Screening of decabromodiphenyl ethane (dbdpe) in lake sediment, marine sediment and peregrine falcon (*Falco peregrinus*) eggs

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Introduction

Decabromodiphenyl ethane (dbdpe) (**Figure 1**) is a brominated flame retardant (BFR) used as an additive to flammable material to decrease the risk of accidental fire. It is used in a broad range of polymers, in products ranging from consumer electronics to wire and cable coatings to insulation foams.

In general terms, BFRs are a controversial group of chemicals. Flame retardants protect lives by increasing fire safety, but at the same time, several of the BFRs are regarded as concerning environmental contaminants. These include polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD). The reasons for concern about BFRs are observed or suspected hazardous environmental behaviour, e.g. high persistence in the environment and adverse biological effects.

Dbdpe is now a commercially important alternative to decabromodiphenyl ether (decaBDE), which is a BFR with similar applications and structural similarities (**Figure 1**). DecaBDE, like the lower brominated PBDEs, has been shown to be ubiquitously present in the environment (**de Wit et al., 2006; Law et al., 2006; Hale et al., 2003; Wang et al., 2007**). The usage of decaBDE in Europe was recently prohibited in electrical and electronic equipment because it is likely to pose a risk to health or the environment (**European Commission, 2003**). This has strengthened the position of dbdpe as a replacement chemical.

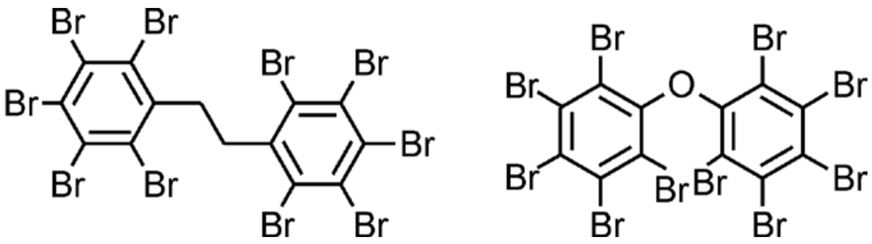


Figure 1. To the left: molecular structure of decabromodiphenyl ethane (dbdpe). To the right: decabromodiphenyl ether (decaBDE).

Dbdpe has been produced and used for more than 20 years (**Umweltbundesamt, 2001**). Presumably there have been considerable emissions to the environment. Nevertheless, few scientific studies have been conducted on the environmental behaviour of dbdpe since its introduction to the market. The main objective of this report is therefore to contribute to scientific understanding of the environmental behaviour and occurrence of dbdpe. The work will help to clarify whether dbdpe poses a threat to human health and wildlife.

This report is built upon three studies. The first is a screening study of dbdpe in sediments from remote Swedish lakes. The objective of that screening survey was to determine whether dbdpe is present in Swedish lake sediments, and thereby available to the organisms dwelling there. Furthermore, the presence of dbdpe in remote lakes would indicate that long range atmospheric transport and deposition of dbdpe had occurred, because the remote lakes are not expected to have any point sources of BFRs. In the second study, marine sediments along a transect from Stockholm Harbour to the outer archipelago were analyzed for dbdpe. Wastewater treatment plants in Stockholm had been shown to emit dbdpe to Stockholm Harbour. The primary objective of this study was to determine if the marine benthic ecosystem outside Stockholm is exposed to dbdpe, and if so, how far out in the archipelago this exposure reaches. In the third study, Peregrine falcon eggs were analyzed for dbdpe. The eggs of this top predatory bird were hypothesized to be early indicators of dbdpe in Swedish wildlife, since they previously have been shown to accumulate high levels of decaBDE. A comparison of dbdpe and decaBDE concentrations in Peregrine falcon eggs would give information about the relative bioaccumulation potential of these two chemicals.

Usage

Dbdpe has been available on the market since the mid-1980s (**Umweltbundesamt, 2001**). One reason for the commercialisation of dbdpe was that it meets the demands of the German dioxin ordinance, which imposes limits for chlorinated and brominated dioxins and furans in commercial products (**Arias, 2001**). In contrast to its predecessor, decaBDE, dbdpe does not have an ether bridge in its molecular structure. This makes it less prone to produce dioxins and furans during pyrolysis conditions, as reviewed by **Kierkegaard** (**2007**).

Common trade names for dbdpe are Saytex 8010 (Albemarle) and Firemaster 2100 (Chemtura). Few statistics on production and sales of the commercial products are available. Europe has no production of its own but in 2001 the imports of Saytex 8010 were estimated to be a few thousand tonnes, primarily to Germany (**Kierkegaard et al., 2007**). However, it can be hypothesized that most of the dbdpe may not be imported as the commercial products, but rather as the additive in its target applications. This has been suggested for decaBDE (**National Chemicals Inspectorate, 2003**).

According to Albemarle, a major expansion of the production capacity for Saytex 8010 was completed during early 2007, and later that year the same company announced another 20% expansion of production of this BFR for January 2008 (**Albemarle Corp., 2007**). For comparison, decaBDE (named Saytex 102E by Albemarle and Great Lakes DE-83R by Chemtura) together with TBBPA and HBCD were the three BFRs with the largest worldwide consumption in 2001 (**Law et al., 2006**). In North America decaBDE was the major BFR, followed by TBBPA and HBCD. In Europe and Asia TBBPA had the highest consumption, followed by decaBDE and HBCD. The total worldwide market demand in 2001 for decaBDE, TBBPA and HBCD was 56100, 119700 and 16700 tonnes, respectively (**Law et al., 2006**).

In China, dbdpe was the second most highly used BFR in 2006 after decaBDE (**Shi, 2009**). The estimated domestic production volumes were 20000, 12000, 4500, and 4000 metric tons for decaBDE, DBDPE, HBCD, and TBBPA-DBPE, respectively. In Japan, a shift in consumption from decaBDE to dbdpe was reported by **Watanabe & Sakai** (**2003**). According to the authors the use of dbdpe surpassed decaBDE in 1997-1998.

Sources, transport and occurrence

BFRs are present in many consumer goods that are used indoors. The BFRs can be released from some of these goods, e.g. via abrasion or direct leakage (“blooming”) of the BFRs from their host polymer. High concentrations of decaBDE in indoor dust have been reported, e.g. 520,000 ng/g d.wt. was reported by **Harrad, et al.** (**2008**). Dbdpe has also been found in indoor dust (**Karlsson, et al., 2007).** Similarly to decaBDE, the environmental transport of dbdpe likely occurs primarily in association with particles as a consequence of its extremely hydrophobic and non-volatile character. This is supported by observations of dbdpe and decaBDE behaviour in an aquatic mesocosm, where both chemicals rapidly were transferred from water to sediment (**Meinecke et al., 2007**). In atmospheric samples collected near the Great Lakes, USA, dbdpe was found mainly in the particulate phase (**Venier & Hites, 2008**).

For chemicals such as dbdpe and decaBDE, wastewater treatment plants (WWTPs) are major filters than modulate the chemical transfer from the technosphere to the environment. The chemicals are transported to the WWTPs from commercial and household sources. In the WWTP they may be transferred together with the particles to the sludge from the waste water. The chemicals may also undergo transformation. There are 3 pathways by which the chemicals can be released to the environment: volatilization to the atmosphere, via the plant effluent to the recipient, and via sludge disposal, e.g. to agricultural soil. From an environmental perspective it is therefore important to determine the release of chemicals from WWTPs, and to understand their behaviour in different treatment steps. For hydrophobic chemicals with low vapour pressure, volatilization is negligible and segregation to sludge is the dominant process. Sludge can thus be an early and sensitive indicator of chemical release from the technosphere, if extensive degradation does not occur.

The behaviour of dbdpe and decaBDE in WWTPs has been evaluated. In Ricklund et al. (2008), the results from a mass balance study in Henriksdal WWTP located in central Stockholm showed that virtually all dbdpe and decaBDE were accumulated in the sludge. The mean levels of dbdpe and decaBDE were 81 and 800 ng/g sludge dry weight (d.wt.), respectively. The mean mass flows of dbdpe and decaBDE to the WWTP were 6.0 g/day and 55 g/day, respectively. Less than 1 % of the influent mass flows left the WWTP via the effluent. The removal efficiency of the BFRs from the wastewater stream was similar to the removal efficiency of particulate material, and it was most efficient in the primary flocculation treatment step (primary treatment > biological treatment step > sand filtration). Based on a mass balance of the sludge, no evidence for degradation during anaerobic digestion was found (the BFR mass flows in the primary sludge and secondary sludge equalled the mass flows in digested sludge). It was concluded that the transfer efficiency of dbdpe from the technosphere to the environment via WWTPs is similar to that of decaBDE.

The transfer behaviour measured at Henriksdal is consistent with observations for decaBDE in other studies. A study of the discharge of PBDEs from a WWTP in California showed that decaBDE was strongly associated with the solids fraction and almost entirely sequestered into sludge (**North, 2004**). More than 90 % overall removal of ΣPBDE (including decaBDE) from wastewater has been reported for a WWTP in Canada (**Rayne & Ikonomou, 2005**). According to the authors of those two studies, degradation of the PBDEs in the WWTPs did not occur. This conclusion is supported in literature by other studies as well (for more information –see below, section for degradation).

Since the discovery of dbdpe in sediment, sewage sludge and indoor air by **Kierkegaard & Björklund** (**2003**), dbdpe has been found in sludge from Spain (**Eljarrat et al., 2005**) and

Canada (**McCrindle et al., 2004**). Recently, a screening survey of dbdpe in international sludge samples was performed (**Ricklund et al., 2008**). In that screening survey, 42 samples collected from 12 different countries were analysed and dbdpe was present in sludge from all countries. It was therefore concluded that this BFR may be a worldwide concern. The highest concentration (216 ng g^{-1} d.wt.) reported was found in the highly industrialized Ruhr area of Germany. Automobile plants connected to the sampled WWTP were suspected to have contributed to this elevated concentration, but otherwise no evidence of elevated levels due to specific point sources was found. Therefore, diffuse leakage from the technosphere (e.g. household dust) may be a major source of the BFRs to the sludge. This has also been suggested for the PBDEs (**de Wit et al., 2006; Law et al., 2006**). In the international sludge samples, the [dbdpe]/[decaBDE] ratio, which ranged from 0.0018 to 0.83, was high in and around Germany where dbdpe imports are known to have been high and substitution of decaBDE with dbdpe is likely to have occurred. Low ratios were found in the USA and the UK, countries that have traditionally been large users of decaBDE. These results show that the [dbdpe]/[decaBDE] ratio can in some cases be useful to reveal trends in the substitution of decaBDE with dbdpe.

In the same study, an estimate of the flux of dbdpe from the technosphere via sludge to the environment within the European Union gave 1.7 ± 0.34 mg annually per person. The corresponding value for decaBDE was 41± 22 mg annually per person. These numbers can be compared with the influent mass flows in the study from Henriksdal (**Ricklund et al., 2008**) if it is assumed that the BFRs are not degraded in the WWTP. For Henriksdal in Sweden, the dbdpe and decaBDE influent mass flows were on average 3.1 and 39 mg annually per person, respectively. Furthermore, the BFR concentrations measured in effluent water in the Henriksdal study (**Ricklund et al., 2008a**) can be combined with the total volume of effluent water to recipients for all Swedish WWTPs (**SCB, 2006**) to roughly estimate the total mass flow of BFRs to recipients. This gives 2.4 to 17 µg/person annually for dbdpe and 22 to 96 µg/person annually for decaBDE.

Besides sludge and air, dbdpe has been reported in the following environmental matrices: tree bark (**Qiu & Hites, 2008**), a benthic food chain from North America (**Law, K. et al., 2006**), Panda bears in China (**Hu et al., 2008**), birds (**Shi et al., 2009**) and bird eggs (**Gao et al.**) from China and North America (**Gauthier et al., 2009**).

Degradation

Degradation of dbdpe in the environment has only been studied to a limited extent. In one recent study by (**Kajiwara et al., 2008**), no marked loss of dbdpe incorporated into high-impact polystyrene (TV casing) was observed during 224 days of exposure to natural sunlight, while the half-life of decaBDE was 51 days. The degradation of decaBDE generated both lower brominated PBDEs and PBDFs. Nevertheless, when a solution of dbdpe was exposed to a fluorescence lamp, nona- and octadiphenylethane congeners were formed (**Kierkegaard et al., 2007**), showing that UV-mediated degradation of this BFR can occur. For decaBDE, UV-induced degradation in solution, silica gel, sand, soil (**Söderström et al., 2004**), sediment and clay minerals (**Ahn et al., 2006**) and indoor dust (**Stapleton & Dodder, 2008**) has been shown to occur. However, when decaBDE is associated with (environmentally relevant) organic matter, photolysis seems to be a slower process; e.g. in presence of humic acids (**Hua et al., 2003**), sediment (**Ahn et al., 2006**), or soil (**Söderström et al., 2004**), compared to when sorbed to (or solved into) more defined matrices. For instance, the half-life of decaBDE in soil was estimated to 150-200 h when exposed to artificial sunlight (**Söderström et al., 2004**).

Thermal degradation in fires may be an important source of degradation products as well. According to the manufacturers, 50 % weight loss (through debromination) can be expected when dbdpe is heated to around 400 ºC. It has been reported that when dbdpe is heated, formation of PBDDs does not occur and only small quantities of PBDFs are formed (reviewed in **Kierkegaard, 2007**). On the other hand, during heating the ethane bridge is susceptible to cleavage, which generates bromotoluenes (**Jakab et al., 2003**). Literature data on the environmental behaviour of bromotoluenes are scarce as well. The halogenated, lipophilic nature of the potential degradation products suggests that they may also be of environmental concern, and that they should also be studied more closely.

The only work addressing biodegradation of dbdpe was the WWTP mass balance described above. In that study, no evidence for anaerobic removal of dbdpe was found. The degradation behaviour of the structurally similar decaBDE may provide some indication for dbdpe. Biodegradation of decaBDE to lower brominated, more potent species has been shown to occur (e.g. **Kierkegaard et al., 1999, 2007a; Mörck, et al., 2003; Steen et al., 2007**). Anaerobic degradation has been purposed as a possible loss process in sewage sludge and sediment. In laboratory experiments where sewage sludge collected from a Swiss WWTP was used as inoculum, decaBDE was shown to undergo anaerobic microbially mediated reductive debromination, though this also was a slow process, with a half life of 700 days (**Gerecke et al., 2005, 2006**). In concordance with this, **La Guardia et al.** (**2007**) found that BDE congener profiles in sludge resembled commercial product formulations and suggested minimal degradation of decaBDE in the WWTP. Furthermore, **Kohler et al. (2008)** showed that the congener patterns of polybrominated diphenyl ethers (PBDEs,) including decaBDE, was steady over time in lake sediments in Switzerland.

Biological uptake and toxicity

DecaBDE is present in many organisms, as summarized by **de Wit et al.** (**2006**) and **Law et al.** (**2006**), and is hence bioavailable. Recent findings of dbdpe in biota provide indications that biological uptake of this BFR also occurs. So far, dbdpe has been found in fish (**Law, K. et al., 2006**), birds (**Shi et al., 2009**), bird eggs (**Gao et al.**; **Gauthier et al., 2009**) and Panda bears (**Hu et al., 2008**). For the Panda bears, exposure was suggested to have occurred via ingestion of dust or food.

In fish and many other aquatic organisms, the gills are often the major uptake route of neutral organic contaminants. Bioaccumulation via the gills is referred to as bioconcentration. (**Hardy, 2004**) concluded that dbdpe together with decaBDE and some other BFRs with a molecular weight >700 g/mole did not bioconcentrate. This result is consistent with the insolubility of dbdpe in the water phase (**Environment Agency, 2007**), which presumably makes the uptake through gills an inefficient process. For aquatic organisms, dietary uptake of dbdpe may therefore be a more relevant route than uptake through the gills.

We are not aware of any studies of the dietary uptake of dbdpe. Oral administration of decaBDE to rats in two Swedish studies (**Sandholm et al., 2003; Mörck et al., 2003**) showed that more than 26 and 10 %, respectively, was taken up by the animals. To a small extent (at most 3.5 %), uptake of decaBDE from the gut has also been observed in fish (**Kierkegaard et al., 1999; Stapleton et al., 2006**). The dietary uptake efficiency of hydrophobic neutral organic chemicals has been shown to vary between classes of organisms (**Kelly et al., 2004**). Typically, lower values have been measured for aquatic poikilotherms (fish) compared to homeothermic carnivores (predatory birds and mammals). Furthermore, the dietary uptake efficiency has been shown to decrease when the log octanol-water partitioning coefficient (K_{OW}) of the chemical exceeds 7 (**Kelly et al., 2004**). Dbdpe has a log K_{OW} estimated to be 13.6 (EPI Suite v4.00, U.S. EPA), so low dietary exposure efficiency might be expected for this chemical, but this has yet to be demonstrated.

The toxicological effects of dbdpe have been investigated to a limited extent. In one study by **Hardy et al.** (**2002**), dbdpe was administered to rats by gavage during 90 days. After sacrificed, an increased size of the liver relative to the body weight was observed. However, this response was not present in animals that were sacrificed after a 28-day depuration period.

The results from a handful of standardized toxicity tests on dbdpe are summarized in an environmental risk evaluation report published by the **Environment Agency** (**2007**) for England and Wales. According to this report, dbdpe appears to have a relatively low toxicity. Nevertheless, in some cases limitations of the test set-ups were identified. This is partly a consequence of the difficulties with using standardized toxicity tests that were not designed for super-hydrophobic chemicals. Briefly, reproduction was reduced in earthworms (lowest observed effect concentration (LOEC) 3.7 was mg/kg d.wt. soil) and growth was inhibited for some plants (onion was the most sensitive, EC25=2.4 mg/kg d.wt. soil). No effects were observed during acute oral and dermal tests on rats and rabbits, respectively. Acute and chronic tests on some fish species did not generate any effects. However, for the fish tests it could not be excluded that the BFR was not present in the water phase, but rather on the test vessel walls (**Environment Agency, 2007**). Chronic tests for sediment-dwelling organisms did not generate any effects. According to the **Environment Agency** (**2007**), toxic effects could have been underestimated since fresh food without dbdpe was provided to the organisms during the whole test period. This was not according to the test guideline and possibly resulted in lower exposure. In summary, toxicological responses of dbdpe have been observed for a few organisms at relatively high doses. In some tests, limitations of the test set-up were identified, which could have reduced the toxicological responses. Consequently, there is a need for more testing of the toxicity of dbdpe.

Investigations conducted for this contract

Methods

Sampling

Lake sediment

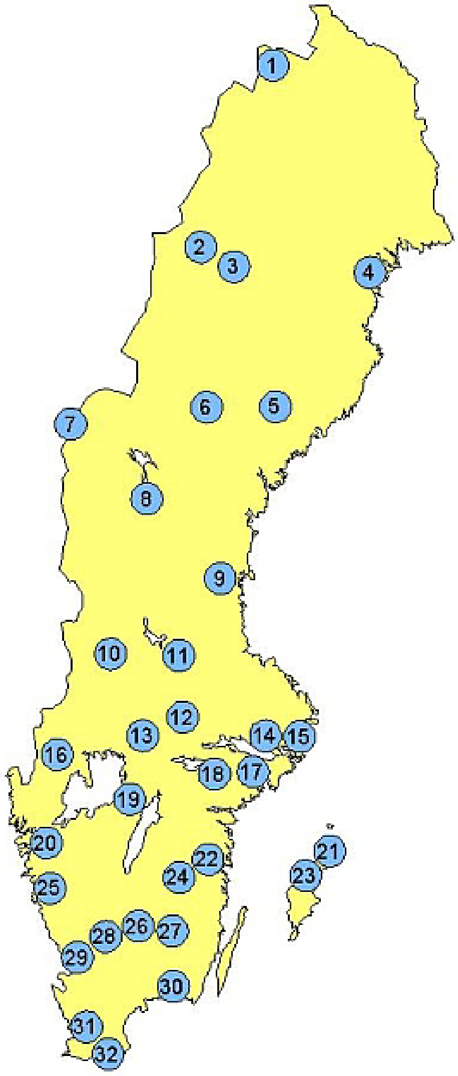
Surface sediment samples from 32 Swedish lakes were collected in 2007. The locations and coordinates of the sampled lakes are shown in **Figure 2**. The samples were collected by the Swedish Museum of Natural History within the national Swedish contaminant programme in lakes. More information about the sampling sites is available at: http://www.nrm.se/download/18.4e32c81078a8d9249800013277/Limniska2002.pdf. Briefly, the lakes were selected using criteria that facilitate comparison of contaminant levels on a regional scale. An attempt was made to exclude factors that can influence chemical concentrations on a local scale, e.g. point sources. The samples were stored in amber glass jars in a freezer (-20 °C). Prior to extraction the samples were lyophilized, ground and mixed.

Marine sediment

Sediment cores from seven different locations (**Figure 3**) were collected along a transect from central Stockholm through the Stockholm archipelago in spring 2008. Sampling was performed from the R/V *Sunbeam*, with the assistance of Per Jonsson. A Gemini twin corer was used to collect the sediment cores. The distinctly laminated sediment cores were sub-sampled, with the slices corresponding to the years 2004-2006 being transferred into glass jars, each covered with alumina foil and sealed with a polyethylene screw top. The sealed beakers were stored in a freezer (-20 °C) until further preparation.

Peregrine falcon eggs

The sampling procedures for the eggs are described in **Johansson** (**2009**)**.** Briefly, the eggs were collected within the Swedish Society for Nature Conservation's inventory program, with permission from the Swedish Environmental Protection Agency. Within this program, eggs that have not been fertilized or have not hatched are collected yearly. Ten pooled egg samples and two individual egg samples, all from the period 2001-2007, were analyzed for dbdpe.



	lake	x-coordinate	y-coordinate
1	Abiskojaure	7582080	1617490
2	Tjulträsk	7317990	1511960
3	Storvindeln	7289600	1560800
4	Brännträsket	7280950	1759260
5	Remmarsjön	7086190	1621320
6	Degervattnet	7085120	1520860
7	Stor-Björsjön	7060830	1322870
8	Stor-Backsjön	6952200	1433830
9	Stensjön	6836730	1540830
10	Gipsjön	6727290	1380820
11	Spjutsjön	6724670	1480310
12	Öv. Skärsj.	6635320	1485710
13	Limmingsjön	6608040	1427420
14	Fysingen	6607490	1618850
15	Tärnan	6606880	1644780
16	Bysjön	6580860	1302640
17	St Envättern	6555870	1588690
18	Älgsjön	6552750	1532340
19	Svartsjön	6516090	1408390
20	Fräcksjön	6452890	1286650
21	Bästeträsk	6425550	1685530
22	Allgjuttern	6424870	1517240
23	Horsan	6420080	1680130
24	Skärgölen	6406090	1486730
25	Lilla Öresjön	6386650	1292430
26	Fiolen	6330250	1422670
27	Hjärtsjön	6325150	1466750
28	Bolmen	6317500	1376100
29	Stora Skärsjön	6286060	1332050
30	Sännen	6244210	1472340
31	Krankesjön	6177600	1351950
32	Krageholmsj.	6153750	1370870

Figure 2. Locations and coordinates (Swedish grid) of sampling stations for lake sediments. Information obtained from the Swedish Museum of Natural History.

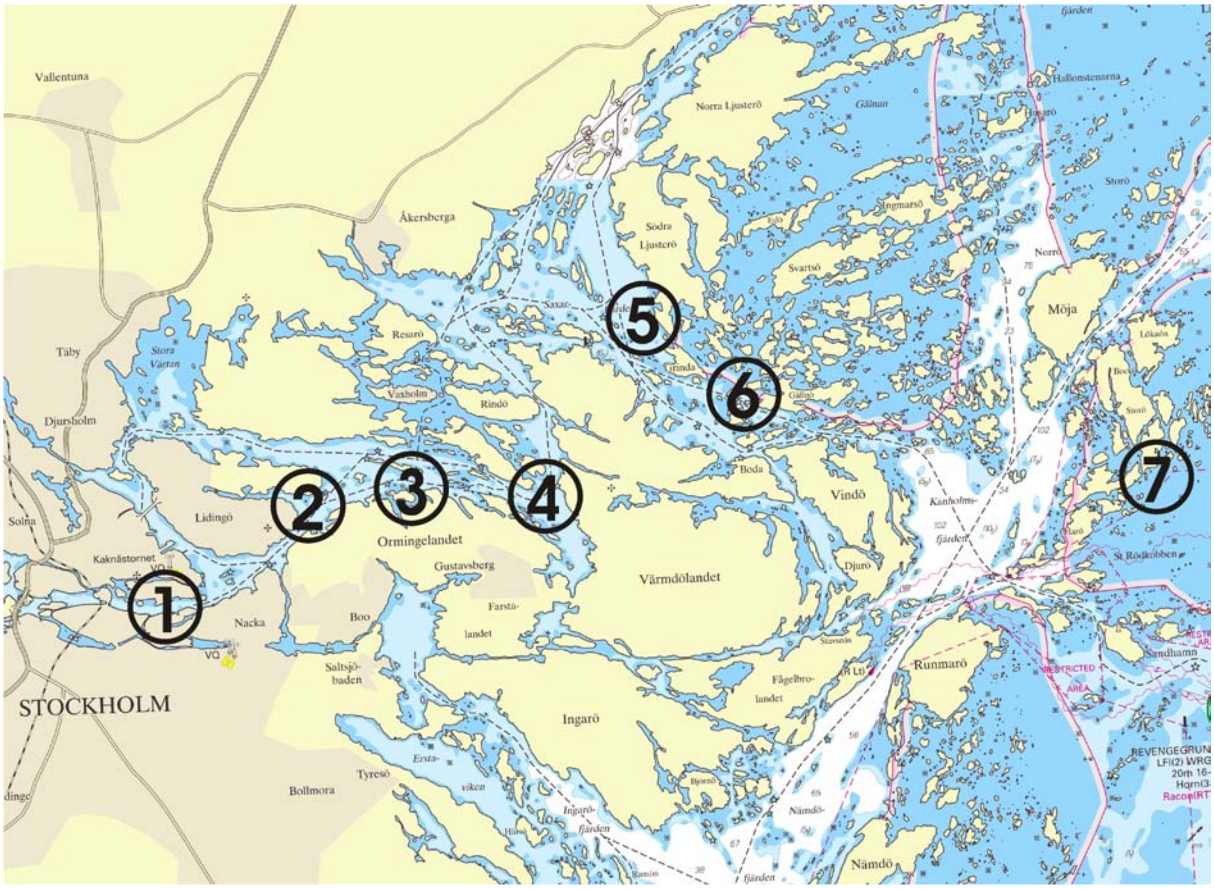


Figure 3. Sampling points for marine sediments in the Stockholm archipelago.

Analysis

Lake sediment

The method used for extraction and cleanup of the lake sediments is described in **ITM-report 59** (**2003**).

Marine sediment

The method developed for analysis of dbdpe in sludge (**Ricklund, 2008**) was used for the marine sediment samples after some modifications. The most significant modification was that the on-line cleanup in the accelerated solvent extractor (ASE) with sulphuric acid treated silica gel was replaced with liquid sulphuric acid treatment of the extract after the extraction. This was necessary since the on-line cleanup is suitable for only small amounts of dried sample (~1 g). For sediment larger amounts of sample (~10 g) are needed to obtain quantifiable amounts of dbdpe. Another modification was that hexane was replaced by dichloromethane (DCM) as the extraction solvent. The ASE parameters were also set slightly differently, i.e. the flush volume was increased to 100 % (from 60 %), to reduce the risk of cross contamination between samples. All chemicals that were used were of analytical grade and were the same as described in **Ricklund et al.** (**2008b**).

Peregrine falcon eggs

The procedures for extraction and cleanup of the Peregrine falcon eggs are described in **Johansson (2009).**

The instrumental conditions and procedures during GC-MS analysis were similar to those described in Ricklund et al. (**Ricklund et al., 2008b**). The identification of native and labelled dbdpe and decaBDE was based on the retention time of the fragment ions monitored. Quantification was performed using 8 point calibration curves of each native chemical. ^{13}C-labeled decaBDE was used as an internal standard for both decaBDE and dbdpe.

Quality assurance

The quality assurance details for the peregrine falcon eggs and the lake sediments are described in **Johansson (2009).** and **ITM-report 59 (2003)**, respectively. In addition, a simple test was performed to estimate the relative recovery of dbdpe and decaBDE to dechlorane, the internal standard that was used in the method for the lake sediments. For the marine sediment, the quality assurance procedures were as follows. Exposure of samples to UV-light was minimized by covering all lamps in the laboratory with UV-protective film. All glassware was pre-heated to >450º C and rinsed with acetone before usage. The ASE-cups were washed and extracted empty before being filled with sample. The laboratory procedures were tested for background levels of dbdpe and decaBDE. Procedural blank samples that included the lyophilisation, extraction and cleanup were analyzed in parallel to the samples. The efficiency of the extraction method was tested with different solvents, i.e. hexane and dichloromethane. The recovery of the internal standard, the relative recovery of dbdpe, and the precision of the method were tested in a small pilot study with replicate spiked sediment samples. In addition, the recovery of the internal standard from the lake sediment samples was also tested. Sample pairs of the marine sediment were analyzed to obtain information about the local variation of BFR concentrations along the marine sediment transect.

Results and discussion

Quality control

Blank samples

For the lake sediments and the Peregrine falcon eggs, no dbdpe was found in the procedural blank samples. For the marine sediments, the solvent was changed from hexane to DCM mainly because fewer problems with background levels have been experienced at our laboratory when DCM has been used. One out of five procedural blank samples contained dbdpe, at 56 pg/sample. DecaBDE was not found in the lake sediment blanks. For the marine sediments, the blank levels ranged from 94 to 186 pg/sample, while for the Peregrine falcon eggs the blank levels ranged from 60 to 170 pg/sample.

Lake sediment: method limitations

In most other studies in which dbdpe have been analyzed, the method had not been optimized for this BFR (**Kierkegaard et al., 2009**). This was also the case with the method used for the lake sediments, described in **ITM-report 59** (**2003**). However, this method is commonly used for screening for PBDEs and was previously used for decaBDE in the same lake sediment samples. Therefore, to enhance comparison of dbdpe and decaBDE concentrations in the lake sediments, this method was considered appropriate for screening of dbdpe as well. Recent observations of the relative behaviour of dbdpe and decaBDE during sample preparation

(**Ricklund 2008, Ricklund et al., 2008a, and 2009b**) supported this assumption. The two BFRs behaved similarly during relatively complex analytical procedures (e.g. packed column separation) and under destructive conditions (i.e. elevated temperature to 100º C), concentrated sulphuric acid and potassium hydroxide treatments). These observations showed furthermore that ^{13}C-decaBDE worked well as a surrogate standard for dbdpe as well as decaBDE. However, in the method for the lake sediments, dechlorane was used as a surrogate standard. The relative recovery of dechlorane compared to dbdpe and decaBDE was therefore tested. The results indicated that corrections were not necessary for a screening study, i.e. the relative recoveries of dbdpe and decaBDE to dechlorane were 0.78 (CV 13%) and 0.74 (CV 9%), respectively (from triplicate samples).

Marine sediment: Extraction efficiency, recovery and precision

Dbdpe and decaBDE have been shown to be relatively easily extracted from sludge (**Ricklund, 2008**) and this was not expected to change with sediment. In a small pilot test, a non-spiked sediment sample was extracted with DCM in three cycles, and the extract from each cycle was analyzed separately. Although exact quantification was not possible, the extracted fractions of dbdpe and decaBDE in cycles 1, 2 and 3 were estimated to be 77, 23 and ~0.1% for both BFRs. This also indicated that the two analytes had a similar relative recovery (see below). This was confirmed by a recovery test, which gave a mean relative recovery of dbdpe to decaBDE of 1.06.

The precision of the method was tested by analysing triplicate samples. The precision, expressed as the ratio between the highest and the lowest obtained BFR concentrations, was 2.1 for dbdpe and 1.9 for decaBDE. The precision of the early version of this method for sludge was assessed in a similar manner using 5 replicate samples (analyzed at different occasions). The max:min quotients were 2.3 for dbdpe and 1.3 for decaBDE (**Ricklund et al., 2008b**). This was considered satisfactory for screening purposes.

Detection and quantification limits

The method limit of detection (LOD) and method limit of quantification (LOQ) for dbdpe were based on 3 and 5 times, respectively, of the noise in field samples. For decaBDE, the LOD and LOQ were calculated from the levels found in the blank samples and defined as the mean plus 3 and 10 times its standard deviation, respectively. The limits are shown in **Table 1**.

Table 1. Limits of detection and limits of quantification for dbdpe and decaBDE. Note that different methods for determination have been applied for the two BFRs.

Sample matrix	dbdpe			decaBDE		
	LOD	LOQ	unit	LOD	LOQ	unit
Lake sediment	100 - 210	170 - 350	pg/g d.wt.	n.a.	n.a.	n.a.
Marine Sediment	33	64	pg/g d.wt.	25	55	pg/g d.wt.
Peregrine falcon eggs	420	700	pg/g l.wt.	2400	5600	pg/g l.wt.

Screening of lake sediment

Dbdpe contamination of lake sediment

The levels found in the Swedish lake sediments are presented in **Figure 4**. Dbdpe was found in 14 out of 31 samples, and the levels varied from <0.10 (i.e. LOD)-1.6 ng/g d.wt.. In 5 of the 17 samples in which the levels were below the LOD, traces of a possible dbdpe peak were observed. In a previous study by **Asplund** (**data reported to the Swedish Environmental Protection Agency**), decaBDE was found at all sample locations but one. The levels ranged from 0.0-2.1 ng/g d.wt. Thus, the results show that dbdpe contamination is widespread in Swedish lake sediment, similarly to decaBDE.

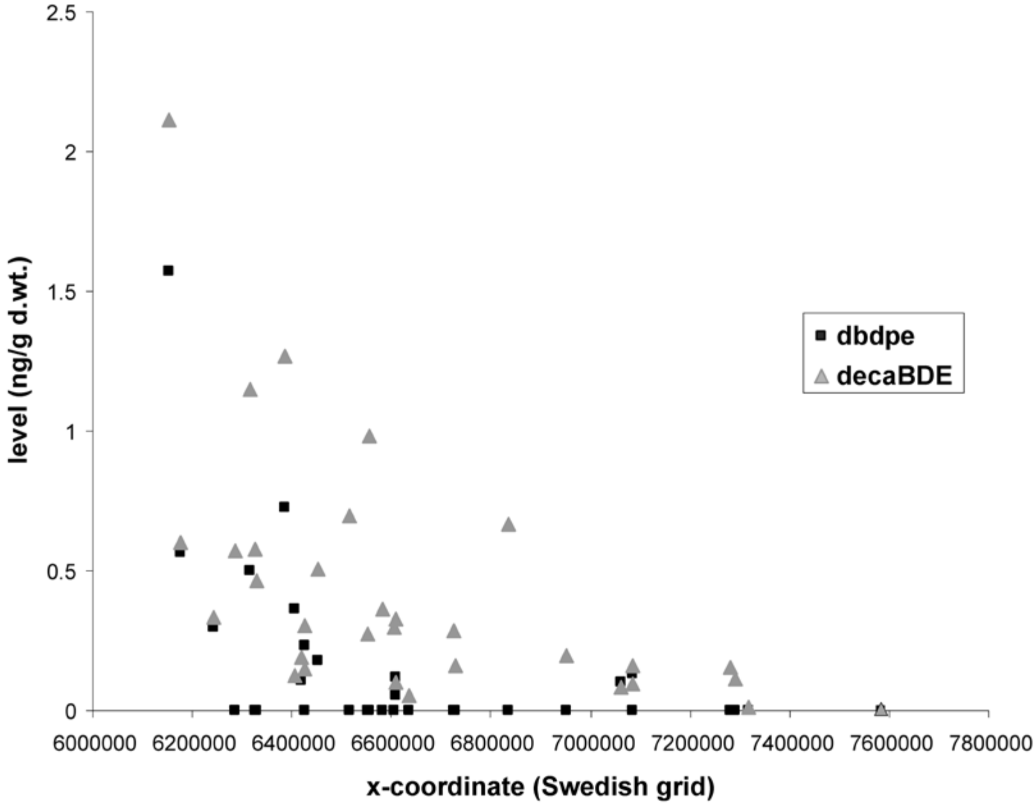


Figure 4. Levels of dbdpe and decaBDE in lake sediments as a function of latitude. Samples with levels >LOQ or between the LOD and LOQ are shown. Samples with levels <LOD are set to zero.

Atmospheric deposition

Based on the assumption that point sources were absent in the immediate vicinity of the lakes, only a diffuse source can explain the presence of the dbdpe and decaBDE in the lake sediments. The lack of clear outliers in the data supports the absence of major point sources. Since dbdpe and decaBDE are prone to sorb to particles due to their high hydrophobicity and low volatility, it is likely that atmospheric deposition of particles contaminated with dbdpe and decaBDE is responsible for the contamination of the lake sediments. Long range atmospheric transport and deposition in remote areas has already been shown to occur for decaBDE (**Bogdal et al., 2008; Breivik et al., 2006; Mariani et al., 2008**). Furthermore, dbdpe has been found in air samples from the USA (**Venier & Hites, 2008**).

To further explore the hypothesis of atmospheric deposition, the ratio [dbdpe]/[decaBDE] was calculated. This was possible for 6 sediments in which the dbdpe levels were above the LOQ. The ratio ranged from 0.28-0.94. This indicates that the level of dbdpe contamination in remote Swedish lakes is close to the level of decaBDE contamination. This is cause for concern, since dbdpe has not been used as long as decaBDE, and since its use is currently increasing.

The range of the [dbdpe]/[decaBDE] ratio, a factor 3.4, is narrow, particularly considering the relatively low precision of the analytical method. A similar ratio of chemical concentrations in the environment can be an indication of similar sources**.** Given the remote locations of these lakes and the known importance of long range atmospheric transport of decaBDE, we conclude that the dbdbe contamination is likely coming from the atmosphere.

For comparison, the [dbdpe]/[decaBDE] ratio measured in different treatment steps at the Henriksdal WWTP ranged between 0.06 and 0.18 (**Ricklund et al., 2008a**). This is lower than measured in the lakes, suggesting that long range atmospheric transport is not the dominant source of dbdpe entering the Henriksdal WWTP. In another study, a much broader range in the [dbdpe]/[decaBDE] ratio was found in international sludge samples (0.0018 to 0.83) **(Ricklund et al.**, **2008b**). The broad range was attributed to differences in BFR usage among countries.

The BFRs present in the Swedish atmosphere may have originated from distant sources. In a study of the accumulation rates of organic contaminants in sediments of remote North American lakes, the long range atmospheric transport of the chemicals was characterized using a parameter called the empirical travel distance (ETD), i.e. the average distance travelled in air until a 63% reduction of the initial chemical concentration in air has taken place **Breivik et al.** (**2006**). The ETD of decaBDE was reported to be 817 km. Therefore, long range transport of decaBDE released to air from sources in other parts of Europe probably influences the BFR levels in the Swedish lake sediments. In the present study, the highest levels of both dbdpe and decaBDE were found among the most southern sampling stations (see **Figure 4**). For decaBDE, a highly significant decrease in BDE209 concentration with increasing latitude was found ($P<<0.01$, both for untransformed and log-transformed concentration values). The decrease was better described with a log-linear regression (R^2~0.5) than with a linear (R^2=0.3). From the log-linear relationship the empirical half distance (EHD, the distance in a north-south direction over which the concentrations change by a factor of two) was estimated to be 300 km. This compared fairly well with the study by Breivik et al., where the EHD for decaBDE was determined to be 566±101 km based on depositional fluxes that had been corrected for sediment focusing. A sound statistical analysis could not be conducted for dbdpe because it could not be detected in many samples. However, **Figure 4** indicates that the trend with latitude was similar in those samples, in which dbdpe was detected.

Marine sediment transect

Levels

The levels found in the marine sediment transect from the Stockholm archipelago are presented in **Table 2**. Dbdpe, as well as decaBDE, were found in all samples. Thus, there is widespread contamination of marine sediment in Stockholm and its archipelago with these BFRs.

An exponential decrease in the concentrations with distance from central Stockholm was observed (**Figure 5**). The highest levels of both BFRs (10 ng/g d.wt. of dbdpe and 80 ng/g d.wt. of decaBDE) were found in the samples taken from central Stockholm (Waldemarsudde). Lower levels were found in the outer archipelago. Furthest out in the archipelago, at Lökholmen, the levels of dbdpe in the sample pair were 0.28 and 0.56 ng/g d.wt., and for decaBDE the corresponding levels were 1.0 and 1.6 ng/g d.wt., which is 20-50 times lower than in central Stockholm. The EHDs of dbdpe and decaBDE along the transect were 14 and 10 km, respectively, meaning that the concentration of each chemical dropped to half of its initial value over this distance. In a similar study (**SITAR, 2007**), a decrease of

PCB and PAH concentrations was observed along approximately the same sediment transect sampled in 2002.

Table 2. Levels of BFRs in marine sediment and coordinates of sampling stations.

Sampling station	**Duplicate**	**Levels** (ng/g d.wt.)		**Coordinate** (WGS-84)	
		dbdpe	**decaBDE**	***x***	***y***
Waldemarsudde	*a*	11	71	*591907*	*180662*
	b	8.6	88		
Käppala	*a*	1.5	25	*592120*	*181440*
	b	1.5	19		
Tegelön	*a*	1.2	6.0	*592150*	*181950*
	b	7.9	19		
Torsbyfjärden	*a*	0.18	1.8	*591937*	*182766*
	b	2.1	9.2		
Saxarfjärden	*a*	0.56	1.6	*592551*	*183239*
	b	0.32	1.9		
Silverkannan	*a*	0.41	1.0	*592373*	*183665*
	b	no data	no data		
Lökholmen	*a*	0.56	1.6	*592091*	*185668*
	b	0.28	1.0		

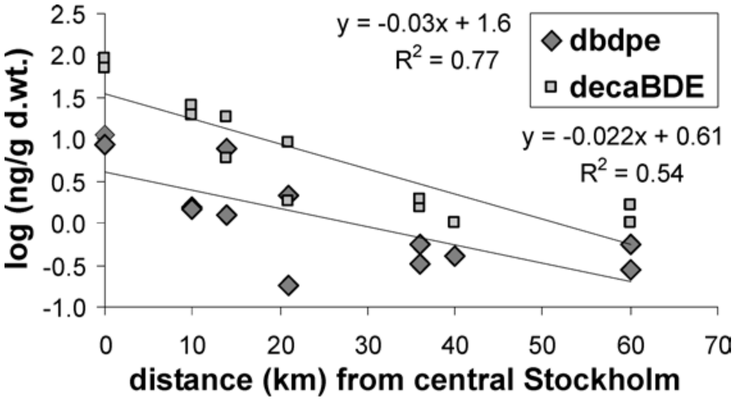


Figure 5. BFR levels in sediment plotted against the approximated travel distance of water masses along the sampling transect from central Stockholm along sediment transect to archipelago, i.e. from west to east.

Potential sources

The sample stations in central Stockholm, Waldemarsudde and Käppala, are presumably impacted by local emissions of BFRs . Several WWTPs are located there, and these plants discharge their effluent within a few hundred meters of the sediment sampling sites. One of these plants, Henriksdal, was recently the subject of a mass balance study (**Ricklund et al., 2008a**), and both dbdpe and decaBDE were found in the effluent at concentrations up to 0.11 and 0.63 ng/l, respectively. The WWTPs are therefore sources of the BFRs to the sediments in central Stockholm. In the present study, the levels of both BFRs in the marine sediment sampled close to the Henriksdal effluent discharge were interestingly just one order of magnitude lower than the levels found in the sewage sludge from the plant in the study from 2008. The ratio [dbdpe]/[decaBDE] also compared well between the sediment and the sludge from that study, The ratio was on average 0.08 and 0.13 in the sludge and 0.13 in the sediment at Waldemarsudde. This is further evidence that Henriksdal is an important source of dbdpe and decaBDE to the sediment.

Further out in the archipelago, at Saxarfjärden via Silverkannan to Lökholmen, i.e. approximately 37 to 62 km by water from Waldemarsudde, the BFR levels reached a "baseline" of 0.28-0.56 and 1.0-1.9 ng/g d.wt., for dbdpe and decaBDE, respectively. These levels are within the range of the lake sediment levels, i.e. <0.10-1.6 and 0.0-2.1 ng/g d.wt., for dbdpe and decaBDE, respectively. Furthermore, the [dbdpe]/[decaBDE] ratio in this transect end member had a fairly similar range (i.e. 0.17-0.40) similar to that in the lake sediments (i.e. 0.28-0.94). Altogether, this suggests that the outer archipelago and the lake sediments have a common source of the BFRs. The atmosphere is a source that would act in a similar fashion on both the lakes and the archipelago.

Differences between dbdpe and decaBDE

Differences in the behaviour of dbdpe and decaBDE were assessed using the [dbdpe]/[decaBDE] ratio along the transect (**Figure 6**). A significant correlation between the ratio and the approximated distance of the sampling stations from central Stockholm was obtained ($P = 0.042$ and $R^2 = 0.33$). This indicates that there have been different sources or different behaviour with respect to degradation of the BFRs to the sediments in central Stockholm compared to those in the outer archipelago. The susceptibility of decaBDE to degradation in natural sediment has been shown to be low (**Kohler et al., 2008; La Guardia et al., 2007**) and cannot explain the correlation. If the atmosphere is the dominant source of the BFRs in the outer archipelago, as argued above, then the correlation indicates that relatively more of the dbdpe is entering sediments from the atmosphere than from urban discharges to water, when compared to decaBDE.

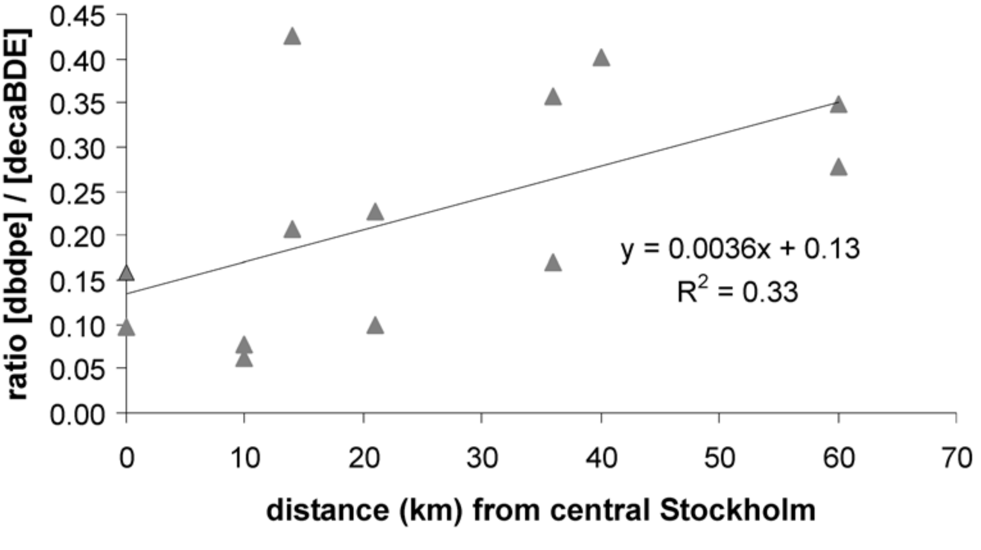


Figure 6. Increase of BFR ratio with approximated distance from central Stockholm along sediment transect to archipelago, i.e. from west to east.

Peregrine falcon eggs

The Peregrine falcon egg samples had been previously analyzed for some BFRs, including decaBDE (**Johansson, 2009**). DecaBDE was detected in most eggs (88.5%) at levels up to 870 ng/g l.wt. Eggs sampled between 2001 and 2007, all with high decaBDE levels, were chosen for analysis of dbdpe in the present study.

Presence of dbdpe in eggs

No traces of dbdpe were found in any of the peregrine falcon eggs. From the baseline noise in two representative GC-chromatograms, the LOD for dbdpe was estimated to be 0.4 ng/g l.wt., or 40 pg/sample. Recently some other data on dbdpe concentrations in bird eggs have been published. Dbdpe was analyzed in herring gull eggs collected between 1982 and 2006 from seven locations around the Great Lakes in North America. It was found at a detection frequency of ~13% in the samples (10-13 eggs/pooled sample) from 1996 and after, at a maximum level at 288 ng/g w.wt. (i.e. approximately 3000 ng/g l.wt.) **Gauthier et al.** (**2009**). This is almost 4 orders of magnitude higher than the LOD in this study. Dbdpe was found in 54% of egg samples (n=67) collected from different aquatic, terrestrial and captive birds in a nature reserve area in China that is highly influenced by industrial discharges (**Gao et al.,** *manuscript accepted for publication*). The samples containing dbdpe had levels up to 2.4 ng/g l.wt., which is 6 times higher than the LOD in this study. In another recent study by **Shi et al.** (**2009**)**,** tissues from birds collected near an electronic waste processing area in China contained dbdpe levels from 9.6 to 124 ng/g l.wt., which is up to 300 times higher than the LOD in this study. In summary, the dbdpe levels in the peregrine falcon eggs are much lower than recently reported levels in other birds. This is somewhat surprising, as the decaBDE levels in peregrine falcons are very high. However, other factors such as the level of dbdpe contamination in the other study areas compared to Sweden and species differences in dbdpe bioaccumulation may explain this result.

Relative bioaccumulation potential

To obtain further insight into the bioaccumulation of dbdpe, its behaviour was compared to that of decaBDE. DecaBDE was found in the same peregrine falcon egg samples at levels ranging from 1.2 to 870 ng/g l.wt. (**Johansson, 2009**). Using the LOD as an upper estimate of the dbdpe concentration, the [dbdpe]/[decaBDE] ratio was calculated to range between <0.00034 and <0.0089. In other words, the decaBDE concentration was between >110 and >2900 times higher than the dbdpe concentration. The sediment analyses provide a measure of the relative levels of dbdpe and decaBDE in the environment. In this case the [dbdpe]/[decaBDE] ratio ranged between 0.28 and 0.94, which is much greater than the ratio in the eggs. To assess the relative bioaccumulation behaviour, the ratio in the eggs was divided by the ratio in the sediments, yielding values of <0.032 to <0.00036. This suggests that decaBDE bioaccumulates at least 30 times more efficiently than dbdpe, while in some eggs it bioaccumulated at least 1000 times more efficiently.

A similar calculation can be done with data from China. **Shi et al.** (**2009**) reported levels of dbdpe and decaBDE in bird tissue as well as in outdoor dust and soil. Using the average [dbdpe]/[decaBDE] ratio in outdoor dust and soil as a measure of the ratio in exposure media, the relative bioaccumulation ratio in bird tissue was calculated. It ranged from 0.25 to 25. In other words, the data from China indicates that the bioaccumulation potential of dbdpe in birds is similar to or higher than for decaBDE. This is in contradiction to the results obtained for the peregrine falcon eggs.

Discussion

There are several possible reasons for the contradictory results on dbdpe bioaccumulation in predatory birds. One is that there are considerable differences in the maternal transfer of chemicals from tissue to egg. The bioaccumulation ratio comparison using the Chinese data was based on levels in tissues, while the peregrine falcon comparison was based on levels in eggs. If there is a low tissue to egg transfer efficiency of dbdpe compared to decaBDE, or for peregrine falcons compared to the birds in the Chinese study, this could explain the contradictory results. The efficiency of the maternal transfer has been shown to vary between species (**Drouillard, 2001**), but this variation is not large enough to explain the contradictory results. There is little information in the literature on the influence of physical chemical properties on the maternal transfer efficiency of very hydrophobic neutral chemicals. However, the similarity in the physical chemical properties of dbdpe and decaBDE make it unlikely that this could explain the very large differences in bioaccumulation behaviour in the Chinese work and this study.

A second possible explanation is species specific differences in the metabolism of dbdpe. If the peregrine falcons were able to rapidly eliminated dbdpe via metabolism, while the other birds were not, this would explain the apparent contradiction. We were not able to find evidence of interspecies differences in metabolic capacity among birds of prey that would be sufficiently large to explain the apparent contradiction, but this cannot be ruled out.

A third potential explanation is that the [dbdpe]/[decaBDE] ratios in sediment do not represent the relative exposure of peregrine falcons to the two chemicals. There may be a unique source of decaBDE that is responsible for the high levels of this chemical in the peregrine falcons.

Finally, the contradictory results may be due to analytical problems. The analysis of dbdpe is very challenging. There are as yet few papers on this subject, and there has been no external quality assurance on the analytical methodology.

Due to these contradictory results, it is not possible at this time to draw firm conclusions about the bioaccumulation of dbdpe in top predators. In lower trophic levels, the available evidence indicates that the bioaccumulation of dbdpe and decaBDE is similar. Bioaccumulation of dbdpe has been demonstrated in a benthic food chain in North America (**Law, K. et al., 2006**), and unpublished work in our laboratory indicates similar bioaccumulation of dbdpe and decaBDE in a benthic / pelagic food web in The Netherlands.

Is dbdpe an environmental problem?

The presence of dbdpe in sediments from remote Swedish lakes and the outer Stockholm archipelago, together with previous data on its presence in dust, international sludge samples and effluent from Henriksdal WWTP, provide evidence that this BFR is widespread and persistent in the environment. Unfortunately, the paucity of toxicological data on this chemical precludes doing a risk assessment, as the potential effects cannot be evaluated.

In the absence of toxicological information, the hazard criteria related to chemical exposure such as persistence, bioaccumulation, and long range transport can be evaluated. The assessment of the absolute magnitude of these criteria is a data intensive undertaking that is only possible for chemicals for which there is a large data base. An alternative is to compare the behaviour of the chemical to a known problem chemical with similar properties. In this report we have to this end frequently compared the behaviour of dbdpe to decaBDE, a chemical with similar properties and one that has now been subject to regulation.

Regarding persistence, there is considerable evidence that dbdpe is persistent in the environment. In particular, the fact that it has reached concentrations in remote Swedish environments that approach those of decaBDE, although it has been in use for a shorter period of time, suggests that dbdpe has an environmental persistence that equals or exceeds decaBDE.

The relative bioaccumulation of dbdpe is less clear. As outlined above, the first two studies of lower trophic levels indicate that the bioaccumulation of dbdpe is similar to decaBDE. However, the evidence for top predators is contradictory. Measurements in predatory birds in North America and China provide evidence that dbdpe does bioaccumulate, and the Chinese work suggests that its susceptibility to bioaccumulation equals or exceeds that of decaBDE. However, the work presented in this report indicates that dbdpe bioaccumulates in peregrine falcons to a much lesser extent than decaBDE. Before conclusions on the bioaccumulation of dbdpe can be drawn, this apparent contradiction must be resolved.

Dbdpe is subject to long range atmospheric transport. This is demonstrated by its presence in remote Swedish lakes, as argued above. There is not a strong data basis to evaluate the efficiency of this process relative to decaBDE. However, the similarity in the decrease in concentrations in lake sediments with increasing latitude between the two chemicals (**Figure 4**) suggests that they possess a similar susceptibility to long range atmospheric transport. This would also be expected for persistent chemicals with similar sources that are transported in the atmosphere primarily in association with particles.

Conclusions –further actions

Dbdpe is a ubiquitous environmental contaminant of the Swedish environment. The available evidence suggests that it has a persistence and a susceptibility to long range atmospheric transport that is similar to the regulated chemical that it is replacing – decaBDE. There is also evidence that it may have a comparable tendency to bioaccumulate. Thus, there is a danger that a problematic chemical – decaBDE – is being replaced with a chemical that is equally problematic with respect to its environmental fate and bioaccumulation behaviour. Hence, further study should be undertaken to better characterize the environmental behaviour of this chemical. The fact that the production and use of this chemicals is growing rapidly and that its concentration in remote Swedish lakes is already approaching that of decaBDE suggests that action is urgent.

We suggest that the following questions are the most urgent priorities:

- Quantify the bioaccumulation of dbdpe in a range of top predators, including humans, and compare this to the bioaccumulation of decaBDE;
- Explore the levels and sources of dbdpe in the atmosphere, with the aim of understanding and rectifying the causes of its high levels in remote Swedish lakes;
- Assess the formation of degradation products of dbdpe, and whether these pose an environmental or human health risk;
- Initiate international quality control programs for the quantification of dbdpe in environmental samples.

Finally, there is a need for toxicity data that allow a better evaluation of the potential adverse effects of exposure to dbdpe.

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