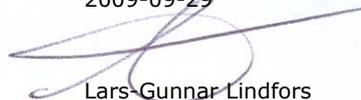


# Screening of Selected Hazardous Substances in the Eastern Baltic Marine Environment

Karl Lilja, Karin Norström, Mikael Remberger, Lennart Kaj,  
Liselott Egelrud, Erika Junedahl, Eva Brorström-Lundén, IVL  
Mebrat Ghebremeskel, Martin Schlabach, NILU  
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Lars-Gunnar Lindfors  
Scientific Director



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<b>Address</b> P.O. Box 21060 SE-100 31 Stockholm	<b>Project sponsor</b> Nordic Council of Ministers
<b>Telephone</b> +46 (0)8-598 563 00	
<b>Authors</b> Karl Lilja, Karin Norström, Mikael Remberger, Lennart Kaj, Liselott Egelrud, Erika Junedahl, Eva Brorström-Lundén IVL Mebrat Ghebremeskel, Martin Schlabach NILU	
<b>Title and subtitle of the report</b> Screening of Selected Hazardous Substances in the Eastern Baltic Marine Environment	
<b>Summary</b> IVL and NILU have during 2008/2009 as an assignment from HELCOM, performed a screening study in the eastern Baltic Sea environment on the occurrence of eight of the substances/substance groups identified as hazardous under the Baltic Sea Action Plan. Of the eight substances or substance classes included in the study, six of them were found above LOQ; organic tin compounds, PBDEs, PFAS, nonylphenol, chlorinated paraffins and endosulfan (endosulfan sulphate). Substances that occurred in fish samples from all sampling sites were; TBT, PBDEs (BDE 47 and BDE 100), PFAS (PFOS), chlorinated paraffins (SCCP), and endosulfan (endosulfan sulphate). Additionally, bisphenol A was found in fish from almost all sampling sites. PFAS (PFOS and PFOA), octylphenol and nonylphenol were found in one, one and six water samples, respectively. No obvious differences in concentrations could be seen between the sampling sites classified as background areas and affected areas. Furthermore, no clear general differences between affected sites could be seen. Concentrations found for the different substances were lower or in the same range as previously reported from other areas of the Baltic Sea, thus the eastern Baltic Sea environment does not seem to be more polluted compared to the Baltic Sea in general. For all the substances, except TBT, concentrations found were below reported PNEC values. However, for TBT, concentrations in several fish muscle samples were close to or above the PNEC value estimated for protection of human health considering consumption of fishery products. Additionally, PFOS levels in fish liver exceeded the PNEC value regarding secondary poisoning of predators in six samples, but PFOS levels in fish muscle were not measured in this study.	
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## Preface

HELCOM launched in March 2008 a screening study on the occurrence of hazardous substances in the eastern Baltic Sea as part of the activities under the Commission's ambitious plan to re-create a healthy Baltic marine environment. As an assignment from the HELCOM project "Screening study on occurrence of hazardous substances in the eastern Baltic Sea", IVL Swedish Environmental Institute Ltd and the Norwegian Institute for Air Research (NILU) have during 2008/2009 performed chemical analysis and assessment of selected chemicals in the eastern Baltic Sea environment (Poland, Lithuania, Estonia and Latvia). The substances included in this investigation are defined as hazardous substances by the HELCOM Baltic Sea Action Plan (BSAP). The project was funded by the Nordic Council of Ministers.

The sampling was carried out by institutes in the different countries. The following persons and institutes have participated:

Ms Leili Järv, Estonian Marine Institute of Tartu University

Mr Juris Aigars, Latvian Institute of Aquatic Ecology

Ms Galina Garnaga, Lithuanian Center of Marine Research

Ms Anna Brzozowska, Institute of Meteorology and Water Management / Maritime Branch (Poland)

Mr Anders Bignert, Swedish Museum of Natural History

The overall objective of the screening was to determine the occurrence and distribution of the selected substances in fish and water in the eastern Baltic environment.

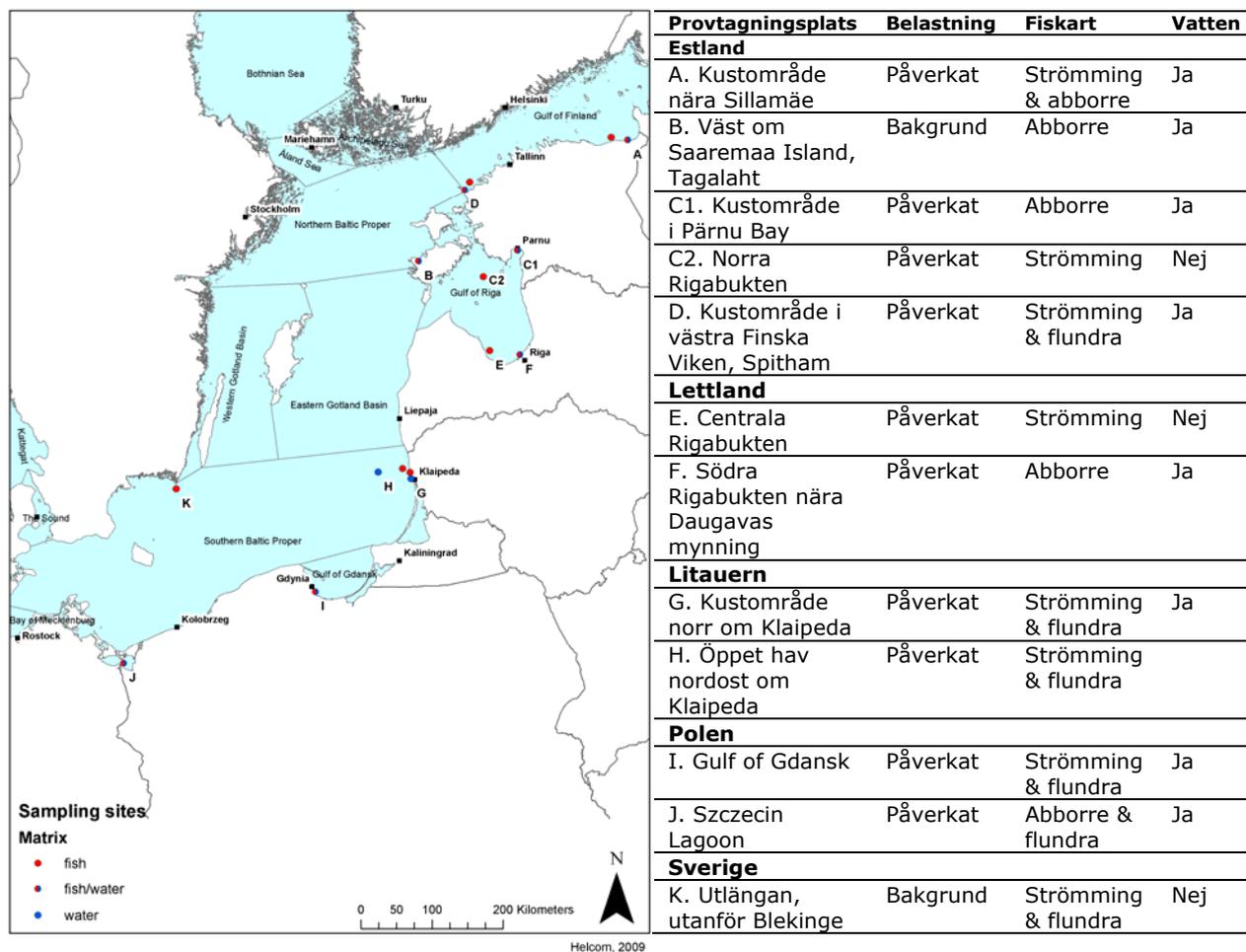


## Sammanfattning

HELCOM lanserade under mars 2008 en screening av farliga ämnen i östra Östersjön som en del av kommissionens ambitiösa plan för att återskapa en god marin miljö i Östersjöområdet. På uppdrag från HELCOM-projektet "Screening study on occurrence of hazardous substances in the eastern Baltic Sea" har IVL Svenska Miljöinstitutet AB och Norsk institutt for luftforskning (NILU) under 2008/2009 analyserat åtta av de ämnen/ämnesgrupper av särskild betydelse för Östersjön utpekade inom HELCOM Baltic Sea Action Plan (BSAP), i prover från Polen, Litauen, Estland, Lettland och Sverige. Inkluderade ämnen/ämnesgrupper var organiska tennföreningar, polybromerade difenyletrar (PBDE), hexabromocyclododecane (HBCDD), perfluorerade substanser (PFAS), nonylfenol (NP) och nonylfenolethoxylater (NPE), oktylfenol (OP) och oktylfenolethoxylater (OPE), klorerade paraffiner (SCCP och MCCP), och endosulfan.

Studien har genomförts för att bidra med data till de nationella program och tematiska utvärderingar av farliga ämnen under BSAP som ska vara genomförda till 2010, samt som stöd för internationellt och nationellt arbete för att uppnå de miljömål avseende farliga ämnen som beslutats inom HELCOM och EU och som skall vara uppfyllda till 2020.

Nedan presenteras de provtagningsplatser från vilka vatten och fisk samlats in.



Helcom, 2009

Uppmätta halter av de ämnen inkluderade i BSAP som analyserats presenteras i tabellen nedan. Ämnen tillhörande sex av de åtta ämnesklasserna inkluderade i studien återfanns i proverna, dessa var organiska tennföreningar, PBDE, PFAS, nonylfenol, klorerade paraffiner, och endosulfan (endosulfansulfat). I fisk från samtliga provtagningsplatser återfanns TBT, PBDE (BDE 47 och BDE 100), PFAS (PFOS), klorerade paraffiner (SCCP), och endosulfan (endosulfansulfat). Dessutom detekterades Bisfenol A i fisk från nästan samtliga platser. I vatten återfanns PFAS, nonylfenol och oktylfenol.

Ämnesgrupp	Ämne	Matris	Detektions-frekvens	Halt
Tributyltenn- (TBT) och trifenyiltenn- (TPHT) föreningar	TBT	Fisk (muskel)	14/23	2.5 - 35 ng/g f.v.
	DBT		4/23	1.8 - 8.2 ng/g f.v.
	DPhT		14/23	1.2 - 24 ng/g f.v.
Polybromerade difenyletrar (PBDE)	BDE 47	Fisk (muskel)	22/23	0.011 - 0.29 ng/g f.v.
	BDE 85		2/23	0.011 - 0.015 ng/g f.v.
	BDE 99		12/23	0.014 - 0.10 ng/g f.v.
	BDE 100		16/23	0.010 - 0.15 ng/g f.v.
	BDE 153		2/23	0.013 - 0.016 ng/g f.v.
	BDE 154		9/23	0.011 - 0.079 ng/g f.v.
Hexabromocyclododecane (HBCDD)	HBCDD	Fisk (muskel)	0/23	< 0.1 ng/g f.v.
Perfluorerade substanser (PFAS)	PFOSA	Fisk (lever)	1/23	1.8 ng/g f.v.
	PFHxS		17/23	0.10 - 1.1 ng/g f.v.
	PFOS		23/23	4.3 - 61 ng/g f.v.
	PFDCS		2/23	0.06 - 0.57 ng/g f.v.
	PFBA		2/23	0.23 - 0.45 ng/g f.v.
	PFHxA		1/23	0.78 ng/g f.v.
	PFHpA		1/23	2 ng/g f.v.
	PFNA		12/23	1.6 - 9.9 ng/g f.v.
	PFDCa		1/23	12 ng/g f.v.
	PFUnA		11/23	0.46 - 15 ng/g f.v.
	PFOS		Vatten	1/9
PFOA	Vatten	1/9	6.0 ng/l	
Nonylfenol (NP) och nonylfenoethoxylater (NPE)	4NP	Fisk (muskel)	2/23	12 - 23 ng/g f.v.
	4NP		Vatten	6/9
Oktylfenol (OP) och oktylfenoethoxylater (OPE)	4-t-OP	Vatten	1/9	1.2 ng/l
Klorerade paraffiner (SCCP och MCCP)	SCCP	Fisk (lever)	23/23	5.2 - 62 ng/g f.v.
	MCCP		3/23	3.9 - 15 ng/g f.v.
Endosulfan	endosulfansulfat	Fisk (muskel)	21/23	0.010 - 0.12 ng/g f.v.

Inga tydliga skillnader i halter kunde ses mellan prover från platser klassificerade som påverkade jämfört med bakgrundsområden. Inga generella skillnader mellan de olika påverkade plaserna kunde heller ses. De högsta halterna av organiska tennföreningar återfanns i fisk från provtagningsplatserna i Polen (Gulf of Gdansk och Szczecin Lagoon) samt i sydöstra Finska Viken (utanför Sillamäe), medan högst halter av PBDE återfanns i Polen (Szczecin Lagoon) och utanför Litauerns kust. För de flesta ämnen var halter i det lägre intervallet i prover från Rigabukten, jämfört med andra områden.

Detekterade halter var generellt lägre eller av samma storleksordning som rapporterats för andra områden i Östersjön, östra Östersjön verkar alltså inte vara mer förorenad. För samtliga ämnen utom TBT och PFOS var uppmätta koncentrationer under rapporterade gränsvärden. För TBT var dock halter i flera muskelprover från fisk nära eller över det gränsvärde som beräknats för skydd av human hälsa vid konsumtion av fisk. PFOS-halter i sex leverprover överskred gränsvärdet satt för skydd mot sekundär förgiftning av toppredatorer, halter av PFOS i muskelvävnad bestämdes dock ej i denna studie.

## Table of contents

1 Aim .....	5
2 Introduction .....	5
2.1 Sources and properties of included substances/substance groups .....	6
2.1.1 Organic tin compounds .....	6
2.1.2 Polybrominated diphenyl ethers (PBDE) .....	7
2.1.3 Hexabromocyclododecane (HBCDD) .....	8
2.1.4 Perfluorinated Substances (PFAS) .....	8
2.1.5 Phenolic Substances – Nonylphenol (NP) and Nonylphenol ethoxylates (NPEs) .....	11
2.1.6 Phenolic Substances – Octylphenol (OP) and Octylphenol ethoxylates (OPEs) .....	12
2.1.7 Chlorinated Paraffins (SCCPs and MCCPs) .....	12
2.1.8 $\alpha$ - and $\beta$ -Endosulfan .....	13
3 Methodology .....	14
3.1 Study area .....	14
3.2 Sampling methods .....	17
3.2.1 Water .....	17
3.2.2 Fish .....	17
3.4 Physiological measurements .....	17
3.5 Analytical methods .....	17
3.5.1 Organic tin compounds .....	17
3.5.2 Brominated Flame Retardants: PBDE and HBCDD .....	18
3.5.3 Perfluorinated Substances .....	18
3.5.4 Phenolic Substances: NP, NPE, OP, OPE & other .....	18
3.5.5 Chlorinated Paraffins .....	19
3.5.6 $\alpha$ - and $\beta$ -Endosulfan .....	19
3.6 Extraction of lipids .....	20
3.7 Quality Assurance/ Control .....	20
4 Results .....	21
4.1 Organic tin compounds .....	21
4.2 Polybrominated diphenyl ethers (PBDEs) .....	22
4.3 Hexabromocyclododecane (HBCDD) .....	23
4.4 Perfluorinated Substances .....	23
4.5 Phenolic Substances: NP/NPE .....	25
4.6 Phenolic Substances: OP/OPE & other .....	26
4.7 Chlorinated Paraffins .....	27
4.8 $\alpha$ - and $\beta$ -Endosulfan .....	28
5 Discussion .....	29
5.1 Organic tin compounds .....	29
5.2 Polybrominated diphenyl ethers (PBDE) .....	31
5.3 Hexabromocyclododecane (HBCDD) .....	31
5.4 Perfluorinated Substances (PFAS) .....	32
5.5 Phenolic Substances NP/NPE .....	32
5.6 Phenolic Substances OP/OPE & other .....	33
5.7 Chlorinated Paraffins (SCCPs and MCCPs) .....	34
5.8 $\alpha$ - and $\beta$ -Endosulfan .....	34
6 Conclusions .....	35
7 References .....	36
Appendix A. Sample characteristics and results .....	41
Appendix B. Sampling manual- Analysis of selected substances in the Eastern Baltic Sea .....	55

## 1 Aim

The overall aim of this project was to provide data on levels of selected hazardous substances in fish and sea water samples collected in the eastern part of the Baltic Sea. Eight substances or substance groups identified by the HELCOM Baltic Sea Action Plan (BSAP) as being of specific concern to the Baltic Sea were included in the study.

Additionally, the project will serve both international purposes (e.g. HELCOM, European Marine Strategy, EU Water Framework Directive) as well as national activities to address hazardous substances in the Baltic Sea. The results will also be used in the revision of the HELCOM monitoring programme on hazardous substances.

The concentration of the hazardous substances found in the eastern Baltic Sea ecosystem will be put in a Nordic perspective using screening data from previous Nordic screening studies and from different national screening studies as well as from other ongoing projects in relation to the EU Water Framework Directive (EU-WFD).

## 2 Introduction

The Baltic Sea Action plan (BSAP) was adopted by a HELCOM Ministerial Meeting in Krakow in November 2007. The theme “hazardous substances” is one of four thematic areas covered by HELCOM BSAP which contain the specific goal to have a Baltic Sea life undisturbed by hazardous substances. The concentrations of hazardous substances should reach levels making the fish safe to eat and to have a healthy wild life.

Most hazardous substances do not occur naturally in the environment. They have adverse effects on the ecosystem like impaired general health status, impaired reproduction of animals and increased pollutant levels in the fish used for human food. HELCOM has defined substances as hazardous if they are toxic, persistent and bio-accumulative (PBT-substances), or very persistent and very bio-accumulative (vPvB). The BSAP includes nine organic substances or group of substance and two heavy metals mercury (Hg) and cadmium (Cd) which specific concern to the Baltic Sea. The main pathways of hazardous substances to the Baltic marine environment are via rivers receiving municipal and industrial waste water, direct municipal and industrial waste water discharges, from rivers receiving leaching waters from the agricultural land as well as via atmospheric deposition.

This screening includes measurements of eight organic substance classes indicated in the BSAP; organic tin compounds (TBT & TPhT), polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD), perfluorinated substances (PFOS & PFOA), phenolic compounds (NP/NPE & OP/OPE), chlorinated paraffins (SCCP & MCCP) and endosulfan, see Table 1. These substances, which are emitted from a variety of different sources, represent chemicals which possess a wide range of chemical and physical properties, which affect their pathway in the environment. Due to the persistency and bioaccumulative properties of several of the substances, biota is considered to be the most relevant matrix to study their presence in the environment. Present information regarding the occurrence of these substances in the Baltic marine environment is mostly scarce. The substances included in each group are presented in more detail in Chapter 2.

Most of the substances in the BSAP are also priority substances in EU Water Framework Directive (WFD)(2000/60/EC)

Table 1. Substance classes within HELCOM BSAP included in this study.

Substance class	Determined in biota	Determined in water
Tributyltin (TBT) and triphenyltin (TPhT) compounds	x	
Polybrominated diphenyl ethers (PBDE)	x	
Hexabromocyclododecane (HBCDD)	x	
Perfluorinated substances (PFAS)	x	x
Nonylphenols (NP) and nonylphenol ethoxylates (NPE)	x	x
Octylphenols (OP) and octylphenol ethoxylates (OPE)	x	x
Chlorinated paraffins (SCCP and MCCP)	x	
Endosulfan	x	

## 2.1 Sources and properties of included substances/substance groups

A short introduction of each of the substances/substance groups are presented based on existing literature.

### 2.1.1 Organic tin compounds

Organic tin compounds are characterized by a Sn<sup>4+</sup> ion to which one to four ligands are attached. They are classified according to the type of ligand and the most common organic tin compounds are butyltins, octyltins and phenyltins. In EU, the use of organotins in 2002 was about 19.000 ton/year. In the same year the use of tri-substituted organotins was about 1600 ton/year. The main use of tributyltin (TBT) in 2002 are as antifouling paints (80%), fungicides, and various biocide uses in preparations and products (<http://www.socopse.se>).

The use of TBT in antifouling paints was banned within EU in 2003. Other applications in northern European countries are for example in diapers, PVC flooring and vinyl papers, earplugs where these compounds mainly occur as impurities (HELCOM, 2009). The use of TBT and TPhT as pesticides and biocides were banned in Sweden in 2003. In Finland and Sweden the total amount of use of TBT decreased from 4 to 0.2 tonnes per year (Finland) and from 1 to 0.4 tonnes per year (Sweden) between 2000 and 2005 (HELCOM, 2009).

The main emission source of organic tin compounds is leaching from ship hulls. Related activities that may cause emissions are sea ship traffic, leaching from contaminated harbor sediments and removal of old antifouling paints.

The environmental partitioning depends on the structure, and the hydrophobicity of the compound increases with increasing number of alkyl groups and the length of the alkyl chain. TBT and triphenyltin (TPhT) adsorb strongly to suspended matter in an aquatic environment and they end up in sediment where their half-lives are from one to a few years slower than in water (HELCOM, 2009).

TBT is the most hazardous of all organic tin compounds with considerable biological effects such as shell malformations of oysters, imposex in marine snails, reduced resistance to infection (e.g. flounder), and it may affect the human immune system (<http://www.socopse.se>). TBT and other organic tin compounds (not DBT and MBT) are endocrine disrupters and TBT may affect the endocrine system of certain marine and freshwater mollusk species at concentrations of 1 ng/L (HELCOM 119, 2009). Previous studies as reviewed in HELCOM (2009) indicate that both TBT and TPhT pose a threat to aquatic marine organisms. The organic tin compounds included in this study are listed in Table 2.

Table 2. Organic tin compounds with their abbreviated names included in this study.

---

Monobutyltin (MBT)
Dibutyltin (DBT)
Tributyltin (TBT)
Monophenyltin (MPhT)
Diphenyltin (DPhT)
Triphenyltin (TPhT)
Monooctyltin (MOT)
Dioctyltin (DOT)

---

### 2.1.2 Polybrominated diphenyl ethers (PBDE)

Polybrominated diphenyl ethers (PBDEs) are used as flame retardants in plastics and to some extent in textiles. The group includes 209 aromatic brominated compounds in which one to ten hydrogens in the diphenyl oxide structure are replaced by bromine. The general formula of PBDEs is:  $C_{12}H_{10-x}Br_xO$ . They are usually numbered from 1 to 209 using the same system as assigned to PCBs (Polychlorinated biphenyls) by Ballschmiter *et al.* (1993).

PBDEs are marketed under three technical products, pentabromodiphenyl ether (PentaBDE), octabromodiphenyl ether (OctaBDE), and decabromodiphenyl ether (DecaBDE), where each commercial product is a mixture of PBDEs with varying degrees of bromination. PentaBDE is considered as priority hazardous substance.

The production and use of PentaBDE and OctaBDE are now banned in Europe; only DecaBDE is still permitted. However, there are stocks of PBDEs in products in service and waste. Main applications of PBDEs were as flame retardants in (in descending order of importance): high-impact polystyrene (HIPS), acrylonitrile butadiene styrene (ABS), flexible polyurethane foam, textile coatings (not clothing), wire and cable insulation, electrical/electronic connectors and other interior parts.

PBDEs do not occur naturally, so all PBDEs in the environment originate from human activities. Current PBDE emissions to water come from waste (disposal and sludge spreading), but some industrial point sources (DecaBDE) as well as fires via extinguishing water might cause local pollution. Atmospheric deposition is an important source of PBDEs to the Baltic Sea today. The PBDE concentrations in the environment may also be due to historical pollution and accumulation.

Penta- and OctaBDE have been phased out and discharges are regulated. One of the remaining issues is PBDE containing waste all the more than they are very stable. Options for reducing emissions are about source control options in industry (DecaBDE), alternatives to PBDEs, and

PBDE containing waste (recycling and disposal) (<http://www.socopse.se/>). The PBDEs included in this study are listed in Table 3.

Table 3. PBDE congener numbering according to Ballschmiter *et al.* (1993) and to International Union of Applied Chemistry (IUAPC).

Congener	IUPAC
BDE 47	2,2',4,4'-tetrabromo diphenyl ether
BDE 85	2,2',3,4,4'-pentabromo diphenyl ether
BDE 99	2,2',4,4',5- pentabromo diphenyl ether
BDE 100	2,2',4,4',6- pentabromo diphenyl ether
BDE 138	2,2',3,4,4',5'- hexabromo diphenyl ether
BDE 153	2,2',4,4',5,5'- hexabromo diphenyl ether
BDE 154	2,2',4,4',5,6'- hexabromo diphenyl ether
BDE-197	2,2',3,3',4,4',6,6'- octabromo diphenyl ether
BDE-201	2,2',3,3',4,5',6,6'- octabromo diphenyl ether
BDE-202	2,2',3,3',5,5',6,6'- octabromo diphenyl ether
BDE-209	2,2',3,3',4,4',5,5',6,6'-decabromo diphenyl ether

### 2.1.3 Hexabromocyclododecane (HBCDD)

Hexabromocyclododecane (HBCDD) is another brominated flame retardant used mainly in plastic materials, textiles and electronics. HBCDD is an additive flame retardant, i.e. the molecule is not chemically incorporated in the polymer. The technical mixture mainly exists of three different isomers,  $\alpha$ -,  $\beta$ - and  $\gamma$ -HBCDD, which are all of environmental interest. In Europe, HBCDD has partially replaced the use of PBDEs and it has undergone an extensive risk evaluation by the Joint Research center of the European Commission. Accordingly, it is classified as persistent, bioaccumulative and toxic (PBT) and it is concluded that there is an environmental threat caused by HBCDD and actions on reducing the environmental concentrations are advised (EU-RAR, 2008).

The global use of HBCDD was estimated to be 15 900 metric tonnes in 1999 and Europe accounts for about 56 % of the total global use (Remberger *et al.*, 2004). As suggested for other additive chemicals, release from polymeric products in use is likely to occur. For products of long service lifetimes, emissions may be possible during the entire product lifetime. According to a qualitative material flow analysis (MFA) there are three potential emission stages in the life cycle of HBCDD products: manufacture, use and disposal (including recycling, incineration and deposit at landfill) (Remberger *et al.*, 2004).

Current HBCDD emissions to water may come from waste water treatment but also some industrial point sources. Atmospheric deposition is a potential source of HBCDD to the Baltic Sea today (Remberger *et al.*, 2004).

### 2.1.4 Perfluorinated Substances (PFAS)

Perfluorinated alkyl substances (PFAS) comprise a large group of industrial chemicals. They consist of a hydrophobic alkyl chain and a hydrophilic functional group. The alkyl chain is partly or fully fluorinated and contains between 4 and 18 carbon atoms. The abbreviations, full chemical names, CAS no and structures of the substances included in the screening are given in Table 4. Due to PFAS unique physical and chemical properties, they have been produced in increasing amounts

since the 1940s and used in a variety of products. The most important applications include surface treatment of textiles, paper, carpet and leather, and performance chemicals, e.g. fire-fighting foams (Jahnke and Berger, 2009).

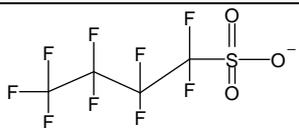
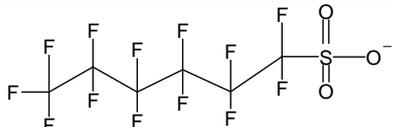
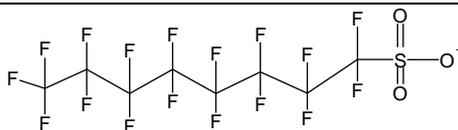
Two major production processes of PFAS have been applied, i.e. electrochemical fluorination (ECF) and telomerisation (Jahnke and Berger, 2009). ECF produce isomer mixtures dominated by the linear isomer but contain several branched isomers. In 2000, the U.S. Environmental protection Agency (EPA) banned PFOS from the US market. 3M phased out its C8-based production in 2002. Since then, the C8 product line has partly been substituted by C4 analogues with similar properties, but which are believed not to bioaccumulate and not to induce toxic effects (Jahnke and Berger, 2009). Also PFOA has been phased out from the production by 3M but is still used in products where no suitable replacement has been found (3M, 2008).

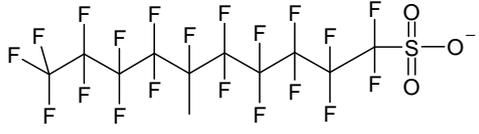
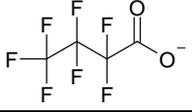
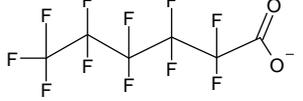
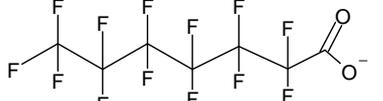
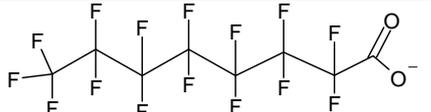
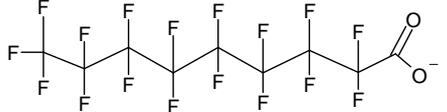
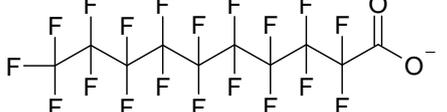
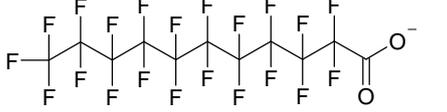
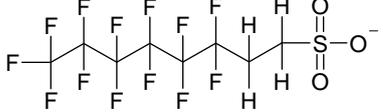
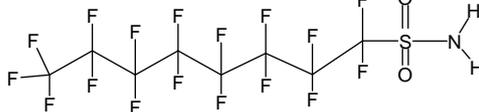
Due to the exceptional stability of the carbon-fluorine bond, a large number of ionic PFAS show high persistence. They are resistant against hydrolysis, photolysis, microbial degradation and metabolism. Several of the compounds have also been found to be toxic and to bioaccumulate. Long-range atmospheric transport of PFAS is considered to be an important pathway.

Perfluorooctane sulfonate (PFOS) has been shown to be toxic to mammals (rats; Rusch *et al.*, 1979, monkeys; Goldenthal *et al.*, 1979). PFOS has also recently been shown to bioaccumulate in fish and mammals (Martin *et al.*, 2003 and 2004) as well as to biomagnify in fish, birds and mammals (Martin *et al.*, 2004, Giesy and Kannan, 2001a-d). PFOS fulfils the criteria for a PBT (persistent, bioaccumulative, toxic) substance (KEMI 2004; OECD, 2002) and has been classified as a POP (persistent organic pollutant) by the Stockholm Convention (UNEP, 2007).

Despite several similarities with PFOS, perfluorooctanoic acid (PFOA) is not considered as a PBT substance, mainly because of studies that indicate low bioaccumulation in fish. However, the low elimination rate of the substance indicates uncertainties about whether this statement is generally applicable in the environment (KEMI 2004).

Table 4. CAS no and chemical structure of selected PFAS substances.

Abbreviation	Chemical name	CAS-no	Structure
PFBS	Perfluorobutane sulfonate	29420-49-3	
PFHxS	Perfluorohexane sulfonate	432-50-7	
PFOS	Perfluorooctane sulfonate	2795-39-3	

Abbreviation	Chemical name	CAS-no	Structure
PFDCS	Perfluorodecane sulfonate	67906-42-7	
PFBA	Perfluorobutanoic acid	375-22-4	
PFHxA	Perfluorohexanoic acid	307-24-4	
PFHpA	Perfluoroheptanoic acid	375-85-9	
PFOA	Perfluorooctanoic acid	335-67-1	
PFNA	Perfluorononanoic acid	375-95-1	
PFDCa	Perfluorodecanoic acid	335-76-2	
PFUnA	Perfluoroundecanoic acid	2058-94-8	
6:2 FTS	1,1,2,2-Tetrahydroperfluoro-octane sulfonate	arbitrary	
PFOSA	Perfluorooctane sulfonamide	754-91-6	

### 2.1.5 Phenolic Substances – Nonylphenol (NP) and Nonylphenol ethoxylates (NPEs)

Nonylphenol is an organic compound of the wider family of alkylphenols and more specific, member of a group called “long-chain alkylphenols”, containing octyl- and nonylphenols and their ethoxylates, and p-dodecylphenol. Long-chain alkylphenols are characterized by having either a straight alkyl chain or a branched alkyl group connected to the phenol. Their names depend on where on the phenol the alkyl group(s) is situated, the length and branching of the alkyl chain. The name "nonylphenol" is used for a number of isomer substances having a phenol ring structure and alkyl chain of C<sub>9</sub>H<sub>19</sub>. Branched 4-nonylphenol is the most descriptive and commercially available NP.

Nonylphenol is a starting substance for production of modified phenolic resins as well as a number of surfactants (emulsifiers) used in technical applications. The surfactant products produced from nonylphenol are called "nonylphenol ethoxylates" (NPEs). NPEs are used as emulsifiers, dispersive agents, surfactants and/or wetting agents and are the primary source of inputs to the sea of NP and NPEs. The main users were the industrial, institutional and domestic cleaning sectors (30 % of EU use).

Releases of NP from production processes are estimated to be low. Rather, the primary source of NP in the environment is considered to be NPEs, which can break down into NP after being released into the environment during their production, their formulation into various other products, and the use of such products. Releases occur to surface water (rivers, lakes, seas and their sediments) via industrial and municipal waste water and waste water treatment plants, via sewage sludge containing NP/NPEs spread on land, and air.

Nonylphenol is a priority hazardous substance of the EU-WFD. Due to the large quantity produced and used annually, its toxicity to aquatic organisms, and concerns that it is not readily biodegradable, a risk assessment on nonylphenol has been carried out by the European Commission. Nonylphenol ethoxylates were also assessed as they are the main pathway of nonylphenol to the environment via their biodegradation in the aquatic environment. The environmental risk assessment for nonylphenol and their ethoxylates indicated the need to reduce the risks associated with their production, their formulation into other products and the end use of these products in a wide range of industries. Based on that review, the European Commission published a Directive (2003/53/EC) to restrict the use of nonylphenol and nonylphenol ethoxylate and preparations containing them. Since January 2005 NP and NPE are banned at concentrations > 0.1% in e.g. industrial and institutional cleaning, domestic cleaning, textiles and leather processing, cosmetic products, and in metal working. Table 5 shows the compounds from this class included in the study.

Table 5. NP and NPE included in this study.

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4-nonylphenol (4-NP)
4-nonylphenol-EO1 (4-NP-EO1)
4-nonylphenol-EO2 (4-NP-EO2)

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### 2.1.6 Phenolic Substances – Octylphenol (OP) and Octylphenol ethoxylates (OPEs)

Octylphenol is like nonylphenol included in the group alkylphenols also called “long-chain alkylphenols, see above. 4-*tert*-Octylphenol (CAS no. 140-66-9) is a high production-volume substance. The European Union consumption was approximately 23,000 tonnes in 2001. It is a chemical intermediate, and is mainly used to make phenolic resins (98%). The remainder is converted into ethoxylates to produce surfactants. It can also be present as an impurity in nonylphenol (with other octylphenol isomers, typically up to a level of around 5%). The phenolic resins are used in rubber processing to make tyres (82%). Minor uses include such as being a component in printing inks and electrical insulation varnishes, and in the production of ethoxylated resins for offshore oil recovery.

Octylphenol ethoxylates are mainly used in emulsion polymerisation, textile processing, water-based paints, pesticide and veterinary medicine formulations, and to produce octylphenol ether sulphates. The parent substance can be reformed in the environment through degradation of the ethoxylate chain.

The substance is a solid (melting point 79-82°C, boiling point 280-283°C). It has a vapour pressure of 0.21 Pa at 20°C, a water solubility of 19 mg/L at 22°C and a log octanol–water partition coefficient (log  $K_{ow}$ ) of 4.12. Hydrolysis and photolysis are believed to be a negligible removal processes for 4-*tert*-octylphenol in the aquatic environment. It is not readily biodegradable, although it is considered to meet the criteria for inherent biodegradation. The log  $K_{ow}$  implies a moderate bioaccumulation potential in aquatic biota, which is supported by measured bioconcentration factor (BCF) values of a few hundred for fish (the estimated BCF is around 600). The substance mainly partitions to soil and sediment when it is released to the environment (Brooke *et al.*, 2005).

Table 6. OP and OPEs included in this study.

4- <i>tert</i> -octylphenol (4-t-OP)
4- <i>tert</i> -octylphenol-EO1 (4-t-OP-EO1)
4- <i>tert</i> -octylphenol-EO2 (4-t-OP-EO2)

### 2.1.7 Chlorinated Paraffins (SCCPs and MCCPs)

Chlorinated paraffins (CPs) are mixtures of polychlorinated *n*-alkanes with the general formula  $C_xH_{(2x+2)-y}Cl_y$  (Bayen *et al.*, 2006). The technical mixtures are named based on chain length,  $C_{10-13}$  as short chained chlorinated paraffins (SCCPs),  $C_{14-17}$  as medium chained chlorinated paraffins (MCCPs), and  $C_{>18}$  as long chained paraffins (LCCPs). The chlorination level varies between 30-72%, and the technical mixtures may contain thousands of isomers, enantiomers and diastereoisomers. SCCPs are classified as a priority hazardous substance group in the EU-WFD. Information regarding use of CPs in HELCOM countries is limited, but the available data together with information for EU-15 indicate decreasing use of SCCPs due to substitution with MCCPs for which the trend is increasing (HELCOM, 2009).

SCCPs and MCCPs are considered persistent and are toxic to aquatic organisms (EU-RAR, 1999; EU-RAR, 2005). The physico-chemical properties of CPs, (affecting their distribution in the environment) depend on carbon chain length and degree of chlorination. CPs are lipophilic with Log  $K_{ow}$  values between 4.39-8.69 for SCCPs and between 5.5-8.2 for MCCPs (Bayen *et al.*, 2006). CPs are thus lipophilic with the potential to bioaccumulate. CPs have been found in aquatic biota

such as plankton, mussels, crustaceans, fish, seals, walruses and whales, in fish eating birds, and also in terrestrial biota such as earthworms, rabbit, moose and reindeer (Bayen *et al.*, 2006; Houde *et al.*, 2008; HELCOM, 2002). Houde *et al.* (2008) have shown that SCCPs and MCCPs bioaccumulate with log BAFs (bioaccumulation factors) between 5.2-7.4, and have the potential to biomagnify and increase in concentration with trophic level. SCCPs and MCCPs have also been found in food stuffs and human milk samples (HELCOM, 2002; Bayen *et al.*, 2006; Thomas *et al.*, 2006). CPs have also been detected in air, water and sediments (Bayen *et al.*, 2006). Their presence in air, and also in biota from remote arctic areas, indicate the potential for atmospheric long range transport (Bayen *et al.*, 2006; Reth *et al.*, 2006).

### 2.1.8 $\alpha$ - and $\beta$ -Endosulfan

Technical endosulfan contains two isomers,  $\alpha$  - and  $\beta$  -endosulfan, in the ratio 7:3. Endosulfan is a broad spectrum insecticide used to treat vegetables, tea, berries, trees, woody plants, cereals, tobacco, rice, sweet corn, grapes, fruit, potatoes, cotton etc. (Schmidt *et al.*, 2001; US EPA, 2005). Endosulfan is formulated as a liquid emulsifying concentrate and wetting powder. It is applied by dip treatment, ground or air spraying from aircraft. The annual use in the U.S. is estimated to 640 000 ton of active substance (US EPA, 2005). Endosulfan is since 2005 banned within EU in plant protection products and is identified as priority hazardous substance under the EU-WFD.

Endosulfan is a semi volatile substance, classified as a POP, and as such may exist in both the vapour and particulate phases of the atmosphere and has potential for long-range transport. According to van Drooge *et al.* (2004), endosulfan is predominantly found in the gas phase, where it may react with hydroxyl radicals, with an estimated half-life of 2 days (HSDB, 2009). The historical global production and use of endosulfan as an insecticide has resulted in its direct release to the environment. Endosulfan is likely to enter the environment mainly via atmospheric long-range transport, followed by deposition to soil and water bodies. When deposited to soil, endosulfan is regarded to be fairly immobile ( $K_{OC}$  of 2,000), but volatilisation from moist soil surfaces may occur. Biodegradation may take place, with reported half-lives of 32 and 150 days in aerobic and anaerobic soils, respectively (HSDB, 2009).

In aquatic systems, the  $K_{OC}$ -value (log  $K_{OC}$  in sediments of 3.6) indicates that endosulfan may adsorb to suspended solids and deposit to sediments. However, the relatively high water solubility also implies that a certain proportion is likely to remain in the water column. Biodegradation may also take place in water, with reported half-lives of 2 and 8 days in aerobic and anaerobic waters respectively. Endosulfan may also undergo hydrolysis (half-lives of 9 to 533 h) (HSDB, 2009).

Endosulfan has not been classified as carcinogenic to humans, but has been shown to induce acute effects such as headache, dizziness, nausea, tremors and unconsciousness. It is toxic to rodents, with reported  $LD_{50}$  values of 18 mg/kg (oral) for rats and 7.4 mg/kg (oral) for mice. Endosulfan has a high tendency to bioconcentrate in aquatic organisms, with reported bioconcentration factors (BCF) of 2650 and 11583. Thus, the substance poses a potential risk to organisms on higher trophic levels (HSDB, 2009).

Endosulfan sulphate is an oxidation product found in technical endosulfan (Walse *et al.*, 2002) but can also be formed due to oxidation by microbes. Oxidation of endosulfan in soil has shown to yield 400 times higher concentrations of endosulfan sulfate than the mother compound (Gonzales *et al.*, 2003).

The structures of endosulfan and endosulfan sulfate are shown in Figure 1.

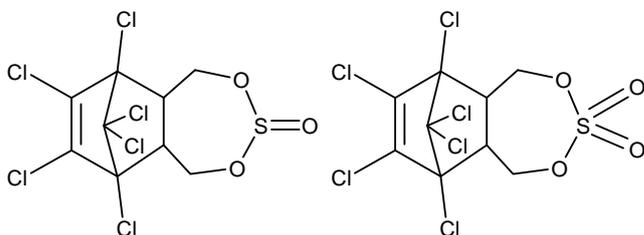


Figure 1. Chemical structures of endosulfan (CAS no 115-29-7) and endosulfan sulphate (CAS no 1031-07-8).

## 3 Methodology

### 3.1 Study area

Water and fish were sampled in the eastern Baltic environment, along the coast from Szczecin Lagoon in the south-eastern Baltic Sea, up to the coastal area near Sillamäe in the eastern Gulf of Finland. In addition, fish samples from Utlängan outside Blekinge in the southern part of Sweden were included in the study. Details of the sampling sites are given in Table 7. The locations of the sampling sites are also presented in Figure 2. Coordinates for the sampling sites are presented in Appendix A, Table A1.

Table 7. Sampling sites for fish and water in the participating countries. Letters in the first column indicate sampling sites shown in Figure 2.

Sampling sites	Estimated major local pressures	Fish species	Sea water
<b>Estonia</b>			
A. Coastal area near Sillamäe in Narva Bay, eastern Gulf of Finland	* City of Sillamäe (17 000 inhabitants, treated waste water) * Burial-place of nuclear waste (500m) * Metal industry (2 km) * Port of Sillamäe -multifunctional port for all cargo groups: oil-products, gas, dry bulk, containers (250 m)	Herring & perch	Same site as for fish
B. Western coast of Saaremaa Island, Tagalaht	No major pressures (background site)	Perch	Same site as for fish
C1. Coastal area in Pärnu Bay (semi-enclosed bay)	* River Pärnu: 51 m <sup>3</sup> /s (annual runoff 1,6 km <sup>3</sup> is equal to the volume of bay) * City of Pärnu (44 000 inhabitants, treated waste water) * Galvanic factory * Ports of Pärnu: 2 cargo port for dry bulk (turf, wood); containers; 2 fisheries harbour (trawlers and small boats)	Perch	Same site as for fish
C2. Northern Gulf of Riga	Very difficult to identify local pressures <sup>1</sup> ; ship traffic	Herring	No water sample
D. Coastal area in western Gulf of Finland, Spitham	Port of Dirhami (4 km): cargo port (wood) and fisheries harbour (trawlers and small boats)	Herring & flounder	Same site as for fish

Sampling sites	Estimated major local pressures	Fish species	Sea water
<b>Latvia</b>			
E. Central Gulf of Riga	Ship traffic	Herring	No water sample
F. Southern Gulf of Riga near estuarine of River Daugava	* River Daugava: average 951 m <sup>3</sup> /s * City of Riga (~700 000 inhabitants, treated waste water) * Port of Riga: port for containers, turf, wood, military port, passenger terminal * Shipbuilding facilities, food processing industry, wood processing industry	Perch	Same site as for fish
<b>Lithuania</b>			
G. Coastal area north from Klaipeda	Curonian Lagoon (plume area); waters of the Curonian Lagoon are affected by the * River Nemunas: average 612 m <sup>3</sup> /s * City of Klaipeda (waste water is treated) * Paperboard plant * Oil terminal * Klaipeda harbour with its intensive ship traffic, ship building and repairing, cargo companies	Herring & flounder	Same site as for fish
H. Open sea area north-east from Klaipeda	Ship traffic	Herring & flounder <sup>2</sup>	Open sea area
<b>Poland</b>			
I. Gulf of Gdansk, near coastline (open area with short retention time)	* River Vistula: average 1400 m <sup>3</sup> /s * Cities of Gdynia, Sopot and Gdansk (altogether 748 000 inhabitants, treated waste waters) * Main industrial branches in Gdynia & Gdansk: shipbuilding, electromechanical, metal processing, engineering, fertilizer & petroleum * Ports & harbors in Gdynia & Gdansk	Herring & flounder	Same site as for fish
J. Szczecin Lagoon (semi-closed area; retention time up to 30 days)	* River Odra: average 685 m <sup>3</sup> /s * City of Szczecin (411 000 inhabitants); its untreated waste waters discharged directly to the Szczecin Lagoon * Main industrial branches in Szczecin: shipbuilding, electromechanical, iron, chemical, plastics and fertilizer industry * Ports & harbors in Szczecin	Perch & flounder	Same site as for fish
<b>Sweden</b>			
K. Utlängen, outside of Blekinge	No major pressures (background site)	Herring & flounder	No water sample

<sup>1</sup> Gulf of Riga is semi-enclosed gulf; the main current flows through the narrow Irbe strait (27 km wide) to North-East and through the very narrow Suur Vin (3 km wide) out. The bay is like a big pot with strong circulation & mixing of the sea water. Thus, it is very hard to identify the local pressures.

<sup>2</sup> Due to metrological conditions fish samples have been taken near the coastline (quite near sampling site G), not from open sea area.

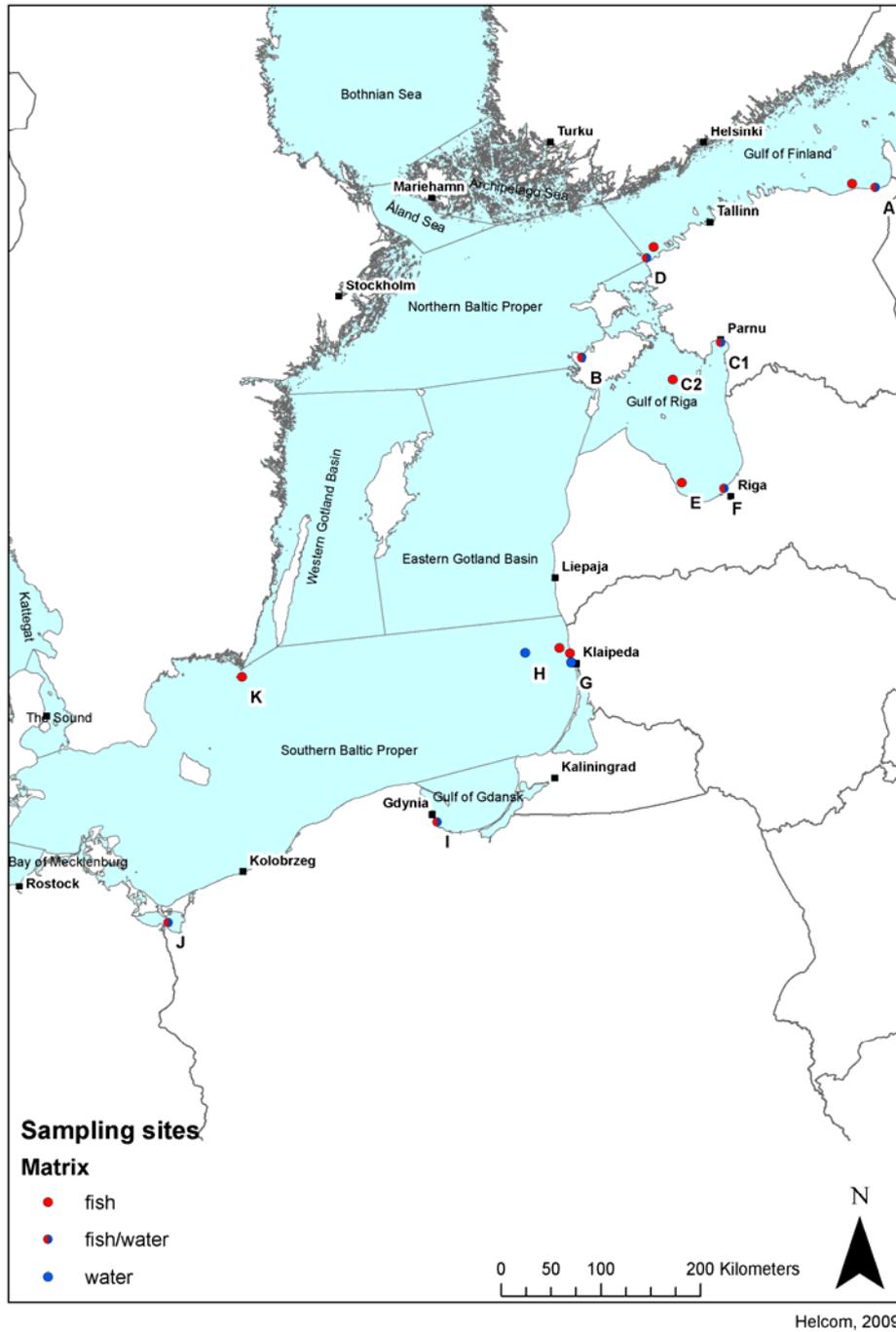


Figure 2. Sampling sites for fish and water in the eastern Baltic environment.

## 3.2 Sampling methods

Sampling of fish and water were performed by participating institutes according to the sampling manual presented in Appendix B. Sampling equipment was provided by IVL Swedish Environmental Institute.

### 3.2.1 Water

Surface water (0-1 m depth) was collected in cleaned and muffled (400°C, 4 h) glass bottles (2 x 1 L) for analysis of phenolic substances, and in cleaned plastic bottles (2 x 1 L) for PFAS analyses. Upon sampling, water samples were stored in refrigerator until (as soon as possible) sent by courier to IVL. In the laboratory plastic bottles were stored frozen, whereas water in glass bottles were acidified (pH < 2) with phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and stored in refrigerator, until further analysis.

### 3.2.2 Fish

Fish were sampled by nets or pelagic trawls. Upon sampling, individual fish were wrapped in muffled (400°C, 4 h) aluminum foil and stored in freezer until sent to the laboratory.

## 3.3 Physiological measurements

After delivery to the laboratory, weight and length measures were taken, and livers and muscle tissue excised. Condition factors (Cf) were calculated as  $Cf = 100 * \text{somatic weight (g) (including liver)} / \text{length}^3 \text{ (cm}^3\text{)}$  and liver somatic indexes (LSI) as  $LSI = 100 * \text{liver weight (g)} / \text{somatic weight (g) (including liver)}$ .

## 3.4 Analytical methods

The extraction and clean up of the samples and the instrumental analyses of organic tin compounds, brominated flame retardants, phenolic substances, and endosulfan were performed by IVL Swedish Environmental Institute. The analytical work for perfluorinated substances and chlorinated paraffins was performed by NILU.

### 3.4.1 Organic tin compounds

Fish homogenate (5 g) and 5 ml water was further homogenized. Internal standards and concentrated hydrobromic acid was added and the mixture was extracted twice with dichloromethane. The extract was dried with sodium sulphate, evaporated to dryness and redissolved in methanol:hexane (1:1). The extract was heated (90°) for 2 h in a closed tube together with sodium tetraethylborate in tetrahydrofuran. After cooling the extract was washed with water, dried with sodium sulphate and analyzed on a 6890N gas chromatograph coupled to a 5973N mass selective detector (Agilent). The injection, 1 µl, was done in splitless mode at 240°C. The fused silica capillary column (VF-5MS 30 m x 0.25 mm i.d. x 0.25 µm film thickness, Varian) was held at 50°C for 3 min., ramped 12°C/min to 300°C and held at 300°C for 10 min. Helium was used as carrier gas. The detector was used in selected ion monitoring mode (SIM) with electron ionisation

energy 70 eV. The analytes were identified by their characteristic retention times and target ions and one or more qualifier ions used to increase specificity.

### 3.4.2 Brominated Flame Retardants: PBDE and HBCDD

Approximately 10 -15 g of each fish homogenate was used for the analysis. The sample was extracted twice with acetone and pentane:diethylether (9:1), 20 min in ultra sonic bath each time. The organic solvent phases were pooled and washed with water. After separation of the phases, the water phase was extracted with pentane:diethylether (9:1). 20% of the organic solvent phase was used for lipid weight determination and the rest is reduced to 3 mL which is cleaned up with sulphuric acid. The hexane fraction is further cleaned up and fractionated applying an alumina column containing 2% water.

The analyses of BDE47 to BDE-183 were performed by GC-MS with splitless injections at an injector temperature of 260 °C. Helium was used as carrier gas with a pressure of 7.6 psi . The GC was fitted with a VF-5MS Varian column (30 m x 250 µm, 0.25 µm phase thickness) and the temperature program was: 50 °C (1 min hold) - 20°/min to 250 °C, 5°/min to 300 °C (15 min hold). The ion source temperature was 150 °C and the transfer line was 280 °C. The instrument was operating in a negative chemical ionization (NCI) mode.

The analyses of HBCDD, BDE-197; 201; 202 and 209 were carried out on a gas chromatograph (HP 5890 A) equipped with an electron capture detector and an auto sampler (Model HP 7376). A fused silica capillary 15 m column Rxi-5ms (Restec; 0.25 mm ID and 0.25 µm phase) was used. The column pressure was 15 psi. The temperature program was as follows: initial temperature 100°C, 1 min hold, 25°C/min to 295°C, and hold for 25 min.

### 3.4.3 Perfluorinated Substances

The fish liver samples (approximately 1 g) were homogenized, extracted with methanol, and further cleaned-up using ENviCarb. Water samples (0.2 L) were extracted onto SPE cartridges (Oasis HLB Plus) and eluted with methanol. The analyses were performed by high-performance liquid chromatography coupled to time-of-flight mass spectrometry (HPLC-Q-TOF-MS). Quantification was performed using the internal standard method.

### 3.4.4 Phenolic Substances: NP, NPE, OP, OPE & other

Approximately 10 g of each fish homogenate was homogenized in acetone and shaken for 30 minutes. The sample was re-extracted twice with pentane:MTBE (1:1). The organic solvent phases were combined and partitioned with 0,1 M H<sub>3</sub>PO<sub>4</sub> containing 0.9% NaCl. The phases were separated and the water phase was extracted with hexane:MTBE (1:1). The pooled organic solvent phase was dried over Na<sub>2</sub>SO<sub>4</sub> and reduced with N<sub>2</sub> to 2 mL. The lipids were reduced by partitioning twice with acetonitrile. This fraction was then diluted with acidic water extracted with hexane:MTBE (1:1). The extract was derivatised using acetic acid anhydride and NaAc. The sample was purified applying a SiO<sub>2</sub> column deactivated with 5% water. The column was eluted with hexane:MTBE (9:1) and then hexane:MTBE (3:1).

Approximately 2000 g water was filtered (glass fiber filter). The filtrate was extracted using a SPE-column (Isolut ENV+, 200 mg) while the filter was extracted separately using acetonitrile and hexane:MTBE (1:1). The SPE-column was eluted with acetonitrile, tetrahydrofuran and

hexan:MTBE (1:1). Water was added and the organic phase was combined with the extract from the filter. The extract was derivatized and purified as described above.

Analysis was performed using a 6890N gas chromatograph coupled to a 5973N mass selective detector (Agilent). The injection, 1  $\mu$ l, was done in splitless mode at 540°C. The fused silica capillary column (VF-5MS 30 m x 0.25 mm i.d. x 0.25  $\mu$ m film thickness, Varian) was held at 50°C for 3 min., ramped 12°C/min to 300°C and held at 300°C for 10 min. Helium was used as carrier gas. The detector was used in selected ion monitoring mode (SIM) with electron ionisation energy 70 eV. The analytes were identified by their characteristic retention times and target ions and one or more qualifier ions used to increase specificity.

### 3.4.5 Chlorinated Paraffins

Liver samples (approximately 3 g) were homogenised with sodium sulphate and extracted with cyclohexane:ethylacetate (1:1). The sample matrix was removed by treatment with sulphuric acid followed by cleanup on silica columns

An HP5890 GC (15 m Restek Rxi 5 ms, 0.25 mm i.d., 0.25  $\mu$ m filmthickness) coupled to a VG AutoSpec, high resolution mass spectrometer was used for all of the analyses. The GC was operated in constant flow mode, 1 mL/min (He), with a temperature program starting at 90°C, then ramping to 245°C by 20°C/min, then to 300°C by 50°C/min, holding that temperature for 3 min. The injector temperature was 260°C. The MS was operated in ECNI mode with argon at a pressure of  $2 \times 10^{-5}$  mbar as reagent gas. To be able to monitor the [M-Cl]<sup>-</sup> ions for each formula group of interest, the MS experiment was divided into five time windows. The quantifications were performed according to the method described by Tomy (1997). The mass Spectrometric Characterization of Polychlorinated n-Alkanes and the Methodology for their Analysis in the Environment.

### 3.4.6 $\alpha$ - and $\beta$ -Endosulfan

Approximately 10 -15 g of each fish homogenate was used for the analysis. The sample was extracted twice with aceton, and pentane:diethylether (9:1) . The organic solvent phases were pooled and washed with water. After separation of the phases, the water phase was extracted with pentane:diethylether (9:1). The organic solvent phase is reduced to dryness by the use of nitrogen gas and re-dissolved in hexane. The hexane phase was partitioned three times with acetonitrile. The combined acetonitrile fraction was diluted by water and extracted with hexane. The hexane was dried over potassium sulphate and purified on a SPE-PSA column (Isolute). The column was eluted with hexane (fraction1,  $\alpha$  -endosulfan), hexane:MTBE (9:1) (fraction 2), and hexane:MTBE (1:1) (fraction 3,  $\beta$  -endosulfan and endosulfan sulphate). Fraction 1 and 3 were pooled for GC-MS analysis.

The analyses were performed by GC-MS with splitless injections at an injector temperature of 240 °C. Helium was used as carrier gas with a pressure of 7.6 psi. The GC was fitted with a VF-5MS Varian column (30 m x 250  $\mu$ m, 0.25  $\mu$ m phase thickness) and the temperature program was: 50 °C (1 min hold) - 15°/min to 200 ° C, 5°/min to 300 °C (2 min hold). The ion source temperature was 250 °C and the transfer line was 280 °C. The instrument was operating in a negative chemical ionization (NCI) mode.

### 3.5 Extraction of lipids

Different methods were used to extract the fish lipids for each substance class. For example for brominated flame retardants, endosulfan and the phenolic substances, the fish homogenates were extracted with acetone, pentane and MTBE, while for perfluorinated substances the fish were extracted with methanol. These extraction methods extract all the organic substances of question but not all kinds of lipids. Especially for lean fish it is easy to discriminate phospholipids if not an appropriate method is used and a too small amount of lipids will be extracted giving overestimated results on lipid weight basis. Jensen *et al.* (2003) developed an extraction method based on isopropanol, diethyl ether and hexane to extract the total amount of lipids. This method was applied in this study for perch, herring and flounder (two samples of each species). Results on lipid content obtained by both methodologies are given in Table A2.

### 3.6 Quality Assurance/ Control

Sampling equipment as well as laboratory equipment was cleaned in accordance with the handling procedures implemented by the project group. Briefly, all glassware, glass fibre filters, sodium sulphate and sodium chloride was cleaned by heating to 400°C for 4 h prior to use. All other equipment was washed with organic solvent before use. The extracts were all time shielded from deposition of dust and particles in the laboratory air. Precautions to be taken during the sampling procedure are presented in Appendix B.

A compound identification was assigned to the peaks observed in the extract chromatogram if two criteria were met. The first criterion was retention time match, i.e. not a greater difference than  $\pm 0.1$  minutes between the known peak in the standard and the unknown peak in the chromatograms. The second criterion was a match in the mass spectrum between the known peak in the standard and the unknown in the extract chromatograms: the ratios of the selected ions in the mass spectrum (target- and qualifier-ions) are within  $\pm 15\%$  of expected / theoretical value.

Quantification was based on comparison of the peak area to the known peak area of the standard analyte. Internal standard (recovery standard added to the samples) approach was used for quantification, thus all reported values were recovery-corrected according to the recovery standard. Acceptable recovery rates for the added recovery standards were accepted if  $\geq 50\%$ .

Analytical method- and field blanks were included for each sample batch analysed to assess background interferences and possible contamination of the samples. Concentrations below field blank levels were treated as not detected. Possible background levels of analytes were subtracted from reported results.

Method blanks were analyzed and the average signal-to-noise ratio (S/N) for the selected compounds were determined. The LOD was calculated as  $S/N = 3$ . The LOQ threshold was derived from the combined threshold values for all field- and laboratory blank values. The highest blank values (field and laboratory blank) was used for LOQ determination ( $LOQ = 5 \times \text{blank}$ ) or 5 times the noise.

The European reference Material ERM-CE477 (mussel tissue) was analyzed for organotin compounds. For MBT, DBT and TBT respectively the results were 95%, 73% and 72% of the certified values. For other compounds values are not given on the certificate.

Calculated measurement uncertainties were estimated according to the Nordtest report TR 537, see Table 8 (Magnusson *et al.*, 2004).

Table 8. Calculated measurement uncertainties.

Substance	Uncertainty (%)
MBT	22
DBT	28
TBT	37
PBDE	15
HBCDD	15
PFAS	20
NP	20
NP-EO1-2	40
OP	15
OP-EO1-2	40
Endosulfan	15
Chlorinated paraffins	?

## 4 Results

The results are presented as concentration bars in maps for each substance class and sampling site as shown in Figure 2. Each bar represents the sum of the detected compounds for the specific substance class. The bars representing the triplicate samples (flounder and herring from Lithuania) are in the figures calculated as the mean value, where values < LOQ are set to LOQ/2. Under each bar a letter indicate the fish species, H (herring), F (flounder) and P (perch).

More detailed information regarding the concentrations is given in Tables A3-A13 in Appendix A where all concentrations for each compound and site are listed. Water concentrations of PFAS and phenolic compounds are total concentrations including particulate fractions. All fish results are presented on fresh weight (f.w.) basis. Results for PBDEs, HBCDD, chlorinated paraffins and endosulfan are also presented on an extractable lipid weight basis. In Table A2, physiological measurements, the measured lipid amounts, as well as the total lipid content determined according to Jensen *et al.* (2003), are presented. The difference in applying different lipid extraction methods is most obvious for lean fish with a lipid content less than 1% (Jensen *et al.*, 2003). This is shown in Table A2, from which it can be seen that for perch and flounder, the extraction for total lipids according to Jensen *et al.* (2003) yields about 30% higher lipid contents compared to the extraction method applied in this study. For herring, approximately the same the lipid content is obtained disregarded extraction method.

### 4.1 Organic tin compounds

TBT and DPhT were found above LOQ in 14 of 23 fish muscle samples each, although not always the same samples. DBT was detected in four samples above LOQ, see Figure 3 and Table A3. The range of TBT concentrations were 2.5-35 ng/g f.w., for DPhT 1.2-24 ng/g f.w. MPhT and TPhT were under LOQ in all samples as well as MOT and DOT. The highest concentrations of TBT were found in herring from the coastal area near Sillamäe (site A), in herring and flounder from the Gulf of Gdansk (site I), and perch from Szczecin Lagoon (site J).

The concentration of TBT was below LOQ in flounder from the background site in Sweden (site K), as well as in flounder from some of the affected sites (site D, G and H). TBT was also below LOQ in perch from the background site in Estonia (site B), as well as in perch from Pärnu Bay (site C2). DBT were however found in these samples.

In the flounder triplicate samples from site G in Figure 2, TBT were below LOQ ( $< 2$  ng/g f.w.) in all three samples, whereas DPHT were found in the range 2.3-3.4 ng/g f.w. DBT were only detected in one of the samples (2.1 ng/g f.w.). TBT was found in two of the herring triplicate samples at 4.2 and 6.4 ng/g f.w., whereas DPHT only were detected in one of the samples (4.4 ng/g f.w.).

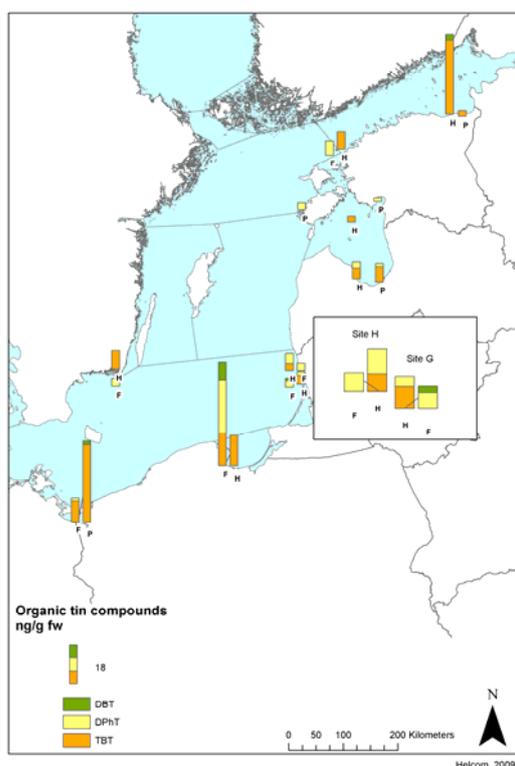


Figure 3. Concentrations (ng/g f.w.) of organotin compounds in fish muscle tissue from the eastern Baltic environment. H=herring, F=flounder and P=perch.

## 4.2 Polybrominated diphenyl ethers (PBDEs)

BDE-47 was most frequently detected of the PBDEs and occurred above LOQ in all fish muscle samples but one of the flounder samples from Lithuania, see Figure 4 and Tables A4 and A5. The concentration range found were 0.011-0.29 ng/g f.w. (1.7-6.1 ng/g l.w.). BDE-99 and BDE-100 were found in 12 and 16 samples in concentration ranges of 0.014-0.054 ng/g f.w. (0.5-1.9 ng/g l.w.), and 0.010-0.15 ng/g f.w. (0.83-4.0 ng/g l.w.), respectively. BDE-85 and BDE-153 were detected in fish from two sampling sites, while BDE-138, BDE-183, BDE-197 and BDE-209 were below LOQ in all samples. Concentrations of PBDEs were higher in herring compared to flounder and perch. The highest concentrations of PBDEs were found in herring from the Gulf of Gdansk (site I) and in herring from the waters outside Klaipeda (site G and H), but no general differences between background and affected sites could be seen.

In the flounder triplicate samples the ranges for BDE-47 and BDE-100 were 0.014-0.021 ng/g f.w. (2.2-2.9 ng/g l.w.) and <0.01-0.010 ng/g f.w. (1.3-1.5 ng/g l.w.), respectively. The ranges in the herring triplicate samples were 0.092-0.18 ng/g f.w. (2.0-5.2 ng/g l.w.) for BDE-47, 0.024-0.036 ng/g f.w. (0.5-1.2 ng/g l.w.) for BDE-99, 0.046-0.11 ng/g f.w. (1.0-4.0 ng/g l.w.) for BDE-100, and 0.021-0.038 ng/g f.w. (0.46-1.1 ng/g l.w.) for BDE 154.

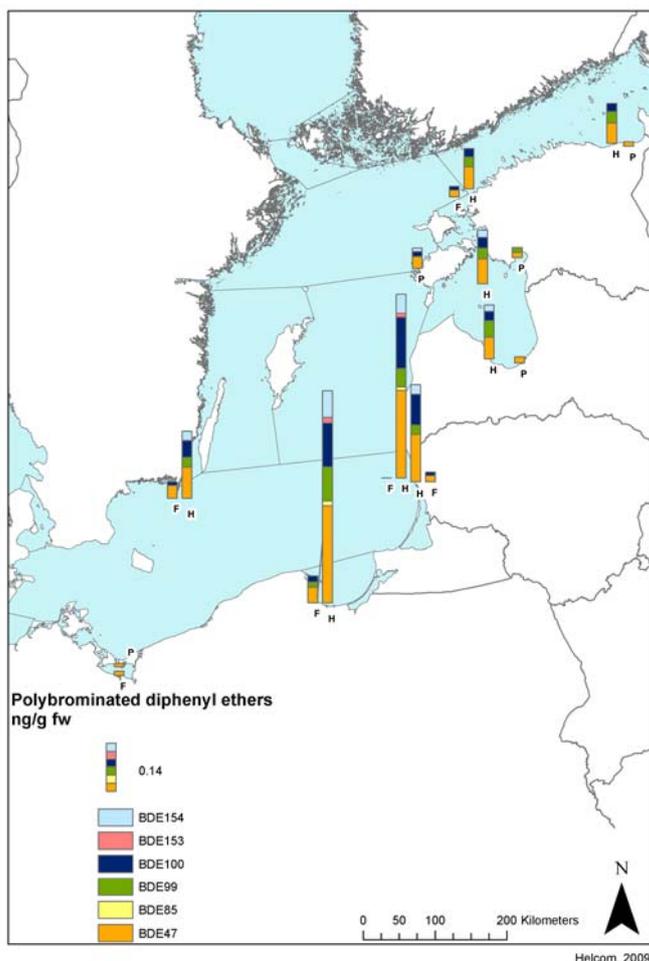


Figure 4. Concentrations (ng/g f.w.) of polybrominated diphenyl ethers in fish muscle tissue from the eastern Baltic environment. H=herring, F=flounder and P=perch.

### 4.3 Hexabromocyclododecane (HBCDD)

HBCDD was below LOQ in all samples (< 0.1 ng/g f.w., < 1.9- < 24 ng/g l.w.), see Tables A4 and A5.

### 4.4 Perfluorinated Substances

PFOS was found in all fish liver samples from all sites in the concentration range 4.3-61 ng/g f.w., see Figure 5 and Table A7. PFHxS was found above LOQ in 17 samples in the range 0.10-1.1 ng/g

f.w. The flounder sample from Lithuania at site H contained most number of substances, in addition to PFOS and PFHxS, also PFDcS, PFBA, PFHxA, PFHpA and PFNA were detected, see table A6 for specific concentrations. The highest concentrations of perfluorinated substances were found in flounder and perch from the Szczecin Lagoon (site J), but no clear differences between affected and background sites could be seen. PFOA was not detected in fish at any sampling site. In general, concentrations of perfluorinated compounds were higher in perch compared to flounder and herring.

In the flounder triplicate samples the ranges for PFOS and PFHxS were 11-20 and 0.40-1.1 ng/g f.w., respectively. The ranges in the herring triplicate samples were 6.1-10 for PFOS and 0.23-0.39 ng/g f.w. for PFHxS.

In water samples, perfluorinated substances could only be found in Szczecin Lagoon (site J). PFOS and PFOA were detected at concentrations of 2.9 and 6.0 ng/L, respectively. For all other sites and substances, the concentrations in the water samples were below LOQ, see Table A7.

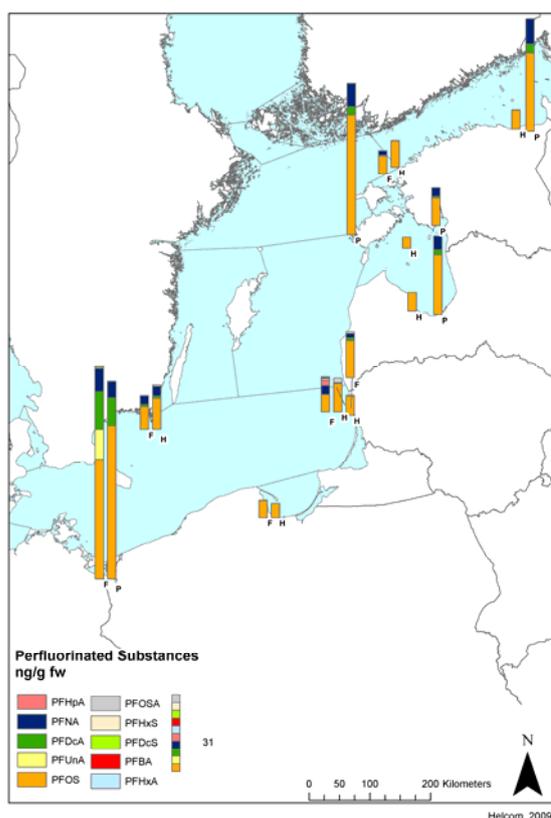


Figure 5. Concentrations (ng/g f.w.) of perfluorinated substances in fish liver tissue from the eastern Baltic environment. H=herring, F=flounder and P=perch.

## 4.5 Phenolic Substances: NP/NPE

4-NP was detected in flounder from Utlängen in Sweden (site K) at a concentration of 23 ng/g f.w. and in flounder sampled north from Klaipeda in Lithuania (site G) at a concentration of 12 ng/g f.w, see Table A9. No detectable concentrations were found in the other fish samples. 4-NP-EO1 and 4-NP-EO2 were below LOQ in all samples.

In the water samples 4-NP were detected above LOQ at six sites, see Figure 6 and Table A8. Concentrations of 4-NP-EO1 and 4-NP-EO2 were below LOQ. Concentrations found at the affected sites varied between <10 ng/l and 66 ng/l, whereas for water from the background site in Estonia (site B) a concentration of 13 ng/l was found.

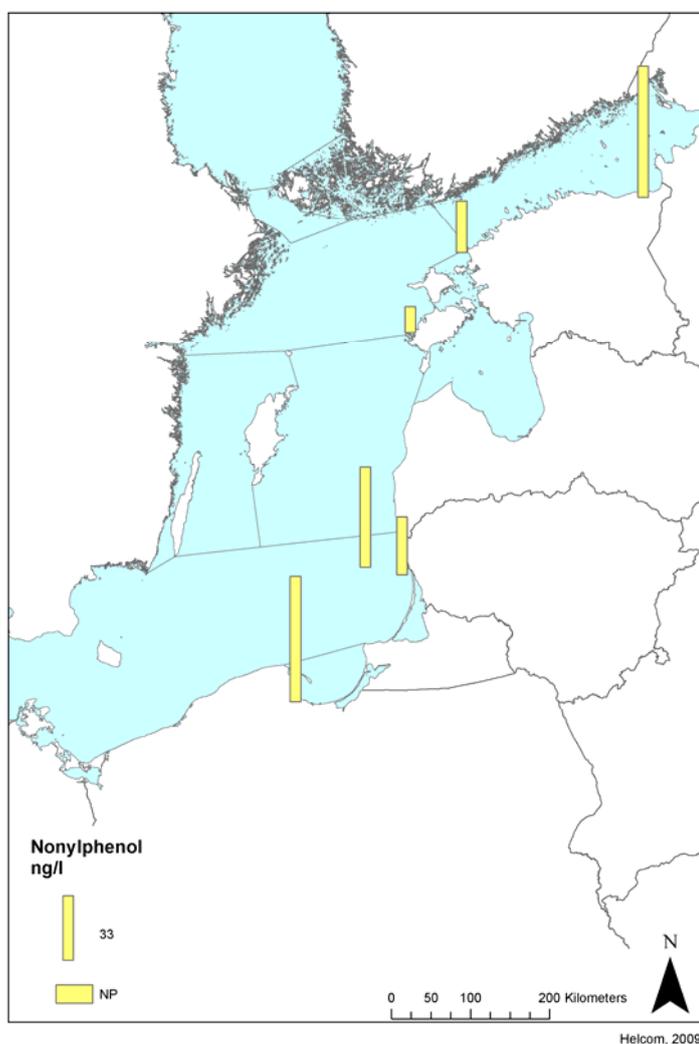


Figure 6. Concentrations (ng/l) of nonylphenol in water from the eastern Baltic environment.

## 4.6 Phenolic Substances: OP/OPE & other

4-t-OP, 4-t-OP-EO1 and 4-t-OP-EO2 were not detected in any of the fish samples, see table A9.

4-t-OP was detected in one water sample (north from Klaipeda, site G) at a concentration of 1.2 ng/L, see Table A7.

Bisphenol A was detected in eighteen of 23 fish muscle samples in the range of 0.6-3.9 ng/g f.w., but concentrations were below LOQ in all water samples, see Figure 7 and Tables A8 and A9. Concentrations in fish were in the same range at affected and background sites, and no differences between species could be seen. In the flounder triplicate samples the range for bisphenol A was 0.98-3.9 ng/g f.w. The range in the herring triplicate samples was <0.6-3.1 ng/g f.w.

Triclosan was below LOQ in all samples, both in water and in fish muscle, see Tables A8 and A9.

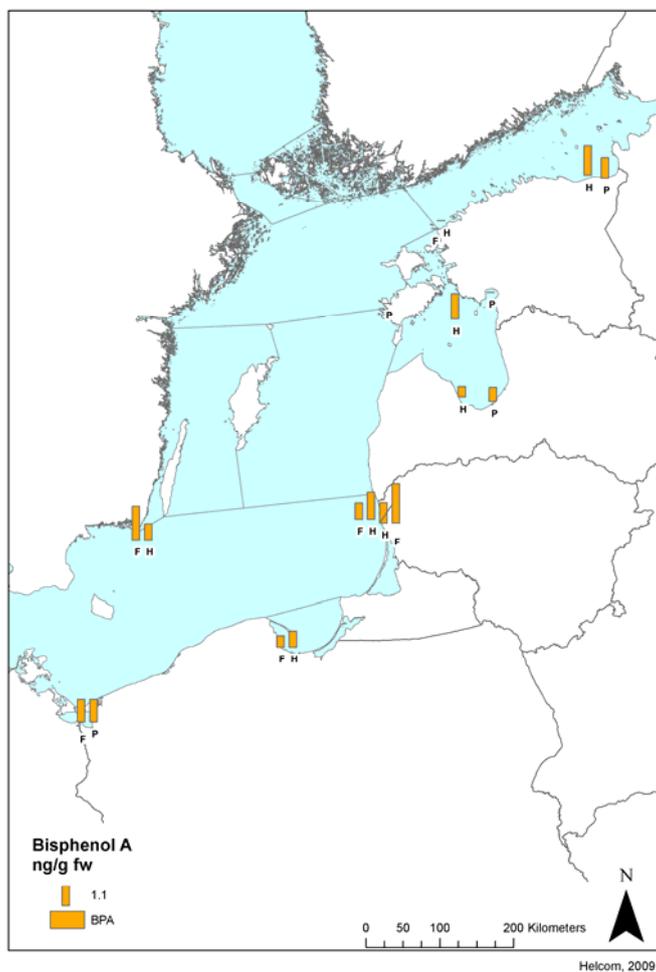


Figure 7. Concentrations (ng/g f.w.) of Bisphenol A in fish liver tissue from the eastern Baltic environment. H=herring, F=flounder and P=perch.

## 4.7 Chlorinated Paraffins

SCCPs were detected in all fish liver samples at concentrations between 5.2 and 62 ng/g f.w. (65-1700 ng/g l.w.), see Figure 8 and Tables A10 and A11. For some liver samples, the tissue amounts were too small for extractable lipids analysis. For these samples, results are only presented on a fresh weight basis. MCCPs were only detected in three perch samples. In samples collected at two sites in Estonia (site B and C) concentrations was 15 and 3.9 ng/g f.w. (290 and 88 ng/g l.w.) respectively, and in Szczecin Lagoon (site J) 8.2 ng/g f.w. (120 ng/g l.w.).

No clear differences in concentrations of SCCPs between sampling sites or between species could be seen.

In the flounder triplicate samples the range for SCCPs was 17-62 ng/g f.w. (520-1700 ng/g l.w.) The range in the herring triplicate samples was 6.5-19 ng/g f.w. (65-210 ng/g l.w.).

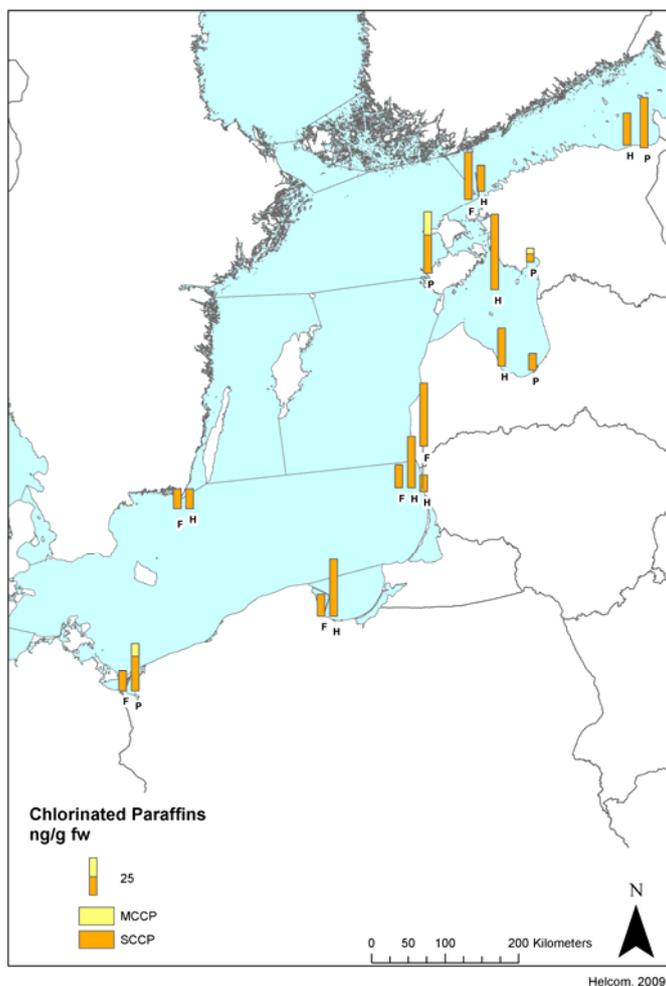


Figure 8. Concentrations (ng/g f.w.) of chlorinated paraffins in fish liver tissue from the eastern Baltic environment. H=herring, F=flounder and P=perch.

## 4.8 $\alpha$ - and $\beta$ -Endosulfan

Both  $\alpha$ - and  $\beta$ -endosulfan were below LOQ in all fish samples, see Tables A12 and A13. Endosulfan sulphate was detected above LOQ in all samples except in herring and perch from Latvia (sites E and F), see Figure 9. The concentration range for endosulfan sulphate was <0.01-0.12 ng/g f.w.

Concentrations of endosulfan sulphate found in herring (0.049-0.12 ng/g f.w.) were higher compared to concentrations found in flounder (0.011-0.022 ng/g f.w.) and perch (0.010-0.013 ng/g f.w.). No differences in concentrations between affected and background sites could be seen.

In the flounder triplicate samples the range for endosulfan sulphate was 0.011-0.014 ng/g f.w. The range in the herring triplicate samples was 0.057-0.088 ng/g f.w.

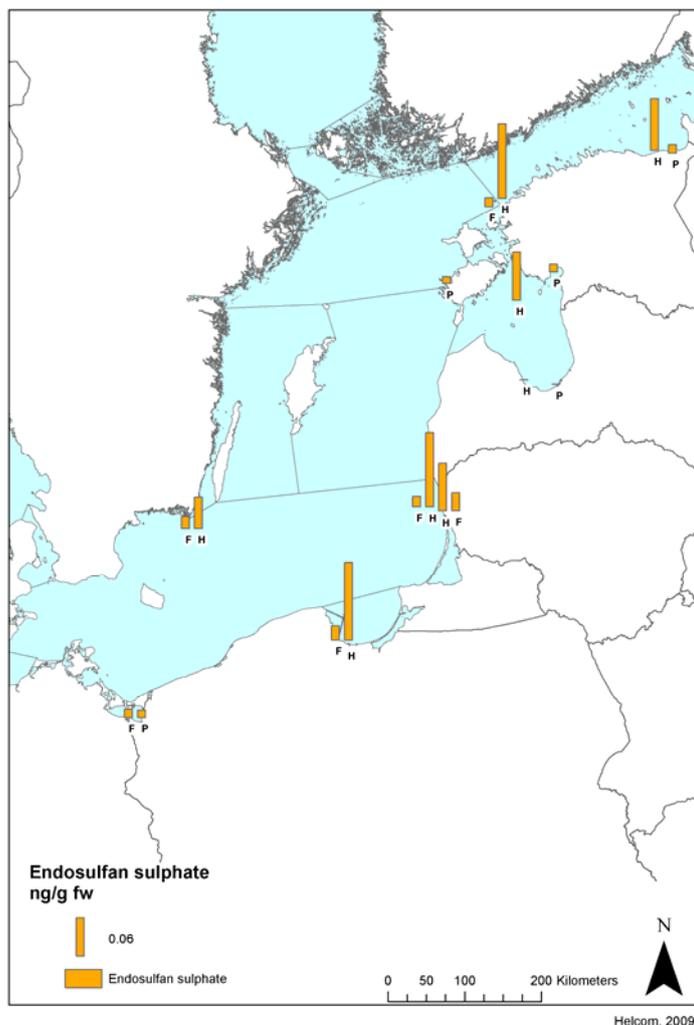


Figure 9. Concentrations (ng/g f.w.) of endosulfan sulphate in fish muscle tissue from the eastern Baltic environment. H=herring, F=flounder and P=perch.

## 5 Discussion

The focus in the discussion is on comparisons between the levels found in this study with levels found in the same species and tissues from previous studies from the Baltic Sea and estimated effect levels.

The levels in fish are discussed and compared mainly on a fresh weight basis (f.w.) but for some contaminants also on a lipid weight basis (l.w). The difference in applying different lipid extraction methods is most obvious for lean fish with a lipid content less than 1% (Jensen *et al.*, 2003). This is shown in Table A2, from which it can be seen that for perch and flounder, the extraction for total lipids according to Jensen *et al.* (2003) yields about 30% higher lipid contents compared to the extraction method applied in this study. For herring, approximately the same the lipid content is obtained disregarded extraction method.

### 5.1 Organic tin compounds

Organic tin compounds have been found in various species from several organism groups sampled in the Baltic Sea. These include seaweeds (eelgrass and bladder wrack) invertebrates (e.g. blue mussel, common whelk and spider crab) various fish species (e.g. eelpout, perch, flounder, herring, cod, sculpin, three-spined stickleback, pikeperch, pike, burbot, bream, whitefish), birds (e.g. mute swan, eider duck, common scoter, great black-backed gull, herring gull, and cormorant), and mammals (harbour seal and harbour porpoise) (see e.g. Falandysz *et al.*, 2002; Rüdél *et al.*, 2003; Senthilkumar *et al.*, 1999; Sternbeck *et al.*, 2006; Strand *et al.*, 2003; Strand & Jacobsen, 2005; Hallikainen *et al.* 2008). Concentrations found differ between species and tissue studied (see e.g. Albalat *et al.*, 2002; Strand & Jacobsen, 2005). Thus, concentrations found in the present study are compared with previous analyses of muscle tissue from perch, flounder and herring. In Table 9, data for the comparison is summarized.

In the present study, TBT was found above LOQ in all but 4 samples, concentration range < 2-35 ng/g f.w. The concentrations found in the present study are similar or in the lower range of what has been previously reported, as presented above.

The use of TBT in antifouling on small vessels was banned 1989 within the EU (1989/677/EC). 2003 new applications of organic tin containing antifouling systems were prohibited on all ships, and since January 2008 there is a complete prohibition under the International Convention on the Control of Harmful Anti-fouling Systems on Ships, adopted by the International Maritime Organization 2003, into force since September 2008 ([www.imo.org](http://www.imo.org)). Despite these restrictions introduced, a study by Eklund *et al.* (2008) on organic tin compound distribution in sediment from a Swedish marina and a harbour suggests that TBT is still being released from pleasure boats. The distribution between butyltin derivatives in sediment in the Port of Gdansk has also indicated new inputs of TBT (Radke *et al.*, 2008). In a retrospective study of TBT in biota from the southern Baltic Sea, no decrease in TBT concentrations could be found over the years 1985-1999 (Rüdél *et al.*, 2003), but recently decreasing concentrations of TBT in mussels have been found at four out of 14 sampling stations within the Danish national environmental monitoring (Dahl and Josefson, 2009).

Table 9. Concentrations of organic tin compounds in muscle tissue from herring, flounder and perch from the Baltic Sea area.

Sampling site	Sampling year	Species analysed	Substance	Concentration	Reference
Gdańsk bay	1990	herring	MBT+DBT+TBT	40 ng/g f.w.	Kannan & Falandysz, 1997
		flounder		316 ng/g f.w.	
Firth of Vistula	1997	herring	MBT+DBT+TBT	78 ng/g f.w.	Senthilkumar <i>et al.</i> , 1999
Gdańsk bay		flounder		83 ng/g f.w.	
Gulf of Bothnia	2001	herring	MBT+DBT+TBT	5-7 ng/g d.w.	Tesfalidet, 2004
			MPhT+DPhT+TPhT	0.3-7 ng/g d.w.	
Northern Baltic Proper, Stockholm archipelago	2001-2002	perch	TBT	6.8-33 ng/g f.w.	Sternbeck <i>et al.</i> , 2006
			DBT	3.1-12 ng/g f.w.	
			MBT	< 0.3-0.8 ng/g f.w.	
			TPhT	39-102 ng/g f.w.	
Gulf of Finland, dredging and disposal sites	2005	perch	TBT	19-38 ng/g f.w.	Vatanen <i>et al.</i> , 2006
			TPhT	12-23 ng/g f.w.	
Finnish coastline, harbours and background	2005-2007	perch	TBT	3.4-81 ng/g f.w.	Hallikainen <i>et al.</i> , 2008
			TPhT	8.1-151 ng/g f.w.	
		herring	DBT	0.4-6.8 ng/g f.w.	
			TBT	4.6-21 ng/g f.w.	
Eastern Baltic marine environment	2008	perch	TPhT	3.6-5.2 ng/g f.w.	This study
			DBT	0.5-1.4 ng/g f.w.	
			TBT	< 2-35 ng/g f.w.	
		flounder	TPhT	< 0.1 ng/g f.w.	
			DBT	< 1.2-1.8 ng/g	
		herring	TBT	f.w.	
			TPhT	< 2-15 ng/g f.w.	
			DBT	< 0.1 ng/g f.w.	
			TBT	< 1.3-8.2 ng/g	
			TPhT	f.w.	
			DBT	< 2-34 ng/g f.w.	
				< 0.1 ng/g f.w.	
				< 1.2-2.6 ng/g f.w.	

Although the concentrations of TBT found in the present study are in the same range or lower compared to previous studies, they might be a cause for concern. PNEC-values for TBT in prey for the protection of predators from secondary poisoning, and human health considering consumption of fishery products, are set to 230 ng/g prey tissue and 15.2 ng/g fishery product respectively

(WFD-EAF, 2005). Concentrations found in the present study are lower compared to the PNEC-value for secondary poisoning of predators, but for several samples close to or higher compared to the PNEC-value considering human health.

## 5.2 Polybrominated diphenyl ethers (PBDE)

BDE-47, BDE-99 and BDE-100 are the most commonly detected PBDEs in fish (Sellström *et al.*, 1998). These three congeners were also found in highest concentration in this study. BDE-47 was detected in all fish samples but one from Lithuania (see Figure 4 and Tables A4 and A5). A general pattern was that, on a fresh weight basis, BDE-47, BDE-99 and BDE-100 were detected in higher concentrations in herring (range for BDE-47 0.060-0.260 ng/g f.w.) compared to flounder and perch (range for BDE-47 <0.01-0.046 ng/g f.w.). This is due to a higher lipid content in herring. If concentrations of BDE-47 based on extractable lipids are compared instead, no differences between species can be seen (1.8-6.1 ng/g l.w. for herring, 1.7-5.2 ng/g l.w. for perch, and < 1.5-4.2 ng/g l.w. for flounder, see Table A5). This was also true for BDE-99 (0.5-1.9 ng/g l.w. for herring, < 1.6-1.7 ng/g l.w. for perch, and < 1.2-1.1 ng/g l.w. for flounder) and BDE-100 (0.83-4 ng/g l.w. for herring, 0.84-2.2 ng/g l.w. for perch, and 1.2-1.5 ng/g l.w. for flounder). The background areas did not show lower levels compared to the areas considered as affected.

Within the Swedish National Monitoring Programme in Marine Biota, mean concentrations in herring sampled over the years 1999-2004 from background sites within the Baltic Sea of 9.9 ng/g l.w. (BDE-47), 2.69 ng/g l.w. (BDE-99) and 1.85 ng/g l.w. (BDE-100) was found, and concentrations seemed to be elevated in the south compared to the north. (Bignert *et al.*, 2007). In perch from the Bothnian Sea, concentrations of 9.0-18 ng/g l.w. (BDE-47), 1.1-1.2 ng/g l.w. (BDE-99), and 2.2-4.8 ng/g l.w. (BDE-100) have been found, whereas in perch from the Western Gotland Basin, concentrations of all three congeners were below LOQ (Sternbeck *et al.*, 2004).

Concentrations found in the present study are in the same range or lower compared to these previous studies.

A PNEC-value for BDE-99 and BDE100, in prey for the protection of predators from secondary poisoning, and human health considering consumption of fishery products, have been estimated to 1000 ng/g f.w. of prey tissue and 274 ng/g f.w. of fishery products, respectively (HELCOM, 2009). Concentrations found in the present study are lower than these values.

## 5.3 Hexabromocyclododecane (HBCDD)

HBCDD was below LOQ (<0.1 ng/g f.w., < 1.9- < 24 ng/g l.w.) in all analyzed fish samples. In previous studies of fish sampled at different sites in the Baltic Sea, HBCDD has been detected in several species as summarized in HELCOM (2009). Within the Swedish National Monitoring Programme in Marine Biota, an increasing trend for HBCDD over the last four decades in Guillemot eggs has been seen (Bignert *et al.*, 2007). In herring, mean concentrations in the range 6-25 ng/g l.w. in fish sampled over the years 1999-2004 from background sites within the Baltic Sea was found, and concentrations seemed to be elevated in the south compared to the north. Sternbeck *et al.*, (2004) found concentrations in the range < 2.4 – 9.8 ng/g l.w. in perch from two Swedish background sites. In the present study, LOQs for perch were in the range <12-<24 ng/g l.w., and for herring in the range < 1.9-< 12 ng/g l.w. Concentrations in herring sampled in the present study thus seems to be lower compared to the results by Bignert *et al.* (2007), whereas for

perch LOQs area above concentrations previously found. All concentrations found in previous studies have been below the estimated PNEC-value of 1530 ng/g f.w. secondary poisoning of predators (HELCOM, 2009).

## 5.4 Perfluorinated Substances (PFAS)

PFOS was detected in all fish species from all sampling sites, concentrations found were in the range 4.3-61 ng/g f.w. liver tissue. There was no trend regarding the concentrations in the different species. The fish sampled at the two background areas did not contain lower levels compared to the affected areas. A PNEC-value regarding secondary poisoning of predators has been estimated to 17 ng/g f.w. (Brooke *et al.*, 2004). The levels of PFOS found in this study exceeded this value in six samples. It should be mentioned that livers and not whole fish are analyzed in this study. PFOA was below the LOQ in all samples.

Levels of PFOS and PFOA in fish from the Baltic Sea are reviewed in HELCOM (2009). Herring and flounder liver concentrations in this study are in the range of what has been found in previous studies. PFOA has in previous studies been detected in livers of flounder and herring with concentrations up to 5 ng/g f.w. but is mostly below LOQ in the studies summarized in HELCOM (2009) as was the case in the present study.

Of the water samples analyzed in present study, perfluorinated substances were found above the LOQ in only one sample. PFOS (2.9 ng/l) and PFOA (6.0 ng/l) was detected in water from Szczecin Lagoon, (site J, Figure 2). The fish collected at the same site contained among the highest levels of PFOS, PFNA, PFDCa and PFUnA, see Figure 5 and Table A6. PFOS and PFOA concentrations in water of the Baltic Sea are reviewed in HELCOM (2009). Both PFOS and PFOA have been detected at several sites outside Denmark, Germany and Finland, but at most sites at concentrations lower than 1 ng/l. However, PFOA has also been found in Denmark and Finland at concentrations in the same range as found in water from Szczecin Lagoon in the present study (Kallenborn *et al.*, 2004). A PNEC value for effects on marine aquatic organisms of 2500 ng/l for PFOS has been reported by Brooke *et al.* (2004), whereas for PFOA, Ji *et al.* (2008) found increased cumulative mortality in progeny of the fish medaka at 100000 ng/l. Concentrations of PFOS and PFOA in the present study are below these values.

## 5.5 Phenolic Substances NP/NPE

4-NP was only detected in fish from two sampling sites, in one of the triplicate flounder samples from Lithuania (site G) and in flounder from Sweden (site K). Concentrations found were 12 and 23 ng/g f.w., respectively. 4-NP-EO1 and 4-NP-EO2 was not detected at all in the fish samples.

NP has previously been found in blue mussel, liver of fish, seal, whale, and in bird eggs from the Nordic environment (Hansen and Lassen, 2008). Concentrations of 43.7-989 ng/g f.w. were found in liver samples from pike collected in the city bay of Helsinki and the coastal bay of Espoo (Finland). Hansen and Lassen (2008) also found NP1EO in two mussel samples (Limfjorden, Denmark and Oslofjord, Norway), and in one liver sample from eelpout sampled in the Roskilde Fjord (Denmark).

A PNEC-value for the protection of predators from secondary poisoning has been estimated to

10 000 ng/g f.w. This is far above the concentrations found in the present study.

In the water samples 4-NP was detected at six sites, with concentrations in the range 13 to 66 ng/l, whereas concentrations of 4-NP-EO1 and 4-NP-EO2 were below LOQ in all samples. NP (branched) has previously been detected in waters from the Nordic environment, at concentrations of 18.8-93.6 ng/L in recipient waters from Denmark and Finland, and in water sampled at background sites in Denmark (Kattegatt) and Sweden (lakes) at concentrations of 22.2-42.1 and 68.3-107 ng/l respectively (Hansen and Lassen, 2008). NP1EO was found in one recipient water from Denmark (60.8 ng/l). The concentrations found in the present study are below the surface water AA-EQS value of 300 ng/l for NP set under the Water Framework Directive (2008/105/EC).

## 5.6 Phenolic Substances OP/OPE & other

4-t-OP, 4-t-OP-EO1 and 4-t-OP-EO2 were not detected in any of the fish samples.

In the water samples, 4-t-OP was only detected in one of the water samples (Lithuania, site G), at a concentration of 1.2 ng/l. The OPEs were both under the LOQ.

4-t-OP and OP1EO have previously been found in biota (in fish liver samples, in mussels, in liver from marine mammals, and in bird eggs) and in water (Hansen and Lassen, 2008). In pike liver samples from Espoo and Helsinki (Finland) and Roskilde Fjord (Denmark), 4-t-OP was found in the range 13.2-355 ng/g f.w., whereas estimated OP1EO concentrations were above 2000 ng/g f.w. 4-t-OP could not be detected (< 1- < 10 ng/l) in water samples from background areas nor in recipient waters (Hansen and Lassen, 2008). However, OP1EO could be found in several recipient waters from Denmark and Finland (1.8-5.7 ng/l) and in water from one Swedish background lake (2.4 ng/l).

A PNEC value for OP have been estimated to 1000 ng/g f.w. for biota, and the AA-EQS set under the Water Framework Directive for surface waters is 10 ng/l (HELCOM, 2009; 2008/105/EC).

Bisphenol A has previously been detected in fish (Finland, Norway and Sweden), mussels (Denmark) and black guillemot eggs (Faroe Islands) in the Nordic environment (Sternbeck and Forsgren, 2007; Hansen and Lassen, 2008). In Pike liver from the City bay of Helsinki, 56.8 µg/kg f.w. have been found (Hansen and Lassen, 2008). Sternbeck and Forsgren (2007) found Bisphenol A concentrations in fish muscle in the same range as the present study. In perch sampled in the Stockholm area, from the Baltic Sea coastal area outside of Stockholm, and in Swedish background lakes, concentrations in the range 0.57-3.01 µg/kg f.w. were found. No differences between urban and background sites could be seen. Bisphenol A was also found in muscle of Cod sampled at Gotland (0.92-4.74 µg/kg f.w.), and in muscle of herring (3.27 µg/kg f.w.) from Landsort (Swedish coastal area, northern Baltic Proper).

Concentrations found in the present study (< 0.6-3.9 ng/g f.w.) were in the same range as those found by Sternbeck and Forsgren (2007) and Hansen and Lassen (2008). No differences between sampling sites or species could be seen.

In water, concentrations were below LOQ (<14 ng/l). In a Nordic screening study, concentrations in the ranges <1-22.3 ng/l and <1-10.8 ng/l have been found in recipient waters and in samples from background areas, respectively (Hansen and Lassen, 2008).

The PNEC values for bisphenol a have been estimated to 33 000 ng/g f.w. for biota and 1600 ng/l for water (EU-RAR 2003). The concentrations found were below these values.

## 5.7 Chlorinated Paraffins (SCCPs and MCCPs)

In the present study, SCCPs were found in all liver samples (5.2-62 ng/g f.w.), whereas MCCPs only were found in three liver samples from perch (3.9-15 ng/g f.w.). No clear regional or species differences in concentrations found could be seen. The concentrations found were lower compared to values reported in previous studies. Both SCCPs and MCCPs have been found in liver samples from cod, flounder and dab from the south-western Baltic Proper and the Kiel Bight (Oehme *et al.*, 2005; Reth *et al.*, 2005). The highest concentrations were found in livers from cod. In liver samples from flounder, SCCPs (C<sub>10</sub>-C<sub>13</sub>) were found in the range 99-221 ng/g f.w. and MCCPs (C<sub>14</sub>-C<sub>17</sub>) in the range 31-206 ng/g f.w. Chlorinated Paraffins have also been determined in muscle tissue from herring and perch sampled in Swedish lakes and along the Swedish coast, but concentrations were below the detection limit (< 2 ng/g f.w.) in all of the samples (Swedish Environment Protection Agency, 2006).

In previous studies concentrations of MCCPs have been found in the same range or higher compared to concentrations of SCCPs (Oehme *et al.*, 2005; Reth *et al.*, 2005). This pattern, reflecting the wider use of MCCPs, has also been found in sediments. Concentrations of MCCPs 1.7-2.4 times higher compared to SCCPs have been found in sediment samples from the south western Baltic Sea (Hüttig and Oehme, 2005). No clear explanations to the divergence regarding concentrations (level and distribution between SCCPs and MCCPs) compared to previous results can be found.

PNEC-values in prey tissue for the protection of predators from secondary poisoning are 16600 ng/g f.w. for SCCPs and 170 ng/g f.w. for MCCPs (EU-RAR 1999; EU-RAR 2005). Concentrations found in liver tissue in the present study were below these values.

## 5.8 $\alpha$ - and $\beta$ -Endosulfan

$\alpha$ - and  $\beta$ -endosulfan was not detected in any of the fish samples in this study. However, endosulfan sulphate was detected in all samples except from the two samples collected in Latvia. In general, endosulfan sulphate was detected in higher concentrations in herring (range < 0.01-0.12 ng/g f.w.) compared to perch and flounder (range < 0.01-0.022 ng/g f.w.) when all sites were compared. No differences in concentrations between sites, geographical or between affected and background sites, could be seen.

Reported measurements of endosulfan in biota are rare. Falandysz *et al.* (2001) analyzed the soft tissue of blue mussel, crab and fish collected from different sites in the Gulf of Gdańsk, but endosulfan was not found. In the Swedish national screening program from 2004 (Palm-Cousins *et al.*, 2005) samples of herring from six coastal sites were used to determine background levels of endosulfan in biota, but concentrations were below LOQ, endosulfan sulphate was found in one fish sample from the northern Uppland (Åland Sea) (7.7 ng/g lipid weight).  $\alpha$ -endosulfan has previously been detected at a level of 0.2-0.5 ng/g in herring (HELCOM, 2009).

Endosulfan is in general not found in water samples in the Baltic sea but endosulfan sulphate has been detected in fish and also in sediment (HELCOM, 2009). Endosulfan sulphate is similarly toxic

as endosulfan. PNEC-values for endosulfan (including endosulfan sulphate) in biota, in prey for the protection of predators from secondary poisoning and in fishery products for the protection of human health, are set to 1000 ng/g prey tissue and 365 ng/g fishery product, respectively (HELCOM, 2009). All concentrations of endosulfan sulphate found in this study are lower than these PNEC-values.

## 6 Conclusions

Of the eight substances or substance classes included in the present screening study six of them were found above LOQ, i.e. organic tin compounds, PBDEs, PFAS, nonylphenol, chlorinated paraffins and endosulfan (endosulfan sulphate). Substances that occurred in fish samples from all sampling sites were; TBT, PBDEs (BDE 47 & BDE 100), PFAS (PFOS), chlorinated paraffins (SCCP), and endosulfan (endosulfan sulphate). Additionally, bisphenol A was found in fish from almost all sampling sites.

No obvious differences in concentrations could be seen between the sampling sites classified as background areas and affected areas. Further, no clear general differences between affected sites could be seen. The highest concentrations of organic tin compounds were found in fish from the Polish sampling sites (site I and J) and the Estonian sampling site in the Gulf of Finland (site A). For PBDEs, the highest concentrations (on a fresh weight basis) were found in Gulf of Gdansk (site I) and outside the Lithuanian coast (site G and H). Concentrations of most substances were in the lower range in the Gulf of Riga (sampling sites C1, C2, E and F) compared to the other areas.

Concentrations found for the different substances were lower or in the same range as previously reported from other areas of the Baltic Sea, i.e. the eastern Baltic Sea environment does not seem to be more polluted.

However, for TBT the concentrations in several fish muscle samples were close to or above the PNEC value estimated for the protection of human health considering consumption of fishery products. Additionally, PFOS levels in fish liver exceeded the PNEC-value regarding secondary poisoning of predators in six samples, but PFOS levels in fish muscle were not measured in this study.

Fish is an appropriate matrix for monitoring of most of the substances included in the present study. However, for NP, OP and their ethoxylates water is probably a more appropriate matrix. 4-NP were found in six of nine water samples but only in two out of 23 fish samples.

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## Appendix A. Sample characteristics and results

Table A1. Sampling site information including sampling dates and coordinates.

Sample ID	Country	Sampling site		Matrix	Species	Sampling date	Coordinates (RT90)
MR 7423	Estonia	A	Coastal area near Sillamäe, eastern Gulf of Finland (affected)	fish	Perch	07-08-2008	6648936; 2173812
MR 7477	Estonia	A	Coastal area near Sillamäe, eastern Gulf of Finland (affected)	fish	Herring	05-10-2008	6654430; 2150802
MR 7419	Estonia	A	Coastal area near Sillamäe, eastern Gulf of Finland (affected)	water		27-09-2008	6648936; 2173812
MR 7421	Estonia	A	Coastal area near Sillamäe, eastern Gulf of Finland (affected)	water		27-09-2008	6648936; 2173812
MR 7429	Estonia	B	Western coast of Saaremaa Island (background)	fish	Perch	27-08-2008	6498501; 1865357
MR 7425	Estonia	B	Western coast of Saaremaa Island (background)	water		28-09-2008	6498501; 1865357
MR 7427	Estonia	B	Western coast of Saaremaa Island (background)	water		28-09-2008	6498501; 1865357
MR 7437	Estonia	C2	Outside of Pärnu Bay in Northern Gulf of Riga (affected)	fish	Herring	09-09-2008	6464522; 1924751
MR 7435	Estonia	C1	Coastal area in Pärnu Bay in Northern Gulf of Riga (affected)	fish	Perch	23-09-2008	6503292; 2005699
MR 7431	Estonia	C1	Coastal area in Pärnu Bay in Northern Gulf of Riga (affected)	water		23-09-2008	6503292; 2005699
MR 7433	Estonia	C1	Coastal area in Pärnu Bay in Northern Gulf of Riga (affected)	water		23-09-2008	6503292; 2005699
MR 7442	Estonia	D	Coastal area in western Gulf of Finland (slightly affected)	fish	Flounder	09-08-2008	6594959; 1938563
MR 7444	Estonia	D	Coastal area in western Gulf of Finland (slightly affected)	fish	Herring	23-08-2008	6605592; 1946794
MR 7438	Estonia	D	Coastal area in western Gulf of Finland (slightly affected)	water		26-09-2008	6594959; 1938563
MR 7440	Estonia	D	Coastal area in western Gulf of Finland (slightly affected)	water		26-09-2008	6594959; 1938563
MR 7355	Latvia	E	Central Gulf of Riga (affected)	fish	Herring	28-07-2008	6363744; 1954831
MR 7354	Latvia	F	Southern Gulf of Riga near River Daugava (affected)	fish	Perch	18-09-2008	6354727; 1996653
MR 7359	Latvia	F	Gulf of Riga, near River Daugava (affected)	water		18-09-2008	6354727; 1996653
MR 7357	Latvia	F	Gulf of Riga, near River Daugava (affected)	water		18-09-2008	6354727; 1996653
MR 7522	Lithuania	G	Coastal area north from Klaipeda (affected), sample 1	fish	Flounder	10-09-2008	6199969; 1828614
MR 7523	Lithuania	G	Coastal area north from Klaipeda (affected), sample 2	fish	Flounder	10-09-2008	6199969; 1828614
MR 7524	Lithuania	G	Coastal area north from Klaipeda (affected), sample 3	fish	Flounder	10-09-2008	6199969; 1828614
MR 7526	Lithuania	G	Coastal area north from Klaipeda (affected), sample 1	fish	Herring	10-09-2008	6199969; 1828614
MR 7527	Lithuania	G	Coastal area north from Klaipeda (affected), sample 2	fish	Herring	10-09-2008	6199969; 1828614
MR 7528	Lithuania	G	Coastal area north from Klaipeda (affected), sample 3	fish	Herring	10-09-2008	6199969; 1828614
MR 7318	Lithuania	G	Coastal area north from Klaipeda (affected)	water		20-08-2008	6196421; 1828918
MR 7320	Lithuania	G	Coastal area north from Klaipeda (affected)	water		20-08-2008	6196421; 1828918
MR 7514	Lithuania	H	Open sea area north-east from Klaipeda (affected)	fish	Flounder	11-09-2008	6206143; 1818578
MR 7515	Lithuania	H	Open sea area north-east from Klaipeda (affected)	fish	Herring	11-09-2008	6206143; 1818578

Sample ID	Country	Sampling site		Matrix	Species	Sampling date	Coordinates (RT90)
MR 7322	Lithuania	H	Open sea area north-east from Klaipeda (affected)	water		20-08-2008	6204060; 1783795
MR 7324	Lithuania	H	Open sea area north-east from Klaipeda (affected)	water		20-08-2008	6204060; 1783795
MR 7449	Poland	I	Gulf of Gdansk, near coastline (affected)	fish	Herring	01-10-2008	6040843; 1681727
MR 7450	Poland	I	Gulf of Gdansk, near coastline (affected)	fish	Flounder	01-10-2008	6040843; 1681727
MR 7445	Poland	I	Gulf of Gdansk, near coastline (affected)	water		30-09-2008	6040843; 1681727
MR 7447	Poland	I	Gulf of Gdansk, near coastline (affected)	water		30-09-2008	6040843; 1681727
MR 7242	Poland	J	Szczecin Lagoon (affected)	water		09-09-2008	5960284; 1404586
MR 7246	Poland	J	Szczecin Lagoon (affected)	fish	Perch	09-09-2008	5960284; 1404586
MR 7247	Poland	J	Szczecin Lagoon (affected)	fish	Flounder	09-09-2008	5960284; 1404586
MR 7244	Poland	J	Szczecin Lagoon (affected)	water		09-09-2008	5960284; 1404586
MR 7520	Sweden	K	Utlängen, outside the Blekinge (background)	fish	Herring	13-10-2008	6202900; 1498900
MR 7521	Sweden	K	Utlängen, outside the Blekinge (background)	fish	Flounder	13-10-2008	6202900; 1498900

Table A2. Physiological data for the fish samples. Length, weight, Condition factors (Cf) and Liver somatic indexes (LSI) are average values.

Sample ID	Country	Sampling site	Species	n	Length (cm) ±SD	Weight (g) ±SD	Cf ±SD	LSI (%) ±SD	% Fat <sup>a</sup> muscle	% Fat <sup>b</sup> muscle	% Fat <sup>a</sup> liver	Comment
MR 7477	Estonia	A Coastal area near Sillamäe	Herring	20	13.8±0.44	18.16±1.77	0.62±0.05	0.81±0.28	2.68		x	liver for 1 ind. missing
MR 7423	Estonia	A Coastal area near Sillamäe	Perch	15	18.3±0.90	74.58±9.04	1.14±0.07	1.36±0.21	0.61	0.92	5.57	
MR 7429	Estonia	B Western coast of Saaremaa Island	Perch	15	17.9±1.03	75.19±13.15	1.18±0.05	1.22±0.31	0.68		5.1	
MR 7437	Estonia	C2 Outside of Pärnu Bay	Herring	20	13.8±0.26	18.15±1.15	0.64±0.04	0.72±0.13	3.00		x	
MR 7435	Estonia	C1 Coastal area in Pärnu Bay	Perch	15	17.9±1.38	70.47±17.92	1.05±0.10	1.63±0.54	0.87		4.42	
MR 7442	Estonia	D Coastal area in western Gulf of Finland	Flounder	10	27.3±1.62	206.83±33.63	0.97±0.08	2.27±0.53	0.83		10.1	
MR 7444	Estonia	D Coastal area in western Gulf of Finland	Herring	20	14.2±0.66	19.85±2.00	0.65±0.04	1.05±0.19	2.53		x	
MR 7355	Latvia	E Central Gulf of Riga	Herring	21	12.3±0.75	14.25±2.12	0.69±0.05	1.14±0.28	3.52		x	
MR 7354	Latvia	F near River Daugava	Perch	23	15.7±0.84	51.11±8.92	1.21±0.08	1.44±0.33	0.41		7.12	
MR 7522	Lithuania	G Coastal area north from Klaipeda, sample 1	Flounder	13	19.7±1.38	79.17±15.02	0.97±0.17	1.68±0.55	0.71		3.9	3 small rotten ind. not dissected
MR 7523	Lithuania	G Coastal area north from Klaipeda, sample 2	Flounder	15	18.5±1.81	68.40±17.03	1.03±0.21	1.69±0.40	0.73		3.6	
MR 7524	Lithuania	G Coastal area north from Klaipeda, sample 3	Flounder	16	18.7±2.33	72.33±24.61	1.01±0.13	1.85±0.47	0.64		3.2	
MR 7526	Lithuania	G Coastal area north from Klaipeda, sample 1	Herring	12	23.3±2.57	103.31±37.51	0.70±0.10	1.53±0.36	3.46		9	3 rotten ind. not dissected
MR 7527	Lithuania	G Coastal area north from Klaipeda, sample 2	Herring	9	22.1±2.98	92.46±28.36	0.79±0.12	1.27±0.32	4.57	4.40	11.5	5 rotten ind. not dissected
MR 7528	Lithuania	G Coastal area north from Klaipeda, sample 3	Herring	10	22.6±3.10	96.65±28.25	0.76±0.11	1.47±0.34	2.66		7.19	
MR 7514	Lithuania	H Open sea area north-east from Klaipeda	Flounder	11	17.4±1.57	64.22±15.64	1.15±0.14	1.73±0.57	0.65	0.94	6.4	
MR 7515	Lithuania	H Open sea area north-east from Klaipeda	Herring	9	17.7±4.47	56.71±48.75	0.78±0.11	1.35±0.38	4.29	4.91	10	Liver from 1 ind. missing, half fish rotten. 2 rotten not dissected
MR 7450	Poland	I Gulf of Gdansk	Flounder	12	31.9±1.56	401.17±28.66	1.18±0.15	2.25±0.46	1.31		16.4	
MR 7449	Poland	I Gulf of Gdansk	Herring	21	22.7±1.45	89.33±16.48	0.66±0.08	0.91±0.37	5.33		9.4	
MR 7247	Poland	J Szczecin Lagoon	Flounder	12	22.1±1.93	129.42±42.98	1.12±0.12	1.07±0.33	0.44	1.05	10.3	
MR 7246	Poland	J Szczecin Lagoon	Perch	22	18.1±1.10	80.65±16.19	1.21±0.12	1.21±0.38	0.59	0.94	7	
MR 7521	Sweden	K Utlängan	Flounder	10	25.3±2.83	169.49±62.00	0.94±0.10	1.85±0.51	0.91		6.3	
MR 7520	Sweden	K Utlängan	Herring	10	19.1±1.58	48.07±16.07	0.62±0.05	1.48±0.36	1.84		5.6	

<sup>a</sup>Extractable lipids method<sup>b</sup>Total lipids method (Jensen *et al.*, 2003)

x Sample amount too small for liver fat analysis

Table A3. Organic tin compounds in fish (ng/g f.w.), &lt; indicate concentrations below LOQ.

Sample ID	Country	Sampling site	Species	MBT	DBT	TBT	MPhT	DPhT	TPhT	MOT	DOT
MR 7477	Estonia	A Coastal area near Sillamäe	Herring	<20	2.6	34	<0.8	<0.91	<0.1	<0.4	<0.4
MR 7423	Estonia	A Coastal area near Sillamäe	Perch	<1	<1.5	2.5	<0.8	<1	<0.1	<0.4	<0.4
MR 7429	Estonia	B Western coast of Saaremaa Island	Perch	<1	<1.3	<2	<0.8	3.1	<0.1	<0.4	<0.4
MR 7437	Estonia	C2 Outside of Pärnu Bay	Herring	<1	<1.4	2.6	<0.8	<1	<0.1	<0.4	<0.4
MR 7435	Estonia	C1 Coastal area in Pärnu Bay	Perch	<1	<1.2	<2	<0.8	1.5	<0.1	<0.4	<0.4
MR 7442	Estonia	D Coastal area in western Gulf of Finland	Flounder	<10	<1.3	<2	<0.8	6.5	<0.1	<0.4	<0.4
MR 7444	Estonia	D Coastal area in western Gulf of Finland	Herring	<10	<1.3	7.9	<0.8	<0.97	<0.1	<0.4	<0.4
MR 7355	Latvia	E Central Gulf of Riga	Herring	<1	<1.2	4.8	<0.8	2.9	<0.1	<0.4	<0.4
MR 7354	Latvia	F near River Daugava	Perch	<1	<1.5	6.9	<0.8	1.5	<0.1	<0.4	<0.4
MR 7522	Lithuania	G Coastal area north from Klaipeda, sample 1	Flounder	<1	<1.3	<2	<0.8	2.3	<0.1	<0.4	<0.4
MR 7523	Lithuania	G Coastal area north from Klaipeda, sample 2	Flounder	<1	<1.3	<2	<0.8	3	<0.1	<0.4	<0.4
MR 7524	Lithuania	G Coastal area north from Klaipeda, sample 3	Flounder	<30	2.1	<2	<0.8	3.4	<0.1	<0.4	<0.4
MR 7526	Lithuania	G Coastal area north from Klaipeda, sample 1	Herring	<1	<1.3	6.4	<0.8	4.4	<0.1	<0.4	<0.4
MR 7527	Lithuania	G Coastal area north from Klaipeda, sample 2	Herring	<15	<1.3	<2	<0.8	<0.9	<0.1	<0.4	<0.4
MR 7528	Lithuania	G Coastal area north from Klaipeda, sample 3	Herring	<1	<1.3	4.2	<0.8	<0.96	<0.1	<0.4	<0.4
MR 7514	Lithuania	H Open sea area north-east from Klaipeda	Flounder	<10	<1.3	<2	<0.8	3.3	<0.1	<0.4	<0.4
MR 7515	Lithuania	H Open sea area north-east from Klaipeda	Herring	<2	<1.3	3.1	<0.8	4.6	<0.1	<0.4	<0.4
MR 7450	Poland	I Gulf of Gdansk	Flounder	<25	8.2	15	<0.8	24	<0.1	<0.4	<0.4
MR 7449	Poland	I Gulf of Gdansk	Herring	<40	<1.3	14	<0.8	<1.4	<0.1	<0.4	<0.4
MR 7247	Poland	J Szczecin Lagoon	Flounder	<1	<1.5	9.8	<0.8	1.2	<0.1	<0.4	<0.4
MR 7246	Poland	J Szczecin Lagoon	Perch	<1	1.8	35	<0.8	<1	<0.1	<0.4	<0.4
MR 7521	Sweden	K Utlängan	Flounder	<1	<1.3	<2	<0.8	3.4	<0.1	<0.4	<0.4
MR 7520	Sweden	K Utlängan	Herring	<2	<1.3	8.5	<0.8	<0.99	<0.1	<0.4	<0.4

Table A4. Brominated flame retardants in fish muscle (ng/g f.w.), < indicate concentrations below LOQ.

Sample ID	Country	Sampling site	Species	BDE-47	BDE-85	BDE-99	BDE-100	BDE-138	BDE-153	BDE-154	BDE-183	BDE-197	BDE-201	BDE-202	BDE-209	HBCDD
MR 7477	Estonia	A Coastal area near Sillamäe	Herring	0.060	< 0.01	0.034	0.024	< 0.01	< 0.01	< 0.01	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7423	Estonia	A Coastal area near Sillamäe	Perch	0.013	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7429	Estonia	B Western coast of Saaremaa Island	Perch	0.035	< 0.01	< 0.01	0.015	< 0.01	< 0.01	0.011	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7437	Estonia	C2 Outside of Pärnu Bay	Herring	0.075	< 0.01	0.032	0.032	< 0.01	< 0.01	0.021	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7435	Estonia	C1 Coastal area in Pärnu Bay	Perch	0.015	< 0.01	0.015	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7442	Estonia	D Coastal area in western Gulf of Finland	Flounder	0.019	< 0.01	< 0.01	0.012	< 0.01	< 0.01	< 0.01	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7444	Estonia	D Coastal area in western Gulf of Finland	Herring	0.065	< 0.01	0.028	0.025	< 0.01	< 0.01	< 0.01	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7355	Latvia	E Central Gulf of Riga	Herring	0.064	< 0.01	0.048	0.029	< 0.01	< 0.01	0.019	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7354	Latvia	F near River Daugava	Perch	0.018	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7522	Lithuania	G Coastal area north from Klaipeda, sample 1	Flounder	0.020	< 0.01	< 0.01	0.010	< 0.01	< 0.01	< 0.01	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7523	Lithuania	G Coastal area north from Klaipeda, sample 2	Flounder	0.021	< 0.01	< 0.01	0.010	< 0.01	< 0.01	< 0.01	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7524	Lithuania	G Coastal area north from Klaipeda, sample 3	Flounder	0.014	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7526	Lithuania	G Coastal area north from Klaipeda, sample 1	Herring	0.18	< 0.01	0.036	0.11	< 0.01	< 0.01	0.038	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7527	Lithuania	G Coastal area north from Klaipeda, sample 2	Herring	0.092	< 0.01	0.024	0.046	< 0.01	< 0.01	0.021	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7528	Lithuania	G Coastal area north from Klaipeda, sample 3	Herring	0.15	< 0.01	0.031	0.11	< 0.01	< 0.01	0.028	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7514	Lithuania	H Open sea area north-east from Klaipeda	Flounder	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7515	Lithuania	H Open sea area north-east from Klaipeda	Herring	0.26	0.011	0.054	0.15	< 0.01	0.013	0.058	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7450	Poland	I Gulf of Gdansk	Flounder	0.046	< 0.01	0.014	0.019	< 0.01	< 0.01	< 0.01	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7449	Poland	I Gulf of Gdansk	Herring	0.29	0.015	0.10	0.13	< 0.01	0.016	0.079	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7247	Poland	J Szczecin Lagoon	Flounder	0.013	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7246	Poland	J Szczecin Lagoon	Perch	0.011	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7521	Sweden	K Utlängan	Flounder	0.038	< 0.01	< 0.01	0.011	< 0.01	< 0.01	< 0.01	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
MR 7520	Sweden	K Utlängan	Herring	0.092	< 0.01	0.029	0.050	< 0.01	< 0.01	0.028	< 0.01	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1

Table A5. Brominated flame retardants in fish muscle (ng/g l.w.), < indicate concentrations below LOQ.

Sample ID	Country	Sampling site	Species	BDE-47	BDE-85	BDE-99	BDE-100	BDE-138	BDE-153	BDE-154	BDE-183	BDE-197	BDE-201	BDE-202	BDE-209	HBCDD
MR 7477	Estonia	A Coastal area near Sillamäe	Herring	2.2	< 0.37	1.3	0.90	< 0.37	< 0.37	< 0.37	< 0.37	< 3.7	< 3.7	< 3.7	< 3.7	< 3.7
MR 7423	Estonia	A Coastal area near Sillamäe	Perch	2.2	< 1.6	< 1.6	< 1.6	< 1.6	< 1.6	< 1.6	< 1.6	< 16	< 16	< 16	< 16	< 16
MR 7429	Estonia	B Western coast of Saaremaa Island	Perch	5.2	0.3	< 1.5	2.2	< 1.5	< 1.5	1.6	< 1.5	< 15	< 15	< 15	< 15	< 15
MR 7437	Estonia	C2 Outside of Pärnu Bay	Herring	2.5	< 1.2	1.1	1.1	< 1.2	< 1.2	0.71	< 1.2	< 12	< 12	< 12	< 12	< 12
MR 7435	Estonia	C1 Coastal area in Pärnu Bay	Perch	1.7	< 1.2	1.7	0.84	< 1.2	< 1.2	< 1.2	< 1.2	< 12	< 12	< 12	< 12	< 12
MR 7442	Estonia	D Coastal area in western Gulf of Finland	Flounder	2.3	< 1.2	< 1.2	1.4	< 1.2	< 1.2	< 1.2	< 1.2	< 12	< 12	< 12	< 12	< 12
MR 7444	Estonia	D Coastal area in western Gulf of Finland	Herring	2.6	< 0.40	1.1	1.0	< 0.40	< 0.40	< 0.40	< 0.40	< 4.0	< 4.0	< 4.0	< 4.0	< 4.0
MR 7355	Latvia	E Central Gulf of Riga	Herring	1.8	< 0.28	1.4	0.83	< 0.28	0.15	0.55	< 0.28	< 2.8	< 2.8	< 2.8	< 2.8	< 2.8
MR 7354	Latvia	F near River Daugava	Perch	4.3	< 2.4	< 2.4	< 2.4	< 2.4	< 2.4	< 2.4	< 2.4	< 24	< 24	< 24	< 24	< 24
MR 7522	Lithuania	G Coastal area north from Klaipeda, sample 1	Flounder	2.8	< 1.4	< 1.4	1.5	< 1.4	< 1.4	< 1.4	< 1.4	< 14	< 14	< 14	< 14	< 14
MR 7523	Lithuania	G Coastal area north from Klaipeda, sample 2	Flounder	2.9	< 1.4	< 1.4	1.3	< 1.4	< 1.4	< 1.4	< 1.4	< 14	< 14	< 14	< 14	< 14
MR 7524	Lithuania	G Coastal area north from Klaipeda, sample 3	Flounder	2.2	< 1.6	< 1.6	< 1.6	< 1.6	< 1.6	< 1.6	< 1.6	< 16	< 16	< 16	< 16	< 16
MR 7526	Lithuania	G Coastal area north from Klaipeda, sample 1	Herring	5.2	0.25	1.1	3.2	< 0.30	< 0.30	1.1	< 0.30	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0
MR 7527	Lithuania	G Coastal area north from Klaipeda, sample 2	Herring	2.0	0.069	0.5	1.0	< 0.22	< 0.22	0.46	< 0.22	< 2.2	< 2.2	< 2.2	< 2.2	< 2.2
MR 7528	Lithuania	G Coastal area north from Klaipeda, sample 3	Herring	5.5	0.24	1.2	4.0	< 0.38	< 0.38	1.1	< 0.38	< 3.8	< 3.8	< 3.8	< 3.8	< 3.8
MR 7514	Lithuania	H Open sea area north-east from Klaipeda	Flounder	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 15	< 15	< 15	< 15	< 15
MR 7515	Lithuania	H Open sea area north-east from Klaipeda	Herring	6.1	0.25	1.3	3.5	< 0.23	0.30	1.3	< 0.23	< 2.3	< 2.3	< 2.3	< 2.3	< 2.3
MR 7450	Poland	I Gulf of Gdansk	Flounder	3.5	< 0.76	1.1	1.4	< 0.76	< 0.76	< 0.76	< 0.76	< 7.6	< 7.6	< 7.6	< 7.6	< 7.6
MR 7449	Poland	I Gulf of Gdansk	Herring	5.4	0.28	1.9	2.5	< 0.19	0.31	1.5	< 0.19	< 1.9	< 1.9	< 1.9	< 1.9	< 1.9
MR 7247	Poland	J Szczecin Lagoon	Flounder	2.9	< 2.3	< 2.3	< 2.3	< 2.3	< 2.3	< 2.3	< 2.3	< 23	< 23	< 23	< 23	< 23
MR 7246	Poland	J Szczecin Lagoon	Perch	1.8	< 1.7	< 1.7	< 1.7	< 1.7	< 1.7	< 1.7	< 1.7	< 17	< 17	< 17	< 17	< 17
MR 7521	Sweden	K Utlängan	Flounder	4.2	< 1.1	< 1.1	1.2	< 1.1	< 1.1	< 1.1	< 1.1	< 11	< 11	< 11	< 11	< 11
MR 7520	Sweden	K Utlängan	Herring	5.0	< 0.54	1.6	2.7	< 0.54	< 0.54	1.5	< 0.54	< 5.4	< 5.4	< 5.4	< 5.4	< 5.4

Table A6. Perfluorinated substances in water (ng/l), < indicate concentrations below LOQ.

Sample ID	Country	Sampling site	6:2 FTS	PFOSA	PFBS	PFHxS	PFOS	PFDcS	PFBA	PFHxA	PFHpA	PFOA	PFNA	PFDcA	PFUnA
MR 7421	Estonia	A Coastal area near Sillamäe	<3	<0.2	<0.4	<0.3	<1.0	<0.2	<2.0	<2.0	<4.0	<5	<2.0	<4.0	<2.0
MR 7427	Estonia	B Western coast of Saaremaa Island	<3	<0.2	<0.4	<0.3	<1.0	<0.2	<2.0	<2.0	<4.0	<5	<2.0	<4.0	<2.0
MR 7433	Estonia	C2 Coastal area in Pärnu Bay	<3	<0.2	<0.4	<0.3	<1.0	<0.2	<2.0	<2.0	<4.0	<5	<2.0	<4.0	<2.0
MR 7440	Estonia	D Coastal area in western Gulf of Finland	<3	<0.2	<0.4	<0.3	<1.0	<0.2	<2.0	<2.0	<4.0	<5	<2.0	<4.0	<2.0
MR 7359	Latvia	F near river Daugava	<3	<0.2	<0.4	<0.3	<1.0	<0.2	<2.0	<2.0	<4.0	<5	<2.0	<4.0	<2.0
MR 7320	Lithuania	G Coastal area north from Klaipeda	<3	<0.2	<0.4	<0.3	<1.0	<0.2	<2.0	<2.0	<4.0	<5	<2.0	<4.0	<2.0
MR 7324	Lithuania	H Open sea area north-east from Klaipeda	<3	<0.2	<0.4	<0.3	<1.0	<0.2	<2.0	<2.0	<4.0	<5	<2.0	<4.0	<2.0
MR 7447	Poland	I Gulf of Gdansk	<3	<0.2	<0.4	<0.3	<1.0	<0.2	<2.0	<2.0	<4.0	<5	<2.0	<4.0	<2.0
MR 7244	Poland	J Szczecin Lagoon	<10	<1.1	<1.0	<1.0	2.9	<0.6	<2.0	<2.3	<4.0	6.0	<3.0	<4.0	<2.0

Table A7. Perfluorinated substances in fish liver (ng/g f.w.), < indicate concentrations below LOQ.

Sample ID	Country	Sampling site	Species	6:2 FTS	PFOSA	PFBS	PFHxS	PFOS	PFDCS	PFBA	PFHxA	PFHpA	PFOA	PFNA	PFDCa	PFUnA
MR 7477	Estonia	A Coastal area near Sillamäe	Herring	< 1.4	< 0.4	< 0.2	< 0.1	7.4	< 0.1	0.23	< 2.3	< 1.8	<2.6	<1.7	<2.0	<1.5
MR 7423	Estonia	A Coastal area near Sillamäe	Perch	< 2.5	<0.8	< 0.2	< 0.1	31	< 0.1	< 1.0	< 2.6	< 1.8	<3.1	9.9	<2.8	3.6
MR 7429	Estonia	B Western coast of Saaremaa Island	Perch	< 1.7	< 0.3	< 0.8	0.18	48	< 0.1	< 0.9	< 1.9	< 2.5	<3.2	9.1	<2.3	3.3
MR 7437	Estonia	C2 Outside of Pärnu Bay	Herring	< 2.0	< 0.5	< 0.4	< 0.2	4.3	< 0.2	< 1.8	< 4.4	< 4.7	<3.9	<3.2	<4.2	<2.6
MR 7435	Estonia	C1 Coastal area in Pärnu Bay	Perch	< 0.8	< 0.1	< 0.2	< 0.07	11	< 0.07	< 0.6	< 1.4	< 1.9	<2.3	3.4	<1.4	0.55
MR 7442	Estonia	D Coastal area in western Gulf of Finland	Flounder	< 0.6	< 0.2	< 0.1	0.10	7.1	< 0.07	< 0.4	< 1.3	< 1.2	<1.2	1.6	<1.2	0.46
MR 7444	Estonia	D Coastal area in western Gulf of Finland	Herring	< 1.7	< 0.3	< 0.2	0.24	10	< 0.2	< 1.1	< 3.0	< 3.1	<3.3	<2.2	<3.1	<2
MR 7355	Latvia	E Central Gulf of Riga	Herring	< 1.6	< 0.6	< 0.3	< 0.2	7.3	< 0.2	< 1.9	< 4.6	< 3.5	<4.1	<3.0	<3.8	<3
MR 7354	Latvia	F near River Daugava	Perch	< 3.2	< 0.9	< 0.4	< 0.2	24	< 0.2	< 1.5	< 3.1	< 3.8	<5.1	5.4	<3.7	2.1
MR 7522	Lithuania	G Coastal area north from Klaipeda, sample 1	Flounder	< 0.7	< 0.6	< 0.1	0.40	11	< 0.07	< 0.5	< 1.5	< 1.6	<1.8	1.7	<1.3	1.5
MR 7523	Lithuania	G Coastal area north from Klaipeda, sample 2	Flounder	< 1.0	< 0.8	< 0.2	0.59	15	< 0.1	< 0.7	< 2.0	< 1.7	<2.1	1.8	<2.1	1.0
MR 7524	Lithuania	G Coastal area north from Klaipeda, sample 3	Flounder	< 1.7	< 0.5	< 0.2	1.1	20	< 0.1	< 1.0	< 2.3	< 2.9	<3.1	<2.7	<2.3	<2.4
MR 7526	Lithuania	G Coastal area north from Klaipeda, sample 1	Herring	< 1.1	< 0.2	< 0.2	0.39	10	< 0.1	< 0.8	< 2.6	< 1.7	<3.3	<1.8	<1.8	<1.5
MR 7527	Lithuania	G Coastal area north from Klaipeda, sample 2	Herring	< 0.6	< 0.3	< 0.1	0.25	6.5	< 0.07	< 0.5	< 1.3	< 0.9	<1.5	<1.4	<1.5	<0.9
MR 7528	Lithuania	G Coastal area north from Klaipeda, sample 3	Herring	< 0.5	< 0.1	< 0.1	0.23	6.1	< 0.05	< 0.5	< 1.3	< 1.2	<1.3	<1.4	<2.6	<0.8
MR 7514	Lithuania	H Open sea area north-east from Klaipeda	Flounder	< 0.8	< 0.6	< 0.1	0.26	6.9	0.06	0.45	0.78	2.0	<1.9	3.5	<2.0	<1.2
MR 7515	Lithuania	H Open sea area north-east from Klaipeda	Herring	< 1.3	1.8	< 0.2	0.30	11	< 0.1	< 1.1	< 2.0	< 2.0	<2.7	<2.4	<2.5	<2
MR 7450	Poland	I Gulf of Gdansk	Flounder	< 0.7	< 0.2	< 0.1	0.16	6.8	< 0.08	< 0.5	< 1.6	< 1.3	<1.6	<1.3	<4.5	<0.9
MR 7449	Poland	I Gulf of Gdansk	Herring	< 0.5	< 0.2	< 0.1	0.19	5.5	< 0.05	< 0.6	< 1.0	< 1.0	<1.3	<1.2	<1.0	<0.7
MR 7247	Poland	J Szczecin Lagoon	Flounder	< 1.3	< 0.5	< 0.2	0.45	48	0.57	< 1.0	< 2.3	< 2.3	<3.1	9.1	12	15
MR 7246	Poland	J Szczecin Lagoon	Perch	< 1.1	< 0.4	< 0.2	0.20	61	< 0.09	< 0.9	< 2.3	< 2.3	<2.4	6.4	<2.3	11
MR 7521	Sweden	K Utlängan	Flounder	< 0.5	< 0.2	< 0.09	0.25	8.9	< 0.06	< 0.4	< 1.2	< 1.3	<1.2	3.3	<1.1	0.88
MR 7520	Sweden	K Utlängan	Herring	< 2.2	< 0.2	< 0.2	0.57	12	< 0.08	< 0.6	< 2.0	< 2.0	<2.9	3.8	<1.5	0.94

Table A8. Phenolic substances in water (ng/l), < indicate concentrations below LOQ.

MR	Country	Sampling site	4NP	4NP-EO1	4NP-EO2	4-t-OP	4-t-OP-EO1	4-t-OP-EO2	Bisfenol A	Triclosan
MR 7419	Estonia	A Coastal area near Sillamäe	66	<20	<10	<0.5	<0.5	<0.5	<14	<1
MR 7425	Estonia	B Western coast of Saaremaa Island	13	<20	<10	<0.5	<0.5	<0.5	<14	<1
MR 7431	Estonia	C2 Coastal area in Pärnu Bay	<10	<20	<10	<0.5	<0.5	<0.5	<14	<1
MR 7438	Estonia	D Coastal area in western Gulf of Finland	26	<20	<10	<0.5	<0.5	<0.5	<14	<1
MR 7357	Latvia	F near river Daugava	<10	<20	<10	<0.5	<0.5	<0.5	<14	<1
MR 7318	Lithuania	G Coastal area north from Klaipeda	29	<20	<10	1.2	<0.5	<0.5	<14	<1
MR 7322	Lithuania	H Open sea area north-east from Klaipeda	50	<20	<10	<0.5	<0.5	<0.5	<14	<1
MR 7445	Poland	I Gulf of Gdansk	63	<20	<10	<0.5	<0.5	<0.5	<14	<1
MR 7242	Poland	J Szczecin Lagoon	<10	<20	<10	<0.5	<0.5	<0.5	<14	<1

Table A9. Phenolic substances in fish muscle (ng/g f.w.), &lt; indicate concentrations below LOQ.

Sample ID	Country	Sampling site	Species	4NP	4NP-EO1	4NP-EO2	4-t-OP	4-t-OP-EO1	4-t-OP-EO2	Bisfenol A	Triclosan	
MR 7477	Estonia	A	Coastal area near Sillamäe	Herring	<10	<20	<10	<1	<1	<1	1.7	<1
MR 7423	Estonia	A	Coastal area near Sillamäe	Perch	<10	<20	<10	<1	<1	<1	1.2	<1
MR 7429	Estonia	B	Western coast of Saaremaa Island	Perch	<10	<20	<10	<1	<1	<1	<0.6	<1
MR 7437	Estonia	C2	Outside of Pärnu Bay	Herring	<10	<20	<10	<1	<1	<1	1.5	<1
MR 7435	Estonia	C1	Coastal area in Pärnu Bay	Perch	<10	<20	<10	<1	<1	<1	<0.6	<1
MR 7442	Estonia	D	Coastal area in western Gulf of Finland	Flounder	<10	<20	<10	<1	<1	<1	<0.6	<1
MR 7444	Estonia	D	Coastal area in western Gulf of Finland	Herring	<10	<20	<10	<1	<1	<1	<0.6	<1
MR 7355	Latvia	E	Central Gulf of Riga	Herring	<10	<20	<10	<1	<1	<1	0.6	<1
MR 7354	Latvia	F	near River Daugava	Perch	<10	<20	<10	<1	<1	<1	0.81	<1
MR 7522	Lithuania	G	Coastal area north from Klaipeda, sample 1	Flounder	12	<20	<10	<1	<1	<1	1.9	<1
MR 7523	Lithuania	G	Coastal area north from Klaipeda, sample 2	Flounder	<10	<20	<10	<1	<1	<1	3.9	<1
MR 7524	Lithuania	G	Coastal area north from Klaipeda, sample 3	Flounder	<10	<20	<10	<1	<1	<1	0.98	<1
MR 7526	Lithuania	G	Coastal area north from Klaipeda, sample 1	Herring	<10	<20	<10	<1	<1	<1	3.1	<1
MR 7527	Lithuania	G	Coastal area north from Klaipeda, sample 2	Herring	<10	<20	<10	<2	<1	<1	<0.6	<1
MR 7528	Lithuania	G	Coastal area north from Klaipeda, sample 3	Herring	<10	<20	<10	<1	<1	<1	1.5	<1
MR 7514	Lithuania	H	Open sea area north-east from Klaipeda	Flounder	<10	<20	<10	<1	<1	<1	0.95	<1
MR 7515	Lithuania	H	Open sea area north-east from Klaipeda	Herring	<10	<20	<10	<1	<1	<1	1.6	<1
MR 7450	Poland	I	Gulf of Gdansk	Flounder	<10	<20	<10	<1	<1	<1	0.67	<1
MR 7449	Poland	I	Gulf of Gdansk	Herring	<10	<20	<10	<1	<1	<1	0.96	<1
MR 7247	Poland	J	Szczecin Lagoon	Flounder	<10	<20	<10	<1	<1	<1	1.3	<1
MR 7246	Poland	J	Szczecin Lagoon	Perch	<10	<20	<10	<1	<1	<1	1.3	<1
MR 7521	Sweden	K	Utlängan	Flounder	23	<20	<10	<1	<1	<1	2.0	<1
MR 7520	Sweden	K	Utlängan	Herring	<10	<20	<10	<1	<1	<1	0.95	<1

Table A10. Chlorinated paraffins in fish liver (ng/g f.w.), < indicate concentrations below LOQ.

Sample ID	Country	Sampling site		Species	SCCP	MCCP
MR 7477	Estonia	A	Coastal area near Sillamäe	Herring	21	< 2.6
MR 7423	Estonia	A	Coastal area near Sillamäe	Perch	33	< 0.35
MR 7429	Estonia	B	Western coast of Saaremaa Island	Perch	25	15
MR 7437	Estonia	C2	Outside of Pärnu Bay	Herring	49	< 4.5
MR 7435	Estonia	C1	Coastal area in Pärnu Bay	Perch	5.2	3.9
MR 7442	Estonia	D	Coastal area in western Gulf of Finland	Flounder	31	< 2.0
MR 7444	Estonia	D	Coastal area in western Gulf of Finland	Herring	17	< 0.6
MR 7355	Latvia	E	Central Gulf of Riga	Herring	25	< 1.6
MR 7354	Latvia	F	near River Daugava	Perch	11	< 0.3
MR 7522	Lithuania	G	Coastal area north from Klaipeda, sample 1	Flounder	46	< 0.46
MR 7523	Lithuania	G	Coastal area north from Klaipeda, sample 2	Flounder	62	< 0.57
MR 7524	Lithuania	G	Coastal area north from Klaipeda, sample 3	Flounder	17	< 0.67
MR 7526	Lithuania	G	Coastal area north from Klaipeda, sample 1	Herring	19	< 1.9
MR 7527	Lithuania	G	Coastal area north from Klaipeda, sample 2	Herring	7.5	< 0.74
MR 7528	Lithuania	G	Coastal area north from Klaipeda, sample 3	Herring	6.5	< 0.30
MR 7514	Lithuania	H	Open sea area north-east from Klaipeda	Flounder	15	< 0.26
MR 7515	Lithuania	H	Open sea area north-east from Klaipeda	Herring	34	< 0.25
MR 7450	Poland	I	Gulf of Gdansk	Flounder	14	< 1.0
MR 7449	Poland	I	Gulf of Gdansk	Herring	37	< 0.49
MR 7247	Poland	J	Szczecin Lagoon	Flounder	13	< 2.8
MR 7246	Poland	J	Szczecin Lagoon	Perch	23	8.2
MR 7521	Sweden	K	Utlängan	Flounder	13	< 0.27
MR 7520	Sweden	K	Utlängan	Herring	13	< 0.35

Table A11. Chlorinated paraffins in fish liver (ng/g l.w.), < indicate concentrations below LOQ.

Sample ID	Country	Sampling site		Species	SCCP	MCCPs
MR 7477	Estonia	A	Coastal area near Sillamäe	Herring	NA <sup>a</sup>	NA <sup>a</sup>
MR 7423	Estonia	A	Coastal area near Sillamäe	Perch	590	< 6.3
MR 7429	Estonia	B	Western coast of Saaremaa Island	Perch	490	290
MR 7437	Estonia	C2	Outside of Pärnu Bay	Herring	NA <sup>a</sup>	NA <sup>a</sup>
MR 7435	Estonia	C1	Coastal area in Pärnu Bay	Perch	120	88
MR 7442	Estonia	D	Coastal area in western Gulf of Finland	Flounder	310	< 20
MR 7444	Estonia	D	Coastal area in western Gulf of Finland	Herring	NA <sup>a</sup>	NA <sup>a</sup>
MR 7355	Latvia	E	Central Gulf of Riga	Herring	NA <sup>a</sup>	NA <sup>a</sup>
MR 7354	Latvia	F	near River Daugava	Perch	150	< 4.2
MR 7522	Lithuania	G	Coastal area north from Klaipeda, sample 1	Flounder	1200	< 12
MR 7523	Lithuania	G	Coastal area north from Klaipeda, sample 2	Flounder	1700	< 16
MR 7524	Lithuania	G	Coastal area north from Klaipeda, sample 3	Flounder	520	< 21
MR 7526	Lithuania	G	Coastal area north from Klaipeda, sample 1	Herring	210	< 21
MR 7527	Lithuania	G	Coastal area north from Klaipeda, sample 2	Herring	65	< 6.4
MR 7528	Lithuania	G	Coastal area north from Klaipeda, sample 3	Herring	90	< 4.2
MR 7514	Lithuania	H	Open sea area north-east from Klaipeda	Flounder	230	< 4.1
MR 7515	Lithuania	H	Open sea area north-east from Klaipeda	Herring	340	< 2.5
MR 7450	Poland	I	Gulf of Gdansk	Flounder	85	< 6.1
MR 7449	Poland	I	Gulf of Gdansk	Herring	390	< 5.2
MR 7247	Poland	J	Szczecin Lagoon	Flounder	130	< 27
MR 7246	Poland	J	Szczecin Lagoon	Perch	330	120
MR 7521	Sweden	K	Utlängan	Flounder	210	< 4.3
MR 7520	Sweden	K	Utlängan	Herring	230	< 6.3

<sup>a</sup>Due to low sample amounts, extractable lipids could not be determined for some samples.

For these samples, results are only presented on a fresh weight basis.

Table A12. Endosulfan in fish muscle (ng/g f.w.), < indicate concentrations below LOQ.

Sample ID	Country	Sampling site	Species	$\alpha$ -endosulfan	$\beta$ -endosulfan	Endosulfan sulphate
MR 7477	Estonia	A Coastal area near Sillamäe	Herring	< 0.2	< 0.2	0.080
MR 7423	Estonia	A Coastal area near Sillamäe	Perch	< 0.2	< 0.2	0.013
MR 7429	Estonia	B Western coast of Saaremaa Island	Perch	< 0.2	< 0.2	0.010
MR 7437	Estonia	C2 Outside of Pärnu Bay	Herring	< 0.2	< 0.2	0.075
MR 7435	Estonia	C1 Coastal area in Pärnu Bay	Perch	< 0.2	< 0.2	0.012
MR 7442	Estonia	D Coastal area in western Gulf of Finland	Flounder	< 0.2	< 0.2	0.014
MR 7444	Estonia	D Coastal area in western Gulf of Finland	Herring	< 0.2	< 0.2	0.12
MR 7355	Latvia	E Central Gulf of Riga	Herring	< 0.2	< 0.2	< 0.01
MR 7354	Latvia	F near River Daugava	Perch	< 0.2	< 0.2	< 0.01
MR 7522	Lithuania	G Coastal area north from Klaipeda, sample 1	Flounder	< 0.2	< 0.2	0.011
MR 7523	Lithuania	G Coastal area north from Klaipeda, sample 2	Flounder	< 0.2	< 0.2	0.014
MR 7524	Lithuania	G Coastal area north from Klaipeda, sample 3	Flounder	< 0.2	< 0.2	0.011
MR 7526	Lithuania	G Coastal area north from Klaipeda, sample 1	Herring	< 0.2	< 0.2	0.077
MR 7527	Lithuania	G Coastal area north from Klaipeda, sample 2	Herring	< 0.2	< 0.2	0.088
MR 7528	Lithuania	G Coastal area north from Klaipeda, sample 3	Herring	< 0.2	< 0.2	0.057
MR 7514	Lithuania	H Open sea area north-east from Klaipeda	Flounder	< 0.2	< 0.2	0.016
MR 7515	Lithuania	H Open sea area north-east from Klaipeda	Herring	< 0.2	< 0.2	0.12
MR 7450	Poland	I Gulf of Gdansk	Flounder	< 0.2	< 0.2	0.022
MR 7449	Poland	I Gulf of Gdansk	Herring	< 0.2	< 0.2	0.12
MR 7247	Poland	J Szczecin Lagoon	Flounder	< 0.2	< 0.2	0.013
MR 7246	Poland	J Szczecin Lagoon	Perch	< 0.2	< 0.2	0.011
MR 7521	Sweden	K Utlängan	Flounder	< 0.2	< 0.2	0.018
MR 7520	Sweden	K Utlängan	Herring	< 0.2	< 0.2	0.049

Table A13. Endosulfan in fish muscle (ng/g l.w.), < indicate concentrations below LOQ.

Sample ID	Country	Sampling site	Species	$\alpha$ -endosulfan	$\beta$ -endosulfan	Endosulfan sulphate
MR 7477	Estonia	A Coastal area near Sillamäe	Herring	<7.5	<7.5	3.0
MR 7423	Estonia	A Coastal area near Sillamäe	Perch	<33	<33	2.2
MR 7429	Estonia	B Western coast of Saaremaa Island	Perch	<29	<29	1.5
MR 7437	Estonia	C2 Outside of Pärnu Bay	Herring	<6.7	<6.7	2.5
MR 7435	Estonia	C1 Coastal area in Pärnu Bay	Perch	<23	<23	1.4
MR 7442	Estonia	D Coastal area in western Gulf of Finland	Flounder	<24	<24	1.7
MR 7444	Estonia	D Coastal area in western Gulf of Finland	Herring	<7.9	<7.9	4.6
MR 7355	Latvia	E Central Gulf of Riga	Herring	<5.7	<5.7	<0.3
MR 7354	Latvia	F near River Daugava	Perch	<49	<49	<2.4
MR 7522	Lithuania	G Coastal area north from Klaipeda, sample 1	Flounder	<28	<28	1.5
MR 7523	Lithuania	G Coastal area north from Klaipeda, sample 2	Flounder	<27	<27	1.9
MR 7524	Lithuania	G Coastal area north from Klaipeda, sample 3	Flounder	<31	<31	1.7
MR 7526	Lithuania	G Coastal area north from Klaipeda, sample 1	Herring	<5.8	<5.8	2.2
MR 7527	Lithuania	G Coastal area north from Klaipeda, sample 2	Herring	<4.4	<4.4	1.9
MR 7528	Lithuania	G Coastal area north from Klaipeda, sample 3	Herring	<7.5	<7.5	2.1
MR 7514	Lithuania	H Open sea area north-east from Klaipeda	Flounder	<31	<31	2.5
MR 7515	Lithuania	H Open sea area north-east from Klaipeda	Herring	<4.7	<4.7	2.7
MR 7450	Poland	I Gulf of Gdansk	Flounder	<15	<15	1.7
MR 7449	Poland	I Gulf of Gdansk	Herring	<3.8	<3.8	2.3
MR 7247	Poland	J Szczecin Lagoon	Flounder	<45	<45	2.9
MR 7246	Poland	J Szczecin Lagoon	Perch	<34	<34	1.9
MR 7521	Sweden	K Utlängan	Flounder	<22	<22	2.0
MR 7520	Sweden	K Utlängan	Herring	<11	<11	2.7

## Appendix B. Sampling manual- Analysis of selected substances in the Eastern Baltic Sea

### Precautions to be taken in advance of sampling to avoid contamination

Cosmetic formulations contain various chemicals that potentially can contaminate the samples. Do not use products such as antiperspirant, eye shadow, hair spray, or skin lotions on the day of sampling. Only specially cleaned sampling containers provided by the laboratory should be used.

To check for contamination sampling blanks are used. The sampling blank to be used for water contains MilliQ-water, the sampling blank to be used for fish sampling contains granulated diatomaceous earth. The sampling blanks should not be emptied or filled. They shall only be opened and closed at the time of sampling.

### *Equipment provided per sampling site*

2 x 1L glass bottles  
2 x 1L plastic bottles  
1 glass bottle field blank  
1 plastic bottle field blank  
1 glass jar with granulated diatomaceous earth (field blank for fish)  
Nitrile gloves  
Plastic bags  
Muffled Al-foil (packed in Al-foil)

### A. Sampling of water

Background information on water sampling sites in each country has been given in Annex 1 (Table 1).

- Arrange the sampling bottles to be used, 2x1L glass bottles and 2x1L plastic bottles (and, if the site is selected for blank sampling, 1 glass and 1 plastic sampling blank) on a clean spot on the sampling site. Put on the supplied gloves.
- Immediately before sampling open the lid of the sampling container (and the sampling blanks).
- Take water samples from 0-1 m surface layer with clean sampler, which is preferably specifically designed for water sampling (*e.g.* Ruttner sampler).
- Fill the sample container. If the Al-foil protecting the lids of the glass bottles is ruptured replace it with new Al-foil. Close the lid on the sample bottles (and sample blanks).
- Mark bottles with sample name/identity (same for all bottles from same locality).
- Put each bottle in a plastic bag.
- Fill in the sample protocol.
- Store the samples in refrigerator (5-10°C).

## B. Sampling of fish

Background information on fish sampling sites, targeted fish species and length ranges in each country has been given in Annex 1 (Tables 1 & 2). The primary target fish are Perch, Herring and Flounder but if these species are not caught are turbot, pike-perch and pike the secondary choice (Annex 1; Table 1 & 2).

Number of fish needed / sample depends on species and size. The expected need is:

Perch: 15 – 20 cm (~ 3+ - 4+ years): 15 fish

Herring: 14 – 19 cm (~ 2 - 3 years): 20 fish

Flounder: 24 – 34 cm (~ 3+ - 5+ years): 10 fish

Pike: Local estimate (~ 3+ - 5+ years): 10 fish

Pike-perch: Local estimate (~ 3+ - 4+ years): 5 fish

Turbot: Local estimate (~ 3+ - 4+ years): 5 fish

The minimum numbers of fish/ species is 10 individuals.

If fish individuals with targeted length range are not caught, fish individuals as close as possible to targeted length range will be sampled.

- Put on the supplied gloves.
- Open the lid of the sampling blank.
- Wrap each fish individually in Al-foil provided. Do not open or in any other way process fish!
- Close the lid of sampling blank.
- Put each pooled sample/the Al-foil packages in a plastic bag.
- Mark the sample with name/identity.
- Fill in the sample protocol.
- Store the samples in freezer (-18°C).

## Storage and transport

Store fish samples frozen and water samples refrigerated. Send to the laboratory as soon as possible in such a way that the samples will reach the laboratory within one day (DHL or equivalent courier services). Send samples in the same containers used for the provided sampling material, one box for fish samples and one box for water samples. Make sure to insulate glass bottles properly to avoid breakage during transport. Use dry ice, alternatively cold clamps, to keep fish samples frozen during transport. Label of content to be simply “water and fish samples”.

When sending the samples please send also an e-mail including a list specifying the samples to Mikael Remberger ([mikael.remberger@ivl.se](mailto:mikael.remberger@ivl.se)) and Karl Lilja ([karl.lilja@ivl.se](mailto:karl.lilja@ivl.se)).

## Address

IVL Swedish Environmental Research Institute  
Mikael Remberger Vallhallavägen 81; 114 23 Stockholm; Sweden.

## Analysis of selected substances in the Eastern Baltic Sea - Sample protocol

Sample name/identity	Sample type (water/fish)	Species (for fish)	Coordinates sampling site	Sampling date	Used sampling equipment	Comments
Field blank 1	water	-				
Field blank 2	water	-				
Field blank 3	Silica particles	-				

Responsible person:

Shipped to IVL:

Received at IVL:

### Address

IVL Swedish Environmental Research Institute  
 Mikael Remberger  
 Valhallavägen 81  
 114 23 Stockholm  
 Sweden

When sending the samples, please send an e-mail including a list specifying the samples to Mikael Remberger ([mikael.remberger@ivl.se](mailto:mikael.remberger@ivl.se)) and Karl Lilja ([karl.lilja@ivl.se](mailto:karl.lilja@ivl.se)).