PRESSURE

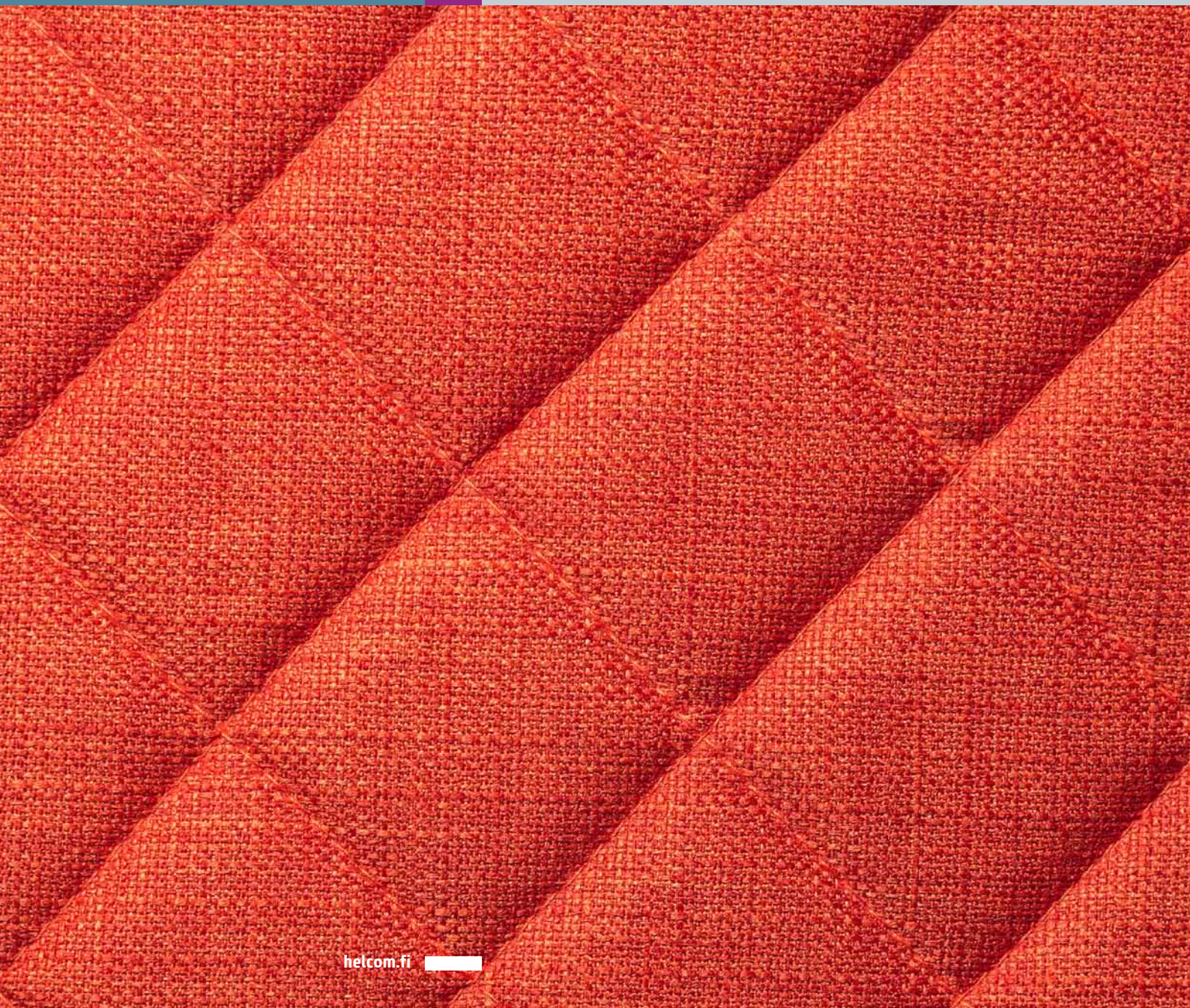
Polybrominated diphenyl ethers (PBDEs)

in the Baltic Sea

Baltic Marine Environment
Protection Commission

Hazardous substances

BSEP n°172



Polybrominated diphenyl ethers (PBDEs) in the Baltic Sea – Sources, transport routes and trends

This report was written to support the update of the HELCOM Baltic Sea Action Plan (BSAP). The BSAP is a programme to restore good ecological status of the Baltic marine environment by 2021 and was adopted in 2007 by all the HELCOM Contracting Parties. The study addresses the thematic area "Hazardous substances".

It provides background information that is relevant in the process of evaluating the efficiency of currently implemented measures, and for suggesting additional measures, needed to achieve good environmental status in the Baltic Sea.

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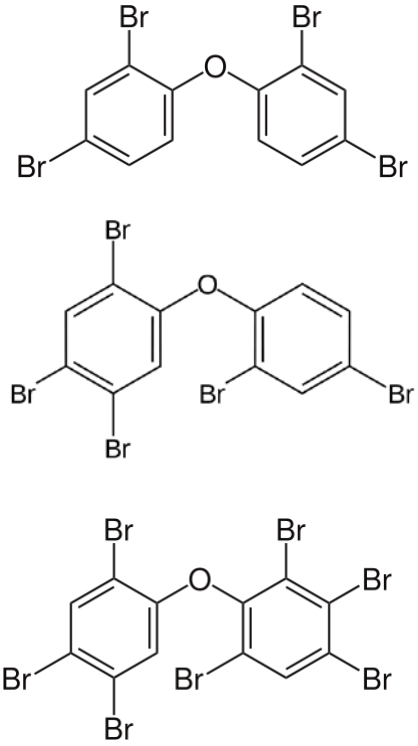
Content

Background

Brominated flame retardants (BFRs) are used as additives in various materials to prevent ignition and delay spread of fire. National and international standards for fire safety exist (e.g. materials should not ignite by small flames or smouldering cigarettes) for some product groups such as electrical equipment, industrial packaging, upholstered furniture, curtains, electronic household appliances and electrical cables, and BFRs have been used extensively to meet these standards (Abbasi, 2015).

Commercial mixtures

Polybrominated diphenyl ethers (PBDEs) are a group of BFRs that has been produced since the 1970s and have been used in materials such as plastics, foams and textiles (Abbasi, 2015). The PBDEs are typically not chemically bound to the materials and therefore migrate from products to indoor and ultimately outdoor environments (Abbasi, 2015). The molecules consist of two phenyl rings connected by an ether linkage, and have various numbers of bromine atoms bonded to the rings; 209 congeners are possible and high congener-numbers indicate high degree of bromination. The congeners containing four bromines are referred to as tetraBDEs, while those that contain five bromines are referred to as pentaBDEs and so on. PBDEs have been produced in three commercial (c-) mixtures with different level of bromination, i.e. the mixtures are consisting of congeners with various number of bromines: c-pentaBDE, c-octaBDE and c-decaBDE. Several variants of the mixtures have been manufactured by different producers, with different composition of PBDE congeners (La Guardia et al., 2006). Congeners that occurred in historically important pentaBDE technical products by >5% weight investigated by LaGuardia et al. include congeners 47, 99, 100, 153; mainly the tetra BDE47 and penta BDE99) (La Guardia et al., 2006). The c-octa mixtures analysed consisted mainly of BDEs number 183 (hepta) and a number of octaBDEs (197, 196, 203), nonaBDEs 206, 207, decaBDE (209) and also hexaBDE 153. Some c-octa products however contained nearly 50% BDE209 (La Guardia et al., 2006). The c-deca was mainly congener 209 (La Guardia et al., 2006). The typical homologue composition of the commercial mixtures as summarized by UNEP (UNEP, 2017) is shown in Table 1.



Examples of PBDE congenes – BDE-47, BDE-99 and BDE-183.

***Table 1**. Typical PBDE homologue distribution in PBDE products. Adopted from (La Guardia et al., 2006).*

Commercial mixture	Congener % (weight)						
	tetraBDE	pentaBDE	hexaBDE	heptaBDE	octaBDE	nonaBDE	decaBDE
c-pentaBDE	24–38	50–60	4-8				
c-octaBDE			10–12	44	31–55	10–11	<1
c-decaBDE						<3	97–98

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PBDEs have been used as flame retarding additives in various materials such as plastics, foams and textiles and are still emitted from in-use products, buildings and waste.

Properties

PBDEs are toxic, hydrophobic and persistent molecules. The log KOW values (octanol-water partition coefficients) of the most commonly studied PBDEs range from 5.96 (BDE28) to 9.16 (BDE209), log KOA from 9.68 to 16.4 for the same congeners (Yue and Li, 2013). The environmental fate of organic chemicals depends largely on the mode of emission, i.e. to which environmental compartment they are released. PBDEs tend to be transported to soil and sediment when emitted to air; when emitted to soil they tend to stay there and when emitted to water they are transported to sediment; a higher degree of bromination enhances water to sediment and air to soil transport (Palm et al., 2002). The majority of globally emitted PBDEs are likely stored in soil and water, environmental compartments where half-lives are greater for heavier congeners compared to the lighter (less brominated) ones (Schenker et al., 2008b). In air, however, heavier PBDEs have shorter half-lives than the lighter PBDEs due to debromination by direct photolysis (Schenker et al., 2008b; Söderström et al., 2004). Heavy PBDEs also have lower vapour pressures, making them more easily washed out of the atmosphere, which potentially leads to a lower long range transport potential of the heavier PBDEs (Breivik et al., 2006; Schenker et al., 2008b). Field measurements however confirm their presence also in pristine areas and the mechanism for long range transport (i.e. particle bound or gaseous) is still debated (Degrendele et al., 2018; Li et al., 2016). Debromination of heavy PBDEs contributes to the environmental pool of lower-brominated PBDEs which are formed in the degradation process (Söderström et al., 2004). Based on model calculations and observed congener patterns in the environment, the contribution to concentrations of pentaBDEs in air in temperate regions by debromination of decaBDE has been estimated to be 3 - 20%, although this fraction may have increased with the phase out of primary pentaBDE emissions (Schenker et al., 2008b). Biomagnification in food chains is commonly observed for PBDEs, although for the heavier PBDEs (e.g. BDE209) bioaccumulation is not as strong as indicated by the high log KOW values, likely due to metabolism in organisms (La Guardia et al., 2007; UNEP, 2007, 2006), limited dietary absorption efficiency of these superhydrophobic substances (due to steric hindrance or slow diffusive membrane passage over stagnant boundary layer of water) (Kierkegaard, 2007) and/or a distribution between biotic tissues that is not correlated to lipid content (Airaksinen et al., 2015; Kuo et al., 2010; Wan et al., 2013).

It is notable that the partitioning behaviour of PBDEs between gas and particulate phases in the atmosphere is complex and not well understood. The models available cannot accurately predict the fractions of different PBDE congeners that are present as a gas and adsorbed/absorbed to particles at various temperatures and levels of atmospheric suspended particles (Degrendele et al., 2018). The common assumption of KOA-dependent equilibrium gas-particle partitioning seems to overestimate the particle bound fraction of commonly analysed PBDEs (except for BDE28), in particular for the highest brominated PBDEs with the highest KOAs (Degrendele et al., 2018; Li et al., 2016). This uncertainty regarding how much of the PBDEs in air that occur in gas phase versus attached to particles influences conclusions regarding removal rates from the atmosphere (via wet and dry deposition and degradation, which differs for gases and particle bound PBDEs) and mechanisms for long range atmospheric transport.

Legislation

GGermany and Sweden were among the countries that first discussed the need to regulate PBDEs. Industrial users in Germany agreed to voluntarily phase them out in 1986, and the use was further restricted in 1993; the Swedish Chemicals Agency was commissioned by the Swedish government to assess the risks of brominated flame retardants and work for the phase-out of PBDEs during the 1990's (Kemikalieinspektionen, 2003; Prevedouros et al., 2004).

Today, the production and use of PBDEs are restricted both at EU-level and globally. Tetra, penta, hexa and heptaBDEs are called persistent organic pollutant (POP)-BDEs and were listed in 2009 under Annex A of the Stockholm convention, meaning production and use of these substances shall be eliminated; use of recycled materials containing POP-BDEs is allowed until 2030 for a few convention Parties (the EU withdrew its registration for this exemption in July 2019). DecaBDE was initially not listed under the Stockholm convention, however BDE-209

The production and use of PBDEs is nowadays restricted, although exemptions exist.

Photo: Anders Ludvigson/Mostphotos

can degrade by debromination to POP-classified lower brominated PBDEs (Earnshaw et al., 2013; Schenker et al., 2008b; Zeng et al., 2010). The EU POPs Regulation EU 2019/1021 (repealing EC No 850/2004) implements the Stockholm Convention.

The use of c-pentaBDE and c-octaBDE in electronic products was restricted in the EU's legislation which aims at restricting the use of hazardous substances in electrical and electronic equipment (EEE), i.e. the RoHS directive decided in 2003 (Directive 2002/95/EC). It was amended to restrict use of decaBDE in 2008. PBDEs were included on the first Water Framework Directive (WFD) priority list presented in year 2008, however with an environment quality standard (EQS) defined only for major constituents of c-pentaBDE (congener numbers 28, 47, 99, 100, 153 and 154) (Directive 2008/105/EC). In Russia, imports of c-penta, -octa and -decaBDE as chemical products and as part of finished articles have been banned since 2010, although this did not include a ban on production and use; whether this has occurred is not clear (Toropovs, 2011). According to Russia at the 58th Meeting of the HELCOM Heads of Delegation however, brominated diphenyl ethers are imported into the Russian Federation for use as flame retardants in industrial products. Russia has signed and ratified the Stockholm Convention, however not the restrictions on PBDEs which are added as amendments of Annex A.

DecaBDE was identified as SVHC under REACH in 2012, and eventually added to Annex A of the Stockholm Convention in 2017, however with several exemptions: for use in certain parts of legacy vehicles (until end of service-life or year 2036), aircrafts (before 2022), polyurethane foam (PUR) for building insulation and textile products that require anti-flammable properties (however us is not allowed in clothing and toys). According to the Stockholm convention, c-decaBDE can still be used as an additive in plastic housings (casings) and parts used for heating home appliances, irons, fans, immersion heaters that contain or are in direct contact with electrical parts or are required to comply with fire retardancy standards, at concentrations lower than 10 per cent by weight of the part (Stockholm Convention).

Production and use

The global production of PBDEs has been estimated to 1300-1500 kilotonnes (kt) until year 2005. The majority of this amount was c-decaBDE (1100 kt) and equal amounts each of c-penta and c-octaBDEs (100 kt) (UNEP, 2010). A more recent estimate of cumulative historical production until 2020 is 1600 kt c-deca, 175 kt c-penta and 130 kt c-octaBDE (Abbasi et al., 2019). Production of c-pentaBDE and c-octaBDE stopped in 2004, whereas c-decaBDE was still produced in 2017 (UNEP, 2017), but supposedly not after 2018 (Abbasi et al., 2019). Annual global production of PBDEs peaked in 2003 (Abbasi et al., 2019).

c-pentaBDE. Production of c-pentaBDE occurred in Israel, the United States, China and EU. Production in the EU ceased in 1997, and c-pentaBDE was thereafter mainly produced in the US and China until 2004 when production stopped (UNEP, 2017). Ca 85 kt c-pentaBDE was used in the US and 15 kt in Europe (UNEP, 2017), c-penta produced in China after 1996 (<10 kt) was also used in China (Abbasi et al., 2019). Most (>90%) c-pentaBDE was used as additives in PUR foam. Of this 36% was used in automotive production (e.g. seating, head rests, car ceilings, acoustic systems, back-coating of textiles; this polyurethane foam typically contained 0.5-1% c-pentaBDE) and 60% in furniture upholstery (in these applications, PUR foam contained typically 3-5% c-pentaBDE) (UNEP, 2017).

Most c-pentaBDE was applied in PUR foam used in furniture upholstery and automotive production (e.g. seatings and car ceilings).

c-octaBDE was produced in the Netherlands, France, the United States, Japan, the United Kingdom and Israel until 2004. In the EU, 95% of the use was in acrylonitrile-butadiene-styrene (ABS) polymers, which were mainly used for plastic housings/casings of electric and electronical equipment (e.g cathode ray tube housings, copying machines, printers), with typical concentrations of 12-18 wt% in these plastics. The major use of ABS polymers was in electronics, and a minor fraction was used in the transport sector (UNEP, 2017).

c-decaBDE. The global production of c-decaBDE peaked in year 2002 (~66 kt/year produced), in Europe the industrial consumption peaked in the 1990s (Earnshaw et al., 2013) and ceased after 1999 (although import in products continued) (UNEP, 2014). Between 1999 and 2003, Europe had ca 14% of the global c-decaBDE market (Earnshaw et al., 2013). China's production was 41.5 kt/year in 2005, but it decreased to 20 kt/year after 2012 due to declining international demand (Abbasi et al., 2019). In the US, main producers and importers agreed to end all uses of c-decaBDE by the end of 2013 (UNEP, 2014). The global production is likely to have ceased after 2018 (Abbasi et al., 2019). C-decaBDE has been used to protect textiles: mainly upholstery, window blinds, curtains, mattress textiles, different types of tents, marquees and canvasses (ECHA, 2012). Typically, c-decaBDE make up ca 2-8% of the fabric weight, and is applied to the reverse side of the fabric as a coating (ECHA, 2012). C-decaBDE has also been used in plastics e.g. housings of computers and TV sets, wires and cables, pipes and carpets (typically 10-15% of material weight) (UNEP, 2014). In Europe, 52% of the c-decaBDE has been sold in textiles and 48% in plastics. The c-decaBDE containing textiles and plastics have been used in motor vehicles, construction materials, electrical and electronic equipment, and textile products (UNEP, 2014).

It has been estimated that ca 3 and 0.7% of total cumulative penta+octaBDE and decaBDE mixtures productions have been emitted to the environment in 2018, respectively (Abbasi et al., 2019). Only a small fraction of the produced PBDEs have been destroyed through incineration and during waste water treatment; the majority of the productions is stored in landfills and dumpsites (Abbasi et al., 2019).

Sources and pathways to the Baltic Sea

Several modelling studies have assessed emissions and the transport pathways of PBDEs globally, but also in the European region (Abbasi et al., 2019; Birgul et al., 2012; Earnshaw et al., 2015; Prevedouros et al., 2004; Schenker et al., 2008a) and in the Baltic Sea region (Andersson et al., 2016; Bartnicki et al., 2016; Mattila and Verta, 2008). Commonly, emission scenarios include only emissions to air, and the atmospheric concentrations and deposition are modelled and compared to atmospheric monitoring data. Emissions however occur also to soil and surface water.

Major sources and mode of emissions

c-pentaBDE

There are only a few studies published assessing the current sources of PBDEs in Europe. A study estimating and comparing emissions to several environmental compartments and making projections for year 2020 for Switzerland was published in 2008 and can give an indication about major emission sources in Europe (Morf et al., 2008). Emissions of BDE47, which is a main component in c-pentaBDE, in Switzerland were estimated to always have occurred mainly (>50%) to air (primarily from use of products, from volatilization from landfills and destruction), with an increasing importance of emissions from landfills and destruction over time (Morf et al., 2008). Emissions to soil (mainly from destruction and landfills) and water (mainly from WWTP effluents) were predicted to contribute roughly 25% and 15% of total environmental emissions by 2020, respectively (Morf et al., 2008).

Landfills are sources of PBDEs.

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Abbasi et al. studied global atmospheric emissions from production of BFRs, use of products and waste, and presented results for various regions in the world including Europe (Abbasi et al., 2019). They estimated that the in-use stock (e.g. in various products, including construction materials) is currently the main source of BDE28, 47, 99, 153, and 183 (Σ5PBDEs) to the atmosphere both globally and in Europe. The second most important source in industrialized countries (including Europe) was production until it ceased in the beginning of the 2000s, whereas in less industrialized countries the second most important source was, and still is, inappropriate waste treatment.

The above-mentioned studies used the total consumption of PBDEs in Europe as a starting point and distributed the consumed mass to the major use categories (electronics, foam and carpets, construction, transportation, textiles). PBDE-containing product mass flows were modelled including use-phase, waste phase, global trade and waste export. In another study, the COHIBA project, a different approach was taken. Inventories and emissions from different sources were calculated independently, based on activity rates (e.g. yearly amount of sludge applied in agriculture, mass of steel produced, mass of e-waste collected etc.) in combination with emission factors (e.g. kg PBDE released /kg e-waste) (Andersson, 2012). The COHIBA project estimated yearly c-pentaBDE emissions to European (EU27) agricultural soil via sludge (400-1500 kg), to indoor air from PUR foam and electronic appliances (in total 9600 kg, but only small emissions from private homes to outdoor air, at most 24 kg), to air from steel production (3-33 kg) and accidental fires in e-waste recycling facilities (0.2 – 500 kg), and to surface water from WWTP effluents (<1 – 216 kg) (Andersson, 2012). The total estimated emissions to air reported in COHIBA were 5-85 kg (although it is not clear how this range was derived), which was considerably lower than the mass deposited from the atmosphere to land calculated from measured deposition fluxes (275 – 22860 kg) in the same project. This indicates that long range atmospheric transport is a major source of c-pentaBDE in air (Andersson, 2012). In COHIBA, emissions to soil dominate both high and low emission scenarios, in contrast to findings by Morf et al. (Morf et al., 2008), which show that air emissions dominate. The relative proportions between emissions to air and water (i.e. greater importance of air emissions (>70%) compared to emissions via WWTP effluents (<30%)) however agree in these studies. Atmospheric deposition was estimated in COHIBA to contribute 63-87% of total emissions to inland surface water in Europe (Andersson, 2012). Note that the COHIBA emission estimates include sources that are not included in other studies of PBDE emissions in Europe, i.e. release from accidental fires in e-recycling facilities and during steel production. The uncertainty in these estimates is large and the importance of these sources is not confirmed in other studies.

The fraction of indoor c-pentaBDE that escapes the indoor environment to the outdoor air is predicted to be small in the COHIBA substance flow analysis, and only private homes are included in the estimation of indoor environments as a source to the outdoor air. This probably leads to an underestimation of the relative importance of in-use products. Björklund et al. estimated that Swedish emissions from public buildings (0.26 – 8.7 kg/year for sum of c-pentaBDE constituents BDE-28, -47, -99, -153) were ca 10 times higher than emissions from private homes (0.024 – 0.92 kg/year) (Björklund et al., 2012). This estimation did not include industrial buildings. Björklund et al. (Björklund et al., 2012) estimated total c-pentaBDE emissions to air in Sweden, partly including the

PBDEs emitted in the indoor environment reach the outdoor air via ventilation.

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Photo: Per Strand/Mostphotos

In-use stock of products and construction materials are still major sources of PBDEs emitted to the environment.

same sources and using the same emission factors as COHIBA, and concluded that ca 80% of total annual emissions to air in Sweden is from indoor air. Note that this estimation did not include long range atmospheric transport from other regions. Other studies of PBDEs in air have shown an "urban pulse" with higher concentrations in urban areas than in rural locations (Newton et al., 2015). However, this pattern was only observed in soil for higher brominated congeners (octa-decaBDEs) (Newton et al., 2015). The same study found that a net deposition from air to soil occurs, probably due to ongoing contamination of outdoor air via ventilation of indoor air combined with background air contamination. Another study also concluded that revolatilization from land did not likely influence atmospheric PBDE concentrations at a background site in Central Europe (Czech Republic) (Degrendele et al., 2018). In other words, secondary emissions from PBDEs deposited on land likely do not govern atmospheric concentrations in Europe.

EMEP modelling has also identified long range atmospheric transport as an important source of c-pentaBDE in air in the Baltic Sea region (Bartnicki et al., 2016). BDE99 was used as an indicator of c-pentaBDE as it constitutes ca 45-50% of the commercial mixture. The emission scenario assumed a concentration decrease over time (decline rate) by a factor 7 from year 2000 to 2014 and was derived from another modelling study that estimated c-pentaBDE emissions in the European region based on monitoring data, and predicted a decline from 1700 to 250 kg during this time period. The geographical distribution of emissions in the EMEP region was based on another emission estimate for c-pentaBDE in the year 2000. The modelled concentrations of BDE99 in air were within a factor 2-3 of the observed concentrations at four EMEP monitoring sites, which can be considered a good agreement. The total mass of BDE99 deposited to the Baltic Sea surface was estimated to ca 2.4 kg in 2014, which would translate into ca 5 kg c-pentaBDE. As a comparison, deposition of c-pentaBDE constituents (BDEs 28, 47, 99, 100, 153 and 154) to the Baltic Proper alone ten years earlier (2004) was estimated to be 70 kg based on measurements of atmospheric deposition, i.e. a factor 14 higher deposition (Ter Schure et al., 2004). EMEP modelling predicted that Germany contributes 21% of total BDE99 deposition over the Baltic Sea, Poland 12% and Russia 9%. Great Britain contributes

somewhere between 7-9%. Emissions in HELCOM countries were estimated to contribute 63% of the total annual BDE99 deposition over the Baltic Sea (Bartnicki et al., 2016). Field measurements of atmospheric levels of PBDEs in Central Europe indicate that the highest levels are observed in air masses that have stagnated over the European continent, rather than those coming from the North Atlantic (Degrendele et al., 2018).

Other modelling studies have used the POPCYCLING-Baltic model to simulate fate of PBDEs in the Baltic Sea (Andersson et al., 2016; Mattila and Verta, 2008; Palm et al., 2004). Palm et al. included only emissions to air in the emission scenario, and predicted air concentrations of BDE47 (main component in c-pentaBDE) in good agreement with atmospheric monitoring data but underestimated concentrations in sediments (Palm et al., 2004). The authors hypothesized that degradation rates in soil and sediment used in the calculations were overestimated, and dismissed lacking emissions to water via e.g. WWTP and landfill leachates as explanation for these underestimations because also soil concentrations were underestimated in their simulations. They referred to previous studies showing that concentrations in coastal and off-shore sediments are similar (indicating that atmospheric deposition is the major source) and suggested that waterborne emissions are only of local importance. Measurements of c-pentaBDE in sediments (dry weight basis) in Stockholm City compared to nearby lakes and in the archipelago have indeed indicated a higher contamination in the city (Jonsson, 2015). Recently published results of monitoring of c-pentaBDE in off-shore sediments (dry weight basis) showed homogenous concentrations throughout the Baltic Sea in sediments sampled in 2008, but larger variability between stations in 2014 (Josefsson and Apler, 2019). The possibility of underestimated rates of atmospheric deposition as explanation

Conclusions regarding major sources and transport routes for PBDEs in the Baltic Sea are uncertain due to lacking information on emissions and behaviour of PBDEs in the environment.

Photo: Natalija Rumiantseva/Mostphotos

for underestimated sediment concentrations was not discussed by Palm et al. (Palm et al., 2004). However, in similar modelling assessments of PBDEs performed in the COHIBA project, atmospheric deposition was found to be relatively more underestimated than air concentrations (Palm Cousins, 2012), and current models' inability to accurately predict particle bound deposition for the broad range of PBDEs has been highlighted (Degrendele et al., 2018). Another study suggests that underestimation of sorption to soil and sediments in the POPCYCLING-model is partly responsible for the model underperformance as inclusion of black carbon (which increases the sorption capacity) in the model increased the predicted concentrations in these compartments (Mattila and Verta, 2008).

Note that the COHIBA project (Palm Cousins, 2012) performed similar modelling assessments as Palm et al. (Palm et al., 2004) of major transport routes to the Baltic Sea, however only based on emissions from the project partner countries (which had several gaps in their inventories) and not including PBDEs reaching the Baltic Sea via long range atmospheric transport, which is a major source. Conclusions regarding major sources and transport routes from these modelling studies are hence uncertain.

c-decaBDE

Earnshaw et al. has published emission estimates for BDE209, the main constituent of c-decaBDE, in Europe (Earnshaw et al., 2013). These were for year 2020 estimated to occur mainly (ca 2/3) to air; of this ca 90% was particle bound emissions during unloading of waste and disturbances caused by vehicles operating at landfills, and 10% gaseous loss from landfills (Earnshaw et al., 2013). Contributions from particle bound emissions during product use and recycling were expected to cease in 2020. The remaining emissions were estimated to be released to water (ca 1/3, mainly from landfill leachates >60%) and only small emissions to soil, mainly via application of sludge in agriculture (>80% of all soil emissions) (Earnshaw et al., 2013). Other older emission scenarios for BDE209 referred to by Earnshaw et al. have estimated a relatively larger proportion of emissions occurring to soil, however the uncertainly in emissions to air is large (Earnshaw et al., 2013). In a more recent emission inventory of BDE209 conducted by Abbasi et al. and published in 2019, the in-use stock was instead estimated to be the primary source to atmospheric emissions in Europe in 2020 (Abbasi et al., 2019). The latter study also estimated ca 60% higher peak emissions to air in the mid 2000s than the previous study by Earnshaw et al. (Earnshaw et al., 2013). These two studies hence come to different conclusions regarding the current sources of BDE209 in air. The latter assumed differentiated product life-times for various product categories, whereas in the previous study 10 years life-time was used for all products, leading to a smaller in-use stock compared to the Abbasi-study. Earnshaw et al. on the other hand separated evaporative and particle bound losses from in-use products and landfills (leading to higher emission factors assumed), whereas the model employed by Abbasi et al. assumed all emissions to be evaporative, i.e. abrasion of products and escape of dust from landfills to the atmosphere were not considered (Abbasi et al., 2019; Li and Wania, 2016).

The COHIBA project estimated emissions of decaBDE to in total 6-150 kg to outdoor air, 60-1800 kg to inland surface water, 3500 – 111000 kg to land (agricultural and forest soil). The emissions to air originated mainly from steel production (5-130 kg, also reported by COHIBA to

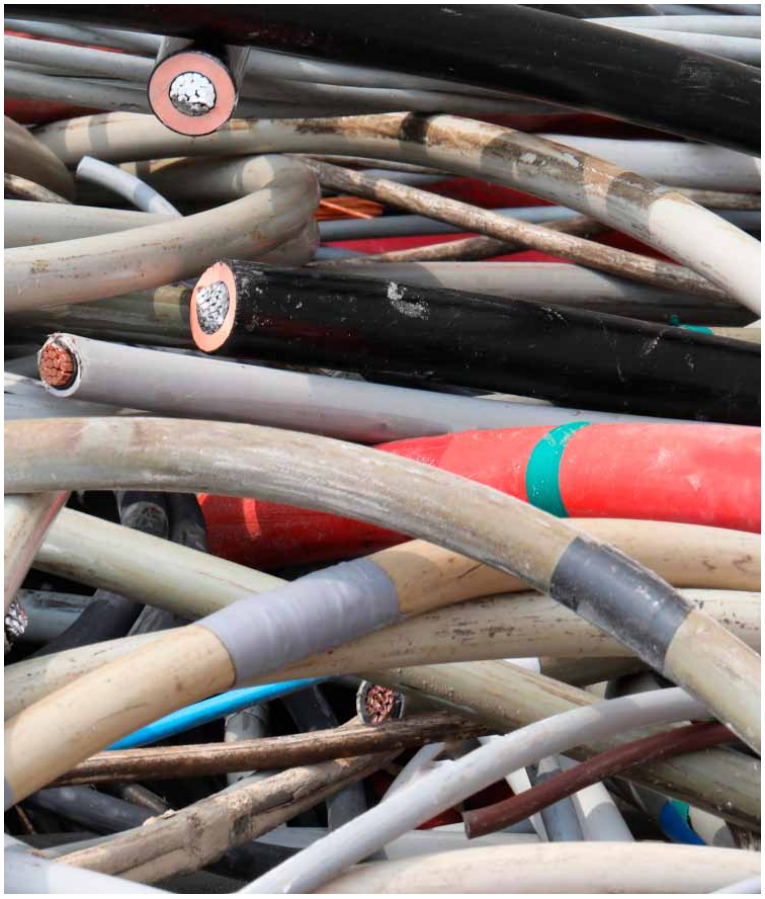

Photo: Mostphotos

DecaBDE has been used in many applications, including cables and wires.

contribute 73 – 94% or air emissions), dismantling and crushing of electronics (0.02-13 kg), accidental fires in electronic waste (5-81 kg, 2.5 – 5%) and from indoor air in private homes (15 kg, 16%). For indoor air, electrical appliances accounted for 100% of the estimated emissions, for inland surface water 90-97% of decaBDE came from atmospheric deposition (Andersson, 2012).

Björklund et al. estimated 10-fold higher emissions from Swedish public buildings than private homes also for BDE209 (0.012-1.2 and 0.83 – 31 kg/year from private homes and public buildings, respectively), and calculated that ca 85% of emissions to outdoor air (excluding long range atmospheric transport) in Sweden was from indoor air escaping through ventilation (Björklund et al., 2012). In a follow-up study, a considerably lower emission rate from indoor to outdoor air was predicted using a model; the differences were explained by a higher ventilation rate used to calculate outflows from public buildings and by higher concentrations in offices and public buildings measured in the previous study compared those predicted by the model (Cousins et al., 2014). In fact, the modelling study predicted that the removal of chemicals via indoor processes such as vacuuming and wet mopping exceeded transport via ventilation to the outdoor. This loss mechanism is not considered in the emission estimates in the two studies by Abbasi et al. (Abbasi et al., 2019) and Earnshaw et al. (Earnshaw et al., 2013) discussed above, where all emissions from the in-use product stock are assumed to enter the outdoor air instantly. A recent modelling study by Li et al. indicated that for PCB153 (log KOA = 9.44), the loss in indoor environments (e.g. degradation, dust removal during cleaning) is small compared to the fraction that is transported to outdoor air (Li et al., 2018), although for BDE209 (log KOA = 16.4), which partitions more strongly to dust, this conclusion may not hold true.

Note that waste containing PBDEs, mainly BDE209 in e-waste and vehicles, has been exported to less industrialized regions (i.e. Africa, Central and South America) where it has been reused or disposed of using inappropriate techniques such as open burning. This trade is estimated to increase global annual emissions of BDE209 by 5-15% after 2010, however this is not predicted to impact emissions in industrialized regions like Europe (Abbasi et al., 2019).

Status in the Baltic Sea

The status of the Baltic Sea with respect to PBDEs is evaluated based on congeners 28, 47, 99, 100, 153 and 154, i.e. main constituents of c-pentaBDE. The Environmental Quality Standard (EQS) threshold value of 0.0085 µg/kg ww biota (sum of BDE 28, 47, 99, 100, 153 and 154) is exceeded at all monitoring stations in the Baltic Sea (HELCOM, 2018). The highest levels are observed mainly in perch in the Finnish monitoring stations in the Bothnian Bay, Åland Sea and Gulf of Finland where fresh weight concentrations are exceeding the EQS by a factor 200 to >1200. High levels are also observed in cod, herring and eelpout in the Arkona Basin, Great Belt, and Kattegat. The EQS is considered to be very low, as it is based on a threshold derived to protect human health, and is not endorsed by the European Food Safety Authority (EFSA) (HELCOM, 2018). A secondary threshold is set for concentrations in sediment of 310 µg/kg dry weight (dw). There are no exceedances of this threshold in the basins where sediment data are available (HELCOM, 2018).

Temporal trends in biota

Fliedner et al. studied PBDEs in herring gull eggs collected annually in Heuweise on the German Baltic Sea coast (Fliedner et al., 2012). C-pentaBDE congeners (sum of BDE 47, 85, 99, 100, 153, and 154) decreased significantly during the study period (1996-2008). For c-octaBDE congeners (sum of BDE 183, 197, 203 and 207) a decline was observed after 2002, while for deca-BDE (BDE 209) an increase was observed. However, these trends were not statistically significant.

As part of the Swedish environmental programme, a number of c-pentaBDE congeners (BDE 28, 47, 99, 100, 153 and 154) are monitored in herring muscle, cod liver, perch, eelpout, blue mussel and guillemot egg sampled in the Baltic Sea and on the Swedish West coast (Bignert et al., 2017; Danielsson et al., 2019). Significant increasing concentrations of BDE 47, BDE 99 and BDE 100 were observed in guillemot eggs from the late 1960s until the early 1990s, followed by rapid declines. By the early 2000s the concentrations were comparable to those observed in the 1960s. Between 2007 and 2017, significant annual decreases of 7-8% were observed for BDE47, 99, 100 and 153 in guillemot eggs; the trend was negative but not significant for BDE28, and BDE154 was not measured (Danielsson et al., 2019). Measurements of PBDEs in white tailed eagle eggs indicate that the levels were consequently higher in the northern Bothnian Sea compared to other Swedish coastal zones. This pattern has been observed also for PCBs, PFASs and other organic contaminants monitored (Hellström, 2016).

For other matrices, the trends were not as consistent. Declining trends of BDE 47 and 99 were observed in cod liver sampled outside Gotland (Southern Baltic Sea) and Fladen (Swedish West coast) from 1980 and

1999 to 2016, respectively, however between 2008 and 2017 no significant trends were observed for BDE47. The shorter time periods (2008-2017) analysed for herring data show tendencies of declining trends of BDE 47 in 19 of 22 monitored sites with significant trends in 5 sites (6 – 10% annual decrease). The tendency for BDE99 was declining concentrations in 16/20 sites, with statistically significant trends observed in 5 sites (6 – 10% annual decrease). Tendencies (i.e. not significant) of increasing trends were observed at two and three sites for BDE47 and 99, respectively. The largest number of sites with tendencies of increasing concentrations over time was found for BDE28 and 153, however these trends were significant only in two cases and time trends were significantly decreasing in five and two sites, respectively. In comparison to the Swedish west coast, higher concentrations of BDE 47, 99, and 153 were generally observed in Baltic Sea herring and cod.

Since 2000, BDE 47 and 99 have been monitored in blue mussel from three different sites. Declining trends of BDE 47 and 99 were observed in two of these, while indications of increasing trends were observed in the third. Overall, the data from the Swedish environmental monitoring program indicate that the levels of the measured PBDEs are declining. However, at all study sites the BDE 47 concentration alone is above the EQS defined for the sum of BDE 28, 47, 99, 100, 153 and 154 (0.0085 µg/g wet weight).

In Baltic ringed seal collected between 1974 and 2015, a maximum in overall PBDE concentration (sum of BDE 28, 47, 66, 85, 99, 100, 154 and 153) was observed around the year 2000 (Bjurlid et al., 2018). Time trend analysis of the sum of 14 PBDE congeners (BDE 28-190) in herring sampled along the Finnish coast between 1978 and 2009 suggests that the maxima in overall PBDE concentrations occurred during the late 1980s or early 1990s, although data points from this particular time period are missing (Airaksinen et al., 2014). Over the study period, the relative contribution of BDE 47 and 99 decreased. This trend was compensated by an increase in the proportions of BDE 100 and BDE 154.

ANNUAL CHANGE OF BDE-LEVELS IN HERRING, COD AND GUILLEMOT EGGS (%)						
Herring muscle	**BDE47**	**Years**	**BDE47**	**BDE99**	**Years**	**Basin**
Råneфjärden	-12	2007–2016	-9	-6	2008–2017	Bothnian Bay
N Baltic Proper offshore			-8		2008–2017	Baltic Proper
Landsort	-6,5	1999–2016	-6	-6	2008–2017	Baltic Proper
Utlängan	-5,5	1999–2016	-10	-10	2008–2017	Bornholm Basin
W Hanöbukten			-7	-8	2008–2017	Bornholm Basin
Fladen	-8,3	1999–2016				Kattegat
Väderöarna	-9	1999–2016				Skagerrak
Cod liver	**BDE47**	**Years**	**BDE47**	**BDE99**	**Years**	**Basin**
Gotland	-1,5	2007–2016				Baltic Proper
Fladen	-9,2	1999–2016		-14	2008–2017	Kattegat
Guillemot eggs	**BDE47**	**Years**	**BDE47**	**BDE99**	**Years**	**Basin**
Stora Karlsö			-8	-8	2008–2017	Baltic Proper

Table 2. *Annual change (%) of measured levels in herring, cod and guillemot sampled in the Swedish monitoring program with significant declining trends. Data extracted from (Bignert et al., 2017; Danielsson et al., 2019)*

Photo: NOAA

Photo: David Thyberg/Mostphotos

Levels of c-pentaBDE congeners in Baltic Sea biota such as ringed seals and guillemots are declining.

The overall PBDE concentrations observed in 2009 were comparable to those observed in 1978. In the Gulf of Bothnia, herring PBDE concentrations were about twice as high as in the Gulf of Finland. This was attributed to differences in herring growth rates between the basins.

In a sediment core taken in the Bornholm deep (Southern Baltic Sea), Nylund et al. observed increasing levels of PBDEs from the mid-1940s up until the 1990s (Nylund et al., 1992). The target analytes in this study were BDE 47, BDE 99 and a third congener of unknown molecular structure. In three sediment cores taken in the Stockholm city centre increasing levels of PBDEs (sum of 28, 47, 99, 100, 153 and 154) were observed from 1975 to 2015, whereas in a sediment core taken in the Stockholm archipelago, measurable levels of PBDEs were not observed (Jonsson, 2015). Monitoring of off-shore sediments in 2008 and 2014 did not show significant differences in the total PBDE levels (dry weight basis) between these years due to large spatial variability (Josefsson and Apler, 2019). There was no correlation between PBDE-levels and content of total organic carbon in the sediments. BDE183 was not present above the reporting limit of 0.03 µg/kg dw in any location. BDE209 was below the reporting limit of 0.3 µg/kg ww in all stations in 2014, but higher in 2008 (ranging from <0.5 to >19 µg/kg ww). The sum of BDE 47, 85, 99, 100, 153, and 154 was dominated by BDE47, 85 and 99. The levels of these congeners were significantly higher in the Baltic Proper compared to other basins.

Overall, the reported trends in Baltic Sea biota indicate that the levels of c-pentaBDE congeners are declining. However, for octa- and deca-BDE, temporal trend data are scarce.

Temporal trends in European air

Within the Arctic Monitoring and Assessment Program (AMAP), PBDEs are monitored in air in three European Arctic sites, namely Pallas (Finland, since 2003), Stórhöfði (Iceland, since 2007) and Zeppelin (Svalbard, since 2006). In data reported up until 2012, decreasing trends were observed for BDE 47 in all three sites (half-life 2.6-4.4 years, corresponding to ~23 – 15% annual declines). Additionally decreasing trends were observed for BDE 99 (half-life 2.6-2.9 years) and BDE 100 (half-life 4.0-4.1 years) at Pallas and Zeppelin (Hung et al., 2016). As a consequence of low detection frequencies, no trend was observed for BDE 138. Furthermore, no trends of PBDEs were observed in air sampled on Northern Greenland between 2008 and 2013 (Bossi et al., 2016). The lack of a clear trend was attributed to high inter-annual variability in combination with a short monitoring period (Bossi et al., 2016).

In 4 of 11 monitored sites in Norway and the United Kingdom, declining air levels of BDE 47, 49, 99, 100, 153 and 154 were observed between 2000 and 2008 (Schuster et al., 2010). The half-lives for these congeners spanned from 1.4 to 4.0 years. Temporal trends in air sampled in three United Kingdom locations between 1999 and 2012, demonstrate that a decrease in PBDE levels (sum of congeners 47, 49, 99, 100, 119, 154, 153, 138, 183) has taken place since the period 2001-2003 (Graf et al., 2016). The atmospheric clearance rates for these urban and semi-rural sites were 2.0-3.5 years. These declines were strongly correlated with trends in European emissions estimated by Prevedourous et al. for years 2000 to 2013, suggesting that ongoing releases from articles containing PBDEs controlled the air concentrations (Graf et al., 2016; Prevedouros et al., 2004). However, in a fourth monitored rural site, no statistically significant trend was observed for air concentrations after year 2000 (Birgul et al., 2012; Graf et al., 2016).

Photo: Mostphotos

Monitoring of sludge in Swedish WWTPs indicates declining levels of several c-pentaBDE congeners. For decaBDE, no clear time trend has yet been observed.

As part of the Swedish environmental monitoring program, BDE 47, 99 and 100 have been measured in air and in atmospheric deposition in Aspvreten, Pallas and Råö since 2001, 2003 and 2008, respectively. Although no statistical time trend analysis was applied, a survey of the data generated up until 2017 concluded that trends of these substances generally have decreased over the study period (Fredricsson, Malin Brorström-Lundén, Eva Danielsson et al., 2018; Sjöberg et al., 2016). In the same sites, BDE 209 (monitored since 2009) and BDEs 85, 153, 154 (monitored since 2013) had low detection frequencies and were only sporadically observed in both air and deposition.

In air sampled at a background site in the central Czech Republic between 2011 and 2014, statistically significant declining trends were observed for BDE 99, 100, 153 and 209 (with apparent half-lives of 2.8-4.8 years), but not for lower brominated congeners (BDE 28, 47, 85) (Degrendele et al., 2018). Instead, an increasing trend of BDE 28 was observed. This indicates that environmental levels of higher brominated congeners have declined in response to reduced primary emissions, but that additional sources contribute to ongoing releases of lower brominated congeners. These lower brominated congeners may be formed in the environment via photolytic debromination of higher brominated congeners (Degrendele et al., 2018; Schenker et al., 2008a).

In summary, insignificant or declining trends are observed for the c-pentaBDE congeners commonly monitored in European air, while temporal data on octa- and decaBDE are scarce. The only increasing trend in European air was reported for BDE 28 (Degrendele et al., 2018). This observation suggests that lower brominated PBDEs may be increasing in European air.

PBDEs have also been monitored in sludge from Swedish WWTPs. Between 2004 and 2012, concentrations of BDE 154 and 183 declined annually by 20% (Olofsson et al., 2012), and levels of BDE 47 and 99 also appear to have declined since 2004 (Haglund, 2019). On the contrary, BDE209 in sludge increased by 16% per year 2004 to 2012 (Olofsson et al., 2012), and monitoring in recent years shows no clear trend up to 2017 (Haglund, 2019).

Because the predominant emission sources are currently uncertain, both in Europe and globally, future trends of PBDE concentrations are difficult to predict. However, the temporal trends observed in biota in recent years can give an indication of the time it will take until concentrations drop below the EQS in the Baltic Sea. Figure 1 shows how concentrations of c-pentaBDE in cod and herring at different monitoring stations throughout the Baltic Sea will decline assuming similar decline rates as observed for BDE47 in these species at the Swedish monitoring stations

ESTIMATED TIME FOR BDE-CONCENTRATIONS TO DECREASE IN HERRING AND COD

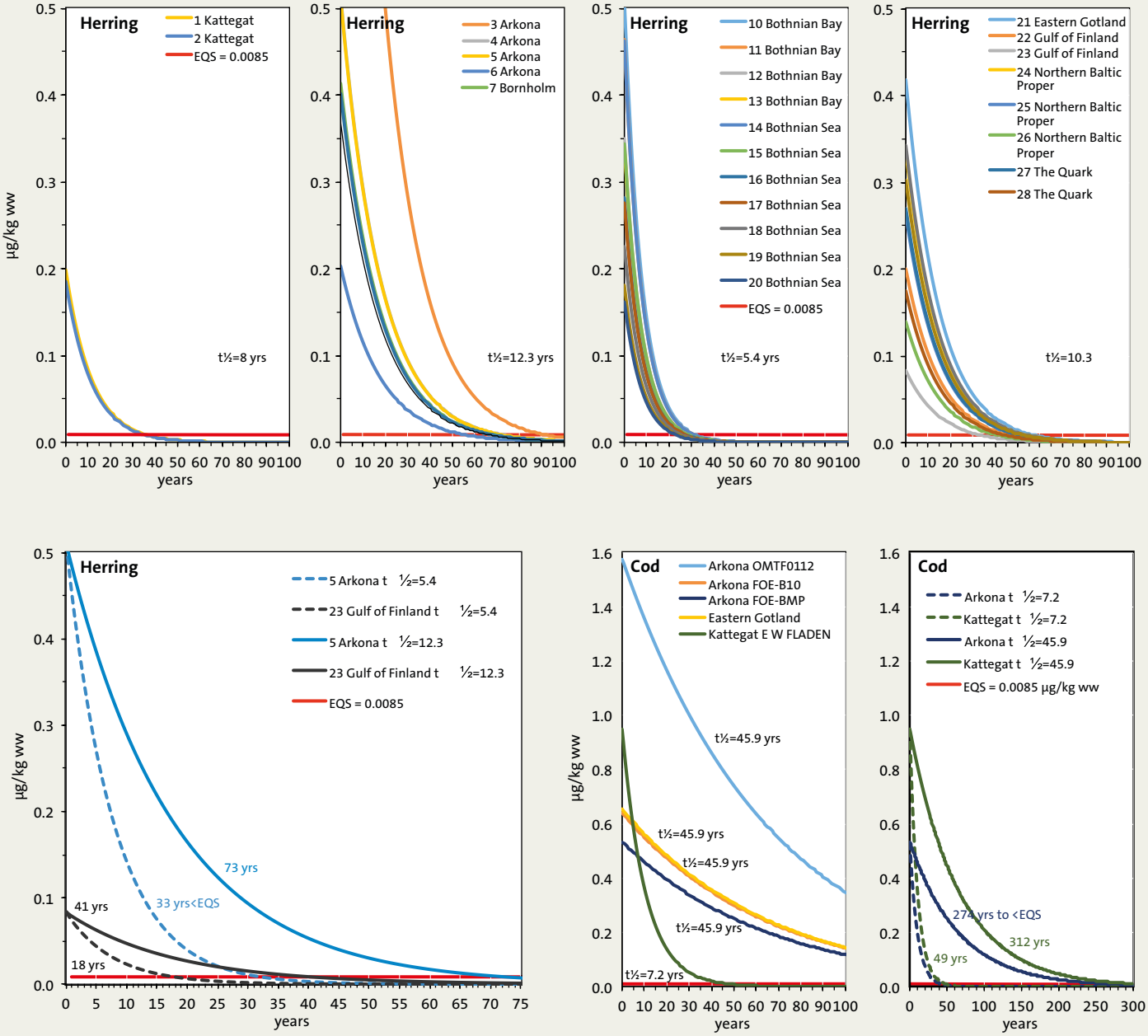

Figure 1. *Estimated time for mean concentrations of PBDEs (sum of congeners 28, 47, 99, 100, 153 and 154) to decrease below the threshold of 0.0085 µg/kg ww fish muscle where this threshold was exceeded in the most recent HELCOM status assessment (performed in 2018) assuming that [PBDE](t)=[PBDE]initial e-kt. The last year of monitoring in the dataset was 2011 to 2016 depending on station. The initial value is the observed concentration at the last year of monitoring or mean log concentration during 3-4 years. The panels in the top row show estimations for herring and assumed half-life for the sea basins. The bottom left panel shows examples of how assumptions regarding half-lives impact predicted time to mean concentrations below the EQS at two monitoring stations. The bottom right panels show the corresponding graphs for cod. Numbers refer to monitoring stations: 1=E W FLADEN, =KULLEN, 3=OMTF0112, 4=Abbekås, 5=FOE-B10, 6=FOE-BMP, 7=LKOL, 8=Utlängan, 9=Västra Hanöbukten, 10=Kinnbäcksfjärden, 11=Kalajoki 1, 12=Harufjärden, 13=Råneåfjärden,14=Gaviksfjärden, 15=Bothnian Sea off shore, 16=Långvindsfjärden, 17=Pori 1, 18=Ängskärsklubb, 19=southwest Vekara, 20=Selkameri Southern, 21=LWLA, 22=Porvoo 1 avomeri, 23=Kotka, 24=Lagnö, 25=N Baltic Proper off shore, 26=Hanko 2, 27=Holmöarna, 28=Storskaret W, 29=Byxelkrok, 30=Landsort. Calculations are made using data available from HELCOM at: http://metadata.helcom.fi/geonetwork/srv/eng/catalog.search#/metadata/cea59caa-d12c-4d3e-a0bc-e5ce0d19f280 and with half-lives reported in (Bignert et al., 2017; Danielsson et al., 2019).*

in the different basins (Bignert et al., 2017). The decline of BDE47 and 99 is similar at all stations with significant trends (Table 2), and these congeners constitute the majority of total c-pentaBDE mass. With the shortest half-lives at the least contaminated monitoring stations, it will take 18 and 43 years for levels in herring and cod to drop below the threshold, respectively. With the longer half-lives observed and in more contaminated fish, it will take considerably longer than 100 years to achieve this.

Conclusions

There are large uncertainties in the available emissions of PBDEs, and to identify the major sources of PBDEs is not straightforward. Different studies come to different conclusions regarding major emission sources in Europe and the Baltic Sea region. Model predictions however indicate that atmospheric deposition is the major transport route of PBDEs found in the Baltic Sea. Although the applied models cannot predict atmospheric deposition accurately, the predictions are likely underestimations in any case.

The major source of PBDEs to the European air is probably still ongoing primary emissions from in-use articles and products and/or waste. Indoor emissions escaping to outdoor air in urban areas are important sources of atmospheric PBDEs, and these PBDEs undergo long range atmospheric transport, also including the heaviest congeners.

Emissions of c-pentaBDE have declined since ca 2004 and c-decaBDE since 2010. The importance of steel production for PBDEs and accidental fires in e-waste recycling facilities for c-pentaBDE is highly uncertain. The importance of landfills as current sources of BDE209 depends largely on assumptions regarding emission factors. Different approaches to calculate particle bound transport arising from unloading of waste and vehicle movements in landfills and assumptions of product service lifetimes give different conclusions regarding the relative importance of these sources. Also, the indoor fate of BDE209 may impact conclusions about the major current sources of this substance.

Environmental time trends in Baltic Sea biota indicate that levels of constituents of c-pentaBDE are declining, for decaBDE and octaBDE time trend data are scarce. It is only the c-pentaBDEs that are included in the HELCOM evaluation of environmental status in the Baltic Sea. Based on observed rates of decline during the last 10-20 years, it will in the best case scenario take ca 18 years for concentrations to drop below the threshold in the least contaminated Baltic Sea herring, however in most locations this will not be achieved for at least 30-40 years or longer.

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References

Abbasi, G., 2015. Story of Brominated Flame Retardants: Substance Flow Analysis of PBDEs from Use to Waste. Available at: https://search.proquest.com/openview/ca6786d28f96b6d15413130415c7f67f/1?pq-origsite=gscholar&cbl=18750&diss=y. University of Toronto (Canada).

Abbasi, G., Li, L., Breivik, K., 2019. Global Historical Stocks and Emissions of PBDEs. Environ. Sci. Technol.

Airaksinen, R., Hallikainen, A., Rantakokko, P., Ruokojärvi, P., Vuorinen, P.J., Mannio, J., Kiviranta, H., 2015. Levels and congener profiles of PBDEs in edible Baltic, freshwater, and farmed fish in Finland. Environ. Sci. Technol. 49, 3851–3859.

Airaksinen, R., Hallikainen, A., Rantakokko, P., Ruokojärvi, P., Vuorinen, P.J., Parmanne, R., Verta, M., Mannio, J., Kiviranta, H., 2014. Time trends and congener profiles of PCDD/Fs, PCBs, and PBDEs in Baltic herring off the coast of Finland during 1978–2009. Chemosphere 114, 165–171.

Andersson, H., 2012. COHIBA WP4 Background paper - Identification of sources and estimation of inputs to the Baltic Sea.

Andersson, H., Palm Cousins, A., Brorström-Lundén, E., Westerdahl, J., Braun, H., Bergfors, L., Pettersson, M., Wickman, T., Jamtrot, A., Parkman, H., 2016. Major sources and flows of the Baltic Sea action plan hazardous substances. WP4 Final Rep. COHIBA Proj. www. cohiba-project. net/publications. Accessed Nov.

Bartnicki, J., Gusev, A., Aas, W., Benedictow, A., 2016. Atmospheric supply of nitrogen, cadmium, mercury, benzo (a) pyrene and PBDEs to the Baltic Sea in 2014. MSC-W Tech. Rep. 1, 2016.

Bignert, A., Danielsson, S., Ek, C., Faxneld, S., Nyberg, E., 2017. Comments Concerning the National Swedish Contaminant Monitoring Programme in Marine Biota, 2017 (2016 years data).

Birgul, A., Katsoyiannis, A., Gioia, R., Crosse, J., Earnshaw, M., Ratola, N., Jones, K.C., Sweetman, A.J., 2012. Atmospheric polybrominated diphenyl ethers (PBDEs) in the United Kingdom. Environ. Pollut. 169, 105–111.

Björklund, J.A., Thuresson, K., Cousins, A.P., Sellström, U., Emenius, G., de Wit, C.A., 2012. Indoor air is a significant source of tri-decabrominated diphenyl ethers to outdoor air via ventilation systems. Environ. Sci. Technol. 46, 5876–5884.

Bjurlid, F., Roos, A., Jogsten, I.E., Hagberg, J., 2018. Temporal trends of PBDD/Fs, PCDD/Fs, PBDEs and PCBs in ringed seals from the Baltic Sea (Pusa hispida botnica) between 1974 and 2015. Sci. Total Environ. 616, 1374–1383.

Bossi, R., Vorkamp, K., Skov, H., 2016. Concentrations of organochlorine pesticides, polybrominated diphenyl ethers and perfluorinated compounds in the atmosphere of North Greenland. Environ. Pollut. 217, 4–10.

Breivik, K., Wania, F., Muir, D.C.G., Alaee, M., Backus, S., Pacepavicius, G., 2006. Empirical and Modeling Evidence of the Long-Range Atmospheric Transport of Decabromodiphenyl Ether. Environ. Sci. Technol. 40, 4612–4618. https://doi.org/10.1021/es060730s

Cousins, A.P., Holmgren, T., Remberger, M., 2014. Emissions of two phthalate esters and BDE 209 to indoor air and their impact on urban air quality. Sci. Total Environ. 470, 527–535.

Danielsson, S., Ek, C., Faxneld, S., Pütz Winkens, K., 2019. The Swedish National Monitoring Programme for Contaminants in marine biota (until 2017 year's data)-Temporal trends and spatial variations.

Degrendele, C., Wilson, J., Kukučka, P., Klánová, J., Lammel, G., 2018. Are atmospheric PBDE levels declining in central Europe? Examination of the seasonal and semi-long-term variations, gas–particle partitioning and implications for long-range atmospheric transport. Atmos. Chem. Phys. 18, 12877–12890.

Earnshaw, M.R., Jones, K.C., Sweetman, A.J., 2015. A first European scale multimedia fate modelling of BDE-209 from 1970 to 2020. Environ. Int. 74, 71–81.

Earnshaw, M.R., Jones, K.C., Sweetman, A.J., 2013. Estimating European historical production, consumption and atmospheric emissions of decabromodiphenyl ether. Sci. Total Environ. 447, 133–142.

ECHA, 2012. ECHA, European Chemicals Agency (2012c). Annex XV dossier. Proposal for Identification of a PBT/vPvB Substance. Bis(pentabromophenyl)ether (decabromodiphenyl ether; decaBDE). July 2012-final. Submitted by the United Kingdom, August 2012. Available at: htt.

Fliedner, A., Rüdel, H., Jürling, H., Müller, J., Neugebauer, F., Schröter-Kermani, C., 2012. Levels and trends of industrial chemicals (PCBs, PFCs, PBDEs) in archived herring gull eggs from German coastal regions. Environ. Sci. Eur. 24, 7.

Fredricsson, Malin Brorström-Lundén, Eva Danielsson, H., Hansson, K., Pihl Karlsson, G., Nerentorp, M., Potter, A., Sjöberg, K., Kreuger, J., Nanos, T., Areskoug, H., Krejci, R., Alpfjord Wylde, H., Andersson, C., Andersson, S., Carlund, T., Josefsson, W., Leung, W., 2018. Nationell övervakning. Sakrapport med data från övervakning inom Programområde Luft t.o.m. 2017. Rapportnummer C 360. ISBN: 978-91-88787-99-6.

Graf, C., Katsoyiannis, A., Jones, K.C., Sweetman, A.J., 2016. The TOMPs ambient air monitoring network–Continuous data on UK air quality for over 20 years. Environ. Pollut. 217, 42–51.

Haglund, P., 2019. Miljöövervakning av utgående vatten & slam från svenska avloppsreningsverk: Resultat från år 2016-2017och en sammanfattning av slamresultaten för åren 2004-2017.

HELCOM, 2018. Polybrominated diphenyl ethers (PBDEs). HELCOM core indicator report. Online. viewed December 2019,https://www.helcom.fi/wp-content/uploads/2019/08/Polybrominated-diphenyl-ethers-PBDEs-HELCOM-core-indicator-2018-1.pdf. ISSN 2343-2543.

Hellström, P., 2016. Rapportering från undersökning av DDT-PCB-HCB-HCH, PBDE-HBCD, PFAS och stabila isotoper i ägg från havsörn 2015.

Hung, H., Katsoyiannis, A.A., Brorström-Lundén, E., Olafsdottir, K., Aas, W., Breivik, K., Bohlin-Nizzetto, P., Sigurdsson, A., Hakola, H., Bossi, R., 2016. Temporal trends of Persistent Organic Pollutants (POPs) in arctic air: 20 years of monitoring under the Arctic Monitoring and Assessment Programme (AMAP). Environ. Pollut. 217, 52–61.

Jonsson, P., 2015. Miljögifter i sediment i Stockholms skärgård och östra Mälaren 2013. Länsstyrelsen.

Josefsson, S., Apler, A., 2019. Miljöföroreningar i utsjösediment–geografiska mönster och tidstrender.

Kemikalieinspektionen, 2003. Swedish Chemicals Agency: Bromerade flamskyddsmedel– förutsättningar för ett nationellt förbud Rapport från ett regeringsuppdrag KEMI 4/03. Available at: https://www.kemi.se/global/rapporter/2003/rapport-4-03.pdf.

Kierkegaard, A., 2007. PBDEs in the environment: Time trends, bioaccumulation and the identification of their successor, decabromodiphenyl ethane.

Kuo, Y.-M., Sepúlveda, M.S., Hua, I., Ochoa-Acuña, H.G., Sutton, T.M., 2010. Bioaccumulation and biomagnification of polybrominated diphenyl ethers in a food web of Lake Michigan. Ecotoxicology 19, 623–634.

La Guardia, M.J., Hale, R.C., Harvey, E., 2007. Evidence of debromination of decabromodiphenyl ether (BDE-209) in biota from a wastewater receiving stream. Environ. Sci. Technol. 41, 6663–6670.

La Guardia, M.J., Hale, R.C., Harvey, E., 2006. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. Environ. Sci. Technol. 40, 6247–6254.

Li, L., Arnot, J.A., Wania, F., 2018. Towards a systematic understanding of the dynamic fate of polychlorinated biphenyls in indoor, urban and rural environments. Environ. Int. 117, 57–68.

Li, L., Wania, F., 2016. Tracking chemicals in products around the world: introduction of a dynamic substance flow analysis model and application to PCBs. Environ. Int. 94, 674–686.

Li, Y.-F., Qiao, L.-N., Ren, N.-Q., Sverko, E., Mackay, D., Macdonald, R.W., 2016. Decabrominated diphenyl ethers (BDE-209) in Chinese and global air: levels, gas/particle partitioning, and long-range transport: is long-range transport of BDE-209 really governed by the movement of particles? Environ. Sci. Technol. 51, 1035–1042.

Mattila, T.J., Verta, M., 2008. Modeling the importance of biota and black carbon as vectors of polybrominated diphenyl ethers (PBDEs) in the Baltic Sea ecosystem. Environ. Sci. Technol. 42, 4831–4836.

Morf, L.S., Buser, A.M., Taverna, R., Bader, H.-P., Scheidegger, R., 2008. Dynamic substance flow analysis as a valuable risk evaluation tool–A case study for brominated flame retardants as an example of potential endocrine disrupters. Chim. Int. J. Chem. 62, 424–431.

Newton, S., Sellström, U., de Wit, C.A., 2015. Emerging flame retardants, PBDEs, and HBCDDs in indoor and outdoor media in Stockholm, Sweden. Environ. Sci. Technol. 49, 2912–2920.

Nylund, K., Asplund, L., Jansson, B., Jonsson, P., Litzén, K., Sellström, U., 1992. Analysis of some polyhalogenated organic pollutants in sediment and sewage sludge. Chemosphere 24, 1721–1730.

Olofsson, U., Bignert, A., Haglund, P., 2012. Time-trends of metals and organic contaminants in sewage sludge. Water Res. 46, 4841–4851.

Palm, A., Brorström-Lundén, E., Breivik, K., 2004. Transport and fate of polybrominated diphenyl ethers in the Baltic and Arctic regions. Nordic Council of Ministers.

Palm, A., Cousins, I.T., Mackay, D., Tysklind, M., Metcalfe, C., Alaee, M., 2002. Assessing the environmental fate of chemicals of emerging concern: a case study of the polybrominated diphenyl ethers. Environ. Pollut. 117, 195–213.

Palm Cousins, A., 2012. COHIBA WP4 Report: Modelling the fate of organic contaminants in the Baltic Sea Application of the POPCYCLING-Baltic model.

Prevedouros, K., Jones, K.C., Sweetman, A.J., 2004. Estimation of the production, consumption, and atmospheric emissions of pentabrominated diphenyl ether in Europe between 1970 and 2000. Environ. Sci. Technol. 38, 3224–3231.

Schenker, U., Scheringer, M., Hungerbühler, K., 2008a. Investigating the global fate of DDT: model evaluation and estimation of future trends. Environ. Sci. Technol. 42, 1178–1184.

Schenker, U., Soltermann, F., Scheringer, M., Hungerbühler, K., 2008b. Modeling the Environmental Fate of Polybrominated Diphenyl Ethers (PBDEs): The Importance of Photolysis for the Formation of Lighter PBDEs. Environ. Sci. Technol. 42, 9244–9249. https://doi.org/10.1021/es801042n

Schuster, J.K., Gioia, R., Breivik, K., Steinnes, E., Scheringer, M., Jones, K.C., 2010. Trends in European background air reflect reductions in primary emissions of PCBs and PBDEs. Environ. Sci. Technol. 44, 6760–6766.

Sjöberg, K., Brorström-Lundén, E., Danielsson, H., Fredricsson, M., Hansson, K., Pihl Karlsson, G., Potter, A., Wängberg, I., Kreuger, J., Nanos, T., 2016. Nationell luftövervakning Sakrapport med data från övervakning inom Programområde Luft tom 2015.

Söderström, G., Sellström, U., de Wit, C.A., Tysklind, M., 2004. Photolytic debromination of decabromodiphenyl ether (BDE 209). Environ. Sci. Technol. 38, 127–132.

Stockholm Convention, n.d. http://chm.pops.int/Implementation/Alternatives/AlternativestoPOPs/ChemicalslistedinAnnexA/tabid/5837/Default.aspx.

Ter Schure, A.F.H., Larsson, P., Agrell, C., Boon, J.P., 2004. Atmospheric transport of polybrominated diphenyl ethers and polychlorinated biphenyls to the Baltic Sea. Environ. Sci. Technol. 38, 1282–1287.

Toropovs, V., 2011. COHIBA Guidance document No. 3 Measures for emission reduction of polybrominated diphenyl ethers (PBDEs) in the Baltic Sea area. Guidance Document compiled under the leadership of the Federal Environment Agency of Germany (UBA) within Work package 5 of CO.

UNEP, 2017. Guidance on best available techniques and best environmental practices for the recycling and disposal of wastes containing polybrominated diphenyl ethers (PBDEs) listed under the Stockholm Convention on Persistent Organic Pollutants. United Nations Enviro.

UNEP, 2014. Report of the Persistent Organic Pollutants Review Committee on the work of its tenth meeting Addendum Risk profile on decabromodiphenyl ether (commercial mixture, c-decaBDE). UNEP/POPS/POPRC.10/10/Add.2.

UNEP, 2010. Technical review of the implications of recycling commercial penta and octabromodiphenyl ethers. Stockholm Convention document for 6th POP Reviewing Committee meeting (UNEP/POPS/POPRC.6/2) Geneva 11-15. October 2010.

UNEP, 2007. Report of the Persistent Organic Pollutants Review Committee on the work of its third meeting Addendum Risk profile on commercial octabromodiphenyl ether. UNEP/POPS/POPRC.3/20/Add.6 United Nations Environment Programme. Available at: http://chm.pops.int/T.

UNEP, 2006. Report of the Persistent Organic Pollutants Review Committee on the work of its second meeting Addendum Risk profile on commercial pentabromodiphenyl ether. UNEP/POPS/POPRC.2/17/Add.1. United Nations Environment Programme. Available at: http://chm.pops.in.

Wan, Y., Zhang, K., Dong, Z., Hu, J., 2013. Distribution is a major factor affecting bioaccumulation of decabrominated diphenyl ether: Chinese sturgeon (Acipenser sinensis) as an example. Environ. Sci. Technol. 47, 2279–2286.

Yue, C., Li, L.Y., 2013. Filling the gap: estimating physicochemical properties of the full array of polybrominated diphenyl ethers (PBDEs). Environ. Pollut. 180, 312–323.

Zeng, X., Massey Simonich, S.L., Robrock, K.R., Korytár, P., Alvarez- Cohen, L., Barofsky, D.F., 2010. Application of a congener- specific debromination model to study photodebromination, anaerobic microbial debromination, and FE0 reduction of polybrominated diphenyl ethers. Environ. Toxicol. Chem. An Int. J. 29, 770–778.

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