



Distr.: General
26 July 2006

English only



**United Nations
Environment
Programme**

**Stockholm Convention on Persistent Organic Pollutants
Persistent Organic Pollutants Review Committee**

Second meeting

Geneva, 6–10 November 2005

Item 6 (a) of the provisional agenda*

**Consideration of chemicals newly proposed for inclusion in
Annexes A, B and C of the Convention: octabromodiphenyl ether**

Octabromodiphenyl ether proposal**

Note by the Secretariat

The annex to the present note contains a proposal by the [European Union and its member States that are Parties to the Stockholm Convention on Persistent Organic Pollutants] for listing octabromodiphenyl ether in Annex A of the Stockholm Convention pursuant to paragraph 1 of Article 8 of the Convention. The annex is being circulated as submitted and has not been formally edited by the Secretariat.

* UNEP/POPS/POPRC.2/1.

** Stockholm Convention, Article 8, paragraph 1.

Proposal for listing

**Octabromodiphenyl ether
(commercial mixture, c-octaBDE)**

in the Stockholm Convention

on Persistent Organic Pollutants

Introduction

Commercial octabromodiphenyl ether (c-octaBDE) is a mixture of several polybrominated diphenyl ethers and congeners. These synthetic brominated compounds have mainly been used as flame retardants. In addition to octaBDE isomers, c-octaBDE contains significant amounts of other component groups (such as penta- and hexabromodiphenyl ethers) with POP characteristics. Specifically, the POP Review Committee recently concluded that pentaBDE meets all the criteria specified in Annex D of the Stockholm Convention, and therefore should be considered as a POP (Decision POPRC-1/3, 2005).

This dossier focuses solely on the information required under paragraphs 1 and 2 of Annex D of the Stockholm Convention and it is mainly based on the extensive EU Risk Assessment Report (European Commission 2003) on c-octaBDE (publicly available at: <http://ecb.jrc.it/existing-chemicals/>) and the risk profile and summary report presented by the European Commission for the UNECE Convention on Long-Range Transboundary Air Pollution (CLRTAP), Protocol on Persistent Organic Pollutants (<http://www.unece.org/env/popsxg/docs/2005/EU%20octaBDE.pdf>). As penta- and hexabromodiphenyl ethers (which have POP characteristics) occur in c-octaBDE, relevant information about these two compounds is also provided, where appropriate.

1 Chemical identity

This proposal concerns the c-octaBDE. There are several components in the commercial product and so any assessment of the commercial product requires an assessment of the individual components. The commercially supplied octaBDE is a complex mixture consisting (as of 2001 within the EU member States) typically of $\leq 0.5\%$ pentabromodiphenyl ether isomers, $\leq 12\%$ hexabromodiphenyl ether isomers, $\leq 45\%$ heptabromodiphenyl ether isomers, $\leq 33\%$ octaBDE isomers, $\leq 10\%$ nonabromodiphenyl ether isomers and $\leq 0.7\%$ decabromodiphenyl ether. The composition of older products or products from non-EU countries may be different from this.

The c-octaBDE is sold as a technical grade under the Chemical Abstracts Service (CAS) Registry number for the octaBDE isomer.

1.1 Names and registry numbers

IUPAC Name: Diphenyl ether, octabromo derivative (octabromodiphenyl ether, octaBDE)

Synonyms: octabromobiphenyl oxide, octabromodiphenyl oxide, octabromo phenoxybenzene and benzene, 1,1' oxybis-, octabromo derivative

CAS Number: 32536-52-0

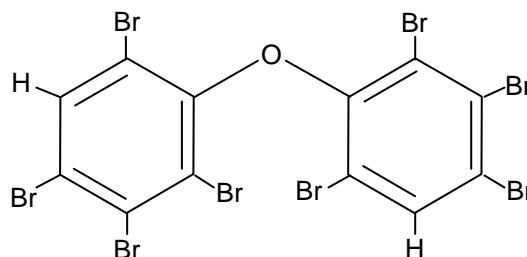
EINECS Number: 251-087-9

1.2 Structure

Molecular formula: $C_{12}H_2Br_8O$

Molecular weight: 801.38

Chemical structure:



2 Persistence

OctaBDE has been found to photodegrade rapidly in a mixture of organic solvents, with a half-life of around 5 hours, but the environmental significance of such a finding is uncertain (European Commission, 2003). Besides, octaBDE is predicted to adsorb strongly onto sediment and soil, which means that only a fraction of this PBDE will be exposed to sunlight, thus having the potential to photodegrade. No information is available on the hydrolysis of octaBDE, but it is not expected to be an important process for octaBDE in the environment.

Regarding biotic degradation, octaBDE is not readily biodegradable in standard tests (no degradation seen over 28 days) and is not expected (by analogy with other brominated diphenyl ethers) to degrade rapidly under anaerobic conditions. Nevertheless, other more highly brominated congeners (deca and nonabromodiphenyl ether) have been found to degrade anaerobically in sewage sludge, although at a very slow rate (Gerecke et al. 2005). As the evidence seems to point that no significant biotic or abiotic degradation may take place in the short term, octaBDE can be considered as persistent.

It's worth noticing that degradation by-products of polybrominated diphenyl ethers (PBDEs) can be lower brominated congeners. For instance, Ahn et al. (2006) showed that decaBDE immobilised on specific soil/sediment and mineral aerosols yielded a number of penta to triBDEs, via octaBDE as an intermediate step. This may pose an additional environmental concern, as these lower brominated diphenyl ethers are usually more toxic and much more bioaccumulative.

It can be concluded that c-octaBDE meet the screening criteria for persistency laid down in Annex D of the Stockholm Convention.

3 Bioaccumulation

The log octanol-water partition coefficient ($\log K_{ow}$) value for the commercial product has been determined to be around 6.29 (European Commission, 2003). Based on its $\log K_{ow}$ octaBDE congener would be expected to be bioaccumulative. However, the experimental result indicates that octaBDE does not bioconcentrate ($BCF < 9.5$), probably due to its large size precluding crossing of cell walls in organisms.

Nevertheless, other brominated diphenyls present in c-octaBDE have been found to have higher BCF, such as:

- around 11 700 – 17 700 for pentaBDE (European Commission, 2003),
- up to 5 600 for hexaBDE (European Commission, 2003),

Thus, lower brominated diphenyls have BCF that meet perfectly the accumulation criteria. As they are not only present in c-octaBDE (penta and hexaBDE make up to 12% of the commercial product) but may also appear as a result of the degradation of the higher brominated diphenyls, c-octaBDE can be considered to fulfil this criterion.

Besides, the EU Risk Assessment Report (European Commission, 2003) shows that brominated diphenyl ethers with bromine contents both lower and higher than octaBDE have been detected in some biota samples, notably predatory birds' eggs. Theoretically, higher brominated congeners shouldn't accumulate, as they are large molecules which are not likely to go through cell walls. However, the work of Sellström et al. (2005), shows a noticeable accumulation of these substances (hepta and decaBDE, amongst other BDEs) in wild falcons. Also Verreault et al. (2005) found certain accumulation of several octaBDE congeners (both, higher and lower brominated) in several environmental samples of two Arctic top predators, and De Wit et al. (2006) reported ubiquity of a variety of PBDEs in the Arctic. Therefore, a similar behaviour could be expected from octaBDE. In addition, other studies (Tomy et al. 2004, Stapleton et al. 2004) mention that biotransformation of PBDEs via debromination can lead to bio-accumulation parameters higher than expected, with the consequent biomagnification risk.

By using the benchmark approach proposed by Scheringer (1997) and Beyer et al. (2000) (which suggests that the intrinsic properties of a substance may be evaluated by studying those of similar substances for which more data exist), it can be concluded that octaBDE meets the screening criterion for bioaccumulation laid down in Annex D of the Stockholm Convention.

4 Potential for long-range environmental transport

In the EU Risk Assessment Report (European Commission 2003), the vapour pressure of c-octaBDE is reported to be 6.59×10^{-6} Pa at 21 °C. Brominated diphenyl ethers as a group all have low vapour pressures, the vapour pressure tending to decrease with increasing bromination. In the same report, the atmospheric half-life for octaBDE is estimated to be 76 days which means that long-range transport is possible for this substance.

Table 1: Water solubility (WS), vapour pressure (VP) and Henry's Law Constant (HLC) (at 25 °C) for c-octaBDE and currently listed POPs.

Substance	WS mg/L	VP Pa	HLC Pa m ³ /mol
c-octaBDE *	0.0005	6.59 x 10 ⁻⁶	10.6
POP-min	0.0012 (DDT)	2.5 x 10 ⁻⁵ (DDT)	0.04 (endrin)
POP-max	3.0 (toxaphene)	27 (toxaphene)	3726 (toxaphene)
POP-2 nd max	0.5 (dieldrin)	0.04 (heptachlor)	267 (heptachlor)

* EU Risk assessment report

Table 1 shows the water solubility, vapour pressure and Henry's law constant for c-octaBDE, in comparison with the maximum and the minimum for currently listed POPs. Henry's law constant, a key property to determine if there is risk of long range environmental transport for a substance, is well inside the range set by the other POPs. Considering this fact together with its half-life, it can be concluded that c-octaBDE is quite likely to undergo long range environmental transport.

There are no monitoring data from remote locations available for octaBDE itself. In general, PBDE concentrations have increased exponentially in arctic biota over the past two decades. The lower brominated congeners (e.g. pentabromodiphenyl ethers and hexabromodiphenyl ethers) present in the c-octaBDE appear to be subject to long-range environmental transport, possibly via the atmosphere, as they are widely found in sediment and biota in remote areas (Environment Canada, 2004).

Regarding other brominated congeners, hepta and decaBDE have been demonstrated to occur in airborne particles in the high arctic (Wang et al., 2005), and the modelling study by Wania and Dugani (2003, as reviewed in European Commission 2004) concluded that decabromodiphenyl ether was likely to be almost exclusively adsorbed to atmospheric particulates that would effectively control the long-range transport behaviour of the substance. Besides, the presence of decaBDE in moss in relatively remote regions of Norway, and in birds and mammals in Polar Regions, has been attributed to long-range particulate transport (European Commission, 2004).

In summary, the data available for lower and higher brominated congeners (some of them also present in c-octaBDE) show that they have potential for long-range environmental transport. Analysis of c-octaBDE's chemical properties seems to support this conclusion, as Henry's law constant is very similar to those of acknowledged POPs. Therefore, it can be expected that c-octaBDE is subject to long-range environmental transport.

5 Adverse effects

The available ecotoxicity data for the c-octaBDE product show little or no effect to aquatic organisms (short-term fish study and a longer-term *Daphnia magna* study) sediment organisms (*Lumbriculus variegatus*) and soil organisms (three species of plant and earthworms *Eisenia fetida*) (European Commission 2003). However, the Risk Assessment Report identified a risk of secondary poisoning via the earthworm route for the hexabromodiphenyl ether component in the c-octaBDE product from the use in polymer applications.

The EU Risk Assessment Report (European Commission 2003) reviews the available toxicological studies on octaBDE. In that report, the lowest no observed adverse effect level (NOAEL) from the available mammalian toxicity data for the c-octaBDE product is determined as 2 mg/kg bw/day in a developmental study with rabbits. Using this data, a predicted no effect concentration (PNEC) of 6.7 mg/kg food was derived in the EU risk assessment. Within the EU, c-octaBDE has been classified as "Toxic", due to its effects on human health, with the risk phrases "may cause harm to unborn child", and "possible risk of impaired fertility".

The presence of lower brominated diphenyl ethers in the c-octaBDE products is of concern also from the human health point of view as they are likely to have a higher potential to cause adverse effects. WHO (1994) and more recently e.g. Birnbaum & Staskal (2004) have reviewed the toxicological data on PBDEs in general.

All the abovementioned risks constitute enough evidence to consider that c-octaBDE meets the criterion for adverse effects. Additionally, the possible formation of brominated dibenzo-p-dioxins and dibenzofurans during combustion or other high temperature processes involving articles containing c-octaBDE is another cause of concern (European Commission, 2003).

6 Statement of the reasons for concern

The fact that c-octaBDE consists of several polybrominated diphenyl ethers and congeners, makes the assessment of POP characteristics more difficult than in the case of a single compound. However, it can be concluded that c-octaBDE meets the criteria for persistence, potential for long range environmental transport and potential to cause adverse effects. The situation with regards to the screening criteria for bioaccumulation is not so clear cut but the commercial product does contain at least a component group that has been confirmed by the POP RC to meet all the screening criteria (pentabromodiphenyl ether). It also contains hexaBDE, another congener with POP characteristics.

A second aspect of concern is that although the higher brominated BPDEs are persistent, there is evidence that they can degrade under some conditions. Lower brominated diphenyl ether congeners have been identified among the degradation products. Since some of the products may be more bioaccumulative and toxic than the parent compound, any significant formation would be a cause for concern.

An additional risk is the possible formation of brominated dibenzo-p-dioxins and dibenzofurans during combustion and other high temperature processes involving articles treated with c-octaBDE flame retardants.

Marketing and use of octaBDE has been prohibited recently in the EU but it is assumed still to be produced and used as a flame retardant in many countries. As octaBDE and its congeners can move far from their sources, single countries or groups of countries alone cannot abate the pollution caused by it. Due to the harmful POP properties and risks related to its possible continuing production and use, international action is warranted to eliminate this pollution.

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