Bromine Science and Environmental Forum

Comments on Track A Review of Octabromodiphenyl Ether nomination under the UNECE LRTAP POPs Protocol

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BSEF is the international organization of the bromine chemical industry, whose remit is to inform stakeholders and commission science on brominated chemicals such as flame retardants.

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Background

The Bromine Science and Environmental Forum (BSEF) is the international organization of the bromine chemical industry, whose remit is to inform stakeholders and commission science on brominated chemicals such as flame retardants. Its members are the world's largest manufacturers of brominated flame retardants used mainly as plastic additives and in coatings for textiles to improve the fire safety of these materials.

BSEF has carefully reviewed the European Commission's (EC) Risk Profile and Summary Report for Octabromodiphenyl Ether (Octa-BDE) as well as the comments prepared by the five experts that performed the technical review of this same document.

Having done so, we wish to respectfully submit our views and provide additional supplemental information that may be useful in the POPs Task Force deliberations during which Octa-BDE is discussed.

Summary

The five technical reviewers are to be thanked for their efforts to critically consider the characteristics of Octabromodiphenyl Ether (CAS Number 32536-52-0; Octa-BDE[1]) against the five criteria for determination of a POP under the LRTAP POPs protocol.

It is notable when comparing the written comments of these five reviewers that each in their own way made judgments regarding the weight of evidence necessary to make a determination that one or more of the criteria were adequately supported. Some of these judgments reached consensus on persistence and on the effects of Hexa-BDE and lower brominated congeners which may be found in commercial Octa-BDE. It is also notable that there were considerable differences not only in interpreting the technical data provided in the EC's Risk Profile, but in interpreting the charge and parameters ("ground rules") under which the reviewers were to operate.

Consequently between the five reviewers there was a wide diversity of opinion regarding the sufficiency of the Risk Profile and whether or not it supported a determination that Octa-BDE should be considered a POP within the context of the LRTAP Protocol.

The following table broadly summarizes the perspectives as a whole for each of the five major criteria for POPs determination under LRTAP.

[1] This CAS number describes a chemical structure that has 8 bromine atoms chemically bonded to the diphenyl ether molecule. This specific chemical structure is not the same as what was made and distributed in commerce as "commercial OctaBDE. See Annex I for chemical composition of the commercial product.

	Persistence	Bio-accumulation	Toxicity	Long Range Transport	Significant Adverse Effects following LRT	Conclusions
Reviewers	**Consensus :** Commercial Octa-BDE is persistent	**Consensus:** <Hepta-BDE are "B" **Consensus:** **>**Hepta-BDE are not "B"	**Consensus:** <Hepta-BDE are "T" **No Consensus:** >Hexa-BDEs	**Consensus:** <Hepta-BDE show LRT **No Consensus:** **>**Hexa-BDE	**No Consensus**[2]	**No consensus: 2 reviewers were not able to reach a clear conclusion and expressed need for further information**
BSEF	Agreed; components of commercial Octa-BDE are persistent	Agreed; components in commercial Octa-BDE with 7 or more Bromines are not "B"	Agreed; those BDEs found in commercial Octa-BDE with 6 or fewer bromine atoms fulfill the "T" criterion	Agreed; components in commercial Octa-BDE with 7 or more Bromines are not likely to undergo LRT(except when particle bound)	Information presented is insufficient to meet the weight of evidence required by EB 1998/2 2(b)	**Certain components in commercial Octa-BDE fulfill the POP criteria; Octa-BDE itself clearly does not.**

As this table indicates, there is clearly a consensus that the EC, in proposing the nomination of commercial Octa-BDE, has not demonstrated in its Risk Profile that commercial Octa-BDE as a whole would fulfill all of the criteria necessary to conclude that this substance should be added to the list of substances which are subject to this protocol. There is greater consensus around the possibility that the EC has demonstrated that HexaBDE and lower congeners may meet most (but not all) the criteria. However these were relatively minor components in Commercial Octa-BDE and are currently being addressed in the LRTAP POP process as components of commercial Penta-BDE.

Conclusion

Given that:

a) Hexa-BDE and Penta-BDE congeners of concern to the EC and the expert reviewers are already being addressed under a concurrent evaluation of Penta-BDE as a LRTAP POP,

b) these components together account for only 12% of commercial Octa-BDE,

c) the potential for bioaccumulation and long-range transport of Hepta-BDEs and Octa-BDEs is low (the major components in commercial Octa-BDE),

d) exposures far from potential sources do not indicate a risk,

e) commercial Octa-BDE was produced only in one UNECE country (US),

[2] Two reviewers indicated there is insufficient data to draw a conclusion. Three others agreed with the EC solely on the basis of the hazards and presence of lower brominated BDEs (<Octa-BDE) in biota or environmental compartments in remote regions.

f) production in the US ceased in 2004,

g) current and/or proposed regulations in North America and Europe forbid further production or use of commercial Octa-BDE,

h) the EC document did not demonstrate that all of the POPs criteria have been met (in particular for Hepta-BDE and Octa-BDE congeners); and

i) there are limited technical resources and therefore a need for prioritization when assessing and addressing nominations of candidate substances.

We would request the POPs Task Force to remove Octa-BDE (CAS #32536-52-0) from the active process of consideration as a POP.

Annex I
Composition of Commercial Octabromodiphenyl ether

(source: July 2002 final risk assessment report on Octabromodiphenyl ether conducted under the EU's Existing Substances Regulation 793/93)

Main components	% by weight			
	up to 1994[a]	1997[c]	2000[d]	2001[e]
Pentabromodiphenyl ethers (CAS 32534-81-9)	10.5-12.0[b]		1.4-12.0[b]	≤0.5
Hexabromodiphenyl ethers (CAS 36483-60-0)		5.5		≤12
Heptabromodiphenyl ethers (CAS 68928-80-3)	43.7-44.5	42.3	43.0-58.0	≤45
Octabromodiphenyl ethers (CAS 32536-52-0)	31.3-35.3	36.1	26.0-35.0	≤33
Nonabromodiphenyl ethers (CAS 63936-56-1)	9.5-11.3	13.9	8.0-14.0	≤10
Decabromodiphenyl ethers (CAS 1163-19-5)	0-0.7	2.1	0-3.0	≤0.7

Note:

a) The 1994 data are taken from WHO (1994).
b) The value is for the total amount of pentabromodiphenyl ether + hexabromodiphenyl ether.
c) The 1997 data are from a composite sample from three suppliers to the EU at that time (Stenzel and Nixon, 1997).
d) The 2000 data are taken from RPA (2001) and represent the composition reported to the OECD under the Voluntary Industry Commitment.
e) The 2001 data represent the mean composition based on random sampling of selected production lots from August 2000 to August 2001 (Great Lakes Chemical Corporation, 2001).

Annex II
Detailed Comments on Reviews

Persistence of Octabromodiphenyl Ether (Octa-BDE) in the context of EB Decision 1998/2

A substance is considered persistent under the LRTAP POPs protocol if it has a half life in water of >2 months or in soil or sediments >6 months. It can be accepted that the components of commercial Octa-BDE are persistent under environmentally relevant biotic and abiotic processes.

However with regard to persistence several reviewers introduced additional information that was not contained in the original Risk Summary prepared by the European Commission. Of note were comments made by Reviewer B regarding the potential formation of lesser brominated congeners arising from the photolytic degradation of Octa-BDE. Reviewer B appropriately notes that while laboratory experiments have demonstrated Octa-BDE's ability to photodegrade, the susceptibility to degrade under environmentally relevant conditions is reduced due to the extreme hydrophobicity of Octa-BDE. Although not explicitly stated, we believe that Reviewer B was intending to convey that this property of Octa-BDE would result in it preferentially partitioning to soils and sediments, effectively removing it from photolytic attack. This is a plausible and reasonable assumption supported by estimates of the log Koc and other physical chemical property data.

While Reviewer B appears to not see photodegradation as a major concern for the fate of Octa-BDE, he found that photodegradation studies of Deca-BDE to be relevant. Two studies are cited (an industry sponsored study done in 2003 at Purdue University and an EPA funded study from the same institution and reported in 2006). However neither of these studies provides any strong evidence for a rate of degradation in soil, sediment or as particle bound substances that is faster than the LRTAP POP criteria. In fact these and others studies have consistently shown that when the higher brominated BDEs are adsorbed to particles the rate of degradation is tremendously slower than when photolyzed in solvents or when on a transparent surface. A field study referenced by Reviewer C by Sellstrom et al on the concentration of Octa through Deca-BDEs in earthworms (see next section) also looked at the brominated BDE patterns in soils where the worms were found and concluded that there was no evidence of photolytic breakdown and goes on to state "The results…show the importance of following up laboratory studies with field studies".

Reviewer C discusses another degradation study using Deca-BDE reported by Gerecke et al in 2005. This study attempted to degrade Deca-BDE into lower brominated species in sewage sludge. While there was some appearance of increasing amounts of Octa-BDE, this only occurred after extending the residence time in the sludge reactor to 238 days (nearly 10X the normal residency time) and with the addition of "primer substances" to encourage the debromination process. Even under these extreme conditions only about 5% of the Deca-BDE was found to change to Octa or Nona-BDE's and there were no "Penta-BDE-like" substances formed. Although intended to evaluate Deca-BDE's

susceptibility for biotic transformation, this study indirectly evaluated Octa-BDE as well and is consistent with modeling and other biologically mediated degradation studies. Highly brominated (e.g. Octa-BDE and higher) BDE's will partition to the sludge and not be readily degraded to the lower BDE's which are commonly found in the environment and biota (Tetra and Penta-BDE's).

Summary: Octa-BDE is likely to be persistent in the context of the POPs Protocol.

Bioaccumulation of Octabromodiphenyl Ether (Octa-BDE) in the context of EB Decision 1998/2

A substance is considered persistent under the LRTAP POPs protocol if it has a BCF or BAF >5000 or a log Kow >5. It can be accepted that the some of the components of commercial Octa-BDE (congeners with 6 or fewer bromine atoms) are likely to be bioaccumulative and should be considered as such.

BSEF agrees completely with all five reviewers who have indicated that the evidence for bioaccumulation of components of commercial Octa-BDE that contain 8 Bromine atoms (Octa-BDE itself and higher) is inadequate, insufficient and not compelling. Therefore these substances should **not** be considered bioaccumulative.

Reviewer C cited Sellstrom et al (2005) and their work looking at Biota-Soil Accumulation Factors (BSAF) as showing "in higher brominated diphenyl ethers a high bioaccumulation factor can be expected." However a closer examination of this paper and the authors own conclusions points to something quite different. Although there was evidence of bioavailability of "higher" BDEs (Octa-BDE and above), the BSAFs were generally <1 (concentration in the earthworm was less than the concentration in the soil, in other words not highly bioconcentrating). The authors stated that the BSAF values correlated reasonably well with the log Kow; substances with the highest Kow's (e.g. Octa-BDEs) had the lowest BSAF's across the range of Kow's from 6 to 9.

Summary: Current information continues to support the view that despite having log Kow's >5, Octa-BDE and more highly brominated species are not highly bioaccumulative.

Toxicity of Octabromodiphenyl Ether (Octa-BDE) in the context of EB Decision 1998/2

A substance is considered toxic under the LRTAP POPs protocol if it has the potential to adversely affect human health and/or the environment. Current toxicity data in mammals and in aquatic species is adequate to support that the lower brominated components found in commercial Octa-BDE may be capable of causing adverse effects on humans or certain aquatic species.

Most of the reviewers and the authors of the risk profile have agreed that the concerns about environmental effects seem to be related to BDE components with 6 or fewer bromine atoms (Hexa-BDEs or lower), which is consistent with the findings of the EU's Risk Assessment which states:

> "The current approach to risk assessment implies that there is no risk of secondary poisoning (with the exception of the hexabromodiphenyl ether component), and the PEC/PNEC ratios are much less than 1 for the commercial octabromodiphenyl ether product itself. Although it appears to be persistent in the environment, the commercial substance is considered to have a low bioaccumulation potential based on the available laboratory data. It also shows no toxicity towards aquatic organisms up to the limit of water solubility, and effects in other organisms are only observed at relatively high concentrations, based on standard laboratory tests."

In regards to human health, speaking of commercial Octa-BDE as a whole, Reviewer B cited the EU Risk Assessment as stating "that for developmental toxicity concerning humans exposed via the environment the MOS (Margin of Safety) calculated is of insufficient magnitude." This Reviewer's comment implies (incorrectly) that potential risks are more widespread than actually stated in the EU Risk Assessment, which stated:

> "Comparison with the NOAEL derived from the developmental toxicity studies (2 mg/kg/day) leads for polymer processing to [MOS] ratios of 182 for local level and 4 762 at the regional level. The ratio derived for **local** exposure is of insufficient magnitude to provide reassurance that adverse health effects will not occur. "

While there were exposure related concerns expressed by the EU, these were limited to humans exposed via the environment in areas relatively close to users/processors of Octa-BDE and for workers exposed occupationally. The EU expressed no concern for developmental effects as a result of exposures **at the regional level**. Since the LRTAP protocol is concerned with exposures to POP substances occurring in remote areas, the EU's comments regarding risks on a regional basis should be given more weight than those concerning risks arising near the source of exposure (the "local environment").

Summary: On purely a hazard basis, it can be accepted that commercial Octa-BDE contains substances that exhibit adverse effects on mammals and aquatic life. But when placed in the context exposure via the environment, there is little evidence that the levels identified in remote areas will present a risk of serious adverse effects (discussed later in more detail).

Long Range Transport of Octabromodiphenyl Ether (Octa-BDE) in the context of EB Decision 1998/2

A substance is considered to exhibit characteristics of susceptibility to long range transport if it has a vapor pressure <1000 Pa and a half life >2 days or there is monitoring data indicating its presence in remote regions. Current information supports the view that commercial Octa-BDE contains lower brominated components that exhibit these characteristics. The higher BDEs (Hepta-BDE and higher) do not exhibit the physical and chemical characteristics of a classic POP (such as PCB's). However there are reports of finding very low concentration of some highly brominated congeners in remote areas. This has been attributed to their adherence to dust particles carried in the global atmosphere.

The EC Risk Profile states "Octa-BDE has not been detected in the monitoring studies from remote regions but polybrominated diphenyl ethers of lower and higher bromination ….are frequently found in such monitoring studies, suggesting significant long range transport." It is on this premise (finding lower and higher PBDE's) that the EC and, several reviewers, have determined that commercial Octa-BDE should be susceptible to long range transport. However, other reviewers did not feel that this information was necessarily adequate to demonstrate that Octa-BDE and higher BDE's were susceptible on the basis of physical property data, particularly in relation to other classic benchmark chemicals which are known to exhibit long range transport.

Reviewer C points out that for the higher brominated PBDE's, the Henry's Law constant indicates volatilization from water is not likely, something that can't be said for more traditional POPs.

Reviewer E summarizes this well in their concluding statement regarding the EC's findings on LRT:

> "Commercial Octa-BDE does not exhibit the semivolatile properties and propensity for LRAT that are the hallmarks of most problematic POPs. Hexa-BDE has been detected more regularly and at higher concentrations in remote locations and may be more likely subject to LRAT. "

This perspective is consistent with the work by Wania and Dugani reported in their article: Assessing the long-range transport potential of polybrominated diphenyl ethers: A comparison of four multimedia models Environ. Toxicol. Chem. June 2003. The authors state:

> "A comparison of LRTP estimates for the PBDEs with those of benchmark chemicals (PCB's) suggests that the lower brominated congeners have a LRTP comparable to that of PCBs known to be subject to significant LRT, whereas the highly brominated congeners have a very low potential to reach remote areas." (Emphasis added)

The presence of lower brominated (Hexa-BDEs and lower species) in remote regions is therefore potentially as a result of similar transport methods seen with PCBs and other classic POP substances. The presence of higher (including Hepta and Octa-BDE) is best explained as a result of movement of particle or migratory species and not due to being semi-volatile like the classic POPs. Reviewer E points out that several recent (2004) publications have demonstrated that transport of higher brominated substances on particles is distinctly different than transport resulting from global distillation of semi-volatile members of the family of BDEs. Reviewer E goes on to say:

> "Finding local concentrations of BDE-183 (a Hepta-BDE) at remote locations is not unexpected and parallels the movement of numerous other contaminants at low levels on dust that can be measured about the detection limit of modern laboratory equipment."

Summary: The available information supports a conclusion that the higher brominated congeners (Hepta-BDE and Octa-BDE):

a) do not have the physical properties that make them susceptible to long range transport and
b) are not present in substantial quantities in remote regions (particularly in relation to substances traditionally know to be susceptible to LRT).

Likelihood of Significant Adverse Effects Resulting from Long Range Atmospheric Transport of Octabromodiphenyl Ether (Octa-BDE) in the context of EB Decision 1998/2

Of the criteria technical reviewers had to work with in making a determination about the sufficiency of the Risk Profile in determining if a substance should be included in the LRTAP POPs protocol, this one has been the most problematic in previous discussions of other substances and it appears to be the same for commercial Octa-BDE.

Some guidance on interpretation of EB 1998/2 Paragraph 2(b) was provided by the WGSR at their October 2005 meeting where they proposed to the Executive Body that "in view of the policy intent of paragraphs 2 (a) and 2 (b) of its decision 1998/2, the phrase "significant adverse human health and/or environmental effects" is understood to mean "likely to be of concern to environmental and human health regulatory agencies". With this in mind, the WGSR indicated an expectation that the technical reviewers would provide an explanation of their basis for deciding a given substance was likely to cause significant adverse effects following long range transport.

Based on a clear lack of consensus among the five reviewers, it seems apparent that the Risk Profile failed to demonstrate that "sufficient information exists to suggest that the substance is likely to have significant adverse human health and/or environmental effects as a result of its long-range transboundary atmospheric transport".

Reviewers A, B & C concluded that the EC's Risk Profile provided "sufficient information" and their comments indicate they did so on the basis of 1) persistence of commercial Octa-BDE in the environment, 2) the adverse effects as reported in toxicological studies, 3) the presence of certain components in the commercial Octa-BDE which are bioaccumulative and 4) the presence of certain BDEs (e.g. Penta-BDEs, Tetra-BDEs) found in remote locations.

In other words, these reviewers came to the conclusion that the potential to exhibit PBT characteristics and the presence in remote regions is sufficient information to suggest that a substance is likely to have significant adverse effects as a result of long range transport.

However, if this were the intent of the Protocol, paragraph 2(b) of EB 1998/2 would not be needed. But Paragraph 2(b) requires that an evaluation be made not only of the relevant properties identified in Paragraph 1(a-d) but a determination whether or not the substance can be expected to cause effects on human health or the environment in these remote regions. Reviewer E shares this view and actually states in his comments that "The [Octa-BDE Risk Profile] focuses on addressing the POPs screening criteria, but does not directly address the EB Decision requirement for the risk profile and technical review to address requirements of EB 1998/2 Paragraph 2(a) and 2(b)."

On that basis, BSEF agrees completely with the particular PBT facts (as previously stated in these and our prior comments). However, the approach of reviewers A, B & C did not:

a) attempt to integrate/compare the concentrations in the environment as a result of long range atmospheric transport relative to the effects concentrations,

b) consider that the specific brominated BDE substances found in remote locations are far more abundant in the commercial Penta-BDE, which was made in much larger quantities and much more widely used than commercial Octa-BDE,

c) take into account that commercial Octa-BDE is no longer made or supplied for use in the UNECE region,

d) explain why environmental and human health regulatory agencies would be concerned about commercial Octa-BDE in light of these circumstances.

Therefore it is our view there is not sufficient information to meet the conditions of Paragraph 2 (b).

It is important to note that BSEF is not alone in this perspective. Both Reviewers D and E expressed their views that there was nothing in the EC's dossier that convinced them that it is likely that serious adverse effects to human health or the environment would arise in remote regions. In fact Reviewer E points out that the primary document used to support the EC's perspective concluded that the risk ratios (PEC/PNEC ratios) for Octa-BDE exposures in the regional environment were all acceptable. Therefore if such is the case on a regional basis, it is difficult to envision how the risks would become unacceptable in more remote regions where exposures would be several orders of magnitude lower.

With respect to human health, the EC's primary reference (the EU Risk Assessment) indicates that there were a small number of exposure related concerns expressed by the EU. However, like the situation with the environmental risks, these were limited to humans exposed via the environment in areas relatively close to users/processors of Octa-BDE and for people handling Octa-BDE in the workplace.

Summary: The EC and those reviewers that supported the EC view relied entirely on hazard information and the presence of selected BDEs in remote areas but clearly stopped short of integrating this into a risk characterization (either qualitative or quantitative). This is not consistent with the wording of EB 1998/2 or guidance that has been provided by the WGSR.

Given the EU's lack of concern for adverse effects on a regional basis in their own risk assessment of commercial Octa-BDE, it is reasonable to conclude there should be even less concern in remote areas where concentrations of Octa-BDE congeners are several orders of magnitude lower.

Therefore, neither the EU's Risk Profile or the 5 reviewers provide sufficient information to support a conclusion that in remote areas, exposures to the Hepta- and Octa-BDE components in commercial Octa-BDE areas are likely to result in serious adverse human health or environmental effects as a result of long range transport.