the knowledge base on contaminant sources in the Baltic region but has also led to an increased awareness of the importance and complexity of source tracking. The identified data gaps in emission estimates introduce high uncertainties in the assessment of sources and potential measures for contaminants and these gaps have to be filled.

Improved quality of emission factors is an important and necessary topic for further development. There is a need for new measurement data both with regards to environmental levels and emission factors. Regular load assessments are needed in the region and harmonisation of methods for measurements and reporting is important.

The COHIBA Project has pointed out a need for the countries in the Baltic Sea region to develop both emission registers and chemical product registers covering the BSAP-substances. Emissions during the service life of consumer articles have been identified as increasingly important and development of reliable emission factors from diffuse sources is also needed.

Models have been shown to be important tools for the estimation of pathways, input and concentrations of the BSAP-substances in the Baltic Sea area, both on local and regional scales. Models are also useful for predicting the outcome of different emission scenarios *e.g.* to evaluate the results of different measures. Future use and development of models for the different BSAP-substances is needed. Emission factors are key input parameters for models and there is also a need for measurement data for model validation (see above) and for sensitivity analysis.

The importance of atmospheric transport and deposition needs to be further assessed both using modelling and by more measurements in the region. However, this is not limited to the Baltic Sea region but is a wider European, as well as, a global issue and should be carried out in a broad international collaboration.

Historically contaminated sites have been pointed out to be important for some of the substances and further work on estimating emissions and the relative importance of these sources is needed.

The work on BSAP-substances in COHIBA has been focused on emitted amounts of the contaminants in the region, thus the possibility that substances with lower emitted volumes could be the most toxic. Future investigations should take into account also the environmental and human effects of the substances in the Baltic Sea and its region.

Future work should include assessments of sources and pathways also for ‘new’ or emerging substances, which have been identified as important contaminants in the region. Many chemicals are globally dispersed and future investigations on hazardous substances in the Baltic Sea region should be carried out with strong links not only to HELCOM but to *e.g.* the EU (REACH/WFD/MSFD) as well as to the UNEP (Stockholm convention).

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The COHIBA Project set out to identify the sources and inputs of 11 hazardous substances of special concern, as detailed in the Baltic Sea Action Plan (BSAP), and to develop measures to reduce emissions of these substances. The overall objective was to support the implementation of the BSAP with regard to hazardous substances, by developing joint actions to reach the goal of the programme.

The present report is the final report of work package (WP) 4: Identification of sources and estimation of inputs/impacts on the Baltic Sea (led by IVL Swedish Environmental Research Institute). The results of WP4 were developed as a joint effort from all partners involved in the WP.

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