

EMEP CONTRIBUTION TO THE PREPARATORY WORK FOR THE REVIEW OF THE CLRTAP PROTOCOL ON POPs

NEW SUBSTANCES:

Model assessment of potential for long-range
transboundary atmospheric transport and
persistence of Hexabromocyclododecane
(HBCDD)

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Model assessment of potential for long-range
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Hexabromocyclododecane (HBCDD)

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INTRODUCTION

Hexabromocyclododecane (HBCDD) is one of the most used brominated flame retardants throughout the world. According to the data of Bromine Science and Environmental Forum (BSEF) (<http://www.bsef.com>), production of HBCDD in Europe in 2001 amounted to 9500 tonnes that is more than 50% from world production. HBCDD is classified as a High Production Volume Chemical. The main use of HBCDD is as an additive-type flame retardant for extruded and expanded polystyrene foam. Other applications include crystal and high-impact polystyrene, resins, adhesives, and coating. HBCDD is a flame retardant for upholstery textiles [*HPV Data Summary and Test Plan for Hexabromocyclododecane (HBCDD)*, 2005].

HBCDD is a potential candidate for the inclusion into the Protocol on POPs to the Convention on Long-Range Transboundary Air Pollution (Twenty-sixth session of the Executive Body held in Geneva in December 2008).

This Technical Note presents additional information for the evaluation of HBCDD as a potential new POP in accordance with the two criteria: potential for long-range transboundary atmospheric transport (LRTP) and persistence. The work is carried out by the request of the Executive Body for CLRTAP

Technical HBCDD mixture consists of a number of stereoisomers. Main stereoisomers, namely α -HBCDD, β -HBCDD and γ -HBCDD have different physical-chemical properties which lead to the different character of their behaviour in the environment. The most complete information on physical-chemical properties of HBCDD stereoisomers is available for γ -HBCDD. The fraction of this stereoisomer in technical HBCDD mixture is about 80%. For these reasons we have included this stereoisomer in the investigation to illustrate differences in the evaluated parameters between technical mixture and particular isomers.

For the evaluation of LRTP and persistence of HBCDD, MSCE-POP multicompartiment hemispheric transport model is used. Detailed information on the structure of the model and parameterisation of the media processes can be found in the EMEP/MSCE reports [see *Gusev et al.*, 2005 and citations therein] and on the Internet (<http://www.msceast.org>).

To estimate LRTP and persistence for HBCDD, the model calculation of its atmospheric transport from a conventional emission point source located in Europe is made for one-year period. Information on physical-chemical properties and degradation rates of this pollutants used for modelling is presented in Annex B.

Presented information is divided into four parts.

1. To evaluate **LRTP** of HBCDD, two numerical characteristics are calculated. The first one is residence time in the atmosphere (**Half-life in air**_{calc} ($T_{1/2}^{air}$)) obtained with allowance of all processes removing the given pollutant from the atmosphere. The second is **Transport Distance (TD)** that is the distance from the source at which annual mean atmospheric concentration of the chemical drops 1000 times compared with the concentration near the source. Additional information on this criterion for HBCDD is provided by the spatial distribution of air pollution caused by the considered conventional point source.

2. **Persistence** in the environment is evaluated by **Half-life in the environment** ($T_{1/2}^{env}$) estimated for HBCDD on the basis of the model simulation of its atmospheric transport taking into account deposition processes, degradation and exchange of the pollutant between main environmental media.

3. The values of TD and $T_{1/2}^{env}$, calculated by the model depend on model characteristics (such as resolution, spatial coverage, etc.). To exclude model peculiarities in evaluating LRTP and persistence of HBCDD with the help of the model dependent TD and $T_{1/2}^{env}$, a comparison of their numerical values against those obtained for an adequately studied “**benchmark substance**” is presented.

4. In **conclusion**, the calculated numerical characteristics of LRTP and persistence of HBCDD are given in relation to the indicative criteria outlined in the Executive Body Decision 1998/2.

Since measurement data in remote regions are mentioned among the criteria for recognizing a substance as a POP, a short review of existing data on levels of HBCDD measured in environmental samples is presented in Annex A to the report. Annex B includes the summary of HBCDD physical-chemical properties used for modelling.

1. LONG-RANGE TRANSPORT POTENTIAL

According to the Executive Body Decision 1998/2 the LRTP criterion for the evaluation of new substances as potential candidates for the inclusion into the Protocol on POPs is characterized by indicative numerical values of their vapour pressure and atmospheric half-life due to degradation. In addition to this criteria model simulations allow evaluating two more characteristics of LRTP, namely half-life in the atmosphere due to all environmental processes and transport distance.

The half-life of HBCDD in the atmosphere can be estimated with the help of modelling as residence time in the atmosphere (Half-life in air_{calc} ($T_{1/2}^{air}$)) obtained on the basis of simulation of their atmospheric transport taking into account not only degradation process in this medium but also all other removal processes. Modelling approach makes it possible to distinguish the most important processes affecting LRTP of a particular considered pollutant in the atmosphere. Additional information on LRTP based also on the model calculations of atmospheric transport is provided by the spatial distribution of air pollution. The latter allows estimating Transport Distance (TD), characterising LRTP of HBCDD as the distance from the source at which annual mean atmospheric concentrations drop 1000 times compared with the concentration near the source. It should be noticed that model estimations of LRTP characteristics takes into account also the process of multi-hop transport (that is, repeating cycle of atmospheric transport, accumulation in environmental media and subsequent re-emission to the atmosphere).

This section contains the main results on evaluation of LRTP criterion for technical HBCDD mixture and stereoisomer γ -HBCDD with the help of above-mentioned characteristics obtained on the basis of the MSCE-POP model calculations.

1.1. Residence time in the atmosphere

To estimate the residence time in the atmosphere, the model calculation of HBCDD atmospheric transport (both for technical HBCDD mixture and for γ -HBCDD) with allowance of such processes as degradation in the atmosphere, partitioning between particulate and gas phases, dry and wet deposition of particles and gaseous exchange with various types of underlying surface is carried out. Emissions to the atmosphere are assumed to be 1 tonne per year from a conventional point emission source located in Europe (5°E; 47.5°N). On the basis of this calculation annual atmospheric balance for HBCDD emitted to the atmosphere is estimated (see Fig. 1).

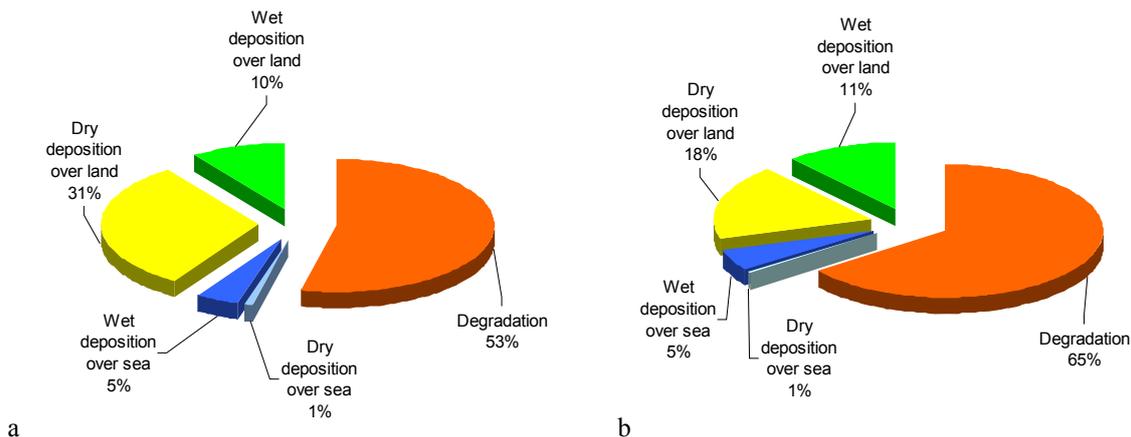


Fig.1. Calculated HBCDD annual balance of removal from the atmosphere:
a – technical HBCDD mixture, *b* – γ -HBCDD

It should be taken into account that the long-range atmospheric transport of HBCDD is affected not only by degradation rate but also by the form in which the substance is present in the atmosphere (gaseous or particle-bound) since particle-bound form degrades in the atmosphere rather slowly. For this form the process of removal from the atmosphere will be governed by deposition velocities to various types of underlying surface.

As seen from the calculated balance, the main process of HBCDD removal from the atmosphere is degradation. Within a year more than a half of the pollutant of the total removal is degraded in the atmosphere (about 53% for HBCDD technical mixture and about 65% for γ -HBCDD). However, wet and dry deposition processes also contribute considerably to the removal from the atmosphere (30 – 40% of total removal are deposited to the land and about 6% is deposited to the sea surface). The presented balance is governed not only by the physical-chemical properties of the considered substance (degradation rate constants, subcooled liquid-vapour pressure values and Henry's law constants) but also by the type of underlying surfaces along the preferable transport pathways and some meteorological parameters.

Calculated value of residence time in the atmosphere (Half-life in $\text{air}_{\text{calc}} (T_{1/2}^{\text{air}})$) occurs to be of about **3 days** for HBCDD (both for technical mixture and γ -stereoisomer).

The numerical value of this characteristic of LRTP for HBCDD mixture and γ -HBCDD meets the existing criterion (atmospheric half-life is greater than two days).

1.2. Spatial distribution of pollution from conventional emission source

Additional information on LRTP of the considered chemicals is provided by the spatial distribution of air pollution by HBCDD estimated by modelling on the basis of their atmospheric transport from the conventional point emission source. Spatial distributions of concentrations of technical HBCDD mixture and of γ -HBCDD in the Northern Hemisphere and in the EMEP domain are given in Figs 2 and 3 below. For convenience, air concentrations are presented in the relative units i.e. as ratios of the concentration calculated in the particular point to the concentration near a source (basic value).

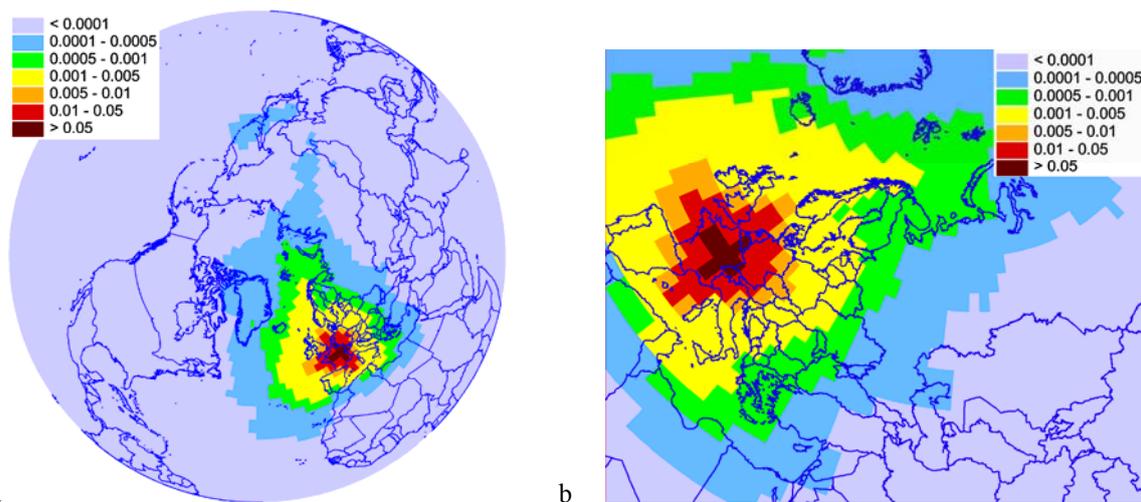


Fig. 2. Spatial distribution of concentrations of technical **HBCDD** mixture in the surface air in the Northern Hemisphere (a) and in the EMEP domain (b), relative units

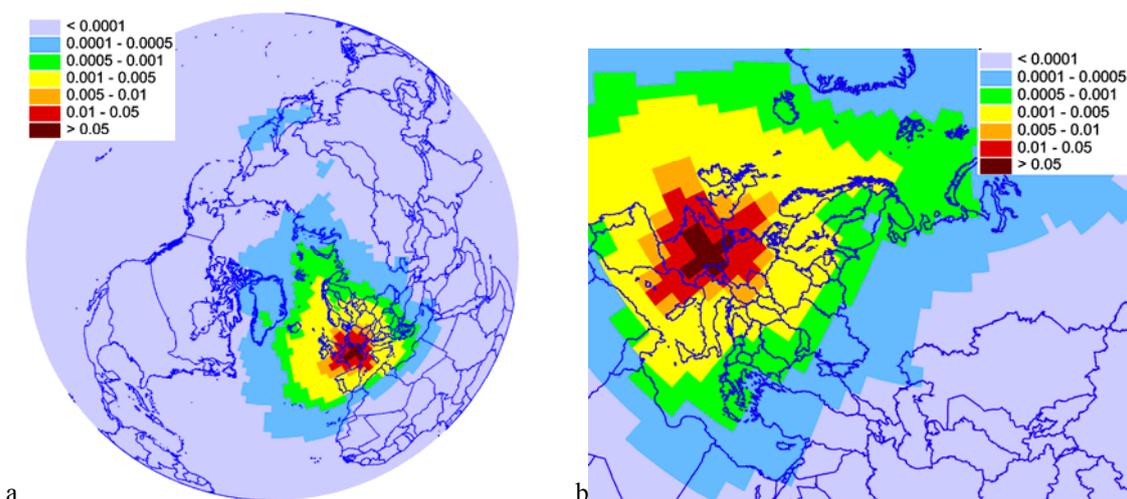


Fig. 3. Spatial distribution of γ -**HBCDD** concentrations in the surface air in the Northern Hemisphere (a) and in the EMEP domain (b), relative units

From the above figures it is seen that spatial distribution of the technical HBCDD mixture and for γ -HBCDD are rather close to each other. The European HBCDD source shows noticeable influence within the European region. The long-range atmospheric transport of this pollutant contributes also to the contamination of the Atlantic region and, partly, the Arctic (Fig. 2a).

The pollution by HBCDD from the considered point source covers the bulk of the area in the EMEP domain (Fig. 2b). The areas where concentrations drop down less than 1000 times reach the Scandinavian Peninsula, the Atlantic Ocean and the Arctic. These areas also include the Mediterranean Sea and partly northern Africa. The levels of air concentrations over many European countries vary from 0.005 to 0.01 of the basic value. The levels of air concentrations amounting from 0.01 to more than 0.05 of the basic value are mostly characteristic of France, Switzerland, Belgium and the Netherlands.

1.3. Transport Distance

At present several model approaches to the evaluation of LRTP of a pollutant by means of different numerical characteristics have been developed and introduced in [Scheringer and Berg, 1994; Scheringer, 1996; Bennett et al., 1998; van Pul et al., 1998; Wania, 1998; Rodan et al., 1999; Beyer et al., 2000; Beyer et al., 2001; Beyer and Matthies, 2001; Leip and Lammel, 2004, etc.]. For example such characteristics are spatial range, spatial scale, transport distance, characteristic travel distance, travelling distance, and so on. In this assessment in addition to the atmospheric residence time of HBCDD, another characteristic demonstrating LRTP of the considered substance is provided by the model estimate of its *Transport Distance* (TD). Numerical values of TD are defined with the help of Eq. 1 as the average distance from the source at which annual mean atmospheric concentration of a chemical in question drops 1000 times compared with the concentration near the point source (as an example See Fig. 3):

$$TD_{0.001} = \sqrt{\frac{S_{0.001}}{\pi}} \quad (1)$$

where $S_{0.001}$ is the area covered by air concentrations dropped less than 1000 times.

It should be noted that such an approach is similar to that suggested in [Rodan et al., 1999].

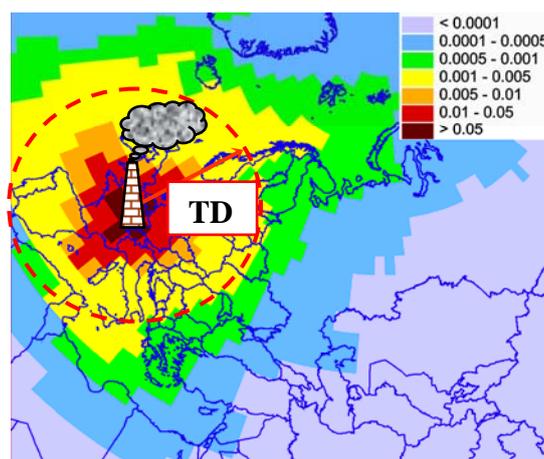


Fig. 3. Definition of the transport distance

The value of TD depends on all of the processes removing the pollutant from the atmosphere such as deposition to the underlying surface (land, sea) and atmospheric degradation. The calculated value of TD for HBCDD together with the half-life in the atmosphere are presented in Table 1.

Table 1. Characteristics of LRTP (*Half-life in air_{calc}* and *Transport Distance*) calculated for HBCDD

Substance	$T_{1/2}^{air}$, days	TD , km
Technical HBCDD mixture	2.6	1883
γ -HBCDD	3.0	1994

Calculations show that the characteristics of LRTP for technical HBCDD mixture and γ -HBCDD stereoisomer are quite close to each other.

The calculated numerical value of $T_{1/2}^{air}$ meet the LRTP criteria of Executive Body Decision 1998/2.

2. PERSISTENCE

The behaviour of a substance in the environment to a large extent is determined by its persistence not only in the atmosphere but also in other environmental media. Its redistribution between air and soil, seawater, sediment, vegetation etc is important for its ability to cause adverse effects to the environment and to be accumulated in the food chain. In this process the main characteristics of a substance is its half-life in the medium under consideration.

In compliance with the Executive Body Decision 1998/2 the persistence of “new substances” in terms of their possible inclusion into the Protocol on POPs is demonstrated by indicative numerical values of their half-life in water, which should be greater than two months, or half-life in soil, which should be greater than six months, or half-life in sediments, which should be greater than six months also.

According to the physical-chemical properties of the considered HBCDD species (technical mixture and γ -HBCDD stereoisomer) used for modelling, half-life in water is about 5 years, so that these substances meet the persistence criteria.

However, in addition to these parameters characterizing the persistence for particular media, multimedia model calculations allow estimating complementary characteristics of persistence in the whole environment - overall residence time or overall environmental persistence [Scheringer, 1996; Webster *et al.*, 1998; Gouin *et al.*, 2000, Klasmeier *et al.*, 2006 etc.]. In this assessment such characteristic as *Half-life in the environment* ($T_{1/2}^{env}$) is estimated for the considered pollutant on the basis of the model calculations of its atmospheric transport taking into account deposition processes, degradation and gaseous exchange between main environmental media.

The model assessment of persistence in the environment for HBCDD is demonstrated by the numerical value of $T_{1/2}^{env}$ calculated with the help of Eq.2 as an inverse value of weighted mean of degradation rate constants k_j in the environmental media (atmosphere, soil, seawater, vegetation, sediments) with weights being the fractions f_j of a pollutant accumulated in j -th medium:

$$T_{1/2}^{env} = \ln 2 / \sum k_j \cdot f_j \quad (2)$$

Here fractions f_j are evaluated on the basis of the model calculations.

Thus, the value of *Half-life in the environment* is affected by the distribution of the total environmental content of HBCDD between main environmental media and the values of its half-life in each particular medium due to degradation process.

The fractions of HBCDD total content in the environment contained in main environmental media (annual means) and relative fractions of the pollutant degraded in each media during a year were obtained on the basis of model simulations for one-year period. It should be noted that seawater includes pollutant content in sediments, and only degradation in forest litter is considered as degradation in vegetation. The distribution of total environmental content of technical HBCDD mixture and γ -HBCDD between environmental media is compared with the amount of pollutant degraded in each media during a year in Fig.4.

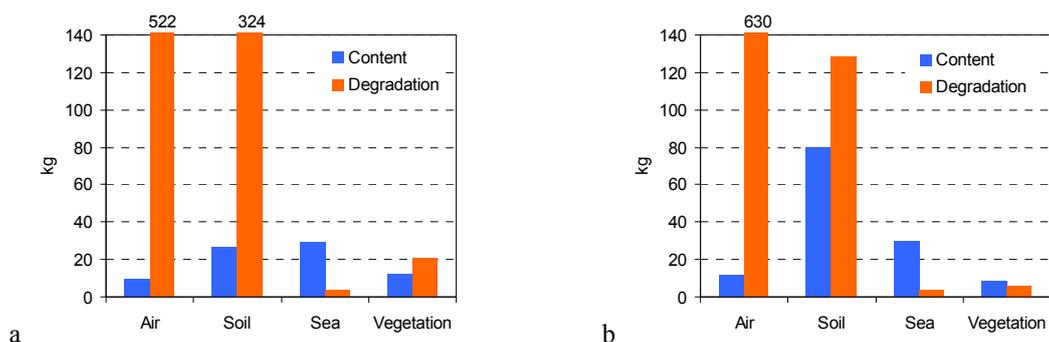


Fig. 4. Annual degradation and media content for HBCDD (a – technical HBCDD mixture, b – γ -HBCDD stereoisomer). Media content is presented as an average over the year.

For technical HBCDD mixture amount of the pollutant accumulated in soil and seawater are approximately the same whereas for γ -HBCDD stereomer the main part of the pollutant is accumulated in soil. The difference between the distribution in the environment media for the two considered HBCDD species is attributed to the difference of soil degradation rates for HBCDD technical mixture (half-life about 35 days) and γ -HBCDD (112 days) [Hexabromocyclododecane as possible POPs, 2008]. Consequently, the degradation of HBCDD technical mixture occurs both in air and soil whereas the degradation of γ -HBCDD is mainly due to the degradation in the atmosphere. The contribution of atmospheric degradation to total degraded mass equals 60% for technical HBCDD mixture and 82% for γ -HBCDD. The contributions of soil degradation are also considerable – 17% for technical HBCDD mixture and 37% for γ -HBCDD.

To evaluate the ability of the considered pollutants to be persistent in the environment, the values of **Half-life in the environment** were estimated on the basis of calculated fractions of total environmental HBCDD mass contained in the environmental media and the values of half-lives in the considered environmental compartments in accordance to formula (2). Obtained estimates of $T_{1/2}^{env}$ are presented in Table 2.

Table 2. Characteristics of Persistence (Half-life in environment) and half-lives of HBCDD in different environmental media

Substance	$T_{1/2}^{env}$, days	Half-life, days		
		Air	Water	Soil
Technical HBCDD mixture	10.7	2	1920	35
γ -HBCDD	19.9	2	1920	111.5

According to the calculated value of *Half-life in the environment*, persistence of HBCDD in the environment can be characterised as relatively low. The highest persistence is characteristic of γ -HBCDD, the lowest – for technical HBCD mixture. For the interpretation of the obtained results it should be taken into account that the values of overall persistence calculated by the model considerably depend on the location of a point source chosen for simulations. In the case if transport from this source passes over water bodies the value of environmental half-life can be essentially greater. Due to relatively high stability of HBCDD in water, this pollutant may cause long-term adverse affect through this medium.

3. COMPARISON WITH BENCHMARK SUBSTANCE

Since the numerical values of $T_{1/2}^{air}$ and $T_{1/2}^{env}$ of particular chemicals are model dependent, one of the possible ways to diminish uncertainties in evaluating new substances proposed by *Scheringer* [1997] and *Beyer et al.* [2000] and discussed at the OECD/UNEP Workshop on the Use of Multimedia Models for the Estimation of Environmental Persistence and Long-Range Transport (Ottawa, Canada, 2001) was to use a “benchmark” approach. This approach suggests that model results on LRTP and persistence are used to compare the pollutants under study with some adequately studied “benchmark substance” with known values of the considered parameters.

This procedure enables assessment of “new substance”, by considering its ranking in terms of persistence or LRTP among the well-known benchmark chemicals. Examples of chemicals ranking and classification approach are described by *Matthies et al.* [1999], and *Bennett et al.* [2001]. Relative approach may also be applicable when the desired outcome is the screening of a large set of existing chemicals, to establish priority classes of substances for further assessment or action.

The comparison of calculated characteristics of LRTP and persistence for HBCDD against those obtained for a benchmark pollutant is presented in this subsection. Benzo[a]pyrene (B[a]P) is used as a benchmark substance. Characteristics of its behaviour in the environment are well studied and clearly meet the UN ECE criteria for POPs. It is already included in the Protocol on POPs and is considered as pollutant of regional concern. All calculations were performed for one-year period from a conventional point source with one and the same location in Europe and one and the same emission intensity.

The considered HBCDD species and B[a]P have been ranked in ascending order according to their values of *Transport Distance* (Fig. 5a) and *Half-life in the environment* (Fig. 5b).

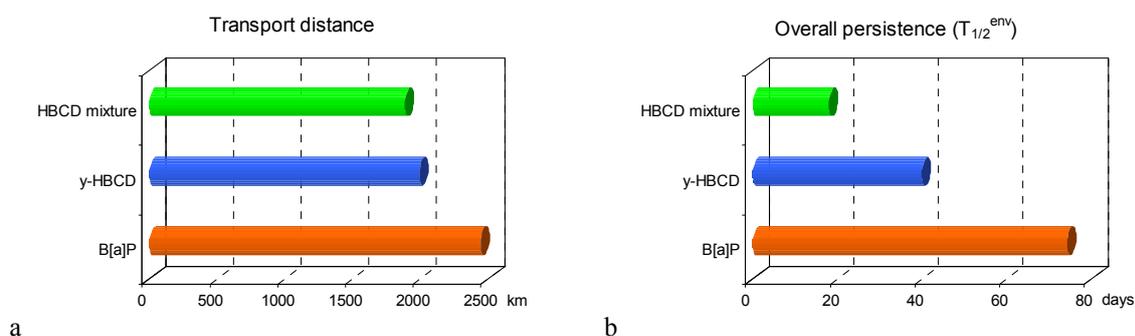


Fig. 5. *Transport distance and Half-life in the environment* calculated for HBCDD species and B[a]P

According to the model calculations of *TD*, the values of Transport Distance for considered HBCDD species are close to that of B[a]P. Hence, hexabromocyclododecane can be classified as a pollutant of regional concern.

It can be seen that values of half-life in the environment for HBCDD and B[a]P are of the same order of magnitude. However, high persistence of the considered substance in water can lead to the values of $T_{1/2}^{env}$ close to that for B[a]P. Thus, from the viewpoint of environmental persistence HCBDD can also be classified as a pollutant of regional concern.

4. CONCLUDING REMARKS

As physical-chemical properties of technical HBCDD mixture are close enough to that of γ -HBCDD, the comparison of HBCDD properties with the LRTP and persistence criteria outlined in the Executive Body Decision 1998/2 with addition of the MSCE-POP model estimates is performed for technical HBCDD mixture (Table 3).

Table 3. Characteristics of LRTP and persistence of HBCDD presented in available published data and obtained by modeling in relation to the indicative criteria outlined in the Executive Body Decision 1998/2

Criterion	Criterion values	Meets the criterion (Yes/No)	Characteristics of Technical HBCDD mixture	Remarks
Potential for Long-Range Transboundary Atmospheric Transport				
Vapour pressure, Pa	< 1000	Yes	6.27×10^{-5} at 21 °C	Presented in IUCLID Data Set, 2005 ¹ , HPV Data Summary and Test Plan for Hexabromocyclododecane (HBCDD) ² , HSDB ³ .
Half-life in air, days	>2	Yes	$1.75^2 - >3.0^3$	Half-life estimated on the basis of rate constant for reaction with OH radical
Half-life in air_{calc}, days		Yes	2.6	$T_{1/2}^{air}$ calculated by MSCE-POP
Persistence				
Half-life in water, months	> 2	Yes	32 - 340667 ²	Half-life due to volatilization from water, estimated (EPI win, V.3.04) ² : River – 2,631 years; Lake – $2.8 \cdot 10^4$ years
Half-life in soil, months	>6	No	0.2 – 4.0	Presented in IUCLID Data Set, 2005 ¹ , HPV Data Summary and Test Plan for Hexabromocyclododecane (HBCDD) ² SVHC Support Document, ECHA, 2008 ⁴
Half-life in sediment, months	>6	No	0.04 – 6.4	Presented in Risk Assessment. Hexabromocyclododecane. Final Draft ⁵
Half-life in the environment, months	-	-	10.7 days	$T_{1/2}^{env}$ calculated by MSCE-POP

¹ IUCLID Data Set [2005] 201-15946, 88 pp.

² HPV Data Summary and Test Plan for Hexabromocyclododecane (HBCDD), CAS No. 3194-55-6, Prepared by American Chemistry Council, Brominated Flame Retardant Industry Panel (BFRIP), 1300 Wilson Blvd Arlington, VA, Original Submission: December 20, 2001, Updated: September, 2003 and March, 2005, 52 pp.

³ HSDB (Hazardous Substances Data Bank, Toxnet) [2008] <http://toxnet.nlm.nih.gov>

⁴ SVHC Support Document, ECHA [2008], 41 pp.

⁵ Risk Assessment. Hexabromocyclododecane. Final Draft [2008] 480 pp.

The results of the model assessment demonstrate the considerable long-range atmospheric transport potential (atmospheric half-life is 2.6 days and relatively low persistence of HBCDD (10.7 days). However, the values of half-life in soil obtained in various experiments vary essentially and, hence, the conclusion on weak persistence of HBCDD in the environment is of a preliminary character.

Transport distance and overall persistence for particular stereoisomers can essentially differ from those for the technical HBCDD mixture. For instance, half-life in the environment calculated for γ -HBCDD equals 19.9 days, which is almost twice higher than the half-life for HBCDD technical mixture.

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LEVELS OF HBCDD MEASURED IN ENVIRONMENTAL SAMPLES

The available data on the environmental concentrations of HBCDD are presented below.

Air concentrations

First data on the presence of HBCDD in the environment were obtained in the beginning of 90th last century. In 2002 Cynhia A. De Wit has published a review on environmental levels of brominated flame retardants [*de Wit, 2002*].

Most widely the presence of HBCDD in the atmosphere of various Sweden regions in 2000 – 2001 was investigated by [*Remberger et al., 2004*]. HBCDD was detected not only in the effluent gases of ventilation systems of enterprises producing of flame retarded extruded polystyrene plastics, textile industry and landfill for construction and demolition waste, but also in background regions in Sweden and Finland. The obtained data are summarized in Table A1.

The investigations of HBCDD content in the atmosphere of 5 various regions in the USA were conducted in 2002 –2003. The obtained concentrations were rather uniform not exceeding – 10 $\mu\text{g}/\text{m}^3$ almost everywhere [*Hoh and Hites, 2005*], see Table A1.

Japan Environmental Agency (JEA) initiated monitoring of application or brominated flame retardants and their occurrence in the environment in the middle 80th. However, HBCDD was not included to the program of investigation of air pollution by new persistent pollutants [*Watanabe and Sakai, 2003*].

The data on HBCDD content in urban regions of Southern China, Guangzhou, were published in 2008. The levels of observed concentrations in this region was somewhat lower [*Yu et al., 2008*] (see Table A1).

The data presented in Table A1 give general impression of contamination levels of HBCDD in the atmosphere but do not allow evaluating the fractions of particular stereoisomers in the mixture. Relations between stereoisomers in the atmosphere were examined in papers by American and Chinese specialists only [*Hoh and Hites, 2005* and *Yu et al., 2008*]. The data on stereoisomer content in the atmosphere over Europe are not available in present.

Water concentrations

Monitoring data for HBCDD in water are limited. By the data from [*Remberger et al., 2004*] HBCDD in water varied from 3 ng/L at the landfill site to 31 ng/L at the public laundry. For seawater, last version of [*Risk Assessment, Final Draft, 2008*] contains the data on HBCDD content on suspended particles in the range from 74 to 472 $\mu\text{g}/\text{kg}$ in the region of Western Scheldt and Term canal (Terneuzen, the Netherlands), respectively, in the vicinity of a production plant.

Soil concentrations

In Sweden the soil samples that were taken outside the extruded polystyrene production plant showed concentrations HBCDD varying from 140 to 1300 $\mu\text{g}/\text{kg dw.}$, and decreased with increasing distance from facility [*Remberger et al., 2004*]. In Norway soil samples collected in 2005 in the Ålesund area, reflecting HBCDD input via deposition were 4 $\mu\text{g}/\text{kg dw}$ (Spjelkavik), 2 $\mu\text{g}/\text{kg dw}$ (Brevik) and 0.1 $\mu\text{g}/\text{kg dw}$ (Godøy) for the sum of α -, β – and γ -HBCDD. γ -HBCDD contributed most to the total HBCDD concentrations [*Hexabromocyclododecane as a possible global POP, 2008*].

Table A1. Levels of HBCDD in air

Sampling location	Sampling data/period	HBCDD, concentrations, pg/m ³	References	Remarks
Sweden, Ammarnäs	1990-1991	6.1	<i>de Wit, 2002</i>	Southern tip of Gotland in the Baltic Seac
Sweden, Hoburgen	1990-1991	5.3	<i>de Wit, 2002</i>	
Sweden, Stockholm,	21.08.2000 - 18.09.2000	76	<i>Remberger et al., 2004</i>	Schoolyard
Sweden, Stockholm	05.01.2001-02.02.2001	610	<i>Remberger et al., 2004</i>	Hudiksvallsgatan 2
Finland, Pallas	25.09.200-02.10.2000	3	<i>Remberger et al., 2004</i>	Northern Finland
	04.01.2001-11.01.2001	2		
Sweden, Aspreven	19.08.2000-18.09.2000	280	<i>Remberger et al., 2004</i>	South of Stockholm
	29.01.2001-12.02.2001	25		
Sweden, Rörvik	28.08.2000-18.09.2000	5	<i>Remberger et al., 2004</i>	West coast
	29.01.2001-12.02.2001	<1		
USA, Sleeping Bear Dunes in Michigan	12.10.2003	8.0	<i>Hoh and Hites, 2005</i>	
USA, Chicago in Illinois	01.08.2003	9.6		
USA, Bloomington in Indiana	09.07.2003	3.6		
	12.10.2003	2.9		
	11.12.2003	2.1		
USA, Rohwer in Arkansas	11.09.2003	11		
USA, Cocodrie in Louisiana	23.12.2003	2.4		
China, city Guangzhou	15-30.06.2004	<u>2.20 – 3.92</u> 3.09	<i>Yu et al., 2008</i>	Typical urban site
		<u>0.28 – 1.18</u> 0.69		Industrial site 1
		<u>0.40 – 1.78</u> 0.89		Industrial site 2
		<u>1.14 – 2.25</u> 1.61		Site background sity

PHYSICAL-CHEMICAL PROPERTIES OF HEXABROMOCYCLODODECANE USED FOR MODELLING

Table B 1. Physical-chemical properties of Technical HBCDD mixture and γ -HBCDD used for modelling

Parameter base values at 10 °C	Numerical value		References
	Technical HBCDD mixture	γ -HBCDD	
Henry's law constant for freshwater, Pa m ³ /mol	0.75*	1.893	For Technical HBCDD mixture Henry's law constant calc with vapor pressure and solubility [<i>Risk Assessment</i> , Final draft, 2008]
Henry's law constant for seawater, Pa m ³ /mol	0.87	2.258	For γ -HBCDD Henry's law constant calc with temperature dependence vapor pressure (estimated on the basis <i>Kruse et al.</i> , 2000) and solubility [<i>Risk Assessment</i> , Final draft, 2008]
Henry's law constant temperature coefficient, K	-	4349.1	
Supercooled liquid saturated vapour pressure, Pa	4.82 × 10 ⁻⁴		Calculated with the help of equations from [<i>Mackay et al.</i> , 1991, vol.1] and data from [<i>Kruse et al.</i> , 2000]
Coefficient of subcooled liquid – vapor pressure temperature dependences, K	4349.12		
OH-radical interaction rate constant, cm ³ /s	5.0 × 10 ⁻¹²		Hexabromocyclododecane as a possible global POP, 2008
Degradation in air constant, s ⁻¹	1.64 × 10 ⁻⁶		Estimated by the model on the basis of [OH] distribution.
Half-life in air, days	4.88		
Degradation in water constant, s ⁻¹	4.18 × 10 ⁻⁹		Calculated using data from <i>HPV Data Summary and Test Plan for Hexabromocyclododecane (HBCDD)</i> , 2005 and SVHC Support Document, ECHA, 2008.
Degradation in soil constant, s ⁻¹	6.44 × 10 ⁻⁷	7.20 × 10 ⁻⁸	
Half-life in soil, days	35	112	
Molar volume, cm ³ /mol	429.6		Calculated using data from <i>Mackay D., Shiu W.-Y. and Ma K.-C.</i> [1997] vol.1
"Octanol-water" coefficient	4.22 × 10 ⁵	1.59 × 10 ⁵	Selected value with <i>Risk Assessment</i> , Final draft, 2008 and <i>Hayward et al.</i> , 2006
"Octanol-air" coefficient	2.87 × 10 ⁹	1.98 × 10 ⁸	Estimated by the relation between K_{oa} , K_{ow} and K_{aw}
Temperature coefficient of K_{OA} coefficient, K	4057.6	4054.8	
Molecular diffusion coefficient, m ² /s			Calculated with the help of equations from <i>Schwarzenbach et al.</i> , 1993
in water	3.73 × 10 ⁻¹⁰		
in the air	3.85 × 10 ⁻⁶		
"Organic carbon-water" partition coefficient, m ³ /kg	172.9	652.8	Calculated with the help of relationship between K_{OC} and K_{OW} [<i>Karickhoff</i> , 1981]
Washout ratio	2.0 × 10 ⁵		Calculated on the basis of [<i>van Pul et al.</i> , 1998]

Values of half-life in water and soil for HBCDD were estimated as averages of data found in publications and available in data bases, HPV Data Summary and Test Plan for Hexabromocyclododecane (HBCDD). CAS No. 3194-55-6 first of all. Besides, in selecting such parameters as Henry's law constant and subcooled liquid-vapour pressure their temperature dependencies were used in the calculations.