EMEP MSC-E Information Note 14/2005

2005

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 Hexachlorobutadiene

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CONTENTS

Удалено: Distant

INTRODUCTION

Hexachlorobutadiene (HCBD) is a chlorinated aliphatic compound widely used in industry. It is a by-product at manufacturing synthetic caoutchouc, rubber and lubrication materials. It is added to transformer oils, hydraulic liquids, and heat carriers. Previously HCBD was widely used in agriculture. Mainly it was used as fumigant and besides as herbicide and insecticide. In the early 80s HCBD production in the USA, Japan and Western Europe was 10 thous.t/y [*Filov,* 1990].

HCBD as a potential candidate for the inclusion into the UN-ECE Protocol on POPs was addressed by the Ad Hoc Expert Group on POPs [*Lerche et al*., 2002]. This year the European Commission has submitted a proposal for amendment to the Protocol with regard to this chemical. In accordance with a suggestion of the Working Group on Strategies and Review that during the 90-day period between the submission of dossier and the twenty-third session of the Executive Body, the dossier on HCBD prepared by national experts [*van de Plassche and Schwegler*, 2005] is available on the Convention's website for comment and submission of additional information by all interested persons or groups. Additional information for the evaluation of hexachlorobutadiene as a potential new POP in accordance with the two criteria: potential for long-range transboundary atmospheric transport (LRTP) and persistence can be provided by modelling.

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A certain experience in the model assessment of the long-range transboundary atmospheric transport and persistence in the environment for a wide range of typical POPs already included in the Protocol on POPs and some potential new POPs [*Shatalov et al.,* 2003*; Dutchak et al.,* 2004*; Mantseva et al*., 2004; *Vulykh et* al., 2004, 2005] is accumulated in the Meteorological Synthesizing Centre-East of EMEP. For the evaluation of LRTP and persistence of pollutants, EMEP/MSCE-POP multicompartment hemispheric transport model is used. To estimate the considered parameters for HCBD, the model calculation of its atmospheric transport from a conventional emission point source located in Europe (10°E; 47.5°N) is made for one-year period. Information on physical-chemical properties and degradation rates of HCBD used for modelling is included in Annex A.

To illustrate LRTP of HCBD, 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 considered pollutant from the atmosphere. The second is ***Transport Distance*** (***TD***) that is the distance from the source at which annual mean atmospheric concentration of a chemical in question drops 1000 times compared with the concentration near the source. Additional information on this criterion for HCBD is provided by the spatial distribution of air pollution caused by the considered conventional point source.

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Persistence in the environment is evaluated by ***Half-life in the environment*** ($T_{1/2}^{env}$) estimated for HCBD 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.

To diminish uncertainties in evaluating LRTP and persistence of HCBD with the help of the model dependent *TD* and $T_{1/2}^{env}$, a comparison of their numerical values against those obtained for B[a]P and HCB as adequately studied “benchmark substances” is presented.

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

Detailed information on the structure of the model and parameterisation of the media processes can be found in the EMEP/MSC-E reports [*Gusev et al*., 2005] and on the Internet (http://www.msceast.org).

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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, which should be greater than two days.

The half-life of "new substances" 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. Advantages of modelling approach are contained in possibility 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 us to estimate *Transport Distance* (*TD*), characterising LRTP of "new substances" as the distance from the source at which annual mean atmospheric concentration drops 1000 times compared with the concentration near the source.

This Chapter contains the main results on evaluation of LRTP criterion for HCBD with the help of above-mentioned characteristics obtained on the basis of the EMEP/MSCE-POP model calculations performed at the hemispheric level.

1.1. Residence time in the atmosphere

To estimate the residence time in the atmosphere, the model calculation of atmospheric transport of HCBD with allowance of such processes as degradation in the atmosphere, partitioning between particulate and gas phases, dry and wet deposition of particles and gas exchange with various types of underlying surface is carried out. Emissions of HCBD to the atmosphere are assumed to be 1 tonne per year from a conventional point emission source located in Europe (10°E; 47.5°N). On the basis of this calculation annual atmospheric balance of HCBD emitted to the atmosphere is estimated. The calculated balance for the processes of HCBD removal from the atmosphere is given in Fig.1.

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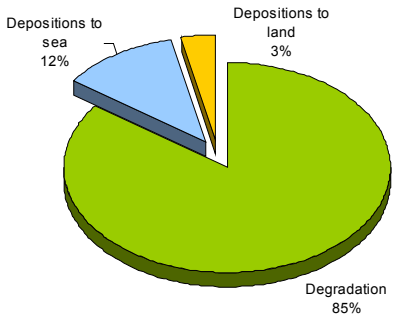


Fig. 1. *Calculated annual balance of HCBD removal from the atmosphere*

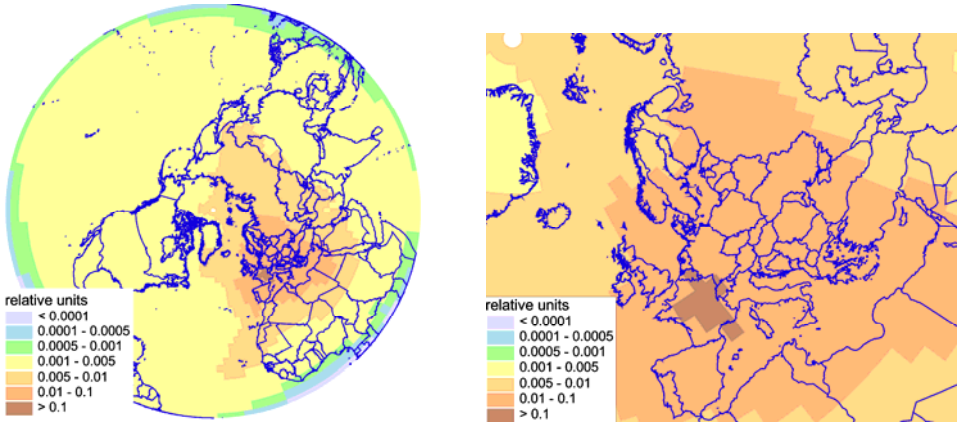
According to the model assessment, the main process of HCBD removal from the atmosphere is degradation. This process affects LRTP of the considered pollutant in the atmosphere much more than deposition does. It was found that 85% of HCBD that removed from the atmosphere within a year degrade and only 15% are deposited to the underlying surface. Only 3% of HCBD is accumulated in soil, and larger fraction (12%) is deposited to seawater.

HCBD is a volatile organic chemical existing in the atmosphere predominantly in the gas phase. Therefore, the degradation rate of HCBD in the atmosphere is defined solely by the rate of its gas-phase interaction with OH radical. According to the literary data, the estimated half-life of HCBD in the Northern and Southern Hemisphere due to this reaction is 840 and 280 days respectively [*Class and Ballschmiter*, 1987]. Using the second-order degradation rate constant equal to $2.24 \cdot 10^{-14}$ cm^3/molec·s taken from [*Howard and Meylan*, 1997] and the average value of OH radical spatial distribution implemented in the model ($8.8 \cdot 10^5$ molecule/cm^3), the atmospheric half-life of HCBD due to the degradation process only is estimated to be 407 days.

The residence time of HCBD in the atmosphere ($T_{1/2}^{air}$) estimated on the basis of model calculations of its atmospheric transport is amounted to 118 days or approximately 4 months. Thus, for this pollutant the numerical value of this characteristic of LRTP obtained by modelling considerably exceeds and fully meets the existing criterion for POPs (atmospheric half-life is greater than two days).

1.2. Spatial distribution of pollution from conventional emission source

The character of calculated atmospheric balance for HCBD is governed by the physical-chemical properties of this chemical and testifies its high ability to the atmospheric transport. In addition, LRTP of HCBD can be also characterised by the spatial distribution of its air pollution obtained with the help of the model simulation. In Fig 2 a, b concentration fields of HCBD in the Northern Hemisphere and EMEP domain are given. 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.



a – Northern Hemisphere *b- EMEP domain*

Fig. 2. *Spatial distribution of HCBD concentrations in the above-ground air in the Northern Hemisphere and in the EMEP domain*

As seen from the model results, HCBD pollution in the atmosphere spreads over extremely long distances. It is obvious that HCBD emitted from the conventional European point source with selected intensity is able to cause the considerable pollution not only of the EMEP domain but also of other continents. Pollution fields with rather high levels of HCBD air concentrations are formed practically over the whole territory of Europe (0.01 – 0.1 of the concentration near a source). Lower levels of air pollution ranging from 0.005 to 0.01 of the basic value reach the Arctic, North-American coast and partly cover Asia and Africa.

Data on HCBD air concentrations are practically absent in the literature. Nevertheless, being rather scarce available measurement data on HCBD air concentrations observed at sampling site located far from emission sources illustrate additionally the high LRTP of this chemical. In particular, this problem was investigated in detail in the framework of studies of global air background pollution by anthropogenic chemicals [*Class and Ballschmiter*, 1987]. The HCBD air concentrations measured within these studies are presented in Table 1.

Table 1. *HCBD measured air concentrations*

Sampling site	Sampling date, month/year	HCBD concentrations
		ng/m^3
Sao Miguel, Azores	6/82	2.3
German Bay	7/82	2.9
Porto Santo	3 and 8/84	1.4; 2.3; 2.9
Portugal (Atlantic)	3/85	2.3
North Atlantic	3/85	2.3; 2.0
Bretagne (France)	9/85	2.3
Tenerife (Coast)	10/85	1.7
Pico Aliero	3 и 6/82	2.3; 3.5
	3 и 8/84	3.5; 1.6
Bermuda	7/85	1.7
Teide	10/85	0.7
Maldives	3/86	0.5; 0.2
South Atlantic	3/85	0.8

On the basis of the results presented in the investigation, mean air concentration calculated for the Northern Hemisphere is equal to 2 $\pm$ 0.58 ng/m^3 and this concentration estimated for the Southern Hemisphere - 0.81$\pm$ 0.35 нг/м^3 [*Class and Ballschmiter*, 1987].

For analytical assessment of HCBD in the environment methods of very high sensitivity should be used. The investigation of air pollution in Canada carried out during 1989-97 could find HCBD only in 2% of samples (total number of samples amounted to 9231) [*Lecloux*, 2004]. Evidently this testifies only that the applied method was not sensitive enough because its lower detection limit was 0.1 μg/m^3 or 100 ng/m^3. Such concentrations are not typical for HCBD. In 1999-2000 under Swedish National Environmental Programme at 3 stations very low HCBD concentrations were recorded – from 2 to 5 pg/m^3 [*Lecloux*, 2004].

A number of samples have been screened in 2003 at the background sites Råö and Pallas for HCBD [*Kaj and Palm*, 2004]. It was found that this pollutant was detected in all analysed air samples with concentration lying in the range from 0.12 to 0.20 ng/m^3 and in atmospheric deposition (0.042 ng/m^2/day), but not in sewage sludge, sediment or common mussel. It should be noted that air concentration of HCB also measured within this study at the same sites are considerably lower changing from 0.012 to 0.086 ng/m^3.

An attempt [*Pankow et al*., 1984] to determine HCBD content in precipitation made in spring (March-April) and in autumn (October-December) of 1982 failed. Not a single sample contained HCBD above the detection limit. It can be partly explained by the fact that existing predominantly in the gas phase and having relatively high values of the Henry's law constant HCBD is supposed to be poorly washed out by the precipitation. Other data on HCBD concentrations in snow and rain were not available.

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1.3. Transport Distance

At present several model approaches to 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 HCBD, 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):

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

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].

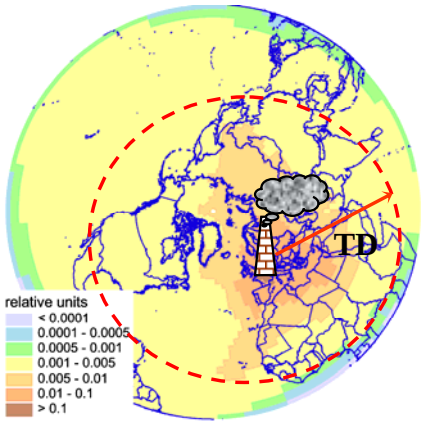

Fig. 3. *Definition of the transport distance*

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. It was found that for HCBD the contribution of degradation process to its removal from the atmosphere is more significant than that of deposition. The calculated value of *TD* for HCBD is amounted to **8784 km**.

Both characteristics of LRTP obtained for HCBD with the help of model calculations are presented in Table 2.

Table 2. *Characteristics of LRTP (**Half-life in air**$_{calc}$ and **Transport Distance**) calculated for HCBD*

Substance	$T_{1/2}^{air}$, days	*TD*, km
HCBD	118	8784

The presented numerical characteristics of LRTP for HCBD fully meet the LRTP criteria of Executive Body Decision 1998/2.

2. PERSISTENCE IN THE ENVIRONMENT

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 the air and soil, seawater, sediment, vegetation etc is important for its ability to be accumulated in the food chain. In this process the main characteristic is its half-life in the media 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. 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, 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 HCBD is demonstrated by the numerical value of $T_{1/2}^{env}$ calculated with the help of Eq.2 as 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:

$$T_{1/2}^{env} = \ln 2 / \sum k_i \cdot f_i \qquad (2)$$

Here fractions f_i 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 HCBD between main environmental media (air, soil, water, sediment and vegetation) and the values of its half-life in each particular medium due to degradation process.

Available information reported on the investigation of HCBD degradation in water is quite limited. There are no data on hydrolysis rate constants and photolysis in surface waters. The half-life of HCBD in water appears to depend on the amount of organic matter in the aqueous media; in natural waters, the half-life is estimated to be 4 - 52 weeks [*Howard et al*., 1991 cited by *Lecloux*, 2004]. Biodegradation processes are also slightly studied. Results of studies of *Tabak et al*., 1981 and *Schröder*, 1987 [cited by *Lecloux*, 2004] suggest that HCBD would biodegrade at a slow-to-moderate rate in aqueous environments. The half-life estimates for this pollutant available in the literature are presented in Table 3.

Table 3. *HCBD half-life in water*

Half – life, days	Notes	Reference
30		*US EPA 2002* cited by *Lecloux*, 2004
3 – 30	River water	*HSDB*, 2001
30 – 300	Lake water and ground water	
28 – 180		*Mackay D. et al.*, 1992, vol. III

The presented values of half-life demonstrating persistence of HCBD in water vary from several days to approximately one year. For model parameterisation the average value of HCBD half-life in water of 100 days is taken.

The half-life of HCBD in soil depends upon the chemical, physical and biological heterogeneity of the soil and climatic conditions [*Lecloux*, 2004]. In particular, Environment Canada, 2000 reports half-lives in soils of 4-26 weeks obtained in a study by *Horward et* al., 1991 on aerobic biodegradation rates. According to [*Mackay et al*., 1992, vol.III] HCBD half-life in soil is from 28 to 180 days. Somewhat higher values – from 104 to 388 days were obtained by *Eisenberg and Mckone* [1998] with the use of CalTOX model. For the model calculation the value of HCBD half-life for degradation in soil was chosen to be equal to 175 days.

For HCBD the distribution of its total content in the environment between main environmental media (annual media balance) and relative fractions of the pollutant degraded in each media during a year (annual degradation balance) were obtained on the basis of 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 model assessment of annual media balance of HCBD in comparison with its annual degradation balance is shown in Fig.4.

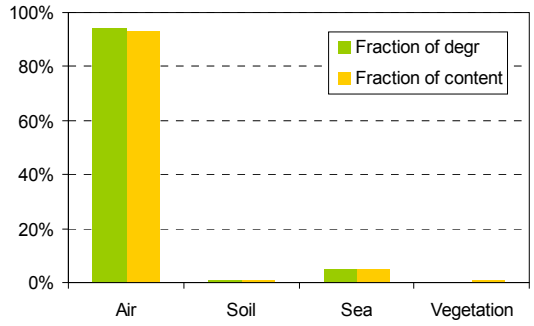

Fig. 4. *Annual degradation and media balances for HCBD*

As it was stated before deposition processes are not very essential for HCBD. By the end of the year the largest fraction of HCBD (about 90%) is contained in the atmosphere. Soil and vegetation equally accumulate HCBD (2% of total environmental content each) and a little bit more (5%) is accumulated in seawater. This shows that the value of the HCBD half-life in the atmosphere is most essential for the evaluation of its residence time in the environment. As a result of calculated intermedia balance of HCBD and the values of its half-life in each of the considered environmental media, the obtained value of *Half-life in the environment* for HCBD is equal to 379 days or approximately 13 months. The calculated estimate of $T_{1/2}^{env}$ together with values of half-life in the separate environmental media used for modelling (for references please see Annex A) are presented in Table 4.

Table 4*. Characteristics of Persistence (Half-life in environment) and half-life of HCBD in different environmental media used for modelling of atmospheric transport*

Substance	$T_{1/2}^{env}$, months	Half-life, months		
		air	water	soil
HCBD	13	14	3	6

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The obtained value of *Half-life in the environment* shows that HCBD posses a rather high persistence in the environment. At that the obtained value of $T_{1/2}^{env}$ is lower than that of half-life in the atmosphere, which take into account degradation processes only, and considerably exceeds those for degradation in water and soil.

3. BENCHMARK APPROACH

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 their ranking in terms of Pov 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 [*ENV/JM/MONO(2004)5*, 2004].

The comparison of calculated characteristics of LRTP and persistence for HCBD against those obtained for benchmark pollutants is presented in this subsection. Benzo[a]pyrene (B[a]P) and hexachlorobenzene (HCB) are used as such benchmark substances in this assessment. Characteristics of their behavior in the environment are well studied and clearly meet the UN ECE criteria. These pollutants are already included in the Protocol on POPs and are considered as pollutants of regional and global concern, respectively. B[a]P and HCB belong to the different groups of pollutants. Due to peculiarities in their physical-chemical properties these substances occur in the

atmosphere mainly in the particulate or gaseous phases, respectively. Thus, for B[a]P dry and wet deposition of particulate phase mainly determine its ability to the long-range transport. In a case of HCB degradation in the atmosphere and gaseous exchange with underlying surface affect most of all LRTP of this pollutant. Distinction of persistence values for these pollutants is determined by difference in distribution of their environmental content between main environmental compartments and values of half-life in these media. According to model calculations, main medium-accumulator for B[a]P is soil but HCB mainly accumulates in seawater. Besides, the larger fraction of HCB than that of B[a]P is contained in the atmosphere. All calculations were performed for one-year period from the conventional point source with one and the same location in Europe and one and the same emissions intensity.

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

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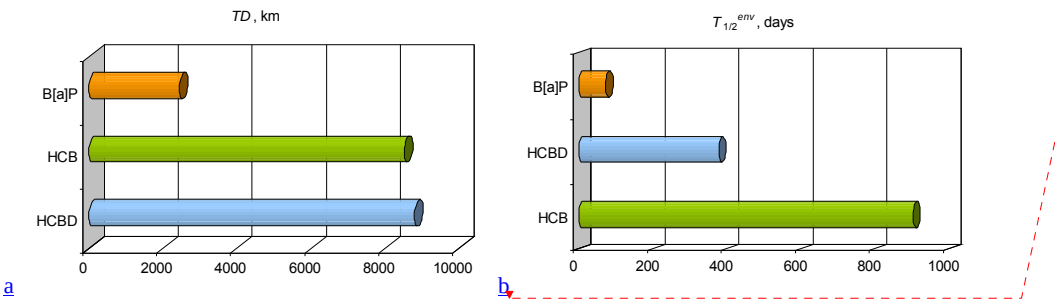

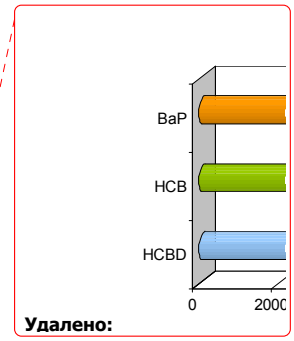

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Fig. 5. *Transport distance and Half-life in the environment calculated for HCBD, B[a]P and HCB*

The ranking of HCBD, B[a]P and HCB with respect to *TD* shows that HCBD has the higher ability to be transported over long distances than B[a]P and the presented numerical value of LRTP for this pollutant is comparable with that of HCB. According to the model calculations of $T_{1/2}^{env}$, persistence of HCBD in the environment is less than that of HCB but considerably exceeds that estimated for B[a]P.

The results of the model evaluation show that HCBD clearly can be viewed as global pollutants. The further assessment of intercontinental transport for this substance is strongly desirable. Thus, according to the results of the present investigation, HCBD meets both the LRTP and persistence criteria for POPs.

4. CHARACTERISTICS OF HCBD LRTP AND PERSISTENCE IN RELATION TO THE INDICATIVE CRITERIA OUTLINED IN EXECUTIVE BODY DECISION 1998/2

Physical-chemical properties of HCBD presented in [*van de Plassche and Scwegler*, 2005] are given in Table 5 in relation to the LRTP and persistence criteria outlined in the Executive Body Decision 1998/2 with additions of the MSCE-POP model estimates. Data on physical-chemical properties of HCBD available in [*van de Plassche and Scwegler*, 2005] and used in the model calculations are given in the Annex A (Tables A1 and A2).

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Table 5. *Comparison of properties of HCBD and criteria of Executive Body Decision 1998/2 based on data [van de Plassche and Scwegler, 2005] and with additions of MSCE-POP model estimates.*

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Criterion	Criterion values	Meets the criterion (Yes/No)	Characteristics of HCBD	Remarks
Potential for Long-range Transboundary Atmospheric transport				
Vapour pressure, Pa	<1000	Yes	20-32 Pa	Presented in v*an de Plassche and Schwegler* [2005]
Half-life in air, days	>2	Yes	200-350 days	
Half-life in air_{calc}, days		Yes	118 days	$T_{1/2}^{air}$ calculated by MSC-E
Persistence				
Half-life in water, months	>2	Yes	Based on scarce and sometimes conflicting information	Presented in v*an de Plassche and Schwegler* [2005]
Half-life in soil, months	>6	Yes		
Half-life in sediments, months	>6	Yes		
Half-life in the environment, months	-	-	13 months (379 days)	$T_{1/2}^{env}$ calculated by MSC-E

The results of the model assessment demonstrate the considerable long-range atmospheric transport potential and persistence of HCBD in the environment. This conclusion is also confirmed by the comparison of calculated numerical characteristics of LRTP and persistence of HCBD against those obtained for B[a]P and HCB well-studied pollutants already included into the Protocol on POPs.

REFERENCES

Bennett D.H., McKone T.E., K. Matthies and W.E. Kastenberg [1998] General formulation of characteristic travel distance for semi-volatile organic chemicals in a multi-media environment. *Environ. Sci. Technol*., vol.32, pp. 4023-4030.

Bennett D.H., Scheringer M., McKone T.E., Hungerbuhler K. [2001] Predicting long-range transport potential: A systematic evaluation of two multimedia transport models. *Environ. Sci. Technol*., vol.35, pp.1181-1189.

Beyer A. and M. Matthies [2001] Criteria for Atmospheric Long-range Transport Potential and Persistence of Pesticides and Industrial Chemicals. Umweltforschungsplan des Bundesministerium fur Umwelt, Naturschutz und Reaktorsicherheit. Stoffbewertung, Gentechnik, Forderkennzeichen (UFOPLAN) 299 65 402.

Beyer A., D. Mackay, M. Matthies, F. Wania and E. Webster [2000] Assessing long-range transport potential of persistent organic pollutants. *Environ. Sci. Tech*., vol. 34, pp. 699-703.

Beyer A., M. Matthies, M. Scheringer and C. Schulze [2001] Comparing assessment methods to determine the environmental spatial scale of organic chemicals. *Environ. Toxicol. Chem*., vol. 20, pp. 922-927.

Class T. and Ballschmiter K. [1987] Global baseline pollution studies. X. Atmospheric halocarbons: global budget estimations for tetrachloroethane, 1,2 – dichloroethane, 1,1,1,2 – tetrachloroethane, hexachloroethane and hexachlorobutadiene. Estimation of the hydroxyl radical concentrations in the troposphere, Fresenius Z. *Anal. Chem*., Bd. 327, S. 198 – 204.

Dutchak S., V.Shatalov, E.Mantseva, O.Rozovskaya, N.Vulykh, M.Fedyunin, W.Aas, K.Breivik and S.Mano [2004] "Persistent Organic Pollutants in the Environment". EMEP Status Report 3/2004.

Eisenberg J.N.S. and Mckone T. [1998] Decision tree method for the classification of chemical pollutants: Incorporation of across-chemical variability and within-chemical uncertainty, *Environ. Sci. Technol*., vol. 32, No.21, pp. 3396 – 3404.

ENV/JM/MONO (2004)5 [2004] Guidance document on the use of multimedia models for estimating overall environmental persistance and long-range transport. Organisation for Economic Co-operation and Development, Environmental Directorate Joint Meeting of the Chemicals Committee and the Working Party on Chemicals, Pesticides and Biotechnology, OECD Series on Testing and assessment, 83 p.

Filov V.A., Ed. by [1990] Hazardous chemicals. Carbohydrates and halogenated derivatives of carbohydrates. Handbook, Leningrad, «*Chemistry*», pp. 517 – 524 (in Russian).

Gouin T., D. Mackay, E. Webster and F. Wania [2000] Screening chemicals for persistence in the environment. *Environ. Sci. Technol*., vol. 34, pp. 881-884.

Gusev A., E. Mantseva, V. Shatalov, O.Travnikov [2005] Hemispheric model (MSCE-Hem) of persistent toxic substances dispersion in the environment. EMEP/MSC-E Technical Note 11/2005.

HSDB (Hazardous Substances Data Bank, Toxnet) [2001] http://toxnet. nlm.nih.gov on September, 2001.

HSDB (Hazardous Substances Data Bank, Toxnet) [2001] http://toxnet. nlm.nih.gov on September, 2001 – CHEMFATe Search Results, http://esc.syrres.com/scripts/CHFcgi.exe

Howard P. H. and Meylan W.P., Ed. by. [1997] Handbook of physical properties of organic chemicals, CRC Press, Inc.

Kaj L. and A. Palm [2004] “Screening av hexaklorbutadien (HCBD) i miljön ". www.ivl.se. IVL report B1543. p. 13 (in Swedish).

Karikhoff S.W. [1981] Semiempirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. *Chemosphere*, v. 10, pp. 833-846.

Lecloux A. [2004] Hexachlorobutadienr-sources, environmental fate and risk characterization, Science Dossier, Euro Chlor representing the chlor-alkali industry, www.eurochlor.org, 43 p.

Leip A. and G. Lammel [2004] Indicators for persistence and long-range transport potential as derived from multicompartment chemistry-transport modelling. *Environmental Pollution*, vol. 128, pp. 205-221.

Lerche D., E. van de Plassche, A. Schwegler, F.Balk [2002] Selecting chemical substances for the UN-ECE POP Protocol, *Chemosphere*, vol. 47, pp. 617-630.

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Mackay D., Wan Ying Shiu, K.C. Ma. [1992] Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals. vol. III, pp. 270- 271.

Mantseva E., S. Dutchak, O. Rozovskaya, V. Shatalov [2004] "EMEP Contribution to the Preparatory Work for the Review of the CLRTAP Protocol on Persistent Organic Pollutants". EMEP/MSC-E Information Note 5/2004.

Matthies M., A.Beyer and D.Mackay [1999] Long-Range Transport Potential of PCB and PCDD/F and their Classification. *Organohalogen Compounds,* vol. 41, pp. 347-351.

Pankow J. F., M.I. Lorne and W.E. Asher [1984] Trace organic compounds in rain. 1. Sampler design and analysis by adsorption/thermal desorption (ATD), *Environ. Sci. Technol*., vol. 18, No. 5, pp. 310-318.

van de Plassche E.J. and Schwegler A.M. [2005] Hexachlorobutadiene. Dossier. Royal Haskoning, The Netherlands, 25 pp.

van Pul W.A.J., F.A.A.M. de Leeuw, J.A. van Jaarsveld, M.A. van der Gaag and C.J. Sliggers [1998] The potential for long-range transboundary atmospheric transport. *Chemosphere*, v. 37, No.1, pp.113-141.

Rodan B.D., D.W.Pennington, N.Eckley and R.S. Boethling [1999] Screening for persistent organic pollutants: techniques to provide a scientific basis for POPs criteria in international negotiations. *Environ. Sci. Technol*., vol. 33, pp. 3482-3488.

Ruelle P. and Kesselring U.W. [1997] Aqueous solubility prediction of environmentally important chemicals from the mobile order thermodynamics, *Chemosphere*, vol. 34, No.2, pp. 275-298.

Scheringer M. [1996] Persistence and spatial range as endpoints of an exposure-based assessment of organic chemicals. *Environ. Sci. Technol*., vol. 30, pp.1652-1659.

Scheringer M. [1997] Characterization of the environmental distribution behavior of organic chemicals by means of persistence and spatial range. *Environ. Sci. Technol*., vol. 31, No. 10, pp. 2891-2897.

Scheringer M. and M. Berg [1994] Spatial and temporal range as measures of environmental threat. *Fresenius Environ. Bull*., vol. 3, pp. 493-498.

Schwarzenbach R.P., P.M. Gschwend and D.M. Imboden [1993] Environmental organic chemistry. John Wiley&Sons Inc., New York.

Shatalov V., M.Fedyunin, E.Mantseva, B.Strukov and N.Vulykh [2003] Persistent Organic Pollutants in the Environment. MSC-E Technical Report 4/2003.

Stephenson R.M. and S. Malanowski [1987] Handbook of the thermodynamics of organic compounds. Elsevier, Science Publishing Co., Inc., New York, Amsterdam, London, pp. 89, 170.

Vulykh N., S. Dutchak, E. Mantseva, V. Shatalov [2004] "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 PentaBDE". EMEP/MSC-E Information Note 10/2004.

Vulykh N., E. Mantseva, V. Shatalov [2005] "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 Endosulfan". EMEP/MSC-E Information Note 10/2005.

Wania F. [1998] The potential of organic chemicals for long range transport and deposition in polar regions based on calculations with a global distribution model. WECC-Report 2/98, WECC Wania Environmental Chemists, Toronto, ON, Canada, p.30.

Webster E., Mackay D. and F. Wania [1998] Evaluating environmental persistence. *Environ. Toxicol. Chem.,* vol.17, pp. 2148-2158.

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Annex

PHYSICAL-CHEMICAL PROPERTIES OF HEXACHLOROBUTADIENE USED FOR MODELLING

Key physical-chemical properties and degradation rates of HCBD presented in [*van de Plassche and Scwegler*, 2005] are shown in Table A1.

Table A1. *Physical-chemical properties of HCBD presented in Dossier on Hexachlorobutadiene [van de Plassche and Scwegler, 2005]*

Physical chemical properties	Numerical values
Vapour pressure, Pa	19.96 – 20.0 [*Mackay et al*., 1998]; 32 [*Syracuse Database*, 2000]
Henrys' Law constant, $Pa \cdot m^3/mol$	1044 – 2604 [*Mackay et al*., 1998]
Octanol-water partition coefficient (log K_{OW})	3.74 – 4.81 – various sources
Half-life, days	
Air	356 [*Syracuse Database*, 2000] 582 – northern hemisphere [*IUCLID dataset, European Chemicals Bureau*, 2000] 194 – southern hemisphere [*IUCLID dataset, European Chemicals Bureau*, 2000]
Water	30 [*US-EPA*, 2001]; 28 – 364 [*Environment and Health Canada*, 2000]
Soil	28 – 182 [*Environment and Health Canada*, 2000]
Sediment	-

The full set of physical-chemical properties and degradation rates of HCBD selected for the model parameterization on the basis of data available in literature is presented in Table A2.

***Table A 2**. Physical-chemical properties of HCBD used for modelling*

Physical-chemical properties	Values	References
Henry' s law constant for fresh water at 10 ºC, Pa m^3/mol	443	*HSDB*, *NIST* [2001]
Henry' s law constant for marine water at 10 ºC, Pa m^3/mol	443	
Coefficient of Henry's constant temperature dependences, K	4700	
Subcooled liquid-vapour pressure at 10ºC, Pa	3.157	*Stephenson and Malanowski* [1987]
Coefficient of subcooled liquid-vapour pressure temperature dependences, K	8787	
Rate constant of the reaction with OH-radical in air, cm^3/(molec·s)	$2.24 \cdot 10^{-14}$	*Howard and Meylan* [1997]
Half-life in air, days	407	*Calc with the use of average value of OH-spatial distribution used in the model:* $[OH^-] = 8.8 \cdot 10^5$ *molec/*cm^3
Degradation rate constant in water, s^{-1}	$8.02 \cdot 10^{-8}$	Estimated
Half-life in water, days	100	
Degradation rate constant in soil, s^{-1}	$4.58 \cdot 10^{-8}$	
Half-life in soil, days	175	
Molar volume, cm^3/mol	167.8	*Ruelle and Kesselring* [1997]
«Octanol-water» partition coefficient at 25 ºC	60256	*Howard and Meylan* [1997]
«Octanol-air» partition coefficient at 10 ºC	$3.2 \cdot 10^5$	Estimated
Coefficient of «octanol-air» partition coefficient temperature dependence, K	4435	
Molecular diffusion coefficients, m^2/s:		Calculated with the help of equations from *Schwarzenbach et al.* [1993]
in water	$7.37 \cdot 10^{-10}$	
in air	$6.18 \cdot 10^{-6}$	
"Organic carbon-water" partition coefficient, m^3/kg	24.705	Calculated with the help of relationship between K_{OC} and K_{OW} given in *Karikhoff* [1981]

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