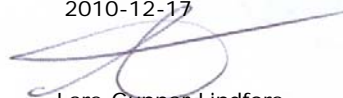


Results from the Swedish National Screening Programme 2009

Subreport 1: Bis(4-Chlorophenyl) sulfone (BCPS)

Karin Norström, Mikael Remberger, Lennart Kaj,
Per Wiklund, Eva Brorström-Lundén
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Lars-Gunnar Lindfors
Senior Adviser

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Summary A screening study has been performed concerning bis(4-Chlorophenyl) sulfone (BCPS). BCPS is a high production volume chemical and is mainly used in the polymer production. It has been detected in biota in several species from the Baltic Sea environment but the source for its detection is unknown. Air, deposition, sediment, fish, effluent and surface were sampled mainly from the Baltic sea region. BCPS was present in all fish samples (perch and herring) and in similar levels as PCB 138 and PCB 153. There was no trend in concentrations between species, country or sampling location. BCPS was detected in all three marine surface samples which may explain the bioaccumulation in biota. It was detected in one air sample in the same magnitude as individual PCB congeners and in one of the WWTP samples. This screening did not clarify the pathways of BCPS to the Baltic Sea. However, the results indicate that distribution is more waterborne rather than airborne.	
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Sammanfattning

En screeningundersökning har utförts med avseende på (4-klorofenyl)sulfon (BCPS). BCPS är en kemikalie som produceras i stora volymer och är klassad som HPVC (high production volume chemical). Det används i produktionen av termostabila polymerer för plastindustrin. Ämnet används t.ex. i mikrovågsugnar, TV-komponenter, inom livsmedelsindustrin och i medicinsk utrustning. BCPS har också tidigare använts i pesticidblandningar. Två andra klorerade och sulfoninnehållande kemikalier ingick också i denna screening, Sulphenone och Tetradifon.

BCPS har tidigare detekterats i fisk, fågel och säl från de nordiska länderna och i miljön runt Östersjön. Speciellt höga koncentrationer uppmättes då i sillgrissla från Östersjön.

Kunskapen om emissionskällor och de viktigaste spridningsvägarna för BCPS är dock begränsad. Provtagningsprogrammet har i denna studie främst fokuserats på Östersjön. Luft, deposition, sediment, fisk, utgående avloppsvatten och ytvatten har provtagits.

Resultaten visar att BCPS fanns i alla fiskprover (abborre och strömming) och att halterna var i samma nivåer som PCB 138 och PCB 153. Det fanns ingen trend i koncentrationer mellan arter, länder eller provtagningsområde. BCPS hittades också i alla ytvatten, från västkusten (Råö), urbant område (Riddarfjärden, Stockholm) och i Stockholms skärgård (Ljusterö) där halterna var högst av dessa tre platser. Detektionen i ytvatten kan förklara att BCPS förekommer i biota från Östersjön. BCPS detekterades i ett luftprov från Aspvreten och i ett avloppsvatten från Estland.

Halterna av Sulphenone och Tetradifon var under detektionsgränsen i alla provmatriser.

Denna screeningstudie kan inte förklara BCPS spridningsvägar till Östersjön. Dock indikerar resultaten att spridning via vatten är mer trolig än spridning via luft.

Summary

A screening study has been performed concerning bis(4-chlorophenyl) sulfone (BCPS). BCPS is a high production volume chemical and the main field of application of BCPS is in production of thermostable polymers for the plastic industry. The field of application is wide, e.g. in microwave ovens, TV components, food industry and medical equipment. BCPS also has a history as a pesticide. Two other chlorinated and sulfone containing compounds, Sulphenone and Tetradifon, were also included in the screening.

BCPS has previously been detected in fish, birds and seal from the Nordic and Baltic Sea environment. Especially high concentrations have been found in guillemots from the Baltic Sea.

The knowledge about emission sources and important pathways for the occurrence of BCPS in the environment is limited. The sampling programme in this study was mainly focused on the Baltic Sea environment. Air, deposition, sediment, fish, surface water as well as effluent water from waste water treatment plants were sampled.

The results from this screening showed that BCPS was present in all fish samples (perch and herring) and in similar levels as PCB 138 and PCB 153. There was no trend in concentrations between species, country or sampling location. BCPS was detected in all three marine surface water samples, from the Swedish west coast (Råö), an urban area (Riddarfjärden, Stockholm) and the Stockholm archipelago (Ljusterö). The highest concentrations occurred in the sample from Ljusterö. The occurrence in marine waters may explain the bioaccumulation of BCPS in biota from the Baltic Sea. BCPS was detected in only one air sample from the Swedish east coast (Aspvreten) in the same magnitude as individual PCB congeners and in one of the WWTP samples from Estonia.

The concentrations of Sulphenone and Tetradifon were below limit of detection in all matrices.

This screening did not clarify the pathways of BCPS to the Baltic Sea. However, the results indicate that the distribution is more waterborne rather than airborne.

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1 Introduction

As an assignment from the Swedish Environmental Protection Agency, a screening study has been performed during 2009/2010. This screening includes bis(4-chlorophenyl) sulfone (BCPS), Dechlorane Plus, UV-filters, benzothiazoles, benzenediamines and benzotriazoles. These substances/substance groups are emitted and distributed in the environment via a variety of sources, e.g. different point sources and/or diffusive sources. The overall objectives of the screening studies are to determine the concentrations of the selected substances in a variety of media in the Swedish environment, to highlight important transport pathways, and to assess the possibility of current emissions in Sweden. Table 1 shows the number of the report where individual results are presented.

Table 1. Substances / substance groups included in the screening

Substance / Substance group	Sub-report #
BCPS	1
Dechlorane Plus	2
UV-filters	3
Benzothiazoles, benzenediamines	separate report
Benzotriazoles	separate report

This sub-report concerns the screening of BCPS, which is a high production volume chemical and mainly used within polymer production. In addition, two other chlorinated and sulphone containing substances, 4-chlorodiphenyl sulfone (Sulphenone) and 2,4,4',5-tetrachlorodiphenyl sulfone (Tetradifon), were included in the screening. Polychlorinated biphenyles (PCBs) were chosen as reference substances.

The screening of benzothiazoles, benzenediamines and benzotriazoles is carried out by IVL and Umeå University in cooperation with the project ChEmiTecs, Organic Chemicals Emitted from Technosphere Articles (www.chemitecs.se).

2 Chemical properties, fate and toxicity

2.1 Properties and fate

BCPS, Sulphenone and Tetradifon are all chlorinated and sulfone containing compounds, see Figure 1. They are neutral and have the potential to bioaccumulate. Due to the sulfone group they are acting as Lewis basis which is utilized in the analytical methodology (Chapter 6.2.1). Their CAS-number, physical and chemical properties are listed in Table 2. Pure BCPS is a crystalline substance at room temperature.

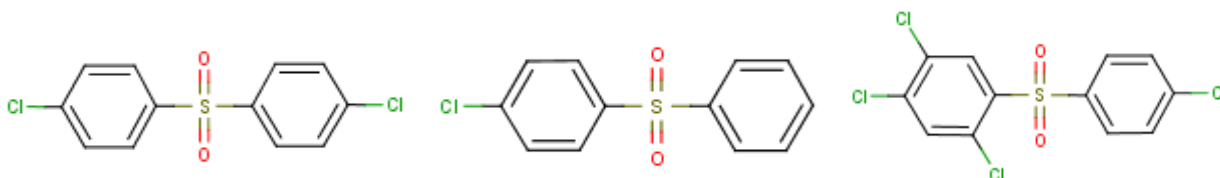


Figure 1. Molecular structure of BCPS, Sulphenone and Tetradifon

Table 2. The physical and chemical properties (ChemIDplus Lite).

	Bis(4-Chlorophenyl) sulfone (BCPS)	4-Chlorodiphenyl sulfone (Sulphenone)	2,4,4',5-Tetrachlorodiphenyl sulfone (Tetradifon)
CAS no.	80-07-9	80-00-2	116-29-0
Molecular formula	C ₁₂ H ₈ SO ₂ Cl ₂	C ₁₂ H ₉ SO ₂ Cl	C ₁₂ H ₆ SO ₂ Cl ₄
Molecular weight (g/mol)	287.16	252.72	
Melting point	147.9 °C	94 °C	148-189 °C
Boiling point	397 °C		
Density	8 g/m ³		
Water solubility		38.2 mg/L (20 °C)	0.078 mg/L
Log Kow	3.9	3.25	4.61

If BCPS is released to air, the estimated vapor pressure of 8.1×10^{-7} mm Hg at 25 deg. C indicates that BCPS will exist in both the vapor and particulate phases in the ambient atmosphere. Vapor-phase BCPS may be degraded in the atmosphere by reaction with photochemically produced hydroxyl radicals. However, the half-life for this reaction in air is estimated to be 27 days, why atmospheric long range transport may take place. BCPS may be removed from the atmosphere by wet and dry deposition.

If released to soil, BCPS is expected to have minor mobility based upon an estimated Koc of 7,600. The estimated Henry's Law constant of 1.4×10^{-7} atm*m³/mole indicates that volatilization from moist soil surfaces is not important. Based upon its vapor pressure, BCPS is not supposed to volatilize from dry soil surfaces.

If released to water, BCPS will most likely adsorb to suspended solids and sediment, based upon the estimated Koc. The estimated Henry's Law constant for BCPS indicates that volatilization from water surfaces will be of minor importance. Hydrolysis is not expected to be an important environmental fate process since BCPS lacks functional groups that hydrolyze under environmental conditions. The information in chapter 2.1 is gathered from Hazardous Substances Data Bank (TOXNET)

2.2 Toxicity

The U.S National Toxicology Program has performed toxicity characterization and carcinogenicity studies of BCPS (Chhabra et al. 2001). BCPS was administered to mice and rats for 14 weeks and for two years (rats only) with no evidence of carcinogenicity and a no observed adverse effect level (NOEL) of 1.5 mg/kg body weight was suggested. Increased liver to body size was shown to be the most prominent effect in the rats.

3 Production and use

BCPS is classified as a high production volume chemical, i.e. it is produced in more than 1000 tonnes per year in at least one of the OECD countries (Organization for economic co-operation and development). The main field of application of BCPS is in production of thermo stable polymers for the plastic industry, such as polysulfones and polyethersulfones (Mark 1988). These polymers have high resistance to burning and in most applications no other flame-retardant additives are needed. Good electrical insulation properties and high resistance to hydrolysis are examples of other properties of these polymers which make the field of application wide, e.g. in microwave ovens, TV components, food industry and medical equipment. BCPS production and use in high temperature plastics may result in its release to the environment through various waste streams.

In the past, BCPS was reported to be used both as a pesticide in Russia (Tarasenko 1969) and as a major contaminant in pesticide production (Harnagea and Badilescu 1965).

BCPS is not produced in Sweden but it is imported as polysulfone or polyethersulfone. During 2006 it was used in nine preparations in Sweden while there is no information from later years (KEMI).

Sulphenone is a low production volume chemical and is probably used within the polymer industry (<http://ecb.jrc.ec.europa.eu/esis/>). Sulphenone also occurs as a pesticide. As a pesticide, 80% of the product is Sulphenone; the rest is BCPS and diphenylsulfone.

Tetradifon is used as a pesticide. The Swedish threshold value is 2 mg/kg for fruit and vegetables. The limit value for drinking water within the EU is 0.1 ug/l (<http://apps.kemi.se/bkmregoff/bkmbld/Tetradi.pdf>). There is no information in the SPIN register at KEMI regarding the use of Sulphenone and Tetradifon.

4 Previous measurements in the environment

BCPS was identified for the first time in the environment in 1995, in perch from the Gulf of Riga (Olsson and Bergman 1995). Since then BCPS has been detected in different fish species from the Swedish part of the Baltic Sea and from Swedish lakes (Norström et al 2004), in grey seal along the Swedish east coast (Norström et al 2004, Larsson et al 2004, in white-tailed sea eagle (Helander et al 2002) and in guillemot from several northern European countries (Norström et al 2004, Jörundsdóttir et al 2006, Jörundsdóttir et al 2009).

The results from a time trend study of BCPS in guillemot eggs showed that highest concentrations occurred in samples from 1970 (1500 ng/g lipid weight in average) and that the concentrations from 1970 to 2001 decreased with 1.6% per year (Jörundsdóttir et al 2006). In humans, BCPS has been detected in the liver (Ellerichmann et al 1998).

The concentrations of BCPS in biota found in the literature are summarized in Table 3.

Table 3. Concentrations of BCPS in biota from the environment

Species	Location	Sampling year	Tissue	BCPS (ng/g fat)	Reference
Fish					
Perch	Latvia	1994	muscle	40-100	Olsson and Bergman 1995
Perch	Latvia	1994-95	muscle	38-100	Olsson et al 1999
Perch	Latvia	1997	muscle	28-190	Valters et al 1999
Salmon	Sweden	1996	muscle	31-33	Norström et al 2004
Perch	Sweden	1998	muscle	15-37	Norström et al 2004
Baltic Herring	Sweden	1996-98	muscle	29-31	Norström et al 2004
Arctic char	Sweden	1996	muscle	1.8	Norström et al 2004
Bream	Germany	1997	muscle	3.5-35	Norström et al 2004
Birds					
White-tailed sea eagle	Sweden	1971-91	egg	n.d-610	Helander et al 2002
Guillemot	Sweden	1989	muscle	1600-1900	Norström et al 2004
Guillemot	Sweden	1971-01	egg	760-2600	Jörundsdóttir et al 2006
Glaucous gull	Norway	2002-04	plasma	5.2-143	Verreault et al 2005
Guillemot	Iceland	2002	egg	5.1-8.8	Jörundsdóttir et al 2009
Guillemot	Faroe Islands	2003	egg	4.5-16	Jörundsdóttir et al 2009
Guillemot	Norway	2005	egg	n.d.-18	Jörundsdóttir et al 2009
Mammals					
Grey seal	Sweden	2000-01	liver	55-700	Larsson et al 2004
Grey seal	Sweden	2000-01	lung	21-98	Larsson et al 2004
Grey seal	Sweden	2000-01	blubber	41-240	Larsson et al 2004

n.d. = not detected

The biomagnifying potential of BCPS seems to be species dependent where birds accumulate BCPS to a higher degree compared to seals. Guillemot and seals from the Baltic Sea both feed on herring but the guillemot shows much higher concentrations of BCPS than the seal (Norström et al 2004), while the opposite is shown for PCB-153. In seals, in a study where BCPS was analyzed in different tissues, it was shown that BCPS had highest retention to the liver (Larsson et al 2004).

BCPS has also been detected in the marine water of the German Bight with concentrations up to 2 ng/L (Bester et al 2001).

Concentrations of Sulphenone and Tetradifon in environmental matrices have not been found in the literature.

5 Sampling strategy and study sites

5.1 Screening program

A sampling strategy was developed in order to determine concentrations of BCPS, Sulphenone and Tetradifon in different matrices. Data on concentrations of BCPS in abiotic matrices is scarce and knowledge about emission sources and important transport pathways for the occurrence of BCPS in biota is limited. The sampling program was focused on the Baltic Sea environment.

Air and deposition were sampled at three background stations; Pallas in Northern Finland, Råö at the Swedish West coast and Aspvreten at the Swedish East coast, 70 km SW of Stockholm, and additionally at an urban location in the city of Stockholm. The measurements at background stations were co-ordinated with measurements carried out within the Swedish Monitoring Programme for Air Pollutants. Surface water was collected at both urban and background sites.

The air, deposition and surface water samples from Stockholm were included to give an indication of possible diffuse emissions from urban area. The measurements at the Swedish West coast were included as a reference to the Baltic Sea.

Effluent water samples from waste water treatment plants (WWTPs) were included both from Sweden and from other countries surrounding the Baltic Sea. Samples from Poland, Finland, Estonia, Lithuania, and Sweden (Kalara, Henriksdal) were collected within the EU-project Control of Hazardous Substances in the Baltic Sea region (COHIBA).

Biota samples from the Baltic Sea both from Sweden and from the Eastern Baltic were included. Perch and herring from Kvädöfjärden, Holmön and Fladen were provided from the specimen bank at the Swedish Museum of Natural History. The herring from Utlängan and the fish from the Eastern Baltic Countries have previously been used within a HELCOM project (Lilja et al. 2009).

The sampling program is summarized in Table 4 and a more detailed description is given in Appendix A.

Table 4. Sampling program

Site	Air	Deposition	WWTP effluent	Surface water	Sedi-ment	Fish	Total
Background	9	8					17
Marine				2	3		5
Diffuse sources						11	11
Urban area	2	2		1	1		6
Municipal STPs							
Sweden			4				4
Other Baltic Sea countries			6				6
Total	11	10	10	3	4	11	49

6 Methods

6.1 Sampling

Air samples were collected using high volume air samplers (HVS) with a flow of approximately 20 m³/hour. Air was sucked through a glass fibre filter (MG160, Munktell) for collection of substances in the particle phase followed by polyurethane (PUF) adsorbent plugs for collection of substances in the gas phase. The sampling was carried out for one week and four weekly samples were pooled to represent an average for one month. Prior to sampling the filters were heated to 350°C, and the adsorbent was cleaned by Soxhlet extraction with acetone. After sampling the filters and PUF plugs were wrapped in aluminum foil and stored in a freezer (-18°C) until analysis. An additional filter and column used as a field blank was sent back to the laboratory unexposed. A share of the sample extract was used for the analyses.

Both wet and dry **deposition** was collected using an open sampler (bulk sampler). This sampler consists of a 1 m² Teflon coated surface with 10 cm high edges. The bottom declines slightly to a central opening where a cassette with an adsorbent (PUF) is attached. The deposition sample includes both compounds in the precipitation and compounds deposited to the collection surface of the sampler. Both the precipitation and the deposited particles are included in the analysis. This type of sampler is used for deposition measurements of organic contaminants within the Swedish national monitoring of air pollutants (Brorström-Lundén, 1995). Before sampling preheated glass fibre filters and ethanol was used to clean the surface and the adsorbent was mounted. After two weeks of sampling the adsorbent was removed and the surface was washed using preheated glass fibre filters and ethanol that was collected. The complete sample consisted of adsorbent, filters and ethanol. A share of the sample extract from the Soxhlet extraction was used for the analyses.

Effluent waters were sampled in 1 L glass bottles and the pH was adjusted to pH 3 with H₃PO₄ and stored at 6 °C.

Surface water samples from the Stockholm archipelago, the Swedish West Coast and the City of Stockholm were sampled in a metal container (30 L) or in glass bottles and stored at 6 °C.

Surface **sediment** (0-2 cm) samples were collected by means of a Kajak sampler. The sediment was transferred into muffled (400 °C) glass jars and stored in a freezer (-20 °C) until analysed.

Fish The fish muscle samples consisted of a homogenate from 10 individuals and they were stored at -18 °C in pre-cleaned glass jars.

All samples are listed in Appendix A.

6.2 Analysis

6.2.1 Sample preparation

Air and Deposition:

The filters and the adsorbents used for air and deposition sampling were Soxhlet-extracted with acetone for 24 hours. The acetone was spiked with surrogate standards. The acetone volume was reduced by rotary evaporation and then diluted with 0.2 M NaCl in water to a final concentration of 25% acetone in water. The mixture was extracted with hexane: methyl-*tert*-butylether (MTBE) (9:1). The samples were cleaned up on a sulphuric acid impregnated (deactivated with water) silica gel column.

Effluent water:

1 L of effluent water was used for the analysis. A SPE C₁₈ column (500 mg, 6 mL) (Isolute) was washed with DCM and activated with MeOH and Milli Q water. The water sample was sucked through the column. The analytes were then eluted with 5 ml MeOH and 5 ml dichloro methane (DCM), collected in one fraction. The extract was evaporated and the solvent changed to hexane before being further cleaned up on a sulphuric acid impregnated (deactivated with water) gel column..

Surface water

Approximately 30 L of water was used for the analysis. The water was spiked with surrogate standard and pumped through polyurethane foam followed by XAD2. The sorbents were then Soxhlet-extracted with hexane:MTBE (1:1) for 6 hours. The organic solvent volume was reduced by rotary evaporation and further cleaned up using a sulphuric acid impregnated (deactivated with water) silica gel column.

Sediment

Sediment samples were extracted according to Nylund et al 1992. 20 g of fresh sediment was extracted with pure acetone and re-extracted with acetone: hexane. The organic solvent was diluted with 0.2 M NaCl in water and finally partitioned with hexane: diethyl ether. After separation of the two phases, the organic solvent phase was reduced to a few ml and cleaned up with concentrated sulphuric acid. The hexane phase was further cleaned up applying a sulphuric acid impregnated silica gel column. This fraction contains the PCBs. The sulfuric acid from the first clean up was diluted with water and extracted with hexane. The hexane phase was then cleaned up applying a silica gel column impregnated with diluted sulphuric acid.

Fish

Fish samples (5 g) were extracted according to Jensen et al 2003. Fish muscle was extracted with isopropanol, diethylether and hexane: diethylether. The organic solvent phase was partitioned with water solution containing NaCl and H₃PO₄. The lipid amount was determined gravimetrically. The samples were then cleaned up in the same way as described for sediment samples.

6.2.2 Instrumentation

The determination of the sulfone containing compounds was made using a 7890A gas chromatograph connected to a 7004A triple quadrupole mass spectrometer (Agilent). The analytical column, HP-5MS 30m x 250 µm, film thickness 0,25 µm (Agilent), was connected via a purged tee to a restrictor connected to the mass spectrometer. This arrangement made it possible to backflush the column when all analytes had been eluted. The injection was made pulsed splitless at 280°C. The column temperature was held at 80°C for 1 min, increased to 300°C at 10°C /min and held at 300°C for 2 min. The transfer line was held at 280 °C. The mass spectrometer was used in SIM mode using CI ionization with methane as reaction gas. The masses for each compound used are summarized in Table 5. A separate seven point linear calibration curve was constructed for each compound and was used for the quantification of the environmental samples.

Table 5. Masses used for detection of the compounds.

	Quantification ion (m/z)	Qualifier ion (m/z)
BCPS	286.1	288.1
Tetradifon	356	358
Sulphenone	252.2	254.2
3-MeSO ₂ -PCB52 (SS)	368	370

The PCBs were determined using a gas chromatograph (Varian Model 3800) connected to an electron capture detector. The analytical column was a 50m long CP-sil 8CB column from Chrompack.

6.2.3 Quality control

All glass equipment were pre-washed and burned at 400 °C for four hours. All solvents used were of highest quality.

For each matrix, two solvent method blanks were prepared in parallel with the samples to assess possible interferences and contamination from the background.

3-MeSO₂-PCB52 was used as surrogate standard (SS) for quantification of all sulfone containing compounds and PCB 53 and PCB 208 were used as SS for the PCBs.

The background contamination in the blank samples was subtracted from the measured sample values and the limit of detection (LOD) was defined as three times the standard deviation of the blank samples noise. No peak for Sulphenone could be seen in the blank samples and LOD was based on the lowest amount that could be detected in the calibration curve. Due to a higher than expected, but constant, background contamination of BCPS at the lab, LOD has been used instead of limit of quantification (LOQ) to report if BCPS is present or not in the samples.

The recovery of the surrogate standard was calculated to ensure the quality of the method. All reported values are recovery-corrected.

Identification of the compounds was made by retention time and that the ratio of the masses between the qualifier and quantification ion have to correspond to the reference standards.

7 Results and discussion

All individual concentrations of BCPS, Sulphenone and Tetradifon are presented in Appendix A. PCB results are presented in Appendix B. The PCB results for air and deposition from Råö, Pallas and Aspvreten were taken from the Swedish Monitoring Program 2009 (NV 2010). sPCB is the sum of PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153 and PCB 180. Samples from the Swedish Monitoring Program where the PCB results have been used are indicated with "SMP 2009" or "SMP 2010 (no PCB results) in Appendix B.

7.1 Air

The atmospheric concentrations of BCPS were below the limit of detection ($\text{LOD} < 2 \text{ pg/m}^3$) at Råö, Pallas and Stockholm. However, at Aspvreten the concentrations were 8400 pg/m^3 in July 2009, 1500 pg/m^3 in November 2009 and 200 pg/m^3 in January 2010. The pump being used at Aspvreten was at these sampling occasions of a different model from the ones being used at Råö, Pallas and Stockholm and may contain parts that release BCPS. The pump at Aspvreten was in May 2010 replaced by a similar pump as is used at Råö and Pallas. A new sample from August 2010 was analyzed and the concentration of BCPS was 1.1 pg/m^3 ($\text{LOD} 0.3 \text{ pg/m}^3$ for this sample). A contamination of the first samples from Aspvreten could not be excluded.

Sulphenone was not detected in any of the air samples ($\text{LOD} < 3 \text{ pg/m}^3$).
Tetradifon was not detected in any of the air samples ($\text{LOD} < 0.6 \text{ pg/m}^3$).

The concentration of sPCB in the sample collected in Stockholm during the summer (48 pg/m^3) was 2-4 times higher, compared to the samples collected during summer months at Aspvreten and Råö. The level of BCPS at Aspvreten (1.1 pg/m^3) was in the same magnitude as the individual PCB congener at the same location.

7.2 Atmospheric deposition

BCPS was below LOD ($< 0.8 \text{ ng/m}^2\text{day}$) at all background locations. In Stockholm the concentration of BCPS was below LOD at the sampling occasion in November 2009 but $32 \text{ ng/m}^2\text{day}$ in January/ February 2010.

Sulphenone was not detected in any of the atmospheric deposition samples ($\text{LOD} < 1.2 \text{ ng/m}^2\text{day}$).
Tetradifon was not detected in any of the atmospheric deposition samples ($\text{LOD} < 0.2 \text{ ng/m}^2\text{day}$).

sPCB in Stockholm was $1 \text{ ng/m}^2\text{day}$, which was approximately the same level as was found at Råö, and about 5 times higher compared to Pallas and Aspvreten.

7.3 WWTP effluent

The only effluent sample that contained BCPS was the effluent water from Estonia (17 ng/L). All other samples were below LOD ($< 8 \text{ ng/L}$).

Sulphenone was not detected in effluent water (LOD < 1.2 ng/L).
Tetradifon was not detected in effluent water (LOD < 1.6 ng/L).

sPCB in the effluent waters ranged between 0-2.8 ng/L. The only effluent water that contained BCPS also had one of the highest levels of Sum PCB, 2.3 ng/L.

7.4 Sediment

The BCPS concentrations in sediment were below LOD (< 4 ng/g d.w.) in all samples.

Sulphenone was not detected in any of the sediment samples (LOD < 5.7 ng/d.w.).
Tetradifon was not detected in any of the sediment samples (LOD < 0.8 ng/d.w.).

PCBs were detected in all sediment samples and highest levels were found in Riddarfjärden (88 ng/g d.w.). The sum PCB concentrations in the three sediments collected outside Gotland ranged between 1.6-6.5 ng/g d.w.. PCB 153 was the dominating congener in the sediment

7.5 Surface water

BCPS was detected in all three surface waters. Sillviken at Ljusterö in the Stockholm archipelago contained the highest concentration, 1.3 ng/l. At Råö and Stockholm (Riddarfjärden) the levels were about three times lower, 0.45 and 0.33 ng/l respectively. The LOD for BCPS in surface water was 0.26 ng/l.

7.6 Fish

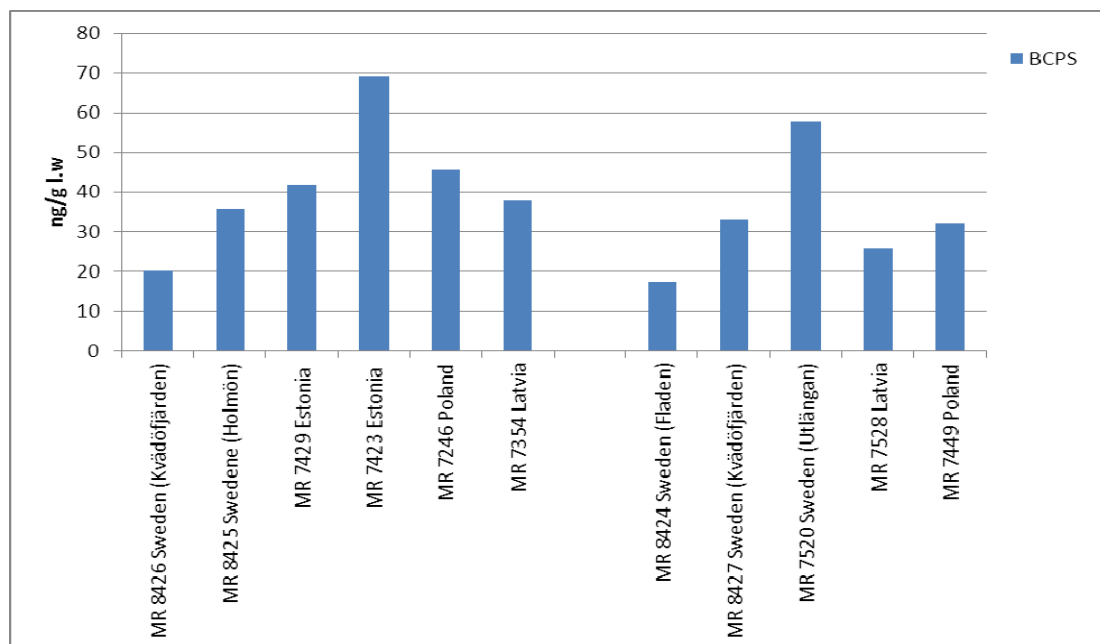


Figure 2. BCPS concentration in perch and herring (ng/g l.w.) sampled in the Baltic Sea, and in the North Sea (Fladen).

BCPS was found in all fish samples and in similar levels in perch and herring. There were no trend in concentrations among species, country or sampling location, Figure 1. This is in agreement with previous studies on different species of fish from the Baltic Sea (Norström et al. 2004). BCPS concentrations in perch from Holmön and Kvädöfjärden were in a previous study 15 and 37 ng/g l.w., respectively (Norström et al. 2004). In Baltic herring and salmon from the same study, the levels were 30 ng/g l.w.. Thus, the concentrations found in this study of the same species sampled in Sweden were in the same range as in the previous study by Norström et al.

Perch from Latvia was sampled near River Daugava. The concentration of BCPS was 37 ng/g l.w.. BCPS in perch from Latvia has been analyzed in several studies (Olsson and Bergman 1995, Olsson et al. 1999, Valters et al. 1999) and the reported concentration was between 28 and 190 ng/g l.w.. The perch in the lower range were sampled close to the sampling point in this study while the perch in the higher range were sampled upstream River Daugava.

Sulphenone and Tetradifon were below LOD (< 4 ng/g l.w.) in all fish samples.

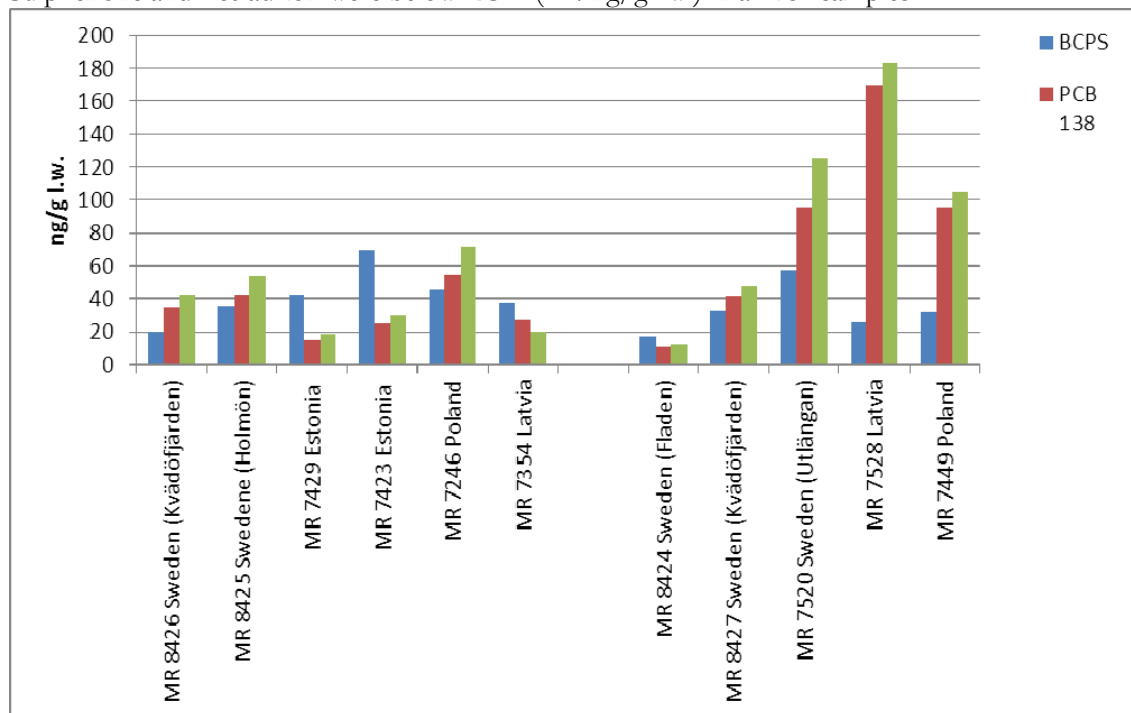


Figure 3. Concentrations of BCPS, PCB 138 and PCB 153 in perch and herring (ng/g l.w.) sampled in the Baltic Sea, and in the North Sea (Fladen).

The BCPS concentrations in the fish in this study were in the same range as the most commonly found PCB congeners in fish, PCB 138 and PCB 153, see Figure 3. In perch from Estonia and Latvia, BCPS occurred in higher concentrations than PCB 153.

The concentrations of PCB 153 in perch and herring from Kvädöfjärden, Holmön and Fladen were in good agreement with the finding of the Swedish Museum of Natural History (NRM 2010).

8 Conclusions

Many of the previous studies on BCPS have been focused on biota from the Baltic Sea. In agreement with previous studies, BCPS was found in all fish samples and in similar levels in perch and herring. There was no trend in concentrations between species, country or sampling location. BCPS was detected in the same range as PCB 138 and PCB 153.

The concentrations of BCPS in most abiotic samples were below LOD.

The WWTP effluent water sample from Estonia contained BCPS, the concentration was 17 ng/L. The concentration in all other effluent samples was below the detection limit (< 8 ng/L).

The atmospheric concentrations at Råö, Pallas and Stockholm were all below the detection limit (<2 pg/m³). At one occasion the level of BCPS at Aspvreten was 1.1 pg/m³ which is in the same magnitude as the individual PCB congeners at the same location. The first sample results at Aspvreten were excluded due to possible contamination.

Atmospheric deposition of BCPS did occasionally occur during one sampling period January/February 2010 in Stockholm, when 32 ng/m²day was measured. The deposition fluxes were below < 0.8 ng/m²day during all other sampling periods, both at urban and background sites. As a comparison, the measured deposition flux of sPCB in Stockholm was 1 ng/m²day.

BCPS was detected in the three surface waters samples, showing that the compound is present in the marine water environment, which may explain the bioaccumulation in fish, seals and birds. The concentrations varied between 0.3 and 1.3 ng/L.

This screening did not clarify the pathways of BCPS to the Baltic Sea. The detection of BCPS in abiotic matrices was below LOD in most of the samples. However, the results indicate that the transport to the environment is waterborne rather than airborne.

Sulphenone and Tetradifon were not detected in any of the samples.

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KEMI: <http://kemi.se>

TOXNET: <http://toxnet.nlm.nih.gov/cgi-bin/sis/search>

<http://apps.kemi.se/bkmregoff/bkmblad/Tetradi.pdf>

Appendix A. Sample information and concentrations of BCPS, Sulphenone and Tetradifon.

Sample ID	Type	Area	Location	Matrix	Sampling date	Lipids (%)	DW, %	Unit	BCPS	Sulphenone	Tetradifon	Comments
MR 8413	Background	Pallas		Air	2010 Jan			pg/m ³	< 2	< 3	< 0.6	
MR 8368	Background	Pallas		Air	2010 July			pg/m ³	< 2	< 3	< 0.6	
MR 8370	Background	Råö		Air	2009 Nov			pg/m ³	< 2	< 3	< 0.6	
MR 8364	Background	Råö		Air	2010 Jan			pg/m ³	< 2	< 3	< 0.6	
MR 8371	Background	Råö		Air	2009 May			pg/m ³	< 2	< 3	< 0.6	
MR 8365	Background	Råö		Air	2009 July			pg/m ³	< 2	< 3	< 0.6	
MR 8407	Background	Aspvreten		Air	2009 July			pg/m ³	8400	< 3	< 0.6	Excluded, see 7.1
MR 8408	Background	Aspvreten		Air	2009 Nov			pg/m ³	1500	< 3	< 0.6	Excluded, see 7.1
MR 8409	Background	Aspvreten		Air	2010 Jan			pg/m ³	200	< 3	< 0.6	Excluded, see 7.1
MR 8944	Background	Aspvreten		Air	2010 Aug			pg/m ³	1.1			LOD 0.3 pg/m ³
MR 8361	Urban	Stockholm	Valhallav. 81	Air	2009-11-05 - 12-07			pg/m ³	< 2	< 3	< 0.6	
MR 8362	Urban	Stockholm	Valhallav. 81	Air	2010-01-19 - 02-16			pg/m ³	< 2	< 3	< 0.6	
MR 8367	Background	Pallas		Deposition	2009 July			ng/m ² day	< 0.8	< 1.2	< 0.2	
MR 8373	Background	Pallas		Deposition	2010 Jan			ng/m ² day	< 0.8	< 1.2	< 0.2	
MR 8372	Background	Råö		Deposition	2009 May			ng/m ² day	< 0.8	< 1.2	< 0.2	
MR 8366	Background	Råö		Deposition	2009 July			ng/m ² day	< 0.8	< 1.2	< 0.2	
MR 8374	Background	Råö		Deposition	2010 Jan			ng/m ² day	< 0.8	< 1.2	< 0.2	
MR 8410	Background	Aspvreten		Deposition	2009 Mars			ng/m ² day	< 0.8	< 1.2	< 0.2	
MR 8411	Background	Aspvreten		Deposition	2009 July			ng/m ² day	< 0.8	< 1.2	< 0.2	
MR 8412	Background	Aspvreten		Deposition	2009 Nov			ng/m ² day	< 0.8	< 1.2	< 0.2	
MR 8415	Urban	Stockholm	Valhallav. 81	Deposition	2009-11-05 - 12-07			ng/m ² day	< 0.8	< 1.2	< 0.2	
MR 8416	Urban	Stockholm	Valhallav. 81	Deposition	2010-01-19 - 02-16			ng/m ² day	32	< 1.2	< 0.2	
MR 8133	Urban	Kalmar	Kalmar WWTP	Effluent	2009-11			ng/l	< 8	< 11	< 1.6	Cohiba
MR 8139	Urban	Stockholm	Henriksdal WWTP	Effluent	2009-11			ng/l	< 8	< 11	< 1.6	Cohiba
MR 8164	Urban	Stockholm	Lidingö WWTP	Effluent	2009-11-19			ng/l	< 8	< 11	< 1.6	
MR 8006	Urban	Umeå	Öhn WWTP	Effluent	2009-09-30 - 10-01			ng/l	< 8	< 11	< 1.6	
MR 7989	Urban	Poland	WWTP 1	Effluent	2009-09			ng/l	< 8	< 11	< 1.6	Cohiba
MR 7991	Urban	Poland	WWTP 2	Effluent	2009-09			ng/l	< 8	< 11	< 1.6	Cohiba

Sample ID	Type	Area	Location	Matrix	Sampling date	Lipids (%)	DW, %	Unit	BCPS	Sulphenone	Tetradifon	Comments
MR 8160	Urban	Finland	WWTP	Effluent	2009-11			ng/l	< 8	< 11	< 1.6	Cohiba
MR 8126	Urban	Estonia	WWTP 1	Effluent	2009-11			ng/l	< 8	< 11	< 1.6	Cohiba
MR 8125	Urban	Estonia	WWTP 2	Effluent	2009-11			ng/l	17	< 11	< 1.6	Cohiba
MR 8106	Urban	Lithuania	WWTP	Effluent	2009-11			ng/l	< 8	< 11	< 1.6	Cohiba
MR 8513	Background	North Sea	Råö	Surface water	2010-04-26			ng/l	0.45	-	-	
MR 8921	Diffuse	Stockholm archipelago	Sillviken, Ljusterö	Surface water	2010-11-22			ng/l	1.3	-	-	
MR 8922	Diffuse	Stockholm	Riddarfjärden	Surface water	2010-11-22			ng/l	0.33	-	-	
MR 7749	Background	North Sea	SE 15	Sediment			30.6	ng/d.w	< 4	< 5.7	< 0.8	
MR 7741	Background	Baltic Sea	SE 6 NE Gotland basin	Sediment			4.43	ng/d.w	< 4	< 5.7	< 0.8	
MR 7742	Background	Baltic Sea	SE 7 NE Gotland basin	Sediment			5.70	ng/d.w	< 4	< 5.7	< 0.8	
MR 7968	Diffuse	Stockholm	Långholmen	Sediment	2009-09-16		11.8	ng/d.w	< 4	< 5.7	< 0.8	
MR 8425	Diffuse	Sweden	Holmön	Fish/ Perch		1.03		ng/g l.w.	36	< 4	< 4	NMR
MR 8426	Diffuse	Sweden	Kväddfjärden	Fish/ Perch		0.95		ng/g l.w.	20	< 4	< 4	NMR
MR 7423	Diffuse	Estonia	Coastal area near Sillamäe	Fish/ Perch	2008-08-07	0.66		ng/g l.w.	69	< 4	< 4	Helcom
MR 7429	Diffuse	Estonia	Western coast of Saaremaa Island	Fish/ Perch	2008-08-27	1.03		ng/g l.w.	42	< 4	< 4	Helcom
MR 7246	Diffuse	Poland	Szczecin Lagoon	Fish/ Perch	2008-09-09	1.00		ng/g l.w.	46	< 4	< 4	Helcom
MR 7354	Diffuse	Latvia	Near River Daugava	Fish/ Perch	2008-09-18	1.11		ng/g l.w.	38	< 4	< 4	Helcom
MR 8427	Diffuse	Sweden	Kväddfjärden	Fish/ Herring		3.88		ng/g l.w.	33	< 4	< 4	NMR
MR 8424	Diffuse	Sweden	Fladen	Fish/ Herring		7.92		ng/g l.w.	17	< 4	< 4	NMR
MR 7520	Diffuse	Sweden	Utlängan	Fish/ Herring	2008-10-13	1.91		ng/g l.w.	58	< 4	< 4	Helcom
MR 7449	Diffuse	Poland	Gulf of Gdansk	Fish/ Herring	2008-10-01	5.32		ng/g l.w.	32	< 4	< 4	Helcom
MR 7528	Diffuse	Lithuania	Coastal area north from Klaipeda	Fish/ Herring	2008-09-10	3.13		ng/g l.w.	26	< 4	< 4	Helcom

Appendix B Table B1: Concentrations of PCBs.

Sample ID	Type	Area	Location	Matrix	Unit	PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153	PCB 180	sPCB	comment
MR 8413	Background	Pallas		Air	pg/m ³	-	-	-	-	-	-	-	-	SMP 2010
MR 8368	Background	Pallas		Air	pg/m ³	-	-	-	-	-	-	-	-	SMP 2010
MR 8370	Background	Råö		Air	pg/m ³	2.1	2.5	1.7	0.63	1.1	1.4	0.43	9.9	SMP 2009
MR 8364	Background	Råö		Air	pg/m ³	-	-	-	-	-	-	-	-	SMP 2010
MR 8371	Background	Råö		Air	pg/m ³	1.4	2.5	1.7	0.64	1.4	1.6	0.53	9.8	SMP 2009
MR 8365	Background	Råö		Air	pg/m ³	2.0	4.3	3.9	1.6	3.3	3.7	1.2	20	SMP 2009
MR 8407	Background	Aspvreten		Air	pg/m ³	2.2	3.2	2.3	0.97	1.1	1.3	0.33	11	SMP 2009
MR 8408	Background	Aspvreten		Air	pg/m ³	1.7	2.0	0.94	0.29	0.43	0.55	0.15	6.1	SMP 2009
MR 8409	Background	Aspvreten		Air	pg/m ³	-	-	-	-	-	-	-	-	SMP 2010
MR 8361	Urban	Stockholm	Valhallav. 81	Air	pg/m ³	13	13	8.6	2.6	4.4	5.3	1.4	48	
MR 8362	Urban	Stockholm	Valhallav. 81	Air	pg/m ³	7.9	7.1	3.8	1.0	1.5	2.0	0.54	24	
MR 8367	Background	Pallas		Deposition	ng/m ² day	<0.01	0.055	0.028	0.013	0.031	0.035	0.017	0.18	SMP 2009
MR 8373	Background	Pallas		Deposition	ng/m ² day	-	-	-	-	-	-	-	-	SMP 2010
MR 8372	Background	Råö		Deposition	ng/m ² day	<0.01	0.30	0.11	0.08	0.30	0.32	0.21	1.3	SMP 2009
MR 8366	Background	Råö		Deposition	ng/m ² day	<0.01	0.32	0.10	0.064	0.24	0.25	0.17	1.1	SMP 2009
MR 8374	Background	Råö		Deposition	ng/m ² day	-	-	-	-	-	-	-	-	SMP 2010
MR 8410	Background	Aspvreten		Deposition	ng/m ² day	<0.03	0.030	<0.03	0.020	0.044	0.041	0.033	0.19	SMP 2009
MR 8411	Background	Aspvreten		Deposition	ng/m ² day	<0.01	0.068	<0.03	0.018	0.034	0.029	0.016	0.19	SMP 2009
MR 8412	Background	Aspvreten		Deposition	ng/m ² day	<0.01	0.035	0.039	0.039	0.059	0.048	0.047	0.27	SMP 2009
MR 8415	Urban	Stockholm	Valhallav. 81	Deposition	ng/m ² day	0.024	0.043	0.11	0.077	0.24	0.20	0.21	0.91	
MR 8416	Urban	Stockholm	Valhallav. 81	Deposition	ng/m ² day	0.016	<0.030	0.11	0.080	0.31	0.28	0.25	1.0	
MR 8133	Urban	Kalmar	Kalmar	Effluent	ng/l	0.38	<0.30	0.38	<0.30	0.31	<0.20	0.26	1.6	
MR 8139	Urban	Stockholm	Henriksdal	Effluent	ng/l	<0.30	<0.30	<0.30	<0.30	<0.20	<0.20	<0.20		
MR 8164	Urban	Stockholm	Lidingö	Effluent	ng/l	<0.30	<0.30	<0.30	<0.30	<0.20	<0.20	<0.20		
MR 8006	Urban	Umeå	Öhn	Effluent	ng/l	<0.30	<0.30	0.40	<0.30	0.292	<0.20	<0.20	0.76	
MR 7989	Urban	Poland	MWWIP 2	Effluent	ng/l	<0.30	<0.30	<0.30	0.21	<0.20	<0.20	<0.20	0.43	
MR 7991	Urban	Poland	IWWIP 2	Effluent	ng/l	<0.30	<0.30	0.61	0.26	0.42	<0.20	<0.20	1.6	
MR 8160	Urban	Finland	Viikinmäki	Effluent	ng/l	0.67	<0.30	0.45	0.57	0.71	<0.20	0.41	2.8	
MR 8126	Urban	Estonia	Kohtla-Järve	Effluent	ng/l	<0.30	<0.30	<0.30	<0.20	<0.20	<0.20	0.031	0.34	

Sample ID	Type	Area	Location	Matrix	Unit	PCB 28	PCB 52	PCB 101	PCB 118	PCB 138	PCB 153	PCB 180	sPCB	comment
MR 8125	Urban	Estonia	Narva	Effluent	ng/l	0.44	<0.30	0.41	0.42	0.39	<0.20	0.26	2.3	
MR 8106	Urban	Litauen	Klaipėdos nafta	Effluent	ng/l	<0.30	<0.30	<0.30	<0.20	<0.20	<0.20	<0.20		
MR 8513	Background	North Sea	Råö	Surface water	ng/l	-	-	-	-	-	-	-		
MR 8521	Diffuse	Stockholm archipelago	Sillviken, Ljusterö	Surface water	ng/l	-	-	-	-	-	-	-		
MR8522	Diffuse	Stockholm	Riddarfjärden	Surface water	ng/l	-	-	-	-	-	-	-		
MR 7749	Background	North Sea	SE 15	Sediment	ng/d.w	<0.15	0.71	0.33	0.39	<0.1	0.15	<0.1	1.6	
MR 7741	Background	Baltic Sea	SE 6 NE Gotland basin	Sediment	ng/d.w	0.34	<0.15	0.70	<0.15	0.84	1.1	0.37	3.3	
MR 7742	Background	Baltic Sea	SE 7 NE Gotland basin	Sediment	ng/d.w	0.49	0.86	1.3	<0.15	1.6	1.7	0.64	6.5	
MR 7968	Diffuse	Stockholm	Långholmen	Sediment	ng/d.w	5.7	20	11	32	<0.1	19	<0.1	88	
MR 8425	Diffuse	Sweden	Holmön	Fish/ Perch	ng/g l.w.	<6	<6	13	16	42	54	23	150	
MR 8426	Diffuse	Sweden	Kvädöfjärden	Fish/ Perch	ng/g l.w	<6	<6	12	17	35	42	11	120	
MR 7423	Diffuse	Estonia	Coastal area near Sillamäe	Fish/ Perch	ng/g l.w	9.2	<6	19	19	25	30	7.8	110	
MR 7429	Diffuse	Estonia	Western coast of Saaremaa Island	Fish/ Perch	ng/g l.w	4.8	<6	7.5	8.0	15	19	4.5	59	
MR 7246	Diffuse	Poland	Szczecin Lagoon	Fish/ Perch	ng/g l.w	<6	<6	20	12	55	72	33	190	
MR 7354	Diffuse	Latvia	Near River Daugava	Fish/ Perch	ng/g l.w	<6	<6	<6	16	27	20	13	76	
MR 8427	Diffuse	Sweden	Kvädöfjärden	Fish/ Herring	ng/g l.w	5.00	11	29	26	41	48	12	17	
MR 8424	Diffuse	Sweden	Fladen	Fish/ Herring	ng/g l.w	2.54	3.8	52	7.1	11	12	1.9	100	
MR 7520	Diffuse	Sweden	Utlängan	Fish/ Herring	ng/g l.w	3.54	10	35	39	96	130	33	340	
MR 7449	Diffuse	Poland	Gulf of Gdansk	Fish/ Herring	ng/g l.w	5.48	14	48	50	96	110	32	350	
MR 7528	Diffuse	Lithuania	Coastal area north from Klaipėda	Fish/ Herring	ng/g l.w	5.29	9.0	48	90	170	18	45	550	