ADDENDUM

to the May 2004
Environmental Risk Assessment Report for
DECABROMODIPHENYL ETHER
(CAS no. 1163-19-5)

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for the Chemicals Assessment Unit, Environment Agency, Wallingford, UK.
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1 INTRODUCTION

Two risk assessment reports for decabromodiphenyl ether have been produced under the EU Existing Substances Regulation. The original risk assessment report was published in 2002 (EC, 2002) and an updated risk assessment was agreed in Spring 2004 at the EU Member State technical and policy level (ECB, 2004). The latter report concluded that further information was required, and in the meantime the Industry has been preparing to carry out the necessary work, as well as carrying out voluntary emissions reduction activity. The Scientific Committee on Health and Environmental Risks (SCHER) gave their opinion on the environment risk assessment on 18th March 2005, and they considered that risk reduction measures should be investigated (SCHER, 2005). Based on the content of the 2004 report, the rapporteur disagreed, and sent the European Chemicals Bureau their response to the SCHER opinion in April 2005.

However, given the uncertainties in the conclusions and the very large amount of scientific literature that continues to be produced on this substance (some of which was cited in the SCHER opinion), the rapporteur believes it is important to regularly review any new information that could affect the conclusions so that it can be rapidly taken into account. This paper reviews all the significant new information that has been published since the updated risk assessment report was agreed in May 2004. This paper only considers the impacts of the information on the conclusions to the environmental risk assessment. Note that the data in the original two risk assessment reports are not explicitly repeated here, and so those two reports should be referred to for further details.

Several of the articles that have been reviewed are extended abstracts from conference proceedings and so do not always contain full experimental details. These are marked as “[ABST]”. The results should be treated with caution until the full details have been formally published in the peer-reviewed scientific literature. This is particularly relevant for papers where analytical monitoring for concentrations of decabromodiphenyl ether in environmental matrices has been carried out. This is because such analyses are difficult and can easily lead to both false positives and negatives, particularly for samples of biota, blood, milk and food (see both ECB (2004) and Section 4).

The date of the last literature search for this paper was June 2005. More recent papers that have been published but not yet reviewed are listed in Section 12.

2 EMISSIONS

2.1.1 New emission data

As agreed by the Competent Authorities, the manufacturing industry has instigated a voluntary initiative known as the Voluntary Emissions Control and reduction Action Programme (VECAP). New codes of good practice for sustainable use of decabromodiphenyl ether in the plastics industry (BSEF, 2004a) and textile industry (BSEF, 2004b; Wragg, 2004) have been issued. The aim of the codes of practice is to ensure improved control of emissions from sites using decabromodiphenyl ether in certain applications.

The code for the plastics industry focuses on emissions during the plastics compounding stage, where handling of powders occurs. The code for the textiles industry focuses on the
formulation and application of backcoatings, and identifies best industry practice for reducing and minimising emissions from the processes.

As part of the VECAP, surveys of the emissions to the environment from sites using decabromodiphenyl ether in textiles and plastics have been carried out in the UK (and it is intended to carry out further surveys in the future). The purpose of these surveys is to identify sources of emissions in the environment, and to quantify the amounts being released. This will provide a baseline so that progress in emissions reduction can be monitored. The results of the first of these surveys have recently become available.

**Textiles**

The survey for the textile industry was carried out in December 2004 and involved member companies of the UK Textile Finishers Association (Wragg, 2005a and 2005b). The members have agreed to adopt the principles of product stewardship, adopt the code of good practice for the textile industry, control emissions, improve the database on emissions from this sector, and to aggregate the results of their surveys into an industry sector report. The first survey was based on one week’s production at each site. Seventeen out of the twenty-two suppliers/users of decabromodiphenyl ether in textiles provided results for the survey (the seventeen respondents consisted of eight processors, four formulators, four formulators/processors and one distributor). These responding companies represented around 95% of the total amount of decabromodiphenyl ether applied to textiles in the UK. The total amount of decabromodiphenyl ether emitted to sewer by these seventeen companies was estimated to be 120 kg/week (equivalent to 0.56% of the total volume of decabromodiphenyl ether used that week). This figure is the combined total for the five companies with reported emissions to sewer. Other waste streams identified included 844 kg/week disposed of as solid waste and 44 kg/week disposed of as waste in empty packaging. The total waste figure was thus 1,008 kg/week (sum of emissions to sewer, solid waste and waste in packaging), which was approximately 4.7% of the total amount of decabromodiphenyl ether used at the sites on the week of the survey.

These figures take into account emission reduction measures taken by the sites over the year 2004 and refer to the situation during the week the survey was taken. It was estimated that, if the survey had been carried out in 2003, the actual emission to waste water would have been of the order of 600 kg/week with total waste figure of 1,500 kg/week.

The returns per site are available (Lambert, 2005). These indicate that one company accounts for around 75% of the reported emissions to sewer. This equates to an emission of around 18 kg/day at this site, assuming five working days per week. The remaining four sites reporting emissions to sewer in the survey all had emissions below 3.6 kg/day (some were considerably lower than this). The emissions to sewer were very low or zero for the remaining twelve sites taking part in the survey.

The Environment Agency’s pollution inventory provides some additional data for the same site that reported the highest emissions in the survey, since it is regulated under the Integrated Pollution Control (IPC) and Integrated Pollution Prevention and Control Regulations (IPPC,

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1 The actual percentage of the industry covered is now higher than indicated by this figure as it is known that a number of companies that did not take part in the original survey have either ceased trading or no longer use decabromodiphenyl ether.

due to have totally replaced IPC by the end of 2007). The reported emissions of total polybrominated diphenyl ethers (PBDE) from the site were 1,400 kg and 2,440 kg (both as bromine) to sewer in 2002 and 2003 respectively (Environment Agency, 2004). The reason for this increase has not been sought. Assuming 300 days operation per year, and that the figures relate solely to decabromodiphenyl ether\(^3\) (which has a bromine content of 83% by weight), these are equivalent to an emission of decabromodiphenyl ether of around 5.6 kg/day (2002) or 9.8 kg/day (2003) to sewer. The rapporteur was informed that the emissions were higher still in 2004, and this is confirmed by the industry survey.

It is of particular note that the Textile Finishers Association believes that the type of textile processing that takes place at the site with the largest emission to sewer is certainly unique within the UK, and most probably within the EU (Lambert, 2005). For example, the company:
- is a ‘disperser’ (i.e. manufactures its own backcoating formulations on-site) as well as a coater,
- applies the backcoatings as a stable foam,
- uses coloured coatings and
- is also a bleaching and dyeing works with a large daily throughput of water.

This combination of factors means that a large number of clean-down operations and changes of coatings occur each day, which is highly unusual in the textile industry. This company is, however, an enthusiastic member of the VECAP and it has been reported that, following the completion of phase one of their decabromodiphenyl ether improvement programme, they have now reduced their annual discharge of decabromodiphenyl ether to sewer by almost 75% compared to the figures given above. This has been achieved by technical changes to some of the processes used, which have removed the need to store coloured compound and discharge coloured washings that could not be recycled. A further reduction will be achieved in 2006 by the reduction of the discharge of foam to drain (i.e foam cannot be re-used and will be collected and disposed of as hazardous waste).

Based on the total emissions from all sites of 120 kg/week in 2004, a very rough estimate of the total amount released can be obtained by assuming that the emissions occur over around 46 weeks/year. This gives an estimated total emission to sewer of 5,520 kg/year (or 27,600 kg/year in 2003) from this source in the United Kingdom. It should be noted that the relevance of this figure is highly uncertain because the underlying survey data were obtained only for one week and it may not be appropriate to scale the data in this way. Based on the emission reduction measures that have occurred as a result of the VECAP, it is likely that the total emissions to sewer in the United Kingdom will be much lower than indicated by the above estimate in future.

It should be noted that, since this was the first survey of its type to be carried out, some “teething” problems became apparent on analysis of the results. For example sites with on-site treatment methods may have reported no emissions to waste water and some double counting of tonnages was apparent (although this would not affect the estimated emissions from each site as these were based on the actual amount used at each site). These problems will be addressed in future surveys. A further survey of the textile industry within the United Kingdom is due to be carried out shortly (around September 2005).

\(^3\) The two other PBDE products were not used in textile applications
**Plastics**

Preliminary results from the survey of the users of decabromodiphenyl ether in plastics have also become available (BSEF, 2005). However, unlike the situation with the textile industry (where the majority of user companies are represented by a single trade association), the companies using decabromodiphenyl ether in plastics in the UK (and the rest of Europe) are not a coherent group and only a relatively small proportion of the companies are members of a national branch (trade) association. Therefore in order to make the scheme workable, the producers of decabromodiphenyl ether firstly set up a UK customer database under strict CEFIC statistical rules and fully in line with the relevant EU anti-trust legislation. The top nine companies (in terms of volume used; these account for around 70% of the decabromodiphenyl ether use volume in the UK in 2003) then agreed to participate in a survey. This survey was started in January 2005 and the initial findings are summarised below. No quantitative emission data were available.

- 75% of the sites had an air aspiration system in place, out of which 65% operated a dust filter. None of the companies measured the specific emissions of decabromodiphenyl ether to air.
- 25% of the sites operated an on-site wastewater treatment facility (physical treatment) before emitting to sewer. All sites surveyed have a consent to emit to sewer (all coordinated with local authority and water company management), but only 75% of the sites actually emitted to sewer. None of the companies measured the specific emissions of decabromodiphenyl ether to sewer and none of the water companies taking waste water from the sites is currently analysing for decabromodiphenyl ether.
- For the dust filters, 55% of the sites partly reprocessed the dust filter content, with the balance being disposed of as chemical waste to special landfill or incinerated.
- Floor sweepings and spills were disposed of as chemical waste at all sites.
- A maximum of 25% of the off-specification material was internally reprocessed with the remaining 75% being disposed of to special landfill.
- One company processed decabromodiphenyl ether in an aqueous dispersion. Empty drums are returned to the supplier or, if the packaging is reused internally, it is cleaned. The waste water goes to an on-site waste water treatment plant before going to sewer. The packaging at other sites is disposed of to special landfill or incinerated.
- The overall process efficiency is estimated to be in the range 95-98%.
- Around 50% of the sites had one or more environmental quality management system in place (or in the process of being implemented).
- Only one company was regulated under the Integrated Pollution Prevention and Control (IPPC) regime.

**Non-European information**

An estimate of the yearly emissions of decabromodiphenyl ether to the atmosphere in Japan has been made by Hirai and Sakai (2004). The total emission was estimated to be in the range 0.12 tonnes/year (low estimate) to 25 tonnes/year (high estimate). The middle estimate was 1.7 tonnes/year. A mass balance model was used to predict the resulting concentrations in air, atmospheric deposition and soil and by comparison of the results of this modelling with the available environmental monitoring data for Japan it was concluded that the actual emissions
of decabromodiphenyl ether into the atmosphere in Japan are most probably around 3 tonnes/year (range 1-7 tonnes/year).

The emissions of decabromodiphenyl ether from plastics processing and recycling facilities have been measured by Sakai et al. (2004). For plastics processing, the levels of decabromodiphenyl ether in flue gas from six facilities were measured (a total of eleven measurements were made). The levels found in the flue gas (measured either at the extruder outlet or a general outlet) were in the range 0.72-170 ng/m³. These data were then used, along with the capacities of the extruder and the decabromodiphenyl ether content in the plastic, to estimate an emission factor from extrusion for three of these sites. The estimated emission factors were in the range $5 \times 10^{-9}$ to $3 \times 10^{-7}$ expressed as a fraction of the decabromodiphenyl ether utilised. The emissions of decabromodiphenyl ether from these three plants were estimated to be 0.025-0.41 mg/hour or 0.22-6.2 g/year.

Similar measurements at seven electrical equipment recycling facilities found the concentration of decabromodiphenyl ether in flue gas to be between 1.9 and 1,400 ng/m³. Emission factors were derived for five of these sites (not including the sites with the two highest concentrations in flue gas; the concentrations at these two sites were 1-2 orders of magnitude higher than found at other sites) as $2.5 \times 10^{-9}$ to $2.9 \times 10^{-7}$ (as a fraction of the decabromodiphenyl ether recycled in the equipment). The total plant emissions were estimated to be in the range 0.38-2.2 g/year for these five sites.

### 2.1.2 Summary and implications for the risk assessment

New quantitative emissions data have been received for textile applications in the United Kingdom following emission reduction activities over the year 2004. New information is also available on the emissions to air from plastics processing and recycling facilities in Japan. These data show that the emissions are low (of the order of grammes per year for each site). A survey of the actual emissions from polymer processing sites in the UK is planned in the near future.

The reported emission to sewer from all but one of the textile sites in the UK is currently <3.6 kg/day per site (and in fact is usually much lower than this figure or close to zero). This is consistent with the generic scenarios contained in the 2002 version of the risk assessment, which were based on information supplied by an industry expert. In that report, an emission of the order of 3 kg/day was assumed for textile compounding and backcoating sites (i.e. 2 kg/day (600 kg/year over 300 days) to waste water at a formulation site and 1 kg/day (300 kg/year over 300 days) to waste water at an application site, with the combined regional emission being 900 kg/year).

It is noted that further emission reduction measures are already underway at the site with the highest of these emissions (installation of an on-site effluent treatment plant), and the emissions from the remaining sites would be <2 kg/day assuming no further emission reduction measures have taken place at these sites.

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4 Figures taken from Section 3.1.1.3 and Table 3.3 of the original published risk assessment report (ECB, 2002). The regional figure is the combined figure for formulation/compounding of the backcoating (regional emission 600 kg/year to landfill/waste water) and application of the backcoating to the textile (regional emission 300 kg/year to landfill/waste water). These figures are higher than the scenarios used in the 2004 version of the risk assessment, which was based on site-specific monitoring data from a limited survey of user sites - the uncertainties over the representivity of the release figures were highlighted.
In contrast, local emissions at the worst-case UK site were around 18 kg/day in 2004, with a total UK emission of around 5,520 kg/year\(^5\). This is much higher than the emissions summarised in both the 2002 and 2004 risk assessment reports. The processing that takes place at this site is not thought to be typical of other textile sites in either the UK or the EU as a whole. It should also be noted that as a result of the VECAP initiative, recent improvements mean that the actual emission from this site will be reduced by almost 75% (i.e. now expected to be around 5 kg/year).

Table 1 provides PECs (calculated using EUSES 2.0.3) and PEC/PNEC ratios based on the worst case releases (both for 2004, and following emission reduction by 75%). It should be noted that this analysis only applies to the processes that occur at one – atypical – site in the United Kingdom, and is probably not representative of the EU.

**Table 1** Revised PECs for textile backcoating formulation and application sites

<table>
<thead>
<tr>
<th>Compartment/scenario</th>
<th>PEC</th>
<th>PNEC(^a)</th>
<th>PEC/PNEC ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Local</td>
<td>Regional</td>
<td>Local</td>
</tr>
<tr>
<td>Surface water(^h)</td>
<td>22.2 µg/l</td>
<td>0.012 µg/l</td>
<td>No PNEC could</td>
</tr>
<tr>
<td></td>
<td>6.2 µg/l</td>
<td></td>
<td>be defined.</td>
</tr>
<tr>
<td>Sediment(^e)</td>
<td>765 mg/kg wet weight (^c)</td>
<td>0.80 mg/kg wet wt. (^d)</td>
<td>≥148 mg/kg wet wt.</td>
</tr>
<tr>
<td></td>
<td>213 mg/kg wet weight (^c)</td>
<td></td>
<td>≥1.5 mg/l</td>
</tr>
<tr>
<td>Waste water treatment plant</td>
<td>0.75 mg/l</td>
<td>Not applicable</td>
<td>≥1.5 mg/l</td>
</tr>
<tr>
<td></td>
<td>0.21 mg/l</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Agricultural soil</td>
<td>305 mg/kg wet weight (^c)</td>
<td>0.19 mg/kg wet weight (^d)</td>
<td>≥87 mg/kg wet wt.</td>
</tr>
<tr>
<td></td>
<td>84.8 mg/kg wet weight (^c)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Secondary poisoning – earthworm food chain</td>
<td>125 mg/kg (^c)</td>
<td>833 mg/kg food</td>
<td>0.15(^e)</td>
</tr>
<tr>
<td></td>
<td>34.7 mg/kg (^d)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note:  
\(^a\) PNEC values are taken from ECB (2004). See main text below regarding the PNEC for sediment.  
\(^b\) The local PECs are based on predicted water concentrations that exceed the actual water solubility of the substance – see main text below.  
\(^c\) Values estimated using a worst case local emission of 18 kg/day.  
\(^d\) Values estimated using a local emission of 5 kg/day, representing the situation following the recently implemented emission reduction measures.

No risks are identified for surface water, WWTP or secondary poisoning from this worst case level of release. A potential risk is identified for the first time for the sediment (based on both the 2004 estimate and the estimate following the implementation of emission reduction measures) and soil compartments (based on the estimate prior to emission reduction measures only). However, there are a number of factors to bear in mind:

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\(^5\) In the calculations this figure has been used as the regional emission to waste water treatment plants from textile backcoating formulation and application. The calculations also take into account the regional contribution from all other sources as outlined in ECB (2004).
- Both the sediment and soil PNECs are only limit values, based on tests where no adverse effects were seen at the highest concentration tested. In other words, they are not true PNECs, and could be substantially higher.

- There is some uncertainty in the calculation of the sediment PECs, because they are based on predicted water concentrations that exceed the actual water solubility of decabromodiphenyl ether. This is theoretically possible if the predicted concentration represents the total (i.e. dissolved plus particulate) concentration of decabromodiphenyl ether and the effluent from the site contains particulate matter. However this does mean that the concentration in sediment is potentially overestimated. If it were assumed that the maximum concentration in the receiving water is 0.1 µg/l (the upper limit to the water solubility), then the equivalent concentration in sediment would be around 3.5 mg/kg wet weight. This would give a PEC/PNEC ratio below 1 using the calculation methods described in the Technical Guidance Document (TGD).

- Nevertheless, it should be noted that previous monitoring studies have shown that decabromodiphenyl ether was accumulating in sediments during the 1990s, as discussed in EC (2002) and ECB (2004). It is therefore possible that levels in sediments downstream of textile sites might be higher than the PECs calculated for the local assessment, which assume that the concentration in sediment is effectively in equilibrium with the concentration in water at the time of release.

- There is also considerable uncertainty over the figure used for the regional estimate of release (and the current emission is likely to be much reduced from this figure owing to the emission reduction measures that have taken place recently under the VECAP). However the analysis undertaken here is relatively insensitive to the regional emission/regional PEC.

- Based on the most recent emission estimates, only sediment might be at risk once emission reduction activity has taken place in accordance with the VECAP.

The generic scenarios given in the 2002 version of the risk assessment appear to be most appropriate for the remaining UK textile sites. These showed no PEC/PNEC ratios greater than 1 for any endpoint (≤ 0.89 for sediment and ≤ 0.59 for soil for a worst case site).

Thus, the newly identified potential risks – based on worst case emissions and a number of uncertainties – appear to be of limited applicability for the textile industry in general, at least in the UK where the VECAP has been a successful tool to reduce emissions. However, it is important to recall that the latest survey data represent a point in time following some level of (voluntary) emission reduction, and that the same activity has not yet taken place in other European countries. The industry’s own estimate is that total UK emissions were around five times higher in 2003 than in 2004. It is therefore possible that current releases at some sites in other European countries could be at a higher level than the 2004 data for the majority of UK sites (and the 2002 risk assessment generic scenarios) suggest.

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6 For sediment, the NOEC was ≥3,841 mg/kg dry weight. For soil, the NOEC was ≥4,910 mg/kg dry weight.
The conclusion for sediment and soil therefore needs to be changed from conclusion (ii) to (i). Further information is now required to refine the assessment, and there are a number of options:

a) For sediment, the PNEC is currently based on the highest concentration tested where no effects were seen in studies with *Lumbriculus variegatus* with an assessment factor of 10. Repeat toxicity testing could be performed to refine the PNEC, using higher test substance concentrations than previously used. The NOEC would have to be above 7,650 mg/kg wet weight to completely remove the concern for the worst case releases (using an assessment factor of 10). This would be equivalent to around 35,190 mg/kg dry weight for sediment (using the default water content currently used for sediment in EUSES 2.0.3\(^7\)). In other words, the substance would make up around 3.5% of the matrix\(^8\). Although the OECD tests methods for sediment organisms\(^9\) do not specify an upper limit to the concentration that could be tested in sediment systems, the results obtained from testing such high concentrations may be difficult to interpret.

b) Given the uncertainties over the calculation of the PEC for this endpoint, monitoring of actual sediment levels downstream from user site discharge points is likely to be the most appropriate way forward in this instance. Firstly, it is important that representative baseline data are collected for aquatic emissions from the textile industry in other European countries as a matter of urgency. Where a potential risk is identified for sediment, monitoring data should be collected downstream from textile application site discharge points, to refine the sediment PECs directly. Neither the monitoring programme designed for the VECAP nor that developed to address the conclusion of the 2004 risk assessment report would provide such sediment data, and so an extension of one or both of these would be required.

c) Although further emission reduction is expected at the worst case UK site, accumulation in sediment means that actual environmental concentrations could actually be higher than predicted. It might be useful to clarify this, for this specific site at least. Sediment core data (where it is feasible to collect a suitable core), rather than spot samples, would also be relevant in this context.

d) Similar considerations apply to soil. The soil PNEC is currently based on the highest concentration where no effects were seen in a study with earthworms using an assessment factor of 50. In this case further toxicity testing covering an additional endpoint (e.g. toxicity to soil microorganisms) may allow the PNEC to be revised sufficiently, provided a suitably high concentration is tested. Based on the PECs calculated here, the NOEC from such a study would have to be above 3,050 mg/kg wet weight to remove the concern (using an assessment factor of 10). This would be equivalent to around 3,470 mg/kg dry weight using the default water content for soil

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\(^7\) It should be noted that the method used for conversion of dry weight to wet weight for sediment has changed in the most recent version of EUSES (version 2.0.3) compared with the version used for the previous versions of the risk assessment (ECB, 2002 and 2004). Using the most recent version of EUSES the NOEC for sediment of >3,841 mg/kg dry weight is now equivalent to a NOEC of 835 mg/kg wet weight. This would lead to a PNEC of 84 mg/kg wet weight using an assessment factor of 10, which would lead to similar conclusions.

\(^8\) Following the recent reduction in emissions at the worst case site, the NOEC would need to be 2,130 mg/kg wet weight (or 9,798 mg/kg dry weight) to remove the concern, i.e. the substance would make up around 1% of the matrix.

\(^9\) Currently OECD methods only exist for sediment toxicity testing with *Chironomus* *sp.*
used in the TGD. This concentration is similar to that which has been tested already (e.g. concentrations of up to 4,910 mg/kg dry weight were tested in an earthworm study, and concentrations of up to 5,349 mg/kg/dry weight were tested in a study with plants). Therefore it should be technically possible to carry out a further study to investigate the toxicity to soil microorganisms at a suitable concentration.

e) It should be noted that, unlike sediment, the emission reduction measures that have occurred recently under the VECAP have reduced the soil PEC/PNEC ratio to below 1 for the worst case emissions. There is therefore currently no need for a soil microorganism toxicity test. However, since emissions in other countries could be higher than the current UK emissions data suggest, the data outlined in point (b) above (and, where relevant, information on sludge disposal practices) is needed before a final decision can be taken.

Depending on the development of the VECAP, some further reduction in emissions might be possible at the site level. The information in this report should be used to inform that process. Local emissions would need to be reduced to <2 kg/day to remove the risk for sediment using the PNEC as back-calculated using the methods in EUSES 2.0.3 (or <3.6 kg/day as back-calculated using the agreed 2002 PNEC of ≥148 mg/kg wet weight). This calculation assumes that the concentration in sediment is in equilibrium with the concentration in water, and does not take into account any possible build-up of levels with time resulting from the persistence of decabromodiphenyl ether.
3 USES

3.1.1 New information

A substance flow analysis of brominated flame retardants (decabromodiphenyl ether and tetrabromobisphenol-A (defined in the study as “tetrabromobisphenol-A and its derivatives”)) in waste TV sets has recently been carried out in Japan (Tasaki et al., 2004). The study investigated the effects on the amounts of the flame retardants that would likely be disposed of in television sets in future years. In order to determine the base-line situation the study investigated the amounts and types of flame retardants that were present in television casings (both front and rear covers). Decabromodiphenyl ether was found to have been first used in the late 1980s for the rear covers of TVs, and in front covers starting from around 1993-1996, but that there was a move in the late 1990s from this flame retardant to tetrabromobisphenol-A-based flame retardants (including its derivatives). Little or no substitution with non-brominated flame retardants was seen (as of 2002). Based on these findings, three scenarios were constructed:

1) Business-as-usual scenario, where it was assumed that the composition of TV sets found in the late 1990s would continue into the future;
2) Non-polybrominated diphenyl ether scenario, where it was assumed that the substitution of decabromodiphenyl ether with tetrabromobisphenol-A-based flame retardants would continue, with total replacement by the end of 2001 assumed; and
3) Non-brominated flame retardant scenario, where it was assumed that from 2003 the brominated flame retardants would be progressively substituted by non-brominated flame retardants, with complete substitution by 2006.

The average lifetime of a TV set in Japan used in the study was 9.8 years based on an analysis of data from survey results of the number of TVs remaining in households. The results of the analysis were determined in terms of the amount of total bromine present in waste TVs over the years 1995 to 2002. For the business-as-usual scenario, the amount of bromine present in waste TVs was estimated to be 246 tonnes in 1995 and this was predicted to rise to 1,204 tonnes in 2000, 2,598 tonnes in 2005, 3,620 tonnes in 2010, 4,091 tonnes in 2015 and 4,463 tonnes in 2020. Tetrabromobisphenol-A-based compounds were estimated to account for 2.8% of the total bromine in 1995, rising to 3.2% in 2000, 12% in 2010 and 13% in 2020. An important driving force behind the predicted increases was the current increase in size of TV sets. For the non-polybrominated diphenyl ether scenario, the amount of decabromodiphenyl ether present in waste TV sets was predicted to peak in 2005 and the amount of tetrabromobisphenol-A-based compounds increases after this time (the amount of decabromodiphenyl ether in waste was predicted to become lower than the amount of tetrabromobisphenol-A-based compounds in 2008). In the non-brominated flame retardant scenario, the amount of bromine in waste TVs was predicted to peak in 2009 and then decrease markedly (falling to around 10% of its 2000 level by 2010).

3.1.2 Summary and implications for the risk assessment

No significant new information related to the uses of decabromodiphenyl ether in the EU has become available.
4 ENVIRONMENTAL LEVELS

The conclusion of the 2004 risk assessment was that further long-term monitoring of the substance and lower PBDE congeners is required in the European environment. Initial sampling has begun, and includes estuarine sediment, sewage sludge, Sparrowhawk (Accipiter nisus) eggs from the UK and Glaucous Gull (Larus hyperboreus) eggs from an Arctic region of Norway. The aim is to establish time trends of concentrations in these matrices over the period of 2005-2014. The first annual report will be made available by industry in the second quarter of 2006. In addition, a pilot project to investigate the feasibility of including air as an additional matrix is underway and will report in the last quarter of 2005. A long-term biomonitoring study in humans is also under development as a result of the human health risk assessment conclusions.

The rest of this section discusses new monitoring data that have been reported outside of these programmes.

When considering the available data on measured levels of decabromodiphenyl ether in the environment it should be noted that the analysis of decabromodiphenyl ether is not straightforward. In particular, a recent (third) international interlaboratory calibration study highlighted that blank problems are significant for decabromodiphenyl ether (de Boer and Wells, 2004). One source of contamination of decabromodiphenyl ether in laboratory blank samples was thought to arise from the presence of decabromodiphenyl ether in dust particles in laboratory air. Björklund et al. (2004) found the column and injection technique used can also have a large influence in the analysis of decabromodiphenyl ether.

4.1.1 Water and sediment

i) Europe

Germany

Sawal et al. (2004 [ABST]) conducted an extensive survey of the levels of polybrominated diphenyl ethers (including decabromodiphenyl ether) in sediments from the River Elbe, Germany, following a flood in August 2002. Surface sediment samples (0-2 cm) were collected from 29 sites (mainly from breakwaters, abandoned channels and harbours) along the course of the River Elbe from Obsiství (Czech Republic) to Hamburg. Decabromodiphenyl ether was found to be the dominant congener present in most of the samples, averaging around 78% of the total polybrominated diphenyl ethers present in the samples from Germany. Three of the samples from the Czech Republic showed a similar congener pattern to those from Germany, but higher percentages of tetra- to hexabrominated congeners (up to 70%) were seen in other samples from the Czech Republic. The concentration of decabromodiphenyl ether found ranged from 0.5 to 17.4 µg/kg dry weight (or 10 to 230 µg/kg on an organic carbon basis). In general the concentrations in the samples from Germany were higher than those in the samples from the Czech Republic, with the highest levels being found near Hamburg. The paper reports that low levels of decabromodiphenyl ether (11 samples; median of 4.2 µg/kg dry weight) were also found in the Hamburg Harbour area in an unpublished study.
Ireland

Kilemade et al. (2004) determined the levels of decabromodiphenyl ether in surface sediments from three polluted sites in Cork Harbour (Douglas (inner harbour), Aghada and Whitegate (both outer harbour)) and from a relatively unpolluted reference site (Ballymacoda). The sediment samples were all intertidal surficial samples (top 1-2 cm) and were sieved (<63 µm) prior to analysis. Decabromodiphenyl ether was not detected in any of the samples analysed (detection limit was 0.1-0.11 µg/kg dry weight).

Norway

A survey of the levels of decabromodiphenyl ether in sediments from Drammens River and the Drammensfjord (both located in an industrialised area in the southeast of Norway) was carried out in 2003 (Schlabach et al., 2004 [ABST]). Decabromodiphenyl ether was found in all sediment samples analysed (seven samples from Drammens River and five samples from Drammensfjord) at a concentration of 3.6-79 µg/kg dry weight (Drammens River) and 6.9-32 µg/kg dry weight (Drammens Fjord). Samples of fish from the area were also collected but the results for decabromodiphenyl ether in these samples were not reported. The highest concentration found in the Drammens River was from what was thought to be an unpolluted site upstream of the industrial area and the paper recommended that this site should be resampled to confirm the level. The highest level found in Drammens Fjord was from a site close to a quay for shipping materials (shredding) from recycled automobiles.

Southern North Sea

Voorspoels et al. (2004a [ABST] and 2004b) determined the levels of decabromodiphenyl ether in sediments from the Belgian North Sea (six locations), the Western Scheldt estuary (9 locations) and several freshwater tributaries (14 locations) of the river Scheldt. The samples were collected to a depth of 20-25 cm. The decabromodiphenyl ether concentrations found were in the range 1.1-24 µg/kg dry weight in samples from the Belgian North Sea (detected in 83% of the samples), 1.5-1,200 µg/kg dry weight in samples from the Scheldt estuary (detected in all nine samples) and <0.1-320 µg/kg in samples from the tributaries of the river Scheldt (detected in 86% of the samples). Decabromodiphenyl ether was the most abundant congener found in the samples accounting for around 95% of the total concentration in the Scheldt estuary samples and 52-99% of the freshwater tributary samples (it was also the predominant congener found in the Belgian North Sea samples). The study also investigated if there was any correlation between the concentrations of decabromodiphenyl ether found and the concentration of lower brominated congeners (expressed as the sum of specific tri- to heptabrominated congeners) found. A statistically significant (p=0.05) positive correlation was found for the samples from marine locations (Belgian North Sea and Scheldt estuary) whereas no correlation between the concentration of decabromodiphenyl ether and that of the lower brominated congeners was evident in the samples from the freshwater locations.

The levels of decabromodiphenyl ether have been determined in surface sediment samples (the <63 µm fraction) from the southern North Sea (Klamer et al. (2005). The levels found were in the range 1-32 µg/kg dry weight. The Western Scheldt upper estuary was thought to be the source of the decabromodiphenyl ether found in the samples.

Verslycke et al. (2005) measured decabromodiphenyl ether levels of 0.24-1.65 mg/kg dry weight in sediment samples from the Scheldt estuary. The samples were collected in
November 2001 and were sieved (<63 µm) prior to analysis. Decabromodiphenyl ether was also found to be present in mysid shrimp from the same area (see Section 4.1.5).

Kierkegaard et al. (2004) found decabromodiphenyl ether to be present at a concentration of 1.28 mg/kg dry weight in a sample of sediment from the Western Scheldt estuary, the Netherlands, collected in 2001.

Spain

Eljarrat et al. (2004) carried out an investigation of the levels of decabromodiphenyl ether in sediments from the River Cinca, Spain. Surface sediments (top 2 cm) were collected from two sites upstream (20 km and 12 km upstream) and two sites downstream (immediately downstream and 30 km downstream) of Monzón (a heavily industrialised town). The level of decabromodiphenyl ether was found to be 2.1 and 2.6 µg/kg dry weight in the two upstream samples, 39.9 µg/kg dry weight in the sample immediately downstream of Monzón and 5.7 µg/kg dry weight in the sample 30 km downstream of Monzón.

United Kingdom

The Central Science Laboratory is currently investigating the causes of chick deformities observed at a Grey Heron Ardea cinerea colony in central England. Decabromodiphenyl ether was added to the suite of chemical analyses to extract additional information from the samples that have been collected. A final report is expected in 2006, but preliminary results for a limited number of samples indicates a concentration range of 5.42-32.56 µg/kg dry weight for freshwater sediment (4 sites) (CSL, 2005). The relationship of these sites to sources of the substance is not yet known.

ii) North America

As part of a study to investigate the uptake of polybrominated diphenyl ethers in infaunal invertebrates, Klosterhaus et al. (2004 [ABST]) determined the levels in sediment downstream of a wastewater treatment facility in Back River (Baltimore, Maryland, USA) and sites close to Hart-Miller Island (a confined sediment disposal facility at the mouth of Back River). The total concentrations of polybrominated diphenyl ethers in the sediments from Back River were in the range ~2,400-9,000 µg/kg dry weight, with the concentrations generally decreasing downstream of the waste water treatment facility. Decabromodiphenyl ether accounted for more than 99% of the total polybrominated diphenyl ethers found in these samples. The total polybrominated diphenyl ether levels in the sediments from Hart-Miller Island were much lower, in the range ~50-160 µg/kg dry weight. Decabromodiphenyl ether accounted for 93-99% of the total polybrominated diphenyl ethers found in these samples.

Wenning et al. (2004 [ABST]) determined the levels of polybrominated diphenyl ether in surface (0-15 cm) and buried sediments (~1.3-10 cm) at several locations in the upper Newark Bay and the lower Hackensack River, New Jersey, USA (a heavily industrialised and urbanised estuary). The levels of decabromodiphenyl ether found were 1.9-6.8 µg/kg dry weight (mean 3.9 µg/kg dry weight) in surface samples from the Lower Hackensack River, 330-700 µg/kg dry weight (mean 500 µg/kg dry weight) in surface samples from the Lower Passaic River confluence, 140-380 µg/kg dry weight (mean 240 µg/kg dry weight) in surface samples from Northern Newark Bay and 0.097-300 µg/kg dry weight in samples from the
Lower Hackensack River confluence (the mean level found was 60 µg/kg dry weight in surface samples and 30 µg/kg dry weight in buried samples at this site).

Song et al. (2004a [ABST] and 2004b) determined the levels of polybrominated diphenyl ethers in dated sediment cores collected in 2001 and 2002 from six locations in Lake Superior. The concentration of decabromodiphenyl ether was found to be in the range 4-17 µg/kg dry weight (or 140-390 µg/kg organic carbon) in the surface sediment samples, and the concentration was found to reduce rapidly with depth. Decabromodiphenyl ether was found to account for about 83-94% by mass of the total polybrominated diphenyl ethers present in the surface samples. The surface flux of decabromodiphenyl ether into the lake was estimated to be around 0.1-0.16 ng/cm²/year and the loading rate of decabromodiphenyl ether into Lake Superior sediments was estimated as 73-135 kg/year. Based on the analysis of the dated sediment cores, an increasing trend was apparent in the estimated flux to the lake from the 1970s onwards, with an increasing trend still being apparent at most of the locations sampled in 2002.

Stapleton et al. (2004c) found that decabromodiphenyl ether was detected at a concentration of 114 µg/kg dry weight in a sample of sediment used as a standard reference material in the United States.

The levels of decabromodiphenyl ether in sediments of tributaries of Lake Ontario have been determined by Kolic et al. (2004b). As well as sediments, the study also investigated the levels of decabromodiphenyl ether in biosolids from nearby waste water treatment sites. The levels in sediment were in the range 6.9-400 µg/kg in six tributary sediment samples and 310-2,000 µg/kg in five biosolids samples.

Baker et al. (2004) examined the levels of decabromodiphenyl ether in estuarine sediments from the Back River (an urbanized tributary to Chesapeake Bay, United States, that receives treated wastewater effluent from a tertiary treatment plant). The samples analysed were surface sediments (to 2 cm) from four locations in the river downstream of the waste water treatment plant. The highest level of decabromodiphenyl ether was found in a sample immediately downstream of the waste water treatment plant (9 mg/kg dry weight or 160 mg/kg organic carbon), with the level falling to 2.4 mg/kg dry weight (68 mg/kg organic carbon) at a distance of 6 km downstream of the plant. Decabromodiphenyl ether accounted for >99.7% of the total brominated diphenyl ethers in these samples.

The levels of total polybrominated diphenyl ether (including decabromodiphenyl ether) have been found to be in the range 0.029-1.05 mg/kg dry weight in suspended solids from the Mississippi River Basin (twenty six sites along the Mississippi River, five of its major tributaries and Lake Itasca) (Raff and Hites, 2004). The actual levels of decabromodiphenyl ether present in the samples was not given but the average decabromodiphenyl ether contribution was estimated to be 96.8% of the total found. Based on the concentrations found, it was estimated that around 8 tonnes of polybrominated diphenyl ether were discharged into the Gulf of Mexico on suspended solids from this river basin in 2002.

The levels of decabromodiphenyl ether in water and surface sediments from the San Francisco estuary have been determined (Oros et al., 2005). The samples were collected in July 2002 and included 33 water samples (taken from approximately 1 m below the surface) and 48 surface sediment samples (to 5 cm) from various locations within the estuary. For the surface water samples, decabromodiphenyl ether was detectable in 32 out of the 33 samples
(the detection limit of all polybrominated diphenyl ethers was given as 0.02-0.2 ng/l) but could only be quantified in 17 of these. The quantifiable levels found were in the range 0.012-0.19 ng/l. Decabromodiphenyl was associated primarily with the particulate phase of these samples. The highest levels of polybrominated diphenyl ethers in general were found in samples from the lower South Bay area. This area receives around 26% of the total waste water effluent from publicly owned treatment works entering the estuary, but only around 10% of the inflow of freshwater into the estuary. In contrast with the water samples, decabromodiphenyl ether was not detectable in any of the 48 sediment samples (detection limit was 1.5 µg/kg dry weight). Samples of bivalves from the same area were also analysed for the presence of decabromodiphenyl ether. These results are summarised in Section 4.1.5.

### iii) Rest of world

Decabromodiphenyl ether has been found to be present in sediments from Pakistan (Khan et al., 2004 [ABST]). The samples analysed were collected from five locations following a transect of the Indus River, and from industrial areas of Karachi Harbour, Korangi Creek and Gizri Creek. Decabromodiphenyl ether was detected in 1 out of the five freshwater sediment samples from the Indus River at a concentration of 1.74 µg/kg dry weight (the detection limit for the samples was in the range 0.02-0.1 µg/kg dry weight), and was found at a concentration of 0.88 µg/kg dry weight in a pooled estuarine sediment sample from the Korangi Creek area, 5.85 µg/kg dry weight in a pooled estuarine sediment sample from Gizri Creek and 6.68 µg/kg dry weight in a pooled oceanic sediment sample from Karachi Harbour.

The levels of decabromodiphenyl ether in surface sediments collected in 2003 from seventeen locations around the coastal area of the Setouchi Sea, Japan, were determined to be in the range 1.3 to 710 µg/kg dry weight (Ohta et al., 2004a [ABST]). The highest levels found were from an area containing many chemical factories.

A recent study on the levels of decabromodiphenyl ether in leachate from landfill sites in Japan has been published (Osako et al., 2004). The samples were collected from the leachate treatment plants present at the landfill sites (samples were taken before treatment, and in some cases also after treatment). The landfill sites sampled included five municipal solid waste landfills (in Japan around 80% of municipal solid waste is incinerated prior to landfill disposal and so the landfills were mostly composed of incineration ash, incombustibles and crushed fragments from bulk wastes (including waste electrical and electronic equipment)), one landfill that received sewage treatment sludge as well as municipal solid waste and an industrial waste landfill (the actual industries served by this landfill were not stated but the landfill contained organic and inorganic sludge, incineration residues and waste plastics). Decabromodiphenyl ether was not detected in any of the samples of raw leachate or treated leachate analysed (the detection limit varied but was generally <1 ng/l for most samples (one raw leachate sample had a detection limit of 50 ng/l)).

#### 4.1.2 Sewage sludge

### i) Europe

**Germany**

Knoth et al. (2004) studied the occurrence and fate of polybrominated diphenyl ethers (including decabromodiphenyl ether) in sewage sludge from municipal waste water treatment
plants from Germany. A total of thirty nine sewage sludge samples from different stages during the treatment process (including primary sludge, secondary excess sludge, and dewatered digested sludge) were collected from eleven treatment plants. The levels of decabromodiphenyl ether were found to be in the range 0.097 to 2.2 mg/kg dry weight, with the mean and 90th-percentile level being 0.43 and 0.78 mg/kg dry weight respectively. Comparison of the ratios of the concentrations of the various lower brominated diphenyl congeners present in the samples found no indication that the bromination pattern of the congeners in the samples changed significantly during the treatment process.

Another study of decabromodiphenyl ether levels in sewage sludge in Germany has been reported by Hamm (2004). In this study, samples of sewage sludge and suspended particulate matter from the effluent were collected from eight municipal waste water treatment plants from central Germany. The concentrations of decabromodiphenyl found are summarised in Table 2. Decabromodiphenyl ether accounted for between 43-79% (in sewage sludge) or 33-58% (in effluent suspended solids) of the total polybrominated diphenyl ethers present.

Table 2  
Levels of decabromodiphenyl ether in sewage sludge from waste water treatment plants in Germany

<table>
<thead>
<tr>
<th>Plant</th>
<th>Concentration in sewage sludge (mg/kg dry weight)</th>
<th>Concentration in suspended matter in effluent (mg/kg dry weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant 1</td>
<td>0.217</td>
<td>0.038</td>
</tr>
<tr>
<td>Plant 2</td>
<td>0.198</td>
<td>0.140</td>
</tr>
<tr>
<td>Plant 3</td>
<td>0.639</td>
<td>0.172</td>
</tr>
<tr>
<td>Plant 4</td>
<td>0.400</td>
<td>0.093</td>
</tr>
<tr>
<td>Plant 5</td>
<td>0.177</td>
<td>0.035</td>
</tr>
<tr>
<td>Plant 6</td>
<td>0.100</td>
<td>&lt;0.011</td>
</tr>
<tr>
<td>Plant 7</td>
<td>0.268</td>
<td>0.032</td>
</tr>
<tr>
<td>Plant 8</td>
<td>0.609</td>
<td>0.181</td>
</tr>
</tbody>
</table>

Spain

The levels of decabromodiphenyl ether in sewage sludge from waste water treatment plants in Spain have been determined (Fabrellas et al., 2004). The samples were collected during 2002 from both urban and industrial treatment plants. The results are summarised in Table 3. Decabromodiphenyl ether accounted for 93-99% of the total polybrominated diphenyl ethers present in the samples. The highest level found was in a sample from an industrial treatment plant from an area with mainly textile manufacturing facilities.

Table 3  
Levels of decabromodiphenyl ether in sewage sludge from waste water treatment plants in Spain

<table>
<thead>
<tr>
<th>Type of plant</th>
<th>Population served</th>
<th>Concentration of decabromodiphenyl ether (mg/kg dry weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed urban/industrial</td>
<td>&lt;500,000</td>
<td>5.43</td>
</tr>
<tr>
<td>Mixed urban/industrial</td>
<td>500,000-1,000,000</td>
<td>0.79</td>
</tr>
<tr>
<td>Mixed urban/industrial</td>
<td>&lt;500,000</td>
<td>1.20</td>
</tr>
<tr>
<td>Urban</td>
<td>&lt;500,000</td>
<td>3.59</td>
</tr>
<tr>
<td>Urban</td>
<td>&gt;1,000,000</td>
<td>5.84</td>
</tr>
<tr>
<td>Industrial</td>
<td>&lt;500,000</td>
<td>18.03</td>
</tr>
</tbody>
</table>
Sweden

A survey of the levels of decabromodiphenyl ether in sewage sludge from Sweden has been undertaken (Nylund et al., 2002 as reported in Kierkegaard et al., 2004). The samples were collected in 2000 (the samples were pooled subsamples collected over a period of around one month) from fifty sewage treatment plants distributed all over Sweden and decabromodiphenyl ether was detected in all samples at a level of 6 to 1,000 µg/kg dry weight.

ii) North America

Decabromodiphenyl ether was found to be present at a concentration of 0.47 to 1.8 mg/kg in ten samples of sewage sludge (the substance was detected in all ten samples) from six locations in Ontario, Canada (McCrindle et al., 2004).

A study of the levels of polybrominated diphenyl ethers (including decabromodiphenyl ether) present in various sludges and other biosolids that can be applied to agricultural land has been carried out in Canada (Kolic et al., 2004a [ABST]). The biosolids analysed included paper biosolids (four samples from two sites), paper biosolids compost (two samples from one site) and manure (six samples from one beef, dairy and poultry site and ten samples from one poultry, pig and horse site). The level of decabromodiphenyl ether found in the paper biosolids was 120-130 µg/kg from one site and 77-79 µg/kg from the other site. The levels found in the paper biosolids compost were 54-80 µg/kg. The manure samples had generally lower, but still detectable, levels of decabromodiphenyl ether, with the concentrations being in the range of not detected (<4 µg/kg) to 12 µg/kg in the beef, dairy and poultry manure and not detected (<0.4 µg/kg) to 3.6 µg/kg in the poultry, pig and horse manure. The paper also investigated the ratios of the concentration of decabromodiphenyl ether to that of the various other polybrominated diphenyl ether congeners present in the composted and uncomposted paper biosolids samples from the same site, and found that the relative amount of decabromodiphenyl ether in the composted sample was lower than in the uncomposted sample and suggested that this may show that decabromodiphenyl ether was degrading with time during the biosolid decomposition/composting process, but that further work would be needed to test this hypothesis. No explanation was given in the paper as to the source of the decabromodiphenyl ether found in the paper biosolids samples.

The levels of decabromodiphenyl ether in biosolids/sewage sludge in plants in the United States have been determined by La Guardia et al. (2004b). The samples were taken from sites using different sludge stabilisation processes, including composting, lime-stabilisation, heat treatment and anaerobic digestion. The concentration of decabromodiphenyl ether found was in the range 308-1,460 µg/kg dry weight in biosolids from three composting plants, 85-553 µg/kg dry weight in biosolids from two lime-stabilisation plants, 1,940-4,890 µg/kg dry weight in biosolids from two heat stabilisation plants and 340-450 µg/kg dry weight in biosolids from four anaerobic digestion plants.

North (2004) investigated the behaviour of polybrominated diphenyl ethers (including decabromodiphenyl ether) at the Palo Alto wastewater treatment plant in the United States. The plant treats approximately 25 million gallons of waste water each day from residential areas (60% of total waste water), industries (10% of total waste water) and commercial businesses and institutions (30% of total waste water). The plant is a tertiary treatment plant...
that discharges into the San Francisco Bay estuary. Samples of aqueous effluent and sludges from the plant were collected over a 3-day period (the individual samples collected were generally composite samples over a 6-hour sampling period). The mean (±standard deviation) concentration of decabromodiphenyl ether found was 1,183(±227) µg/kg dry weight in the sludge and 1.73(±0.65) ng/l in the effluent. The concentration of suspended solids in the effluent was around 1.2 mg/l and the decabromodiphenyl ether in the effluent was thought to be associated with this particulate phase. The mass loading of total polybrominated diphenyl ethers to the San Francisco estuary via the effluent from this plant was estimated to be around 0.9 kg/year, with decabromodiphenyl ether accounting for around 6% of this total.

4.1.3 Soil

Sellström (2005) found decabromodiphenyl ether to be present in a farm soil at a concentration of 2,400 µg/kg dry weight. The soil sample (pooled sample of 30-40 subsamples) was taken in 2000 from a farm that had received sewage sludge from a waste water treatment plant treating waste water from polybrominated diphenyl ether-using textile industries between 1978 and 1982. Further details of this study are reported in Section 6.1.1.

The levels of decabromodiphenyl ether in soil from Japan have been reported by Hirai and Sakai (2004). Decabromodiphenyl ether was reported to be detected in twenty-five out of thirty samples analysed. The mean, median and range of concentrations found were 10 µg/kg, 0.4 µg/kg and 0.06-195 µg/kg respectively. No further details were reported (it is not clear if these soil samples were influenced mainly by atmospheric deposition or sludge application, etc.).

Hayakawa et al. (2004) found decabromodiphenyl ether to be present at a concentration of 9.6 µg/kg in a sample of soil from Kyoto University (in an urban area of Japan) in August 2004. Decabromodiphenyl ether was found to be present in air and wet and dry deposition in the same area (see Section 4.1.4).

Decabromodiphenyl ether has been found at a concentration of 1,026 µg/kg dry weight in soil from an open electronics waste treatment site in Japan (Wang et al., 2005).

4.1.4 Air and dust

i) Europe

Sjödin et al. (2004a [ABST] and 2004b) have determined the levels of decabromodiphenyl ether in household dust samples from Germany (10 samples from mainly northern Germany) and Atlanta, United States (10 samples). The samples were collected from vacuum cleaner bags and sieved by shaking with a sieve with a hole size of ~2 mm. Decabromodiphenyl ether was one of the two most abundant congeners detected, with levels in the samples from the United States in the range 120 to 21,000 µg/kg dust (median level was 2,000 µg/kg dust). The levels found in Germany were much lower, in the range <5 to 410 µg/kg dust (median level was 60 µg/kg dust), and were found to be statistically significantly different to the levels found in the United States (using the U-Test). It should be noted that the levels reported by Sjödin et al. (2004b) for the dust samples from Germany are distinctly lower than the levels reported by Knoth et al. (2003) (as reported in ECB (2004)). Furthermore, using the results of Knoth, no significant difference between the levels in the samples from Germany and from the US could be observed.
ter Schure et al. (2004a) and Agrell et al. (2004) investigated the atmospheric deposition (wet and dry) of polybrominated diphenyl ethers (including decabromodiphenyl ether) at a municipal solid waste incineration plant with electronics recycling and an industrial urban reference site producing asphalt and concrete. The volume weighted mean decabromodiphenyl ether concentration found at the municipal waste incineration plant was 14.4 µg/m³, compared with 14.1 µg/m³ at the reference site. The corresponding atmospheric deposition fluxes at the two sites were 63.8 and 14.7 ng/m²/day respectively. The proportion of decabromodiphenyl ether found in the particulate phase of the air was higher at the municipal solid waste site than at the reference site.

A study of the levels of decabromodiphenyl ether in air in the United Kingdom has been carried out (Wilford et al., 2005a [ABST]). Preliminary work indicated that decabromodiphenyl ether was present at a concentration of 4.9-53 pg/m³ in air samples (collected over three to four days in October-November 2003). The decabromodiphenyl ether was associated mainly with the particulate phase. A follow-up study investigated whether meteorological conditions and air mass back trajectories influenced the levels and the possible breakdown of decabromodiphenyl ether over a one month period (daily particulate phase samples were collected and the gas phase was also sampled for 1 week). The levels were found to vary dramatically over this period (range was ‘not detected’ to 92 pg/m³ with the mean level being 12.5 pg/m³). The levels found appeared to be influenced by regional rather than long-range sources of air masses. The influence of other meteorological factors (such as rainfall, sunshine, average temperature, etc.) on the levels was unclear. The paper concluded that the levels found were generally similar to those found in rural Canada (4-75 pg/m³; Gouin et al. (2005)), urban Sweden (<0.1-190 pg/m³; Agrell et al. (2004)) and urban Japan (<1-48 pg/m³; Hayakawa et al. (2004)).

The levels of decabromodiphenyl ether in air and atmospheric bulk deposition have been determined in samples from a small island (Gotska Sandön) located in the central basin of the Baltic Sea (ter Schure et al., 2004b). The samples were collected during September and November 2001, with air samples being collected over nineteen two-day periods and wet and dry deposition being collected over ten four-day periods. Blank samples (twelve field blanks and nine analytical blanks) were also analysed and the limit of quantification for decabromodiphenyl ether defined as five times the blank value. The volume-weighted mean concentration in air (gaseous phase plus particulate phase) was determined to be 6.1 pg/m³ (range of values 1.1-74.5 pg/m³) and the volume weighted mean concentration in rain (dissolved plus particulate phase) was determined to be 1.7 ng/l (range of values 1.1-6.0 ng/l). The yearly deposition of decabromodiphenyl ether to the Baltic Proper was estimated as 166 kg from these data.

**ii) North America**

Gouin et al. (2004) [ABST] determined the levels of decabromodiphenyl ether in air from Southern Ontario. Samples were collected during the winter and spring of 2002 within a hardwood forest located 115 km northeast of Toronto. The samples were 24-hour samples and samples were taken every six days (from 23 January to 11 April and from 4 May to 6 June) or daily (from 11 April to 28 April). The detection limit of the method used was 9.4 pg/m³. The concentration of decabromodiphenyl ether found in the study ranged from not detected to 105 pg/m³, with the average concentration being 19 pg/m³. The
Decabromodiphenyl ether found in the samples was associated mainly with the particulate fraction of the air samples.

The levels of decabromodiphenyl ether in air and precipitation samples from Canada have been determined by Blanchard et al. (2004 [ABST]). The air samples were collected from Point Petre on Lake Ontario in 2002 (samples were collected over 72 hours every month). Three precipitation samples were collected from Burnt Island on Lake Huron in 2003. The average level of decabromodiphenyl ether in the air samples (gas phase + particulate phase) was found to be 1.8 pg/m³, with decabromodiphenyl ether being found to be associated predominantly with the particulate phase. Decabromodiphenyl ether was found to be present in the precipitation samples at around 5 to 9 ng/l (values read from graph).

A survey of the levels of decabromodiphenyl ether in household dust from the United States has been undertaken (Stapleton et al., 2004a [ABST]). In the study a total of sixteen household dust samples were collected using a handheld vacuum cleaner. Decabromodiphenyl ether was found in all samples analysed at concentrations ranging between 83 µg/kg dry mass to 8,750 µg/kg dry mass, and was found to contribute between 4% and 90% of the total polybrominated diphenyl ethers found in the samples.

A similar (or possibly the same) study is reported by Stapleton et al. (2004b). Here a total of seventeen house dust samples from the US were collected by a small handheld vacuum cleaner in the main family room by vacuuming the rugs or hardwood floors. The dust was passed through a 1 mm mesh. The concentration of decabromodiphenyl ether was found to be in the range 160 µg/kg to 8,700 µg/kg dry mass, with the mean level being 2,100 µg/kg dry mass. Decabromodiphenyl ether was found to contribute between 10 and 86% of the total polybrominated diphenyl ethers found in these samples. Factors that could be affecting the PBDE levels in the dust (e.g. house age, area, number of televisions and computers within the residence, type of flooring (i.e. carpeting versus hardwood floors) and amount of foam-containing furniture) were examined. No significant correlations were apparent. However, the homes with the greatest percentage of decabromodiphenyl ether in dust were all small apartments in which the owners were young professionals with computers that were used frequently (>5 hours per week).

Further details of this study have been recently published by Stapleton et al. (2005). Here household dust samples from 16 homes in Washington DC and one home in Charleston SC were collected between January and March 2004. Lint was also collected (from the lint trap from the clothes drier) from five homes. Decabromodiphenyl ether was found to be present in all samples of household dust in the range 162 to 8,750 µg/kg dry mass, with decabromodiphenyl ether accounting for between 8 and 88% (average 41%) of the total polybrominated diphenyl ethers found. Decabromodiphenyl ether was also found to be present in all five lint samples at a concentration of 58-2,890 µg/kg dry weight.

Stapleton et al. (2004c) found that decabromodiphenyl ether was present at a concentration of 2,050 µg/kg dry mass and 2,230 µg/kg dry mass in two samples of house dust used as standard reference materials in the United States.

Wilford et al. (2005b [ABST]) carried out a survey of the levels of polybrominated diphenyl ethers (including decabromodiphenyl ether) in indoor air samples from homes in Ottawa, Canada. The samples were collected over a three-week period in each home during December 2002 to March 2003 using diffusive samplers. Dust samples from the homes were collected...
from the family vacuum cleaner (the dust samples were sieved using a 150 µm mesh). In addition, seven outdoor air samples were collected from three sites over a three-month period. Only the dust samples appear to have been analysed for the presence of decabromodiphenyl ether and this congener accounted for around 40% of the total polybrominated diphenyl ethers present in dust. The estimated human intake of all congeners from dust ingestion (assuming an adult ingests 100 mg/day of dust) was a maximum of 17,300 ng/day (the 5th-percentile, median and 95th-percentile values were given as 25, 160 and 1,000 ng/day).

McPherson et al. (2004) carried out an analysis of the levels of decabromodiphenyl ether in dust on computers in the United States. The samples were wipe samples taken from the central processing units and monitors of computers. The computers sampled included both old and new models from a range of manufacturers and were located in a variety of different locations (ranging from offices with single computers to computer labs with several computers in the room). In all a total of sixteen samples were analysed. Decabromodiphenyl ether was found in all sixteen samples at a concentration of 2.1-213 pg/cm². The samples were also found to contain nonabromodiphenyl ether (range 1.2-104 pg/cm²) and octabromodiphenyl ether (range 0.38 to 58.2 pg/m²), and a high degree of correlation was found between the levels of decabromodiphenyl ether and the levels of these two other polybrominated diphenyl ethers.

iii) Rest of the world

The levels of decabromodiphenyl ether in air and atmospheric deposition from Japan have been reported by Hirai and Sakai (2004). Decabromodiphenyl ether was reported to be detected in eighteen out of nineteen air samples analysed. The mean, median and range of concentrations found were 10 pg/m³, 7.9 pg/m³ and 0.80-34 pg/m³ respectively. Similarly decabromodiphenyl ether was detected in twenty five out of twenty six samples of atmospheric deposition at levels corresponding to a mean, median and range of atmospheric deposition rates of 39 ng/m²/day, 21 ng/m²/day and 0.3-240 ng/m²/day respectively. No further details were reported.

Hayakawa et al. (2004) determined the concentration of decabromodiphenyl ether in air samples, bulk deposition samples and rainwater samples collected at Kyoto University (in an urban area of Japan). Air samples were collected over two-week periods in August 2000 and January/February 2001, and also over a three-day period in September 2001. A soil sample from the same area was also collected in August 2000 (the soil results are summarised in Section 4.1.3). For the air samples, decabromodiphenyl ether was generally found to be associated with the particulate phase (no decabromodiphenyl ether was detected in the gaseous-phase samples (the detection limit was between 1 and 20 pg/m³ for the gaseous samples)). The levels found in the particulate phase were 15 pg/m³ in samples from August 17-24 2000, 48 pg/m³ in samples from August 24-31 2000, <0.5 pg/m³ in samples from January 22-February 5 2001 and 3.7 pg/m³ in samples from 4-7 September 2001. Decabromodiphenyl ether was also found to be present in bulk deposition (deposition was 1.5 µg/m² in samples from August 17-31 2000, 0.028 µg/m² in samples from January 22-February 5 2001 and 0.011 µg/m² in samples from September 4-18 2001) and rainwater (deposition was 4.8 ng/m² (in particulate phase) and 1.7 ng/m² (in dissolved phase) in samples from August 17-31 2000, 1.5 ng/m² (in particulate phase) and <1 ng/m² (in dissolved phase) in samples from January 26-February 5 2001 and 9.4 ng/m² (in particulate phase) and 11 ng/m² (in dissolved phase) in samples from September 4-18 2001).
4.1.5 Biota

i) Europe

Leonards et al. (2004 [ABST]) investigated the levels of decabromodiphenyl ether in fish from the Western Scheldt estuary and the Wadden Sea. The fish were collected in the spring of 2003 and included samples of sandeel, flounder, sole, goby, herring and whiting. The actual number of samples collected was not stated but decabromodiphenyl ether was reported to be present in 24% of the fish analysed. The levels found in the positive samples were in the range 1.9 to 17 µg/kg lipid.

Verslycke et al. (2005) found that decabromodiphenyl ether was present in mysid shrimp (Neomysis integer) from three sites in the Scheldt estuary. The samples were collected in November 2001. Decabromodiphenyl ether was found to be present in all samples and the level found was 269-600 µg/kg lipid. High levels of decabromodiphenyl ether were found in sediment from the same area (see Section 4.1.1). The mysids were not depurated prior to analysis and so it is possible the levels represent ingestion of contaminated sediment rather than uptake into the organism.

The results of a recent study of the levels of polybrominated diphenyl ethers (including decabromodiphenyl ether) in mussels from the Seine estuary, France has been reported by Johansson et al. (2004 [ABST]). The study used archived freeze-dried samples of Mytilus edulis that had been collected over a 22 year period (1981 to 2003). The samples were collected during the same period of late November or early December each year and the mussels were depurated (depuration time not given) and had the shells removed before storage. Each sample consisted of a pooled sample of around 20 individuals of homogeneous size. The sampling site was located at Villerville and is known to receive a high input of chemical contaminants in general. The results of the analysis are shown in below in 0.

The biomagnification potential of decabromodiphenyl ether has been studied in field samples of fish caught in the Lumparn estuary in the Åland archipelago, Baltic Sea (Burreau et al., 2004). The samples analysed for decabromodiphenyl ether included 8 roach (Rutilus rutilus), 33 perch (Perca fluviatilis) and 25 pike (Esox lucius) muscle samples (approximately 10 g). The trophic position of each species was determined based on the $^{14}$N:$^{15}$N ratios in the fish. The detection limit of the method was ~148 pg per sample (as 10 g of muscle were used this is approximately 14.8 ng/kg fresh weight) and the blank response was subtracted from the reported level. In some cases this resulted in a substantial correction as the amount of decabromodiphenyl ether found in the blank sample was in some cases >20% of the amount found to be present in the muscle sample. This appears to have been the case particularly for the analysis of perch and pike.
Table 4  Time-trend in levels of decabromodiphenyl ether in mussels from the Seine estuary (Johansson et al., 2004)

<table>
<thead>
<tr>
<th>Year</th>
<th>Concentration of decabromodiphenyl ether (µg/kg dry weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1981</td>
<td>0.06</td>
</tr>
<tr>
<td>1986</td>
<td>0.18</td>
</tr>
<tr>
<td>1989</td>
<td>0.14</td>
</tr>
<tr>
<td>1991</td>
<td>0.40</td>
</tr>
<tr>
<td>1993</td>
<td>0.11</td>
</tr>
<tr>
<td>1995</td>
<td>0.05</td>
</tr>
<tr>
<td>1997</td>
<td>0.15</td>
</tr>
<tr>
<td>1999</td>
<td>0.96</td>
</tr>
<tr>
<td>2001</td>
<td>0.31</td>
</tr>
<tr>
<td>2002</td>
<td>0.13</td>
</tr>
<tr>
<td>2003</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Decabromodiphenyl ether was detected in 3 out of the 8 roach samples at a concentration of 0.57-116 µg/kg lipid (median level was 48 µg/kg lipid), in 12 out of 33 perch samples at a concentration of 0.3-31 µg/kg lipid (median level was 13 µg/kg lipid but the blank response was stated to be >20% of sample response), and in 4 out of 25 pike samples at 0.52-4.6 µg/kg lipid (median level was 1.7 µg/kg lipid but the blank response was stated to be >20% of the sample response). The report concluded that there was no correlation between the levels found and trophic position of the fish and so although decabromodiphenyl ether was bioavailable to the fish it was not biomagnified. It should be noted that the relatively large amounts of decabromodiphenyl ether that appear to have been found in the blank samples in this experiment means that the results presented should be treated with caution.

Samples of fish (a total of twenty-three barbel, *Barbus graellsi*) from the River Cinca, Spain, were analysed for decabromodiphenyl ether (Eljarrat et al., 2004). The samples were taken from two sites upstream and two sites downstream of Monzón (a heavily industrialised town). Both liver samples and muscle samples were analysed and decabromodiphenyl ether was not detected in any sample (detection limit was 2-19 ng/kg wet weight). Decabromodiphenyl ether was found to be present in sediments from the same area (see Section 4.1.1).

Samples of adipose from Polar Bears (*Ursus maritimus*) have been analysed for the presence of decabromodiphenyl ether (Gabrielsen et al., 2004). The samples were collected from fifteen individuals from Svalbard in April 2002. Decabromodiphenyl ether was not detected in any of the samples analysed (the detection limit of the method was 0.1 µg/kg wet weight).

The presence of decabromodiphenyl ether in liver samples of Northern Fulmar (*Fulmar glacialis*) has been investigated by Gabrielsen et al. (2005). The samples were collected from birds breeding on Bjornøya during June-July 2003. A total of fifteen samples (six females and nine males) from two colonies were sampled. Decabromodiphenyl ether was detected in one out of the fifteen samples at a concentration of 206 µg/kg wet weight (the detection limit of the method was not given).
A similar study of the levels of decabromodiphenyl ether in the eggs and plasma of Glaucous Gulls (Larus hyperboreus) has been carried out by Verreault et al. (2004). The samples were collected from Bear Island (Bjørnøya). In all a total of 109 plasma samples (57 males and 52 females) and 32 egg samples were collected from two major breeding colonies during May-June 2002 and 2004. Only 89 of the plasma samples appear to have been analysed for decabromodiphenyl ether. Decabromodiphenyl ether was found to be present in 15% (4 out of 32) of the egg samples and 30% (28 out of 89) of the plasma samples. The plasma levels were in the range 202-1,055 µg/kg lipid (or 2.76-14.7 µg/kg wet weight) and the levels found in eggs were in the range 23.2 to 52.5 µg/kg lipid. The report indicates that a blank correction was applied in cases where interferences were seen in the blank samples but it is not clear if this was the case for the decabromodiphenyl ether analysis. In addition the report indicates that the results for decabromodiphenyl ether should be treated with caution as the substance was found to be unstable during the analytical procedure used (resulting in a relatively high detection limit of 2.73 µg/kg wet weight).

Jaspers et al. (2004 and 2005) investigated the levels of polybrominated flame retardants in eggs of the Little Owl (Athene noctua). In all forty deserted or addled eggs were collected between 1998 and 2000 from different nests around Charleroi, Belgium. The contents of the eggs were analysed for mainly lower brominated polybrominated diphenyl ether congeners, but a limited number of samples (the exact number was not given) were also analysed for the presence of decabromodiphenyl ether. Decabromodiphenyl ether was detected in only one sample at 17 µg/kg lipid (the detection limit of the method was 8 µg/kg lipid).

The CSL (2005) study referred to in Section 4.1.1 provides the following preliminary concentration ranges for a small number of biota samples taken in central England:

- Eel: <0.07-0.21 µg/kg whole weight (3 sites, 8 samples);
- Earthworm: <0.06-0.52 µg/kg whole weight (4 sites, 4 samples);
- Heron regurgitate: 0.16-0.73 µg/kg whole weight (4 composite samples); and
- Heron fat: <0.46 µg/kg whole weight (one sample).

It is not clear whether the eel and earthworm analyses included gut contents. For comparison, the earthworm PECs estimated for the secondary poisoning scenario in the 2002 risk assessment report were in the order of 100 mg/kg (and this did not lead to a secondary poisoning risk) (EC, 2002).

**ii) North America**

The levels of decabromodiphenyl ether in Peregrine Falcon (Falco peregrinus) eggs from South Greenland has been determined (Sørensen et al., 2004). The samples analysed were collected between 1986 and 2003 and consisted of 37 samples (addled eggs) from 28 different clutches. Decabromodiphenyl ether was found to be present in all of the samples analysed (36 samples) at a concentration of 3.8-250 µg/kg lipid (the concentrations on a wet weight basis were 0.27-17.0 µg/kg wet weight) with the median level being 11 µg/kg lipid. The study also carried out a time trend analysis of the log-transformed lipid-normalised data. This analysis indicated that the levels appeared to be increasing with time with the slope of the plot of log concentration against year being 0.0582 with a significance of 0.976 (the significance was defined as the probability for the “true” slope to have the same direction (either increasing or decreasing with time) as the fitted line slope). It should be noted that the Greenland Peregrine Falcon populations are thought to winter in Central (females) and South
America (males) and so the levels found are likely to be related to the emission situation along the migratory routes rather than emissions from Europe.

Stapleton et al. (2004c) found that decabromodiphenyl ether was not detected (<1.0 µg/kg wet weight) in samples of whale blubber, fish tissue and mussel tissue used as standard reference materials in the United States.

Oros et al. (2005) determined the levels of decabromodiphenyl ether in bivalves from San Francisco estuary. The samples included resident clams (Corbicula fluminea) from two locations and transplanted oysters (Crassostrea gigas) and mussels (Mytilus californianus) that were collected from an uncontaminated site outside the estuary and housed in groups of 80 in cages at seven (mussels) or five (oysters) locations within the estuary for 90 days prior to analysis. The detection limit of the method used was in the range 1.4-2.8 µg/kg dry weight and decabromodiphenyl ether was not detected in any of the samples analysed.

de Wit et al. (2004) reports that decabromodiphenyl ether was analyzed for but not detected in Western Canadian ringed seals.

The levels of decabromodiphenyl ether in various fish species from Lake Winnipeg, Canada, have been determined by Tomy et al. (2004a [ABST]). Decabromodiphenyl ether was found in all fish sampled (and was found to be the dominant polybrominated diphenyl ether congener present in walleye, perch, burbot and white fish). The concentrations found were ~45 µg/kg lipid in walleye, ~5 µg/kg lipid in whitefish, ~145 µg/kg lipid in perch, ~40 µg/kg lipid in goldeye, ~10 µg/kg lipid in sauger and ~95 µg/kg lipid in burbot (all values read from a graph). All samples were also found to contain 2,2’,3,4,4’,6’-hexabromodiphenyl ether which has been postulated as a metabolite of decabromodiphenyl ether in juvenile lake trout (Tomy et al. 2004b (paper reviewed in 2004 risk assessment report)), although it is not clear if this congener is present in other commercial polybrominated diphenyl ether products.

A sample of fat from a single 3-year-old female Vancouver Island Marmot (Marmota vancouverensis) has been screened for the presence of polybrominated diphenyl ethers (Lichota et al., 2004). The sample was collected in August 2001 and the total concentration of polybrominated diphenyl ethers was found to be 0.78 µg/kg lipid. Decabromodiphenyl ether was found to be the dominant polybrominated diphenyl ether present, accounting for around 67% of the total (i.e. around 0.5 µg/kg lipid). It was, however, indicated that the low analytical recovery in the study may have affected the results and that more analytical work would be needed in order to confirm the result.

### iii) Rest of the world

Rayne et al. (2004) investigated the levels of polybrominated diphenyl ethers in blubber samples from free-ranging killer whales (Orcinus orca) from three distinct communities from the northeastern Pacific Ocean. Blubber biopsies were collected from a total of 39 killer whales (ages ranged from 1 to 69 years) between 1993 and 1996 and the samples were analysed for a suite of 37 polybrominated diphenyl ethers. A total of thirteen tri- to hexabromodiphenyl ether congeners were found to be present in the samples analysed. The actual identity of all of the 37 polybrominated diphenyl ethers analysed for in this study was not given and so it is not clear if decabromodiphenyl ether was not detected in the study or whether it was not determined in the study.
Ohta et al. (2004a [ABST]) carried out a time-trend analysis of the levels of polybrominated diphenyl ethers (including decabromodiphenyl ether) in stock-fish samples of Japanese sea bass and grey mullet from 1986 to 2000. The fish were sampled from Osaka Bay, Japan, and the mouth of the Yamato River (which flows into Osaka Bay). Decabromodiphenyl ether was found to be present in the sea bass samples at a concentration of between 0.36 µg/kg lipid and 89 µg/kg lipid. The highest levels were found in samples for 1991 (74 µg/kg lipid), 1992 (76 µg/kg lipid) and 1993 (89 µg/kg lipid), but had fallen to 0.36-1.2 µg/kg lipid by 1997-1999. The results for grey mullet were not presented in the paper. The demand for decabromodiphenyl ether in Japan was reported to be 2,200 tonnes in 2002, but data for other years was not given and so it is not possible to see how the concentrations found relate to the amounts being used over the period of the study.

Kajiwara et al. (2004 [ABST]) investigated the levels of polybrominated diphenyl ethers (including decabromodiphenyl ether) in cetaceans from Asian waters. The cetaceans sampled (41 samples comprising 7 species) were all found stranded on the coasts of Japan, Hong Kong, the Philippines and India during 1990 to 2001. Decabromodiphenyl ether was not detected in any of the blubber samples (the detection limit was 0.5 µg/kg lipid).

A large survey of the levels of polybrominated diphenyl ethers in farmed and wild salmon from around the world has been undertaken by Hites et al. (2004). In all around 700 samples were analysed and decabromodiphenyl ether was not detected in any sample (detection limit 0.1 µg/kg wet weight). Decabromodiphenyl ether was however found in samples of commercial salmon feed. The actual levels of decabromodiphenyl ether present in the feed was not given but it was reported that the total levels of polybrominated diphenyl ethers in 13 samples of salmon feed were in the range 0.49 to 10.92 µg/kg wet weight, and that the amount of decabromodiphenyl ether present averaged around 15±5% of the total polybrominated diphenyl ethers present.

Watanabe et al. (2004) investigated the levels of polybrominated diphenyl ethers in cormorant (Phalacrocorax carbo) liver (ten samples) and egg (ten samples) from Japan. In addition two samples of fish commonly eaten by the cormorants (gizzard shad (Konosirus punctatus)) were also analysed. The levels of decabromodiphenyl ether in these samples appear to have been below the limit of detection of the method used but no further details of this are given in the paper.

Decabromodiphenyl ether has recently been found to be present in samples of pine needles from Japan (Okazawa et al., 2004). The samples were collected during March 1999 from ten sites in the Tokyo Bay area. Polybrominated diphenyl ethers were found to be present in all samples collected, with decabromodiphenyl ether accounting for >90% of the total present. The highest level of decabromodiphenyl ether (2.3 µg/kg) was found at a site from the inner bay area. The level of decabromodiphenyl ether from a control site (located at the top of the Bousou Peninsula) was 0.37 µg/kg. No quality assurance details are reported.

Decabromodiphenyl ether has been found to be present in livers of Norway rats (Rattus norvegicus; also known as brown rats) from Japan (Takasuga et al., 2004a). Samples were collected from urban areas (two locations in Tokyo), rural areas (two areas in Osaka), a landfill site and a remote island. At each location a composite sample of rat liver from three individuals (seven week old males) was collected. Liver samples from three laboratory-raised Wistar rats were used as a control. The levels of decabromodiphenyl ether found in the livers were 6 µg/kg lipid in the Wistar control rats, 3.6 µg/kg lipid in rats from a remote island,
27 µg/kg lipid in rats from a landfill site, 26 and 73 µg/kg lipid in rats from Osaka and 7.5 and 11 µg/kg lipid in rats from Tokyo. Decabromodiphenyl ether was found to account for a significant proportion of the total polybrominated diphenyl ethers present in the samples (ranging from 4% to around 83% of the total). The paper indicates that two method blanks were also analysed along with the samples, and these blanks did not contain quantifiable amounts of any target contaminant. Norway rats were considered to be good indicator species for human exposure as they feed on human waste and shelter in and around the human environment.

4.1.6 Human foodstuffs

i) Europe

Samples of fish from a market in Germany were analysed for the presence of decabromodiphenyl ether (Paepke and Herrmann, 2004). The samples were bought in summer and autumn 2003 and only the edible parts of the fish were analysed. The results of the analysis are summarised in Table 5.

<table>
<thead>
<tr>
<th>Fish sample</th>
<th>Origin</th>
<th>Lipid content (%)</th>
<th>Concentration of decabromodiphenyl ether (µg/kg lipid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Herring</td>
<td>North Sea</td>
<td>20.7</td>
<td>not detected</td>
</tr>
<tr>
<td>Salmon</td>
<td>Chile</td>
<td>12.7</td>
<td>not detected</td>
</tr>
<tr>
<td>Plaice</td>
<td>North-east Atlantic</td>
<td>2.3</td>
<td>not detected</td>
</tr>
<tr>
<td>Trout</td>
<td>North-east Atlantic</td>
<td>9.6</td>
<td>not detected</td>
</tr>
<tr>
<td>Ocean Perch (Rosefish)</td>
<td>North Atlantic</td>
<td>3.6</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>North Atlantic</td>
<td>3.2</td>
<td>0.04</td>
</tr>
<tr>
<td>Halibut</td>
<td>North-east Atlantic</td>
<td>13.6</td>
<td>not detected</td>
</tr>
<tr>
<td></td>
<td>North Atlantic</td>
<td>11.1</td>
<td>not detected</td>
</tr>
<tr>
<td></td>
<td>North Atlantic</td>
<td>11.2</td>
<td>not detected</td>
</tr>
<tr>
<td>Coalfish</td>
<td>North Atlantic</td>
<td>0.51</td>
<td>0.42</td>
</tr>
<tr>
<td>Pike-perch</td>
<td>Denmark</td>
<td>0.56</td>
<td>2.79</td>
</tr>
<tr>
<td>Victoria Perch</td>
<td>Kenya</td>
<td>1.8</td>
<td>1.04</td>
</tr>
<tr>
<td>Catfish</td>
<td>The Netherlands</td>
<td>3.1</td>
<td>1.18</td>
</tr>
</tbody>
</table>

The analysis was carried out using relatively long (30 m) gas chromatography columns. For quality control a laboratory blank and a quality control pool of human milk fat was run with each batch of ten samples analysed. Quantification was only carried out if the sample values were at least two times the blank values.

ii) North America

A market basket survey of the levels of decabromodiphenyl ether in food has been carried out in the United States (Schecter et al., 2004a, 2004b and 2004c). In all, 32 food samples (including canned milk, liquid baby food, milk powder, fish, meat, eggs, cheese, ice cream, sausage, butter and margarine) from three major supermarket chains in Dallas, Texas, were
analysed for a total of thirteen polybrominated congeners (including decabromodiphenyl ether). The study found that fish samples had the highest overall levels of total polybrominated diphenyl ethers (median level of 1.7 µg/kg wet weight; range 0.009-3.1 µg/kg wet weight), followed by meat products (median level 0.28 µg/kg wet weight; range not detected (<2×10⁻⁴ µg/kg wet weight)-1.4 µg/kg wet weight) and dairy products (median level 0.032 µg/kg wet weight; range 9×10⁻⁴-0.68 µg/kg wet weight). In fish, the dominating congener found was generally 2,2’,4,4’-tetrabromobiphenyl ether (accounting for 40-70% of the total). An exception to this were two catfish samples where 2,2’,4,4’,5-pentabromodiphenyl ether was found to be the dominating congener in one sample and decabromodiphenyl ether was found at a concentration of 1.3 µg/kg wet weight (accounting for around 50% of the total polybrominated diphenyl ethers present) in another sample. In the meat samples, the dominating congeners present were generally 2,2’,4,4’,5-pentabromodiphenyl ether, followed by 2,2’,4,4’-tetrabromodiphenyl ether and other tetra- and pentabrominated congeners. However, decabromodiphenyl ether was the dominant congener found in calf liver, and the third most dominant congener found in chicken liver. Decabromodiphenyl ether was also found to be the dominant congener present in soy instant formula, cheese and margarine. The experimental results for individual congeners were mainly displayed graphically and so it is difficult to determine the exact concentrations of decabromodiphenyl ether in the various samples analysed.

The levels of decabromodiphenyl ether in fish, beef and fowl purchased from shops in northern California in December 2003 and February 2004 have been determined by Luksemburg et al. (2004a [ABST]). The samples included six species of wild marine fish (swordfish, pacific salmon, coho salmon, tuna, petrale sole and tilapia), sea scallops, two species of farm-raised fish (atlantic salmon and catfish fillets and nuggets), ground beef samples from cattle raised on grain-fed and free-range diets, ground deer meat from animals caught in California, breast meat from wild or naturally raised duck, goose and pheasant, ground meat from free-range chicken and turkey and thigh meat from free-range chicken. For the wild fish products, decabromodiphenyl ether was found to be present in all six species at a concentration (all on a wet weight of food basis) of 189-800 ng/kg in swordfish, 504 ng/kg in pacific salmon, 167 ng/kg in coho salmon, 328 ng/kg in tilapia, 161 ng/kg in canned tuna and 123 ng/kg in petrale sole. The concentration in scallop was 220 ng/kg wet weight. Decabromodiphenyl ether was also found to be present in the farm-raised fish species sampled at a concentration (on a wet weight food basis) of 265-411 ng/kg in atlantic salmon, 249-453 ng/kg in catfish fillets and 214 ng/kg in catfish nuggets. For the meat products, decabromodiphenyl ether was not detected in the sample of grain-fed ground beef or ground deer but was present at 113 ng/kg wet weight in the sample of free-range ground beef. For the fowl products, decabromodiphenyl ether was detected at a concentration (again on a wet weight food basis) of 264-417 ng/kg in chicken, 188 ng/kg in duck, 123 ng/kg in goose, 147 ng/kg in ground turkey and 106 ng/kg in pheasant. The limit of quantification of the analytical method used was in the range 10-250 ng/kg wet weight (this refers to the overall detection limit for all polybrominated diphenyl ether congeners included in the study; the exact detection limit for decabromodiphenyl ether was not stated). The results of this study are currently only available in abstract form and certain important information (such as the levels of decabromodiphenyl ether in analytical blanks) are not yet available. As the levels of decabromodiphenyl ether found in many of the samples are close to (or within) the range of the limit of quantification of the method used, and are relatively constant amongst the various food items analysed (which may be indicative of potential blank problems in the analysis), these results should be treated with caution at present until full details of the study are published.
Luksemburg et al. (2004b) reported the same data above but included also results for decabromodiphenyl ether in further products. Decabromodiphenyl ether was not detected in pacific swordfish steak, Atlantic salmon fillet and chicken thighs but was found in yellowfin tuna ahi (39 ng/kg), wild sockeye fillet (41 ng/kg), Alaskan halibut fillet (37 ng/kg) canned tuna (46 ng/kg), ground beef (57 ng/kg), free range ground beef (120 ng/kg), free range chicken (35 ng/kg) and free range ground turkey (41 ng/kg) (all concentrations on a wet weight basis).

The results of a further survey of levels of decabromodiphenyl ether in food in the United States have been reported by Huwe (2004 [ABST]). In this study meat and poultry samples were obtained from large supermarkets in nine cities in the United States during 2001. The report noted that the results for decabromodiphenyl ether in this study are uncertain as large amounts of the substance were also detected in laboratory blank samples (average level in blanks corresponded to around 914 ng/kg sample). The detection limit of the method used was set at three times standard deviation of the blank level (~3,385 ng/kg sample), and the sample data were reported as blank-subtracted values. Decabromodiphenyl ether was not detected in bacon (11 samples) or beef fat (9 samples) but was found in chicken fat (17 samples; range of concentrations not detected – 4,275 ng/kg) and pork fat (11 samples; range of concentrations not detected – 4,120 ng/kg). Given the occurrence of decabromodiphenyl ether in the blanks these results should be treated with caution.

Blake (2005) carried out an investigation of the levels of decabromodiphenyl ether in chicken eggs from around the world. The eggs were collected from locations near to hazardous waste and municipal solid waste incinerators, waste dumps, and locations near to petroleum and other industrial chemical plants. In all a total of twelve composite samples were analysed for polybrominated diphenyl ethers from locations on the Czech Republic, Kenya, Mexico, Mozambique, Philippines, Slovakia, Turkey, Uruguay and the United States. Decabromodiphenyl ether was found at concentrations between 0.8 and 106.8 µg/kg lipid in the samples. Decabromodiphenyl ether appeared to be the dominant polybrominated diphenyl ether congener present in most of the samples.

4.1.7 Humans

This section considers the levels of decabromodiphenyl ether found in the general population. New information relevant to occupational exposure has not been considered in this paper.

i) Europe

A survey of the levels of decabromodiphenyl ether in blood serum from the members of seven families from the United Kingdom has been determined (WWF, 2004a). The samples (40-50 ml each) were collected during June and July 2004 and in all a total of 33 people were sampled. The make-up of the family members sampled included six grandmothers (one person was the grandmother to two of the families), seven mothers, six fathers and fourteen children (eight females and six males). The ages ranged between nine and 88 years. Immediately after sampling, the blood samples were centrifuged (3,000 rpm for 10 minutes) to separate the blood cells and platelets from the serum, and the samples were then frozen for transport to the laboratory for analysis. Blank samples (ultra-pure water) were also taken at the time of sampling. No further details of the sampling and analytical methods used were given. Decabromodiphenyl ether was found to be present in seven of the 33 serum samples
analysed. The seven samples in which decabromodiphenyl ether was detected included one sample from a grandmother, two samples from parents and four samples from children. The range of concentration of decabromodiphenyl ether in the positive samples was from 9.1 to 33.9 µg/kg lipid in the serum (the median of the detected levels was 15.1 µg/kg lipid). An attempt was made in the paper to examine the links between the occurrence of decabromodiphenyl ether and the family’s lifestyles, food consumption patterns and use of everyday products, however the uncertainties over the actual sources of exposure meant that no conclusions could be drawn on this.

WWF (2004b) carried out a survey of the levels in blood samples from fourteen Ministers from thirteen European countries. The samples were collected in June 2004 and were screened for the presence of a total of 103 chemicals, including decabromodiphenyl ether. Decabromodiphenyl ether was found to be present in three of the fourteen samples analysed at a concentration of 11 ng/kg serum, 21 ng/kg serum and 45 ng/kg serum respectively (the detection limit of the method was 5 ng/kg serum).

Vieth et al. (2004) investigated the presence of decabromodiphenyl ether in samples of human milk from Germany. Overall 143 samples of human milk were collected between November 2001 and December 2003. The mothers chosen were placed into two groups based on their diet (omnivores and vegetarians/vegans) to investigate the effects of diet on the concentrations found. Samples were collected during the second week after delivery (first sampling period) and again at around 12 weeks after delivery if possible (second sampling period). At the time of publication a total of 93 samples had been analysed. Decabromodiphenyl ether was found to be present in around 40% (25 out of 62) of the samples from the first sampling period. For the combined data set from both omnivores and vegetarians/vegans, the mean level was 0.17 µg/kg lipid (no difference in the mean level was seen between the omnivore group (mean level 0.17 µg/kg lipid) and the vegetarian/vegan group (mean level 0.17 µg/kg lipid), with the median, 95th percentile and maximum level being 0.10 µg/kg lipid, 0.59 µg/kg lipid and 1.0 µg/kg lipid respectively. The mean levels for the second sampling period was found to be 0.11 µg/kg lipid. The detection limit of the method used was around 0.1 µg/kg lipid and quantification was only carried out if the sample level was at least twice the blank level. Further details of the analytical method and quality control procedure used are given in Paepke et al. (2004).

López et al. (2004 [ABST]) analysed five samples of milk from Swedish women (collected from Stockholm in 2003) as part of a wider study – the results are mentioned below under ‘Rest of the world’.

One additional study has recently been published on the web in Norwegian (SPFO-rapport: 930/2005 TA-2103/2005), and a partial translation has kindly been supplied by SFT (2005). This was a pilot study to analyse blood serum from pregnant women in Norway and Russia. Decabromodiphenyl ether was not detected in any of the samples (n = 10) at a detection limit of 90 pg/ml serum. This was attributed to a high detection limit caused by low sample volume. A follow-up of this study is planned, using sufficient sample volumes for all PBDEs to be measured at a satisfactory detection limit.
ii) North America

Stapleton et al. (2004c) found that decabromodiphenyl ether was not detected (<1.0 µg/kg wet weight) in a sample of human serum used as a standard reference material in the United States.

An analysis of breast milk samples from forty Pacific Northwest mothers (ten each from Montana, Oregon, Washington and British Columbia) has been carried out by Northwest Environment Watch (2004). The samples were collected between April and November 2003. Decabromodiphenyl ether was found to be present in twenty four of the forty samples at levels up to 4.3 ppb fat (4.3 µg/kg fat). The median and mean levels found were 0.4 µg/kg fat and 0.8 µg/kg fat respectively. The detection limit of the method was 0.05 µg/kg fat.

She et al. (2004) analysed sixteen breast milk samples collected from residents of the Pacific Northwest for the presence of decabromodiphenyl ether. Exposure of the samples to UV light was minimized during the sample handling to prevent possible degradation of the decabromodiphenyl ether. The levels of decabromodiphenyl ether found were in the range 0.048-1.5 µg/kg fat, with the median and mean levels being 0.25 and 0.37 µg/kg fat respectively (the number of samples in which decabromodiphenyl ether was detected was not stated). It should be noted that the data in this report is referenced to North West Environment Watch (2004) and so may represent a sub-set of the data from the above study.

iii) Rest of world

A study of the levels of decabromodiphenyl ether in blood and milk from Mexican women has been carried out (López et al., 2004 [ABST]). The samples were taken from both women living in an urban environment (blood plasma samples from five women) and from indigenous rural women (milk samples from seven women). In addition five samples of milk from Swedish women (collected from Stockholm in 2003) were also analysed. The level of decabromodiphenyl ether found in the samples was 4.8-14.6 µg/kg lipid (mean 9.5 µg/kg lipid) in plasma from Mexican women, 0.1-0.6 µg/kg lipid (mean 0.3 µg/kg lipid) in milk from Mexican women and 0.3-0.4 µg/kg lipid (mean 0.4 µg/kg lipid) in milk from Swedish women.

Takasuga et al. (2004b) investigated the levels of decabromodiphenyl ether in human blood from nine married couples in Japan over a two year period. A total of 156 samples were collected in the study, and decabromodiphenyl ether was detected in 102 samples. The average concentration was 9.2 µg/kg lipid, with the median, minimum and maximum level being 6.9 µg/kg lipid, 1.3 µg/kg lipid and 31 µg/kg lipid respectively in the positive samples.

Ohta et al., (2004b) investigated the levels of polybrominated diphenyl ethers in human breast milk samples from Japan. Decabromodiphenyl ether was found to be present in some samples but, as the results are only displayed graphically, the actual concentration of decabromodiphenyl ether present in the samples is unclear.

4.1.8 Summary and implications for the risk assessment

The new information generally confirms the information reported in the previous risk assessment reports (EC (2002) and ECB (2004)). Decabromodiphenyl ether can be found widely in sediments and sewage sludge, where it is frequently the dominant PBDE congener.
present. This is perhaps not especially surprising given its high tonnage, historical widespread dispersive use, persistence and potential for adsorption to organic matter. However, it does appear to be almost ubiquitous in these environments in some parts of Europe.

Sewage sludge is potentially a major source of decabromodiphenyl ether to agricultural land as a result of sludge spreading. The levels of decabromodiphenyl ether found in sewage sludge in the EU in recent studies are generally around 0.1 mg/kg dry weight up to a few mg/kg dry weight. The amount of sewage sludge spread onto agricultural land varies between countries but figures for the EU for 1997 are given in European Commission (2000). These show that of the total amount of sludge generated (~1,995,000 tonnes dry matter/year in 1997), 54% (or ~645,798 tonnes dry matter/year) was applied to agricultural land. Assuming a “typical” decabromodiphenyl ether content of around 1 mg/kg dry weight, this means that around 650 kg of decabromodiphenyl ether would have been applied to agricultural land from this source in one year. It is expected that the substance will be persistent in soil, and indeed Sellström (2005) detected levels of a few mg/kg dry weight in a farm soil in Sweden that last received an input from sludge around 20 years before. Continued sludge application might therefore lead to a potential build-up in soils.

Decabromodiphenyl ether also shows a widespread occurrence in air (predominantly in the particulate phase), albeit at low concentrations (i.e. in the order of several pg/m³). Household dust samples and dust samples from computers have also been shown to contain decabromodiphenyl ether, at levels in the order of parts per million. It could be postulated that dust from sources such as these might make a significant contribution to the levels found in outdoor air, although this has not been investigated.

Decabromodiphenyl ether has again been detected in a wide variety of biota, including aquatic organisms (e.g. aquatic invertebrates, fish, predatory birds and some mammals), as well as in human food items, and human blood and milk. Its presence in the tissues of so many species remains a cause for concern, given the uncertainties over its neurodevelopmental effects. Despite the analytical difficulties, it might be expected to be found in yet more species as more research is performed. However, the results should be viewed in context – monitoring activity for this substance is currently intense, especially when compared to most industrial chemicals. Though widespread, the levels of the substance are typically in the region of several parts per billion, confirming that it is bioavailable but not permitting conclusions to be drawn over potential bioaccumulation in the food chain. One study that has attempted to look at biomagnification in aquatic food chains concluded that although decabromodiphenyl ether was bioavailable to fish it was not biomagnified, although problems with blanks in this experiment mean that this statement should be treated with caution.

No new time trend studies for Europe are available, but two studies (one for sediment and one for Peregrine Falcon eggs) provide some evidence for increasing concentrations of decabromodiphenyl ether in the environment related mainly to emission sources in North America. A comparison of the emissions (and trends in emissions) between Europe and North America has not been made, so the relevance of these findings to Europe is unknown. It was noted in the previous risk assessments that sediment levels in Europe were increasing with time during the late 1990s.

Several studies have reported concentrations in human foodstuffs, mainly from North America. The results are broadly similar to the regional levels estimated using the EUSES
model in EC (2002), although levels in meat seem to be a lot lower than predicted (600 µg/kg). It was noted that the predictions were uncertain. Levels in chicken eggs are not estimated using the TGD models, but they appear to be comparable to the levels being found in wild bird eggs.

There is further confirmation that the substance is present in Arctic environments, and it is clear that decabromodiphenyl ether is being transported to remote regions. Whilst air might be expected to be the most likely medium of transport (e.g. the presence in moss (cf ECB, 2004) is hard to explain by any other route), the situation is complicated by the fact that the substance binds to particulates in air. Some particulates may be readily removed from the atmosphere, but atmospheric particulates in the range of 0.1 to 1 µm diameter have an atmospheric half-life of the order of one week (approximate range one day to one month). This is long enough for the particulates to be transported many thousands of kilometres (Harrison, 2005). The presence of decabromodiphenyl ether in animal species in the Arctic is not itself indicative of long-range transport via the air. For example, migratory species may themselves act as sources of transport of decabromodiphenyl ether to remote regions (a mechanism that has recently been suggested for certain other substances such as DDT, whereby the substance is deposited in the Arctic in bird excrement from migratory species (Blais et al., 2005)). Overall the available data provide clear evidence that decabromodiphenyl ether is undergoing long-range transport to polar regions, most probably via the atmosphere (but other mechanisms could be involved).

One of the main issues of concern for decabromodiphenyl ether is the possible formation of more toxic and accumulative metabolites by degradation and metabolism. This is considered in detail in the 2004 risk assessment (ECB, 2004), and the new laboratory data on degradation and uptake, accumulation and metabolism of decabromodiphenyl ether is summarised in Sections 5 and 6 of this report. However, this aspect is also considered in some of the recent monitoring studies. For example, one new study (Tomy et al., 2004a) has identified a hexabrominated diphenyl ether congener in fish that has been postulated as a possible metabolite of decabromodiphenyl ether. However, the interpretation of such findings is complicated by the fact that this congener may be present in some other commercial polybrominated diphenyl ethers (or indeed could be formed from the degradation/metabolism of polybrominated diphenyl ethers other than decabromodiphenyl ether in the environment). Similarly Kolic et al. (2004a) suggested that degradation of decabromodiphenyl ether during the biosolids decomposition/composting process could be an explanation for the changes in the relative ratios of congeners seen in composted and uncomposted biosolids, although the authors thought that further work was needed to test this hypothesis.
5 DEGRADATION

5.1.1 Biotic degradation

La Guardia et al. (2004a [ABST]) determined the distribution of polybrominated diphenyl ether congeners (tetra- to decabromodiphenyl ether) in various environmental samples in order to investigate whether degradation (debromination) of decabromodiphenyl ether was occurring. The samples were collected close to a plastics-related facility in the United States where decabromodiphenyl ether was used and included influent and effluent from a waste water treatment plant at the site, as well as surface water, sediment and fish from a nearby receiving stream. The concentrations of decabromodiphenyl ether found were 12.1 µg/l in the effluent from the waste water treatment plant, 10.2 µg/l in the stream water, 79.9 µg/kg dry weight in sediment, 492 µg/kg lipid in Pumpkinseed (Lepomis gibbosus) collected from the stream but it was not detected in Mosquitofish (Gambusia holbrooki). Many other congeners were also found in these samples, but it was not possible to determine conclusively if their presence was related to the possible degradation of decabromodiphenyl ether. The concentrations in water found in this study are well in excess of the water solubility of decabromodiphenyl ether and so probably reflect decabromodiphenyl ether adsorbed onto suspended matter.

Parsons et al. (2004) investigated the potential for the anaerobic degradation of decabromodiphenyl ether in sediments. The sediment samples used were taken from Hansweert in the Western Scheldt (an area known to be contaminated with decabromodiphenyl ether). The experiments were carried out using suspensions of the sediment (20 g of sediment in 60 ml of anaerobic media) spiked with decabromodiphenyl ether at a concentration of 14 mg/kg. The spiked sediment was incubated in the dark at room temperature under anaerobic conditions. Sterilized control samples were also run. At appropriate times, duplicate sediment samples were analysed for polybrominated diphenyl ethers. A decrease in the concentration of decabromodiphenyl ether in the sediment was seen over the first two months incubation. The results are displayed graphically in the paper (as a percentage of that spiked with time); this shows that the concentration of decabromodiphenyl ether fell from around 23-25% of the nominally spiked concentration at day 0 to around 7-8% by around day 25-50, reaching around 5% of the nominally spiked concentration after >200 days. There is no explanation in the paper as to why the actual concentration at day 0 is <25% of the nominally spiked amount. Furthermore a similar decrease in concentration with time was found in the sterile control. The paper indicates that this decrease may have resulted from incomplete sterilisation of the control sediment (no details of how sterilisation was carried out are given), as methane was produced from the control sediment after addition of lactic, pyruvic and acetic acids.

The GC-MS chromatograms of extracts of the sediment showed that, as well as the decrease in the peak corresponding to decabromodiphenyl ether, two new peaks appeared. These were tentatively identified as nonabromodiphenyl ethers (the actual congeners were not identified). No indication was given as to the amounts of these debromination products that were formed in the test.

Few other experimental details are given (notably there are no details on how the decabromodiphenyl ether was spiked onto the sediment or the background levels of decabromodiphenyl ether (and other brominated diphenyl ethers) in the sediments used). It should be noted that there are some uncertainties with this test that are not clearly explained.
in the paper. For example, the concentration of decabromodiphenyl ether at day 0 appears to be around 25% of the nominally added amount. In addition, the degradation seen in the sterile controls means that the results of this test should be treated with caution. In view of the limited details available for this study, and the fact that they appear to show some serious shortcomings in the test, the results are not considered further in this report.

The degradation of decabromodiphenyl ether in sewage sludge under anaerobic conditions has been studied by Gerecke et al. (2004 [ABST] and 2005). The experiments were carried out in 100 ml glass serum bottles each containing a 1 cm layer of glass beads. The bottles were spiked with stock solutions of decabromodiphenyl ether (98% purity; 10 nmole added to each bottle), alpha-hexachlorocyclohexane (used as a positive control; 10.5 nmole added), and five “primers” (4-bromobenzoic acid, 2,6-dibromobiphenyl, tetrabromobisphenol-A, hexabromocyclododecane and decabromobiphenyl (around 9-11 nmol of each was added)). Two experiments were also carried out using either BDE-206 (2,2’,3,3’,4,4’,5,5’,6-nonabromodiphenyl ether or BDE-207 (2,2’,3,3’,4,4’,5,6,6’-nonabromodiphenyl ether). The solvent was allowed to evaporate overnight (the solvent used was not stated) and then starch (20 mg), yeast (50 mg) and 20 ml freshly collected digested sewage sludge (from a plant serving 45,000 people in Dübendorf, Switzerland) was added. The sludge used had a pH of 7.6, a 3% dry weight solids content and was contaminated with decabromodiphenyl ether (the concentration in the sludge was 58 nmole/l; the amounts of other brominated diphenyl ethers present in the sludge were not stated). The total amount of decabromodiphenyl ether in the system (spiked and from the sewage sludge) was 11.2 nmol/bottle. The bottles were then tightly capped and incubated in the dark at 37°C for up to 238 days. During the experiment (both incubation and analysis) exposure to light was kept as low possible (for example windows and fume hoods were covered with a UV filter foil). Control experiments were carried out using heat-sterilized sludge.

Gas production was found to occur in all sample bottles indicating that methanogenic conditions were present. No gas production was found in the sterile controls.

The amount of decabromodiphenyl ether remaining in the bottles was determined at various times during the experiment. The amount of decabromodiphenyl ether was found to decrease by around 30% (from the initial amount of 11.2 nmole/bottle to 7.9 nmole) after 238 days incubation in the experiments with primers. The observed disappearance was found to be statistically significant at the 95% confidence level, and corresponded to a pseudo-first-order reaction rate constant of $1 \times 10^{-3}$ day$^{-1}$. No significant degradation of decabromodiphenyl ether was seen in the sterile controls. The positive control (alpha-hexachlorohexane) was found to degrade with a rate constant of 0.4 d$^{-1}$ indicating that the microbial community in the experiment were able to degrade halogenated compounds.

The study also investigated the amounts of several lower brominated congeners present at various times in the study. The decabromodiphenyl ether used in the study contained traces of three nonabrominated congeners (BDE-206 (~2% on a molar basis) and BDE-207 (~0.4% on a molar basis) and BDE-208 (2,2’,3,3’,4,4’,5,5’,6,6’-nonabromodiphenyl ether; ~0.04% on a molar basis) but octabromodiphenyl ether congeners were not detected (detection limit used was 0.005 nmole/sample which was equivalent to a concentration of ≤6,000 ppm in the decabromodiphenyl ether sample) in the decabromodiphenyl ether used. During the incubations both nonabromodiphenyl ethers (BDE-207 and BDE-208) and a number of octabromodiphenyl ethers were formed. The amount of BDE-208 present in the system was found to increase by greater than ten times (from an amount below the limit of quantification
to 0.15 nmole/bottle) and the amount of BDE-207 increased from 0.024 nmole/bottle to 0.16 nmole/bottle). Similarly the amount of octabromodiphenyl ethers increased from an amount below the limit of quantification to 0.21 nmole/bottle. No statistically significant (95% confidence level) increase in the amount BDE-206 was seen in the experiment resulting either from a very low formation rate from decabromodiphenyl ether or as a result of further degradation of BDE-206 itself. No nonabrominated or octabrominated diphenyl ethers were found to be formed in the sterile controls. Overall at least 0.5 nmole/bottle of transformation products were formed within 238 days incubation, indicating that at least 5% of the decabromodiphenyl ether initially present in the system had degraded to lower brominated congeners.

The mass balance from the experiment showed that around 3 nmole/bottle of decabromodiphenyl ether degraded (from the initial amount of 11.2 nmol/bottle) but the amounts of octabromodiphenyl ether and nonabromodiphenyl ether congeners formed only accounted for around 0.5 nmole/bottle. There was no evidence of the formation of other, lower brominated, congeners (such as heptabromodiphenyl ethers) in the experiments. Explanations for this discrepancy could include formation of other unidentified transformation products, formation of bound (non-extractable) decabromodiphenyl ether residues, or imprecisions in the analytical procedure used.

Experiments without primers showed that similar degradation products were formed but that the rate of degradation of decabromodiphenyl ether was approximately half of that found in the experiments with primers outlined above. The experiments with BDE-206 and BDE-207 both showed that the substances were degraded to octabromodiphenyl ethers but no rate constants for the reaction could be determined. Evidence was also presented that BDE-208 undergoes a similar degradation.

The results of this study appear to show that debromination of decabromodiphenyl ether proceeded most readily by loss of bromine from the para- (4-position) and meta-position (3- or 5-position) as shown by the formation of BDE-208 and BDE-207 (although degradation by loss of bromine from the ortho-position (leading to the formation of BDE-206) could not be entirely ruled out).

Gerecke et al. (2005) also carried out a preliminary study to investigate if decabromodiphenyl ether degraded in a full-scale anaerobic digester. Grab samples were taken from the inlet and outlet of the anaerobic digester from the same sewage treatment plant used for the inoculum source in the above experiments. These grab samples were analysed for the presence of lower brominated congeners. The concentrations of BDE-208 and BDE-207 were found to increase relative to that for BDE-206 between the inlet samples and the outlet samples, showing a similar pattern to that found in the laboratory experiment. However the authors cautioned that as the residence time in the reactor was 28 days one set of grab samples does not provide unequivocal evidence that degradation of decabromodiphenyl ether was the source of these congeners in the samples.

5.1.2 Abiotic degradation

Keum and Li (2005) investigated the reactivity of decabromodiphenyl ether with several reducing agents including powdered zero valent iron or iron sulphide, or a solution of sodium sulphide. The experiments with zero valent iron and iron sulphide were carried out by adding 1 ml of a solution of decabromodiphenyl ether in ethyl acetate (to give a final concentration
of 50 mg/l) to 5 g of powdered iron or iron sulphide in a capped amber glass vial. The solvent was removed under a gentle stream of nitrogen and 10 ml of deionised water was added. The vial was capped and incubated at 30°C on a rotary shaker (60 rpm). Control solutions (without the iron powders) were prepared in a similar manner. Samples were extracted and analysed for the presence of polybrominated diphenyl ethers after 3 hours and 0.5, 1, 2, 3, 5, 7, 14 and 40 days incubation. All experiments were carried out in triplicate. The experiments with sodium sulphide were carried out using a similar system except decabromodiphenyl ether (50 mg/l) was suspended directly in 10 ml of a sodium sulphide solution (sodium sulphide concentration was 200 mg in 10 ml of water).

In the experiments with zero valent iron, decabromodiphenyl ether was rapidly transformed to lower brominated congeners. Around 90% of the decabromodiphenyl ether initially added was converted to mono- to hexabrominated congeners after 40 days. Little degradation of decabromodiphenyl ether was seen in the control solutions.

The analysis of the samples (by gas chromatography with either an electron capture detector or mass spectrometric detector) found that a large number of congeners were present (a total of 112 peaks were found). These included around forty polybrominated diphenyl ethers, which are commonly found in environmental samples (and for which chromatographic reference/standard compounds were available), with around a further thirty-six peaks being tentatively identified as di- to hexabrominated diphenyl ethers (these accounted for around 2-3% of the total peak area).

The time profile of the degradation reaction with zero valent iron showed that heptabromo- and higher brominated diphenyl ether congeners were the most abundant degradation products during the initial stages of the experiment (accounting for >50% of the total polybrominated diphenyl ether congeners present up to day 5), but the proportion of the lower brominated congeners (mono- to hexabromodiphenyl ethers) gradually increased with time (with a concomitant decrease of the higher brominated congeners), and by day 40 of the experiment, the tri- and tetrabrominated congeners were the most dominant polybrominated diphenyl ethers present. At the end of the experiment the mass balance of the identifiable congeners had decreased to around 44.9% of the total, with the amount of unidentifiable congeners accounting for around 40-50% of the initial molar amount of decabromodiphenyl ether. Thus the overall mass balance was around 85-95% at day 40 (the estimate for unidentifiable congeners takes into account assumptions of the detector response for the unidentified congeners). The results of the experiment are summarised in Table 6. Analysis of the product profile suggested that ortho- and meta-substituted bromines were more susceptible to debromination by this reaction than those in the para- position.

Experiments were also carried out using 2,4-dibromodiphenyl ether, 2,4,4’-tribromodiphenyl ether, 2,2’,4,4’-tetrabromodiphenyl ether, 2,3’,4,4’-tetrabromodiphenyl ether and 2,2’,4,4’,6-pentabromodiphenyl ether using the same zero valent iron system. These all were found to undergo a similar debromination reaction, but the rate of the reaction was found to decrease with decreasing number of bromines, indicating that as the debromination proceeds, the lower brominated diphenyl ether products formed become increasingly more stable.
Table 6  Degradation of decabromodiphenyl ether by zero valent iron (Keum and Li, 2005)

<table>
<thead>
<tr>
<th>Congener</th>
<th>Relative abundance (% of initial amount of decabromodiphenyl ether added)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 hours</td>
</tr>
<tr>
<td>Tribromodiphenyl ethers</td>
<td></td>
</tr>
<tr>
<td>2,2',4'-</td>
<td>ND</td>
</tr>
<tr>
<td>2,4,4'- + 2',3,4'-</td>
<td>ND</td>
</tr>
<tr>
<td>Tetrabromodiphenyl ethers</td>
<td></td>
</tr>
<tr>
<td>2,2',4,4'-</td>
<td>ND</td>
</tr>
<tr>
<td>2,3',4,4'-</td>
<td>ND</td>
</tr>
<tr>
<td>Pentabromodiphenyl ethers</td>
<td></td>
</tr>
<tr>
<td>2,2',4,4',5'-</td>
<td>ND</td>
</tr>
<tr>
<td>2,2',4,4',6'-</td>
<td>ND</td>
</tr>
<tr>
<td>Hexabromodiphenyl ether</td>
<td></td>
</tr>
<tr>
<td>2,2',3,4,4',5'-</td>
<td>ND</td>
</tr>
<tr>
<td>2,2',4,4',5,5'-</td>
<td>ND</td>
</tr>
<tr>
<td>2,2',4,4',5,6'-</td>
<td>ND</td>
</tr>
<tr>
<td>Heptabromodiphenyl ethers</td>
<td></td>
</tr>
<tr>
<td>2,2',3,4,4',5,6'-</td>
<td>ND</td>
</tr>
<tr>
<td>2,3,3',4,4',5,6'-</td>
<td>ND</td>
</tr>
<tr>
<td>Others</td>
<td></td>
</tr>
<tr>
<td>Othersa</td>
<td>ND</td>
</tr>
<tr>
<td>Decabromodiphenyl ether</td>
<td>100.04</td>
</tr>
<tr>
<td>Sumb</td>
<td>100.04</td>
</tr>
</tbody>
</table>

Notes:  
a) Other polybrominated diphenyl ethers for which standards were available.  
b) Sum refers to identifiable congeners (for which standards were available). The amount of unidentifiable congeners was estimated to be around 40-50% of the initial amount of decabromodiphenyl ether added at day 40.  
ND = not detected.

The experiments with iron sulphide and sodium sulphide also showed transformation of decabromodiphenyl ether to lower brominated congeners but at a slower rate than found with zero valent iron. For example, 2% and 33% of the decabromodiphenyl ether had degraded after 14-days in the experiments with iron sulphide and sodium sulphide respectively compared with 90% in the experiment with zero valent iron. Although the degradation rate was slower with sodium sulphide, the congener profile of the degradation products was found to be similar to that obtained with zero valent iron.

The results clearly demonstrate a stepwise debromination reaction was occurring with zero valent iron, the rate of which slows with decreasing numbers of bromine atoms. No hydroxylated products were seen in this experiment.

10 Fewer details of these experiments were reported in the paper than for the experiments with zerovalent iron. The authors of the paper have been contacted and they have kindly provided further details of the concentrations of lower brominated diphenyl ethers found in these studies. The results are shown in Appendix A and confirm that significant amounts of lower brominated congeners were found.
Eriksson et al. (2004a) studied the photochemical degradation of decabromodiphenyl ether and fourteen other polybrominated diphenyl ether congeners in methanol/water (80/20 mixture) using artificial UV light in the sunlight region. Studies were also carried out using pure methanol or tetrahydrofuran as solvent, and the degradation of decabromodiphenyl ether was also investigated in water (with and without the presence of humic acids).

The decabromodiphenyl ether used in the study had a purity of >98%. The experiments were carried out in a cylindrical vessel with a 20 watt fluorescent tube placed longitudinally through the middle. The methanol/water solutions of decabromodiphenyl ether used were prepared by firstly dissolving the substance in tetrahydrofuran and then diluting 1 ml of this solution in 2 litres of a mixture of methanol and water (80:20). The initial decabromodiphenyl ether concentration was <1 µM in all experiments. The preparation of the solutions for the experiments with water was carried out by firstly preparing a saturated solution of decabromodiphenyl ether in ethanol. Around 20 ml of this solution was then transferred to a conical flask (and a solution of humic substances (50 mg in 10 ml of ethanol) was added if being used) and approximately 10 ml of the ethanol was then evaporated. After this the flask was filled with 2 litres of water and heated at 80°C for 1 hour. Once cooled the solution was used directly in the photolysis experiment (the final humic substances concentration would thus have been around 25 mg/l and traces of ethanol would also likely have been present (i.e. <5 to <10 ml/l; it is not clear however, how much ethanol would have been lost by heating at 80°C)). All experiments were carried out in at least duplicate.

Decabromodiphenyl ether was found to photodegrade in all test systems used. The first order rate constant for the reaction was determined to be around $4 \times 10^{-4}$ s$^{-1}$ in the methanol/water mixture (half-life around 0.5 hours), $6.5 \times 10^{-4}$ s$^{-1}$ in pure methanol (half-life around 0.3 hours), $8.3 \times 10^{-4}$ s$^{-1}$ in pure tetrahydrofuran (half-life around 0.23 hours), $3 \times 10^{-5}$ s$^{-1}$ in water with humic acid (half-life around 6.4 hours) and $5 \times 10^{-6}$ s$^{-1}$ in pure water (half-life around 39 hours). For the experiment in methanol/water the UV-visible spectrum for decabromodiphenyl ether showed some overlap with the solar spectrum up to a wavelength of around 320 nm. The $\lambda_{\text{max}}$ for decabromodiphenyl ether was at 306 nm with an extinction coefficient of 2,450 cm$^{-1}$ M$^{-1}$. The quantum yield for the disappearance of decabromodiphenyl ether in the methanol-water system was determined to be 0.14.

Experiments with other brominated diphenyl ethers showed that the rate of photodegradation decreased with decreasing degree of bromination, and was also influenced in some cases by the bromine substitution pattern. The rate of photodegradation of polybrominated diphenyl ethers in the methanol/water mixture was found to be consistently around 1.7 times slower than that in pure methanol and around 2-3 times slower than that in tetrahydrofuran. The photodegradation half-life found for decabromodiphenyl ether in methanol/water was 0.5 hours, which was considerably shorter than that found for 2,2’-4,4’-tetrabromodiphenyl ether (half-life 12 days).

Degradation of decabromodiphenyl ether in the methanol/water system was found to occur by consecutive debromination down to hexabromodiphenyl ethers. For example all three possible nonabrominated diphenyl ethers, at least seven octabromodiphenyl ethers (five of which were major chromatographic peaks), eight heptabromodiphenyl ethers (two of which were major peaks), small amounts of hexabromodiphenyl ethers but no mono- to pentabromodiphenyl ethers were detected after 100 minutes irradiation. Products with less than six bromine atoms were also formed and these were tentatively identified as brominated
dibenzofurans and possibly methoxylated brominated dibenzofurans. The experiments in pure methanol, tetrahydrofuran and water containing dissolved humic substances give rise to an almost identical set of products, although a higher proportion of pentabromodibenzo-furans were evident in the experiment with dissolved humic substances. The experiments using water-only were reported to be very difficult to carry out, and it is possible that the disappearance seen could have resulted from adsorption to the glass wall since no degradation products were apparent in these experiments.

Bezares-Cruz et al. (2004) have studied the photodegradation of decabromodiphenyl ether dissolved in hexane by natural sunlight. For the kinetic experiments the solutions of decabromodiphenyl ether (initial concentration 2-5 µM) was exposed to direct solar radiation on the roof of a building (40°29’N; 86°59.5’W) in the afternoon in both July and October. Separate experiments (using larger amounts of solution) were also carried out in order to identify the degradation products (the maximum exposure time in these experiments was 34 hours over seven days). In addition experiments were also carried out using pure samples of several lower brominated diphenyl congeners. The total irradiance during the kinetic experiments was measured close to the exposure site at 300, 305.5, 311.4, 317.6, 325.4, 332.4 and 366 nm at 3-minute intervals.

Decabromodiphenyl ether was found to degrade rapidly on exposure to sunlight, with the concentration being reduced to 5% of the initial concentration after 45 minutes exposure in October and to <1% of the initial concentration after 30 minutes exposure in July. The substance was found to be stable in dark controls over this period. The degradation reaction was found to follow first order kinetics. The molar absorptivities for decabromodiphenyl ether were determined to be 2,418 M⁻¹ cm⁻¹ at 300 nm, 2,181 M⁻¹ cm⁻¹ at 310 nm and 1,142 M⁻¹ cm⁻¹ at 320 nm and it was concluded that light centred at 320 nm was most responsible for the degradation of decabromodiphenyl ether under the conditions used. The first order reaction rate constants were determined to be 1.86×10⁻³ s⁻¹ in July (giving a half-life of 6.2 minutes) and 1.11×10⁻³ s⁻² in October (giving a half-life of 10 minutes). Taking into account the total irradiance during the two experiments, the second order reaction rate constants were estimated as 4.1×10⁻³ einstein mol⁻¹ s⁻¹ for the July experiment and 2.6×10⁻³ einstein mol⁻¹ s⁻¹ for the October experiment. The average reaction quantum yields were 0.48 and 0.46 for the July and October experiments respectively.

The degradation was found to proceed via reductive debromination to form lower brominated congeners. Over forty polybrominated diphenyl ether degradation products were apparent in the experiments with decabromodiphenyl ether, with over twenty-one of these having identical chromatographic retention times to known polybrominated diphenyl congeners. For example, after eighteen minutes irradiation in early afternoon in October all three possible nonabromodiphenyl ether and several octabromodiphenyl ethers were found to be formed, followed by formation of successively less brominated congeners as the irradiation time increased. The congener 2,2’,4,4’-tetrabromodiphenyl ether (BDE47) was detected as a degradation product after 20 hours irradiation in July and 27.8 hours irradiation in October, and several other of the lower brominated diphenyl ethers that are commonly found in environmental samples were also detected (e.g. 2,2’,3,4,4’-pentabromodiphenyl ether (BDE85), 2,2’,4,4’,5-pentabromodiphenyl ether (BDE99), 2,2’,4,4’,6-pentabromodiphenyl ether(BDE100), 2,2’,3,4,4’5’-hexabromodiphenyl ether (BDE138), 2,2’,4,4’,5,5’-hexabromodiphenyl ether (BDE153) and 2,2’,4,4’,5,6’-hexabromodiphenyl ether (BDE154)). In general the rate of photodegradation was found to decrease with decreasing bromine substitution.
The report concluded that the photolysis reaction of decabromodiphenyl ether in natural waters can be expected to be attenuated by sorption of decabromodiphenyl ether onto colloidal particles, by light attenuation by humic materials, and as a result of lower concentrations and/or less favourable hydrogen donors being present in natural waters. The authors of the paper indicated, however, that further, on-going, studies were being carried out to investigate the photoreactivity of decabromodiphenyl ether dissolved in humic acid solutions, and that early results from these studies indicated that similar initial degradation products were being formed under these conditions, but over periods of days rather than minutes as found in the hexane solvent.

Rahm et al. (2005) studied the rates of nucleophilic substitution of a series of polybrominated diphenyl ethers (including decabromodiphenyl ether) using sodium methoxide in a methanol/N,N-dimethylformamide solution. The purpose of the study was to determine the inherent susceptibility of the chemicals to such reactions (including hydrolysis). For the sequence of chemicals from decabromodiphenyl ether to pentabromodiphenyl ether, the rate constant for the reaction was found to decrease by roughly a factor of 10 for each bromine removed. It was concluded that as bromine groups are electron-withdrawing, and bromide is a good leaving group, fully brominated decabromodiphenyl ether is highly susceptible to nucleophilic aromatic substitutions but that this susceptibility decreases with decreasing degree of bromination. It should be noted that although this approach can be used to establish the relative susceptibility of the polybrominated diphenyl ethers as a group to nucleophilic substitution by a hard nucleophile (such as methoxide, hydroxide, etc.), the conditions used in the study means that it is not possible to ascertain whether such substitution reactions (e.g. hydrolysis) would occur in the environment.

5.1.3 Summary and implications for the risk assessment

The potential degradation of decabromodiphenyl ether by debromination to lower PBDE congeners is of high concern. Many of these substances are considered to be persistent, bioaccumulative and toxic (PBT) or very persistent and very bioaccumulative (vPvB), as defined in the Technical Guidance Document (particularly certain tetra-, penta- and hexaBDE congeners\footnote{The data are reviewed in the EU risk assessments for penta- and octabromodiphenyl ethers (EC, 2001 & 2003). Based on the available laboratory test data, these substances are considered to be persistent in the environment with mineralization half-lives of >2 months in water and >6 months in soil and sediment. Measured bioconcentration factors for fish are up to 5,600 l/kg for the hexaBDE components, and 11,700-17,700 l/kg for pentaBDE components. This identifies them as vPvB substances. For the commercial pentaBDE product, the 21-day Daphnia NOEC was 0.0053 mg/l, which meets the toxicity criterion. There are mammalian toxicity concerns too.}). Several significant new studies on the degradation of decabromodiphenyl ether in the laboratory have become available since the 2004 risk assessment was completed.

1. The study by Gerecke et al. (2005) is a good quality study that clearly demonstrates that debromination can take place microbially under anaerobic conditions. The reaction rate was relatively slow even though favourable conditions were used (e.g. a temperature of 37°C with a relatively high inoculum concentration). Debromination of at least 5% of the initial decabromodiphenyl ether added to the system was seen over 238 days’ incubation. The main debrominated diphenyl ether products found in the study were nonabromodiphenyl ethers and octabromodiphenyl ethers. It cannot
be ruled out that lower brominated products might be formed over longer incubation periods.

2. The study suggested that debromination of decabromodiphenyl ether proceeds most readily by loss of bromine from the para- (4-position) and meta-position (3- or 5-position) (although loss of bromine from the ortho- (2-position) was not completely ruled out by the authors). This has some important consequences for the debrominated products that could be formed as a result of such reactions. For example, the congeners that are most commonly found to occur in biota (such as 2,2,4,4'-tetrabromodiphenyl ether (BDE-47), 2,2',4,4',5-pentabromodiphenyl ether (BDE-99), 2,2',4,4'-6-pentabromodiphenyl ether (BDE-100), 2,2',4,4',5,5'hexabromodiphenyl ether (BDE-153), 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE-154) etc.) all have bromine atoms in the 4-position on both aromatic rings (and some have bromine atoms in the 5-position as well). Thus, if loss of bromine from the para-position is one of the main anaerobic degradation routes for decabromodiphenyl ether, then the products from this degradation route are unlikely to be the congeners that are most commonly found to occur in biota. Nevertheless, this does not rule out the possible formation of other congeners with similar properties to the latter.

3. It should be noted that although the test system is more environmentally relevant than earlier experiments using organic solvents, it is not in itself representative of sewage treatment processes (which have much shorter sludge retention times of around 20 days) or environmental conditions in general. Nevertheless, such conditions could potentially occur in landfill sites (which are anaerobic and methanogenic, and can experience elevated temperature), although the rates of degradation would be expected to be much lower than found in the test system used by Gerecke et al. (2005) (e.g. because the substance will be present in landfill sites mostly in articles, and microbial populations will differ substantially from those used in this test). In addition it would be expected that the reaction products would remain strongly sorbed to organic matter in such situations. Potential releases from landfill sites would be difficult to quantify in any case due to the complex characteristics and interactions that exist, and the usefulness of monitoring data would be limited by the presence of other PBDE products from historical uses. The relevance of the findings is therefore limited.

4. Two new photolysis studies are available for decabromodiphenyl ether (Eriksson et al. (2004a) and Bezares-Cruz et al. (2004)). These studies essentially confirm the results of earlier studies (see EC (2002) and ECB (2004)), which show a rapid debromination of decabromodiphenyl ether to lower brominated congeners occurring in organic solvents, with the rate of reaction decreasing as the number of bromine atoms declines. However, importantly, both new studies have investigated the photodegradation of decabromodiphenyl ether further using aqueous-based systems. Although not described in as much detail as the experiments in organic solvent, both Eriksson et al. (2004a) and Bezares-Cruz et al. (2004) found that the products of photodegradation of decabromodiphenyl ether in water-based systems (sometimes with added dissolved humic acids) were similar to those formed in organic solvents, but were formed at a slower rate. Furthermore, Eriksson et al. (2004a) found that in water-based systems, the debromination of decabromodiphenyl ether proceeded
down to hexabromodiphenyl ether and that products with less than six bromine atoms were also formed and were tentatively identified as brominated dibenzofurans.

5. Although these new data provide additional evidence that decabromodiphenyl ether could photodegrade to form more toxic and accumulative products in the presence of water, it is not possible to extrapolate these results directly to the environment for a number of reasons (as outlined by Bezares-Cruz et al. (2004)). These include sorption of decabromodiphenyl ether onto colloidal particles in the environment, the attenuation of light by humic materials (and other materials) in the environment and the generally lower concentrations and/or less favourable hydrogen donors present in natural waters compared with the conditions used in the laboratory studies. Similar conclusions were drawn in the previous risk assessment report:

“Overall, although it can be concluded that formation of lower brominated diphenyl ethers and brominated dibenzofurans can occur from the photolysis of decabromodiphenyl ether in the environment, the actual significance of the process is likely to be limited owing to the lack of exposure to light of the bulk of decabromodiphenyl ether in the environment. It is considered unlikely that such photolysis reactions of decabromodiphenyl ether could explain the current widespread occurrence of tetra-, penta- and hexabromodiphenyl ether congeners in the environment. Instead, it is much more likely that this is mainly the result of the emissions of the commercial penta- and octabromodiphenyl ether flame retardants. However any photolysis of decabromodiphenyl ether that does occur in the environment could make a (probably small) contribution to the levels of the lower brominated diphenyl ether congeners and also possibly brominated dibenzofurans present in the environment.”

This conclusion would therefore still seem to be appropriate based on the new photolysis data.

6. The final important new degradation study is that by Keum and Li (2005). This found that decabromodiphenyl ether was debrominated reasonably rapidly in water using a variety of reducing agents (some of which are found in the environment). In this case many lower brominated congeners were formed including those that are commonly found in biota (such as BDE-47, BDE-99, BDE-100, BDE-153, BDE-154). Still, the actual conditions used in these experiments are not directly related to those in the environment. For example, Vangheluwe (2005) pointed out that:

- The mechanism is unlikely to be important in marine sediments, because the excess of sulphate ions in seawater would act as a competing (and preferred) electron acceptor.
- High concentrations of powdered iron or iron sulphide were used in the experiments – in the case of iron sulphide, the levels used were around at least one order of magnitude higher than the concentrations typically encountered in freshwater sediments.
- The tests were conducted at 30°C – the temperature in the field is much lower (the TGD assumes a standard temperature of 12°C).
Iron sulphide is present in the solid phase in anaerobic sediments, and sediment particles tend to be coated with organic carbon (to which the substance would adsorb), which would reduce the area available for reaction.

7. The relevance of the experiment to environmental conditions is therefore uncertain. However, there are numerous similar reductants (e.g. iron-bearing minerals and sulphide ions, etc., some of which may be water-soluble) present in anaerobic conditions in both sediments and soils, and these are predicted to be the major environmental compartments to which decabromodiphenyl ether will distribute. Thus, although the rates and extent of reaction seen in this laboratory study cannot be extrapolated directly to the environment, similar reactions can not easily be ruled out (although it is not possible to estimate the extent or rate of such reactions).

8. A 32-week anaerobic biodegradation study in a sediment-water system was reported in the 2002 risk assessment report (EC, 2002). Overall, decabromodiphenyl ether was found to be stable under the conditions used in the test. There is no information on the sulphide content of the test sediment, so the experiment does not provide any additional information about the significance of this reaction pathway.

9. Appendix F of the 2002 risk assessment report considered the evidence for dehalogenation under various conditions for a number of substances. In experiments with polychlorinated biphenyls (PCBs), dechlorination has been demonstrated under methanogenic but not sulfidogenic conditions. Sulfidogenic conditions usually exist between the aerobic surface layers and the deeper methanogenic layers of sediments. It was concluded that if anaerobic debromination of the PBDEs occurs in the environment under similar conditions to the dechlorination of PCBs, any products formed are more likely to be present in the deeper methanogenic layers of the sediment, and rapid exchange between this layer and the aerobic sediment and water phases would be expected to be limited. However, the new data from Keum and Li (2005) suggest that this might not be the case.

10. Appendix F of the 2002 risk assessment report also reported evidence that dehalogenation requires an adaptation period during which enzyme induction occurs in the microorganisms, and that this process may be dependent on the presence of a high concentration of the halogenated compound. Since the levels of decabromodiphenyl ether are increasing in sediments with time, the potential for such adaptation could be increasing, although this is speculative.

In summary, the new data provide clear evidence that debromination of decabromodiphenyl ether to form lower brominated congeners can occur under certain conditions in laboratory tests, but the results are difficult to extrapolate to the environment.

On the other hand, it is important to examine the evidence from field experience. Decabromodiphenyl ether is clearly very persistent under many conditions (e.g. see the results of Sellström, 2005). There is some circumstantial evidence from the available monitoring data (see Section 4) that decabromodiphenyl ether might degrade (or be metabolised) to lower brominated congeners in the environment, although none of these data are conclusive in this respect. For example, Voorspoels et al. (2004a [ABST] and 2004b) investigated the correlation between the concentrations of decabromodiphenyl ether and
lower brominated congeners (expressed as the sum of specific tri- to heptabrominated congeners) found in various sediments. A statistically significant (p=0.05) positive correlation was found for the samples from marine locations (Belgian North Sea and Scheldt estuary) whereas no correlation between the concentration of decabromodiphenyl ether and that of the lower brominated congeners was evident in the samples from the freshwater locations. Similarly Kolic et al. (2004a) suggested that degradation of decabromodiphenyl ether during the biosolids decomposition/composting process could be an explanation for the changes in the relative ratios of congeners seen in composted and uncomposted biosolids, although the authors thought that further work was needed to test this hypothesis.

Importantly, results of a number of sediment core monitoring studies were reported in the previous risk assessment reports, and these did not provide any evidence of debromination (in either freshwater or marine environments). In addition, the degradation studies reported above appear to result in a wide distribution of congeners. This pattern is not reflected in environmental samples, which are always dominated by the congeners present in the various commercial products. Nevertheless, the pattern could be masked for this very reason. In summary, the available monitoring data provide little evidence for debromination being a significant degradation mechanism for decabromodiphenyl ether in the environment (and hence a major source of lower brominated congeners).

Consequently the new data serve to reinforce the existing concerns, but do not lead the rapporteur to conclude that there is actually a risk. The conclusions of the previous assessment therefore remain essentially the same, but additional investigations are necessary. The rapporteur recognises that there are uncertainties in drawing this conclusion.

It is possible in principle to carry out further degradation testing to investigate the possible formation of lower brominated congeners under environmentally relevant conditions. However, several such tests have already been performed (see EC (2002) and ECB (2004)), and these did not suggest any significant debromination. In addition, given the complexities of the likely degradation routes and possible degradation systems, it is considered that even with extended testing, it might still be difficult to predict the actual amounts of any given degradation product that may be formed from decabromodiphenyl ether in the environment.

It is therefore recommended that the existing monitoring programmes be continued, but that in particular:

- they include analysis of lower PBDE congeners (especially those observed in the degradation experiments reported here) in all relevant samples. Clearly, the contribution from the now banned commercial penta- and octabromodiphenyl ether products will remain a confounding factor, but correlations between congeners in environmental samples should be established if possible; and
- data on the sulphide content of sediments are collected at the same time as sampling is performed; if none of the current sediment sampling locations have elevated sulphide concentrations, further sampling in sulphide-rich areas should be performed, with collection of sediment cores for comprehensive analysis.

In Section 2 it was indicated that some further sampling of sediment might be required specifically related to textile processing sites. Given concerns over debromination, it would be
sensible to analyse for lower PBDE congeners as well as decabromodiphenyl ether in such cases. Of course, if lower congeners were detected, a reference site upstream of the discharge would also need to be investigated for comparison, since there are other known sources of these substances.

The rapporteur also undertakes to continue to monitor the literature for significant new data on a quarterly basis, and will remain in contact with researchers who are performing additional degradation experiments (see Section 12).

6 UPTAKE AND ACCUMULATION

6.1.1 New information

The absorption of decabromodiphenyl ether from diet by grey seals (Halichoerus grypus) has been studied by Thomas et al. (2005) {note: preliminary results from this study were reported in the 2004 risk assessment}. Three captive (wild) juvenile grey seals were fed a constant diet of herring (from the North Sea) for three months prior to the start of the study. After this time the seals were fed fish taken from one batch caught in the North Sea for a further three months (each seal consumed between 1 and 2.5 kg fresh weight of fish each day). During the second month, seals were fed a supplement of 12 µg decabromodiphenyl ether per day (the decabromodiphenyl ether was dissolved in cod liver oil in a capsule) and in the final month of the study the seals were fed a control (unspiked) oil capsule each day. Samples of the fish used, and a blood sample and a 24-hour feces sample from the seal, were analysed on a weekly basis for the presence of polybrominated diphenyl ethers. In addition a blubber biopsy was taken from each seal at three times during the study.

Decabromodiphenyl ether was not found to be present in any of the fish samples used in this study. However, decabromodiphenyl ether was found to be adsorbed from the diet when the diet was supplemented with cod liver oil capsules containing decabromodiphenyl ether. The average net absorption for decabromodiphenyl ether found in the study was 89% (range 57-97%). Decabromodiphenyl ether was not found to be present in blood during the first month of the study (when the seals were fed fish alone), and could not be detected in blood three days after the diet was supplemented with decabromodiphenyl ether. However measurable levels of decabromodiphenyl ether was found in blood by day 45 of the study and decabromodiphenyl ether could still be detected in blood at the end of the study (i.e. 1 month after the supplementary feeding of decabromodiphenyl ether had ceased). The maximum concentration in blood occurred between five and eleven days after cessation of the supplementary feeding (the level reached was around 1,000 µg/kg lipid; values read from a graph), and had declined to around 14-15% of the maximum value by day 83 of the study (the depuration half-life in blood was estimated to be around 8.5-13 days from these data).

Decabromodiphenyl ether was also found to be present in blubber samples within three days of the start of the supplementary feeding with decabromodiphenyl ether, and was still present in blubber at the end of the study (it was estimated that around 11-15% of the cumulative amount of decabromodiphenyl ether ingested during the study (~320 µg per seal) was still present in blubber at this time).

Lebeuf et al. (2004 [ABST]) investigated the possible metabolism of decabromodiphenyl ether to lower brominated congeners in marine fish (Atlantic tomcod (Microgadus tomcod))
following pre-treatment with a cytochrome P450 inducer with a high potency to induce the liver detoxification system (PCB-126). The fish used in the study (175-250 mm) were captured in the St. Lawrence estuary in November and acclimated to laboratory conditions (salinity 30 ppm and temperature of 6-7°C) until the start of the experiment the following May. During this period the fish were fed *ad libitum* with frozen capelin twice per week. At the start of the test eight groups of 25 fish were placed into 500 litre fibreglass tanks. Fish from half the tanks were then anaesthetized and were injected with PCB-126 (dose 25 ng/g of fish in corn oil; fish from the remaining tanks received a dose of corn oil alone). After three weeks, the fish from two out of the four tanks that had received PCB-126 and the fish from two out of the four tanks that had received corn oil alone were injected with decabromodiphenyl ether (dose 400 ng/g fish; fish from the remaining tanks received a dose of corn oil alone). After a further seven weeks, groups of seven to eight fish from each tank were sampled and analysed for the presence of decabromodiphenyl ether and several lower brominated diphenyl ether congeners (di- to hexabromodiphenyl ethers).

The level of decabromodiphenyl ether present in the liver at the end of the study was 412 µg/kg lipid in the fish pre-exposed to corn oil alone and 726 µg/kg in the fish pre-exposed to PCB-126. The transfer efficiency of decabromodiphenyl ether to the liver was estimated to be 4.6±4.6%. For the lower brominated congeners the study determined the relative ratio of the concentration of each congener to that of 2,2',4,4'-tetabromodiphenyl ether (the absolute concentrations were not reported). No significant difference was found in this ratio between the fish pre-exposed to PCB-126 and then decabromodiphenyl ether and those pre-exposed to PCB-126 and then corn oil alone (the control population), except for one congener (2,2',4,4',5,5'-hexabromodiphenyl ether) which was slightly, but statistically significantly, enriched compared to the control population. Overall it was concluded that the fish exhibited very limited capacity to metabolise decabromodiphenyl ether to lower brominated congeners.

The study indicates that none of the lower brominated congeners examined in the study were detectable in the decabromodiphenyl ether sample used in the study. However it is clear from the paper that lower brominated congeners were also present in the control fish population (i.e. the fish receiving BCP-126 and then corn oil alone) and the paper does not indicate if other sources (such as the food or corn oil used in the study) contained any of the lower brominated congeners studied.

The formation and retention of hydroxylated polybrominated diphenyl ether metabolites in rat blood has been studied following exposure to a mixture of seven polybrominated diphenyl ethers (Malmberg *et al.*, 2004). A group of ten rats were given a single intraperitoneal dose of an equimolar (3 µmol/kg body weight for each substance) mixture of 2,2’,4,4’-tetabromodiphenyl ether, 2,2’,4,4’5-pentabromodiphenyl ether, 2,2’,4,4’,6-pentabromodiphenyl ether, 2,2’,4,4’5,5’-hexabromodiphenyl ether, 2,2’,4,4’,5,6’-hexabromodiphenyl ether, 2,2’,3,4,4’,5’,6-heptabromodiphenyl ether and decabromodiphenyl ether. The substances were administered using an emulsion of 0.16 g soya phospholipon/Lutrol (16:34, w/w)/ml water. The levels of the polybrominated diphenyl ethers and metabolites in blood plasma was determined both 24 hours and five days after exposure. The mean concentration of decabromodiphenyl ether in plasma was found to be 1,200 pmol/g fresh weight 24 hours after exposure and this fell to 60 pmol/g fresh weight five days after exposure. A total of sixteen hydroxylated (three of which were dominant) and two dihydroxylated polybrominated diphenyl ether metabolites were identified in the plasma
samples. As the rats were exposed to a mixture of polybrominated diphenyl ethers it is not possible to distinguish which metabolites, if any, originated from decabromodiphenyl ether.

The SCHER opinion indicated that information was available showing the uptake of decabromodiphenyl ether by earthworms from soil. The researchers who carried out this work have been contacted and some further details of this study have been received (Sellström, 2005). In the study, samples of soils and earthworms were taken from three research stations and two private farms in southern Sweden in 2000. The soils from the research stations were amended with controlled amounts of sewage sludge (last applications in 1997 or 1998), with some plots receiving no sludge (reference areas). At one of the farms the soil was treated with sewage sludge from a plant receiving waste water from polybrominated diphenyl ether-using textile industries between 1978 and 1982. The other farm soil was not amended with sludge (but was located near the river Viskan (which contains sediments with measurable polybrominated diphenyl ether contents) and is flooded on a regular basis (including the summer before the sampling took place). Again reference areas from these parts (either an area where no sludge had been applied or that had not been flooded) were also sampled. The soil samples analysed were pooled samples (30-40 subsamples taken to a depth of 0-20 cm making up each pooled sample). The earthworms were collected from the same areas as the soil samples and were allowed to clear the gut and then washed prior to analysis. The levels of decabromodiphenyl ether found in the reference soils were in the range 0.014-0.7 µg/kg dry weight (0.46-10 µg/kg on a dry weight ignition loss (IG) basis). The levels in the soil exposed or treated soils were expressed as a ratio to the reference soil for the same location. These ratios were >1 for all sites, and were generally highest for the farm sites. For example, the levels of decabromodiphenyl ether in one of the sludge amended experimental soils were around eight times higher than the corresponding reference soil, and the levels in the flooded farm soil were around 200 times higher than the reference soil for that farm. The highest overall levels of polybrominated diphenyl ether were found in the sludge amended farm soil. The levels of decabromodiphenyl ether found in this soil were around 2,400 µg/kg dry weight (34,000 µg/kg IG). The corresponding concentration in the earthworms was 5,200 µg/kg lipid. It should be noted that these samples were taken around 20 years after sewage sludge was applied to the soil at this site, and implies a high persistency of decabromodiphenyl ether in this soil.

The biota-soil accumulation factor (BSAF – calculated as the concentration in worm on a lipid basis/concentration in soil on an IG basis) was found to be similar in all soils, except for the flooded soil (which resulted in a lower BSAF). The actual BSAFs for decabromodiphenyl ether were not stated but it was indicated that the BSAF for higher brominated congeners (octa- to decabromodiphenyl ether) were in the range 0.3-2, with the factor generally decreasing with increasing bromination. These results show that decabromodiphenyl ether can be transferred from soil into earthworms.

6.1.2 Summary and implications for the risk assessment

As reported in the previous risk assessment report, although the substance meets the screening criteria for being potentially very bioaccumulative (vB) it does not meet the actual confirmatory criteria based on bioconcentration factor (BCF) data from aquatic tests. The new data show that decabromodiphenyl ether is bioavailable from food and can be taken up by earthworms from soil, but there is no new information about biomagnification potential. As discussed in Section 4.1.8, one study that has attempted to look at biomagnification in aquatic food chains concluded that although decabromodiphenyl ether was bioavailable to
fish it was not biomagnified, although problems with blanks in this experiment mean that this statement should be treated with caution.

The metabolites of decabromodiphenyl ether (if any) are unclear. As discussed in Section 4.1.8, there is some limited evidence for the formation of lower brominated congeners from the metabolism of decabromodiphenyl ether in fish, although this is by no means certain or proven at this stage.
7 TOXICITY

7.1.1 New information

The possible neurotoxicity of decabromodiphenyl ether is discussed in the 2004 risk assessment report. Following on from the findings for decabromodiphenyl ether, Eriksson et al. (2004b) investigated the neurotoxicity of several other highly brominated diphenyl ethers (including a nonabrominated diphenyl ether congener). As the commercial decabromodiphenyl ether contains up to around 3% nonabrominated congeners it is relevant to consider these findings here. The test system used was similar to that used for decabromodiphenyl ether. In the study neonatal NMRI-male mice were exposed on postnatal day 3 or day 10 to a single oral dose of 2,3',4,4',5,6'-nonabromodiphenyl ether (PBDE 206) at a concentration of 18.5 mg/kg body weight. The mice were observed for spontaneous behaviour at an age of two months, and learning and memory was observed in a Morris water maze at an age of three months. Effects on spontaneous behaviour (locomotion, rearing and total activity in 2-month old mice) and learning and memory (in 3-month old mice) were observed in mice exposed on postnatal day 10. Few other details are currently available on this study. It is not possible to derive a no effect level for these effects from this single dose study.

Decabromodiphenyl ether is currently being studied for possible endocrine disrupting effects in the FIRE project by the Cluster of Research into Endocrine Disruption in Europe (CREDO, 2005). The pre-screening phase of this study has recently been completed. This pre-screening phase investigated the endocrine disrupting potency of several brominated flame retardants (including decabromodiphenyl ether) using a battery of in vitro bioassays with endpoints such as hormone-receptor mediated gene transcription, cell proliferation and interference in hormone metabolism via competitive protein binding and inhibition or induction of enzyme activity. The actual results of the studies are not yet available but decabromodiphenyl ether was placed in a group of chemicals that showed almost no in vitro endocrine disrupting potency in any of the assays preformed. However, owing to the high production volumes and environmental abundance of decabromodiphenyl ether, further in vivo toxicity studies are scheduled to be carried out in the near future with decabromodiphenyl ether.

7.1.2 Summary and implications for the risk assessment

The available (in vitro) information on the endocrine disrupting effects of decabromodiphenyl ether indicates that it has only a very low potential for causing effects on the endocrine system. However, further work is being planned to investigate this endpoint in vivo.

A nonabromodiphenyl ether (a main impurity in the commercial decabromodiphenyl ether product) has been shown to cause neurotoxic effects in mice. However, the method used was similar to that used for decabromodiphenyl ether itself and so would be subject to the same uncertainties as the study with decabromodiphenyl ether (see ECB, 2004).
Borgnes and Rikheim (2004) investigated the combustion of electrical and electronic plastic waste at three full-scale waste incineration plants in Norway. The plants studied were two larger plants for mixed municipal waste and one smaller plant for shredded industrial waste. The brominated waste used in the study was waste from a plant for demolition of electrical and electronic equipment. This waste was estimated to contain approximately 1% by weight bromine (of which polybrominated diphenyl ethers accounted for around 80%; the actual polybrominated diphenyl ethers present were not stated but it is likely that decabromodiphenyl ether would account for a significant fraction of this). The experiments were carried out using the normal waste feed for the plant mixed with varying proportions (between 0% and 20%) of the brominated waste.

Analysis of the waste streams from one of the larger incinerators indicated that the total outflow of brominated flame retardants from the incinerator was <0.001% by weight of the total amount of brominated flame retardants in the waste mixture fed to the plant. The concentration of total brominated flame retardants in the flue gas from the plant was 14-22 ng/Nm$^3$ (Nm$^3$ = Normal m$^3$ at standard temperature and pressure (20°C and 1 atmosphere). Decabromodiphenyl ether was reported to make the largest contribution to the measured levels of total brominated flame retardants. This is equivalent to a total emission of 0.9-1.4 mg/hour or around 0.010 kg/year. Decabromodiphenyl ether was also found to be present in the bottom ash from the plant. The flue gas concentration of total brominated flame retardants at the smaller plant was <5 ng/Nm$^3$.

The flue gas was also analysed for the presence of halogenated dibenzo-$p$-dioxins and furans. It was concluded that increasing the content of brominated flame retardants in the waste stream did not result in a significant increase in the emissions of chlorinated, brominated or mixed chlorinated/brominated dibenzo-$p$-dioxins and furans. The levels were always below the EU threshold value for incineration of waste. It was concluded that the incineration efficiency and the operating conditions of the flue gas treatment systems are of greater importance to the resulting emission levels for halogenated dibenzo-$p$-dioxins and furans than the bromine content of the waste.
9 SUMMARY OF CONCLUSIONS

Two aspects have been considered. The first is the conclusion for sediment and soil based on the PEC/PNEC approach for textile use of decabromodiphenyl ether. The second, and more important, aspect is the conclusion for the PBT assessment, relating to the formation of more hazardous degradation products.

i) Use in textile applications – PEC/PNEC approach

The conclusion for sediment and soil should be changed from conclusion (ii) to (i).

This applies to the assessment of worst case releases, based on an atypical site in the United Kingdom. Emissions at other UK sites are all now comparable to the scenarios given in the 2002 version of the risk assessment, which did not lead to risks. However, this is the situation following emission reduction activity, and the current levels of emission at other textile sites in the EU could be higher. It is recommended that representative baseline data for aquatic emissions from the textile industry in other European countries are collected as a matter of urgency (and, where relevant, information on sludge disposal practices). Further sediment monitoring downstream from textile application site discharge points might be required as a result to refine the PECs where a potential risk is identified. It would be useful to clarify whether the actual sediment concentrations are higher than predicted at the worst case UK site.

A decision on the need for further toxicity tests at a suitable concentration would be taken following the collection of better emissions data.

ii) PBT conclusions

Decabromodiphenyl ether continues to be a potential, though not proven, source of lower PBDE congeners that are considered to be PBT or vPvB substances. The conclusion in the 2004 risk assessment report does not need to be changed by the new data, but it is recommended that the existing monitoring programmes:

- include analysis of lower PBDE congeners (especially those observed in the degradation experiments reported here) in all relevant samples; and
- collect data on the sulphide content of sediments at the same time as sampling is performed; if none of the current sediment sampling locations have elevated sulphide concentrations, further sampling in sulphide-rich areas should be performed, with collection of sediment cores for comprehensive analysis.

Given concerns over debromination, it would be sensible to analyse for lower PBDE congeners in cases where samples are collected for chemical analysis related to textile processing sites (see above). If lower congeners were detected, a reference site upstream of the discharge would also need to be investigated for comparison, since there are other sources of these substances.

The rapporteur also undertakes to continue to monitor the literature for significant new data, and will remain in contact with researchers who are performing additional degradation experiments (see Section 12).
REFERENCES


Bureau S., Zebühr Y., Broman D. and Ishaq R. (2004). Biomagnification of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) studies in pike (Esox lucius), perch (Perca fluviatilis) and roach (Rutilus rutilus) from the Baltic Sea. Chemosphere, 55, 1043-1052.


Luksemburg W., Wenning R., Maier M., Patterson A. and Braithwaite S. (2004b). Polybrominated diphenyl ethers (PBDE) and polychlorinated dibenzo-p-dioxins (PCDD/F) and biphenyls (PCB) in fish, beef, and fowl purchased in food markets in Northern California, USA. Organohalogen Compounds, 66, 3982-3987.


SFT (2005). Personal communication to the Environment Agency from Marit Kopangen, Norwegian Pollution Control Authority (SFT). Translation of:


OTHER PAPERS THAT DID NOT CONTAIN SIGNIFICANT NEW INFORMATION RELEVANT TO THE ENVIRONMENTAL RISK ASSESSMENT

N.B. It should be noted that some of these references might still be useful for the human health assessment.


Andersen O-K. (2004). Biomarker response and plasma-protein expression signatures (PES) in mussels (Mytilus edulis), cod (Gadus morhua) and turbot (Scophthalmus maximus) exposed to PBDE-47, Bisphenol A and DAP. Abstract from “Third International Workshop on Brominated Flame Retardants, BFR2004”, University of Toronto, Canada, June 6-9, 2004. [contains information mainly on lower brominated congeners]


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Bodin N., Abarou A., Defour S. and Fraisse D. (2004). PCBs, PCDD/Fs and PBDEs in crustaceans from different French coastal sites. Organohalogen Compounds, 66, [contains information on lower brominated congeners only]


Fängström B., Strid A. Athanasiadis I., Grandjean P., Weihe P. and Bergman Å. (2004). A retrospective time trend study of PBDEs and PCBs in human milk from the Faroe Islands. Organohalogen Compounds, 66, 2829-2833. [contains information on lower brominated congeners only]


Guvenius D. M., Aronsson A., Ekman-Ordeberg G., Bergman A. and Noren K. (2003). Human prenatal and postnatal exposure to polybrominated diphenyl ethers, polychlorinated biphenyls, polychlorobiphenylols, and pentachlorophenol, Environ Health Perspect., 111, 1235-1241. [data indicate that the higher brominated PBDEs do not pass the human placenta to the same extent as do the lower brominated congeners. Data concerning decabromodiphenyl ether are not presented]


Harrad S. and Hunter S. (2004). Spatial variation in atmospheric levels of PBDEs in passive air samples on an urban-rural transect. Organohalogen Compounds, 66, 3786-3792. [contains information on lower brominated congeners only]


Jenssen B. M., Sørmo E. G., Salmer M. P., Bæk K., and Skaare J. U. (2004). Brominated flame retardants (BFRs) in the Arctic marine food chain. Abstract from “Third International Workshop on Brominated Flame Retardants, BFR2004”, University of Toronto, Canada, June 6-9, 2004. [mainly contains information mainly on lower brominated congeners – may have found decabromodiphenyl in polar bears – these are probably the same results already given in the RAR]


Kuramochi H., Meada K. and Kawamoto K. (2004). Physicochemical properties of selected polybrominated diphenyl ethers and comparison with some brominated aromatics and PCDDs. Organohalogen Compounds, 66, 2420-2425. [contains information on lower brominated congeners only]


Larsen G., Huwe J., Low M., Rutherford D. and Hakk H. (2004). Binding of 2,2′,4,4′,6-pentabromodiphenyl ether (BDE-100) and/or its metabolites to mammalian biliary carrier proteins. Organohalogen Compounds, 66, 3877-3882. [contains information on lower brominated congeners only]


Ruokojärvi P., Koistinen J., Herve S. and Vartiainen T. (2004). Mussel incubation in the monitoring of PCDDs, PCDFs, PCBs, PBDEs and PCNs in two Finnish watercourses. Organohalogen Compounds, 66, 1829-1833. [contains information on lower brominated congeners only]

Ryan J. J. and van Oostdam J. (2004). Polybrominated diphenyl ethers (PBDEs) in maternal and cord blood plasma of several Northern Canadian populations. Organohalogen Compounds, 66, 2579-2585. [mainly related to human health assessment; lower brominated congeners only – did look for decaBDE but appears to have been not detected]


Schuhmacher M., Kiviranta H., Vartiainen T. and Domingo L. L. (2004). Concentrations of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in breast milk of women from Catalonia, Spain. Organohalogen Compounds, 66, 2560-2566. [contains information on lower brominated congeners only]


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Van Leeuwen S., Traag W. and de Boer J. (2004). Monitoring of brominated flame retardants, dioxins, PCBs and other organohalogen compounds in fish from the Netherlands. Organohalogen Compounds, 66, 1764-1769. [contains information on lower brominated congeners only]


WWF (2005). The tip of the iceberg: Chemical contamination in the Arctic. WWF Detox Campaign. [no significant new data]


12 FURTHER PAPERS THAT HAVE NOT YET BEEN REVIEWED

The published literature on polybrominated diphenyl ethers is increasing all the time. The review of papers included in this update was carried out during May/June 2005. Since then, a number of further papers have been published or are in press. These are listed below. They have not yet been reviewed as part of this update (this will be done in any future updates).

The Norwegian Polar Institute and Veterinary Institute is currently performing a trend-analysis on levels of decabromodiphenyl ether (amongst other substances) in bird eggs from 1983, 1993 and 2003 from two remote sites in northern Norway (Finnmark and Lofoten). Two species (Atlantic Puffin and Herring Gull) are involved. The results are expected to be available during the summer 2005. One additional monitoring study has recently been published on the web in Norwegian (Kartlegging av utvalgte nye organiske miljøgifter 2004), and a partial translation has kindly been supplied by SFT (2005). This was received too late for inclusion in this report, but will be included later. The report gives monitored concentrations of the substance (and other PBDEs) in:

- untreated and treated landfill leachates,
- treated water from waste water treatment plants,
- sediments linked to landfills,
- sludge from sewage treatment plants,
- freshwater sediments,
- freshwater fish,
- marine surface sediments,
- blue mussels, and
- cod liver.

The rapporteur is also aware that further relevant studies are being planned or are underway by the US EPA, Environment Canada (including anaerobic degradation in Lake Ontario sediments under normal, fortified and nutrient rich conditions) and other researchers, notably Dr H. Stapleton at the US National Institute of Standards & Technology/Duke University, and Professor Li’s group in Hawaii. The results of these studies are not yet available. In addition further information is being generated under the EU Fire project.

**Literature list**


Jaspers V. L., Covaci J. V. L., Voorspoels S., Dauwe T., Eens M. and Schepens P. (2005). Brominated flame retardants and organochlorine pollutants in aquatic and terrestrial predatory birds of Belgium: levels, patterns, tissue distribution and condition factors. Environ. Pollut., in press. [it is likely that these are the same data as already included in the assessment]


Verreault J., Gabrielsen G. W., Chu S., Muir D. C. G., Andersen M., Hamaed A. and Letcher R. J. (2005). Flame retardants and methoxylated and hydroxylated polybrominated diphenyl ethers in two Norwegian Arctic top predators: Glaucous Gulls and Polar Bears. Environ. Sci. Technol., in press. [it is likely that these are the same data as already included in the assessment]


\(^{12}\) Further topics discussed at this (or perhaps a similar) forum, but for which no information has so far been obtained include:
- Hardy M., Decabromodiphenyl ether/oxide metabolism in fish and mammals: contribution to lower brominated diphenyl ethers
- Nyden M., Stapleton H. and Dodder N., Measurements of the photolytic breakdown of decabromodiphenyl ether in plastics;
- Ranken P., Hardy M. and Landry S., Decabromodiphenyl oxide/ether (BDE-209) in consumer electronics: contribution to lower brominated diphenyl ethers in the environment
APPENDIX A  FURTHER INFORMATION ON THE KEUM AND LI (1995) STUDY

The following further information has been kindly supplied by the authors of this paper in relation to the experiments with iron sulphide and sodium sulphide.

The experiments of reductive debromination of decabromodiphenyl ether by iron sulfide and sodium sulfide were done with three replicates. Sixteen debromination products were identified and quantified with proper PBDE standards that were available (see Table below). The correlations of variation averaged 15% or less for iron sulfide and sodium sulfide treatments.

<table>
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<tr>
<th>Substitution</th>
<th>BDE-No</th>
<th>Concentration (ppm)</th>
<th>Iron sulfide</th>
<th>Sodium sulfide</th>
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<td></td>
<td></td>
<td></td>
<td>Mean</td>
<td>Std. deviation</td>
</tr>
<tr>
<td>2,4',6-tetraBr</td>
<td>BDE-75</td>
<td>ND*</td>
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<td>ND</td>
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</table>

* ND, not detected in all triplicate samples; **BDE-99 was found only in one sample.