

**EMEP CONTRIBUTION TO THE PREPARATORY WORK FOR
THE REVIEW OF THE CLRTAP PROTOCOL ON PERSISTENT
ORGANIC POLLUTANTS**

NEW SUBSTANCES:

**Model assessment of potential for long-range transboundary
atmospheric transport and persistence of
PentaBDE, Endosulfan, Dicifol, HCBd, PeCB, PCN**

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INTRODUCTION

In the recent years MSC-E collaborated with the Task Force on POPs contributing to the preparatory work for the review of the POP Protocol.

To support the work on peer review of dossiers of new substances that were be proposed by Parties for inclusion into annexes to the Protocol, model evaluation of long-range atmospheric transport potential and persistence of a number of new substances, namely PentaBDE, endosulfan, dicofol hexachlorobutadien (HCBd) pentachlorobenzene (PeCBz) and polychlorinated naphthalenes (PCN), was done by MSC-E and delivered to the Task Force on POPs. The results of this work are summarized in the present report.

Here evaluation of long-range transport potential (LRTP) and overall persistence (P_{ov}) for the above-listed substances is presented.

In addition to the evaluation of long-range transport potential and overall persistence, spatial distributions of air concentrations of the considered POPs originated from a conventional point source located in Europe provide complementary information on the main directions of atmospheric transport. This information allows evaluating the regions most affected by these substances from a given conventional emission source.

I. METHODOLOGY OF LRTP AND P_{OV} EVALUATION

Finally, evaluated long-range transport potential and overall persistence of the above-listed substances were compared with that of two well-known substances – benzo(a)pyrene (B[a]P) and hexachlorobenzene (HCB) – used as benchmark substances of regional and global concern, respectively.

To characterize long-range transport potential, model estimates of half-life of the considered pollutants in the atmosphere ($T_{1/2}^{air}$) calculated with allowance of all processes removing them from the atmosphere are used. LRTP is also illustrated by *Transport Distance* (TD).

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 residence time of dicofol in the atmosphere, another characteristic demonstrating LRTP of the considered substance is provided by the model estimate of its *Transport Distance*. Numerical values of *TD* are defined with the help of Eq. I.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 source (as an example See Fig. I.1.):

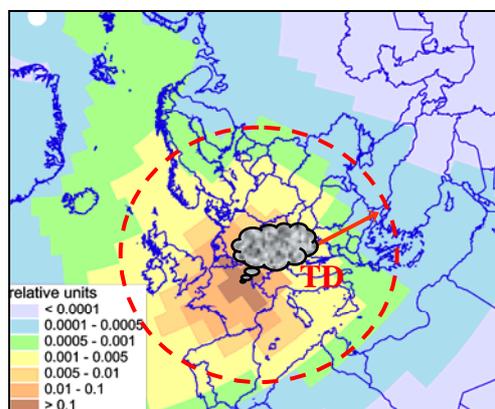


Fig.I.1. Definition of the transport distance

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

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].

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 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.

Overall persistence is enumerated by half-life in the environment ($T_{1/2}^{env}$) estimated for the considered substances on the basis of the model calculations of their atmospheric transport taking into account deposition processes, degradation and exchange of a pollutant between main environmental media. The numerical value of $T_{1/2}^{env}$ is calculated with the help of Eq. 1.2 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:

$$T_{1/2}^{env} = \ln 2 / \sum k_j \cdot f_j \quad (1.2)$$

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

Thus, the value of $T_{1/2}^{env}$ is affected by the distribution of the total environmental content of the particular pollutant between main environmental media (air, soil, water, sediment and vegetation) and the values of their half-life in each particular medium due to degradation process.

II. PENTABROMODIPHENYL (PentaBDE)

Pentabromodiphenyl ether (PentaBDE) is a brominated flame retardant widely used all over the world. This commercial product is within the scope of interest of the Task Force on POPs as a potential new POP. Preliminary risk profile of PentaBDE prepared by national experts [Peltola and Ylä-Mononen, 2001] testifies that its characteristics meet the criteria outlined in the Executive Body Decision 1998/2 and it may be a candidate for the inclusion into the UNECE Protocol on POPs. Additional information on the evaluation of this product in accordance with the two criteria: potential for long-range transboundary atmospheric transport (LRTP) and persistence can be provided by the model assessment.

PentaBDE is a mixture of individual congeners belonging to the groups of tri-, tetra-, penta-, hexa- and heptabromodiphenyl ethers with different physical-chemical properties depending on a number and position of bromine atoms in the molecule of diphenyl ether. In this assessment we stand at two BDE congeners (BDE-47 and BDE-99), which are the major components of PentaBDE (more than 70% w/w).

For the evaluation of PentaBDE potential for the long-range transboundary atmospheric transport and persistence in the environment, a multicompartment hemispheric transport model EMEP/MSCE-POP is used. A multicompartment approach is conditioned by the ability of POPs to be accumulated in soil, seawater and vegetation with subsequent re-emission. For modelling of the atmospheric transport of considered substances the information on their physical-chemical properties (see II.5), as well as meteorological and geophysical data are used. More detailed information on the structure of the model and parameterisation of the media processes can be found in the EMEP/MSCE-E reports [Shatalov et al., 2003; Dutchak et al., 2004] and on the Internet (<http://www.msceast.org>).

To estimate LRTP and persistence of BDE-47 and BDE-99 with the help of the EMEP/MSCE-POP model, the calculations of their transport from a conventional point emission source located in Europe (France) were made for one-year period.

II.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 vapor pressure and atmospheric half-life, which should be greater than two days. The half-life of the pollutants in air (*Half-life in air_{calc}* ($T_{1/2}^{air}$)) can be estimated on the basis of model calculations of their atmospheric transport.

The values of LRTP are strongly influenced by such environmental processes as degradation, deposition, gas/particle partitioning, and gaseous exchange with underlying surface. The annual balance of the removal of the considered congeners from the atmosphere of the Northern hemisphere is shown in Fig. II.1. Of note that such balance is characteristic not only for annual period but also for the time framework determining half-life in air.

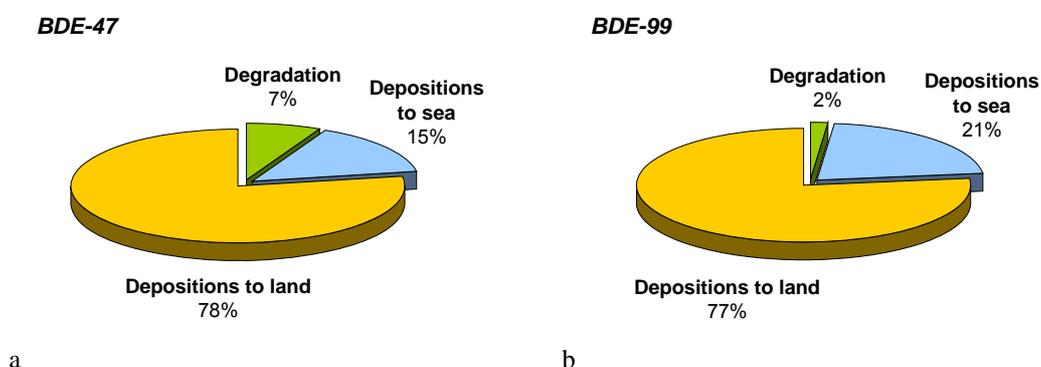


Fig. II.1. Calculated annual balance of BDE-47(a) and BDE-99 (b) removal from the atmosphere

The main process of BDE-47 removal from the atmosphere is depositions to land and seawater (78 and 16% of the annual emissions, respectively). At that only about 7% are degraded in the atmosphere. For BDE-99 degradation process takes about 2% of the annual emissions, the most part is deposited to land (77%) and sea (21%). The character of the calculated balance for the considered congeners is governed by their physical-chemical properties. The difference in degradation rate constants, subcooled liquid-vapour pressure values and Henry's law constants for the considered congeners mainly determines the difference in the balance and correspondingly in calculated values of $T_{1/2}^{air}$ (See Table II.1). As seen from the removal balance, deposition processes to a greater extent affect LRTP of these pollutants than degradation process does. Nevertheless, the two-time difference in degradation rate constants of the congeners leads to the noticeable difference in the calculated values of their *Half-life in air_{calc}*. The highest values of $T_{1/2}^{air}$ were found for BDE-99; then come BDE-47. Of note that the numerical values of this characteristic of LRTP for both congeners fully meet the existing criterion (atmospheric half-life is greater than two days).

Table II.1. Characteristics of LRTP (*Half-life in air_{calc}*) calculated for BDE-47 and BDE-99

Congener	$T_{1/2}^{air}$, days
BDE-47	7
BDE-99	11

To illustrate the model estimates of *Half-life in air*_{calc} for the congeners under consideration visually, the calculated fields of air pollution formed by their annual emissions from a conventional point source with intensity 1 t/y located in France can be used. For convenience, we present air concentrations of BDE-47 and BDE-99 in the relative units so that the maximum value equals 1 near the source (basic value). Spatial distributions of air concentrations provide complementary information on the main directions of their atmospheric transport and the regions most affected by BDE-47 and BDE-99 pollution from the conventional emission source.

The spatial distribution of air pollution by BDE-47 in the Northern hemisphere and in the EMEP domain given in relative units is presented in Fig. II.2a,b.

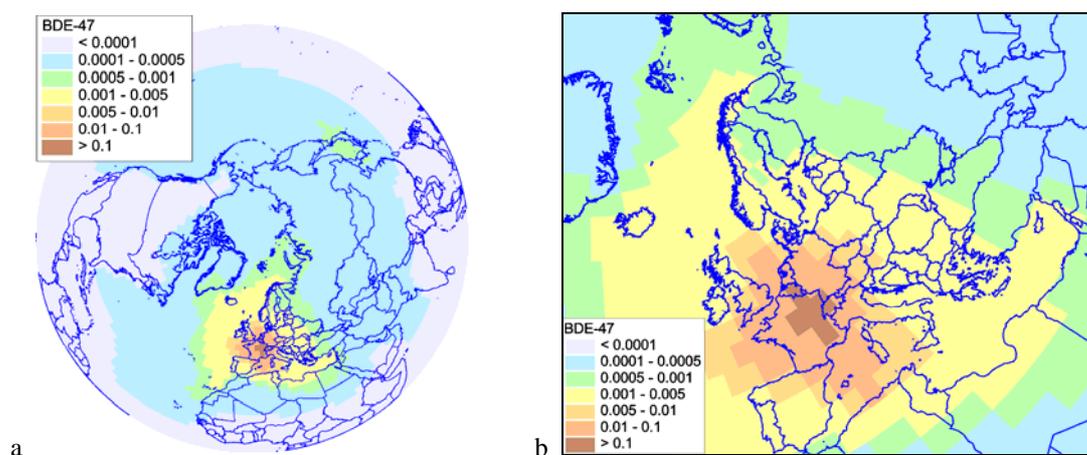


Fig. II.2. Spatial distribution of BDE-47 concentrations in the above-ground air in the Northern Hemisphere and in the EMEP domain

The pollution by BDE-47 from the point source covers the whole territory of the EMEP domain. For this congener the area where concentrations drop down less than 1000 times reach the Arctic. These areas also include Mediterranean Sea and northern Africa. The levels of air concentrations over the major part of European countries vary from 0.001 to 0.1 of the basic value. The levels of air concentrations amounting from 0.01 to more than 0.1 of the basic value are mostly characteristic of France, Switzerland, Belgium, the Netherlands and some regions of other neighbour countries: the United Kingdom, Germany, Spain and Italy.

The spatial distribution of air pollution by BDE-99 in the Northern hemisphere and in the EMEP domain from the conventional point source presented in Fig. II.3a,b.

On the assumption of equal emissions BDE-99 pollution in the atmosphere spreads over longer distances than that of BDE-47. The area with concentrations 1000 times less than that near the source covers the considerable part of the Arctic, Atlantic Ocean, Asia and Africa. The pollution fields with rather high levels of air concentrations are formed practically over the whole territory of Europe (0.005 – 0.1 of the basic value). The highest values of air concentrations (0.01 - >0.1 of the basic value) are observed in France, the United Kingdom, Belgium, the Netherlands, Germany, Spain, Italy, Switzerland, Austria and the Czech Republic.

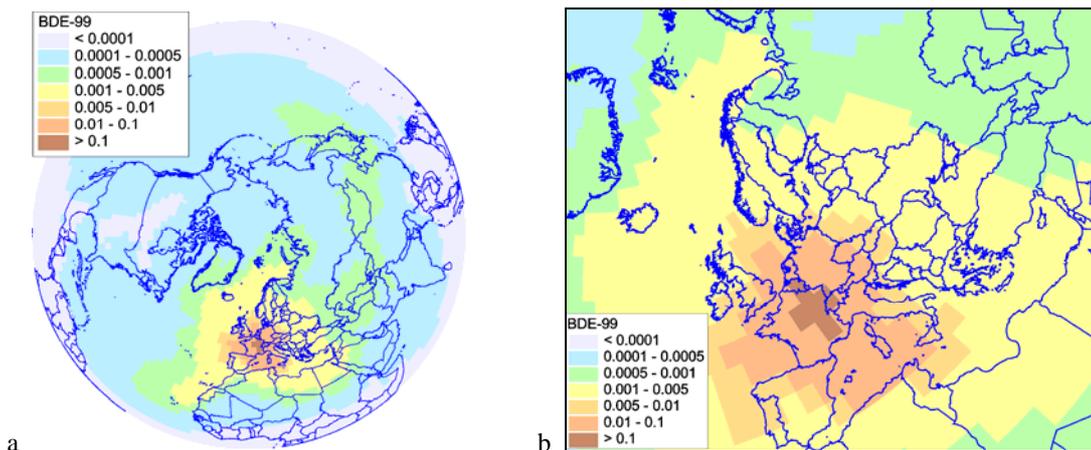


Fig. II.3. Spatial distribution of BDE-99 concentrations in the above-ground air in the Northern Hemisphere (a) and in the EMEP domain (b)

Due to peculiarities in the physical-chemical properties of BDE-47 and BDE-99, their ability to the atmospheric transport is somewhat different.

To characterize LRTP of BDE-47 and BDE-99 the numerical values of *Transport Distance* calculated on the basis of the spatial distributions of air pollution caused by emissions from the conventional point source are demonstrated in Table II.2. For the sake of comparison, values of *Half-life in air_{calc}* obtained for the considered congeners taking into account the main processes removing a pollutant from the atmosphere (degradation, depositions and gaseous exchange with underlying surface) are also shown in Table II.2.

Table II.2. Characteristics of LRTP (*Half-life in air_{calc}* and *Transport Distance*) calculated for BDE-47 and BDE-99

Congener	$T_{1/2}^{air}$, days	TD, km
BDE-47	7	2300
BDE-99	11	2800

According to the calculated values of $T_{1/2}^{air}$ and TD, BDE-99 possesses higher LRTP than BDE-47.

II.2. Persistence

For the congeners under consideration the distribution of their total content in the environment between main environmental media (annual media balance) and relative fractions of these pollutants 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 annual media balance of BDE-47 in comparison with its annual degradation balance is shown in Fig. II.4.

As it was stated before, deposition processes are very essential for all considered BDE congeners. Within a one-year period the most part of BDE-47 total content in the environment (more than 50%) is accumulated in soil. Its content in seawater and vegetation equals 17 and 26%, respectively. Atmospheric content of this congener totals to 5% only. So, soil is the main medium accumulating this pollutant and the value of this congener half-life in soil is very important for evaluation of its persistence in the environment. However, due to the high rate constant for degradation in air the relative fraction of BDE-47 degraded in the atmosphere is equal to that in soil (approximately 40%) and considerably exceeds the relative fraction of its content in air. That leads to the fact that degradation process occurring in the atmosphere strongly reduces BDE-47 accumulation in other media via gaseous exchange. Thus, the calculated value of its $T_{1/2}^{env}$ is affected not only by relatively low rate constant in the medium with maximum pollutant content but to a larger extent by BDE-47 degradation rate constant in the atmosphere.

For BDE-99 the distribution of its environmental total content between environmental media is compared with its relative fractions degraded in each media during a year in Fig. II.5.

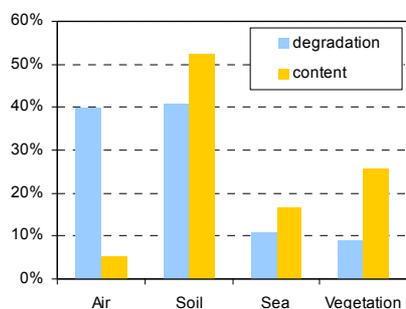


Fig. II.4. Annual degradation and media balances for BDE-47

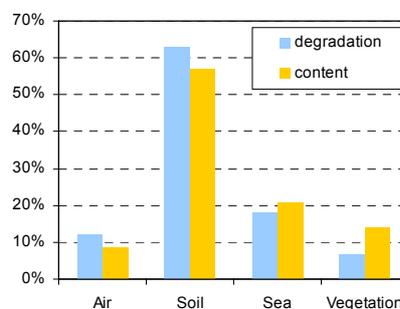


Fig. II.5. Annual degradation and media balances for BDE-99

As in the case with BDE-47 the largest fraction of BDE-99 (approximately 57%) is accumulated in soil within a year. As distinct from BDE-47 seawater accumulates BDE-99 more effectively than vegetation does (21 and 14% of total environmental content, respectively) and a little bit more fraction of this congener (9%) is contained in the atmosphere. However, for BDE-99 the relative fraction of the pollutant degraded in the atmosphere (only about 12%) is much less than that for BDE-47. At that the relative fractions of BDE-99 degraded in air and soil (63% for soil) exceed the fraction of its content in these media. This shows that the degradation processes (both in air and soil) considerably affect BDE-99 accumulation in the environmental media. The value of BDE-99 half-life in soil is the most essential for evaluation of its $T_{1/2}^{env}$.

To evaluate the ability of the considered pollutants to be persistent in the environment, the values of *Half-life in the environment* for BDE-47 and 99 were estimated on the basis of calculated media balances and the values of half-lives in the considered environmental compartments. Obtained estimates of $T_{1/2}^{env}$ are presented in Table II.3.

Table II.3. Characteristics of Persistence (*Half-life in the environment*) calculated for BDE-47 and BDE-99

Congener	$T_{1/2}^{env}$	
	days	months
BDE-47	166	5.5
BDE-99	184	6.1

According to the model results BDE-99 is more persistent congener than BDE-47. Due to rather high ability of the congeners to accumulate in soil and seawater these components of PentaBDE should be considered as pollutants that may cause long-term adverse effects on living organisms in these media. Besides, high values of relative fractions of their total content in the environment are observed in vegetation.

II.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” substance. This approach suggests that modelling 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.

The comparison of calculated characteristics of LRTP and persistence for the considered congeners against those obtained for benchmark pollutants is presented in this subsection. All calculations were performed for one-year period from the conventional point source with one and the same location (France) and one and the same emissions intensity.

Benzo[a]pyrene (B[a]P) and hexachlorobenzene (HCB) were used as such benchmark substances in this assessment. Characteristics of their behavior in the environment are well studied and clearly meet UN ECE criteria. They 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, HCB mainly accumulates in seawater.

The considered BDE congeners, B[a]P and HCB have been ranked in ascending order according to their values of *Transport Distance* (Fig. II.6a) and *Half-life in the environment* (Fig. II.6b).

According to the model calculations of **TD**, LRTP of BDE-99 is found to be higher than that of B[a]P but much less than that of HCB. BDE-47 also can be transported over long distances comparable with that of B[a]P. Thus, these congeners forming the most part of PentaBDE content are found to be pollutants with potential for long-range atmospheric transboundary transport to be viewed at least at regional/hemispheric level.

The ranging of the considered congeners and benchmark pollutants with respect to $T_{1/2}^{env}$ values to some extent differs from that obtained on the basis of **TD**. BDE-47 and BDE-99 are found to be much more persistent in the environment than B[a]P and are in respect to this characteristic in between B[a]P and HCB. Thus, they can be considered as pollutants which after being emitted in the atmosphere are able to have a long-term exposure in the environment and correspondingly due to their high toxicity - adverse effect on human beings and ecosystems.

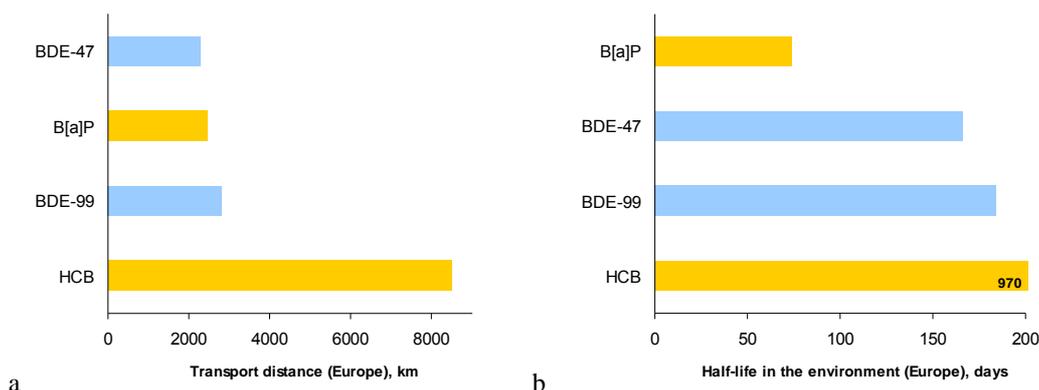


Fig. II.6. Transport distance and Half-life in the environment calculated for BDE congeners, B[a]P and HCB

Thus, according to the results on ranking the considered substances, the long-range transport potential and persistence of PentaBDE is comparable with the adequately studied “benchmark” pollutants already included into the Protocol on POPs.

II.4. PentaBDE characteristics of LRTP and persistence in relation to the indicative criteria outlined in Executive Body decision 1998/2

Characteristics of LRTP and persistence of BDE-47 and BDE-99 as the major components of PentaBDE presented in [Peltola and Ylä-Mononen, 2001] and obtained by the model calculations are given in Table II.4 in relation to the indicative criteria outlined in the Executive Body Decision 1998/2.

Thus, according to the data presented in [Peltola and Ylä-Mononen, 2001] and modeled values of *Half-life in air_{calc}* BDE-47 and BDE-99 fully meet the criterion for Potential for Long-Range Transboundary Atmospheric Transport. Calculated values of their *Half-life in the environment* testify that these congeners can be persistent in the environment during approximately 6 months that is comparable with criterion values of half-life outlined in the Executive Body Decision 1998/2 for environmental media such as soil and sediments.

Table II.4. Characteristics of LRTP and persistence of BDE congeners presented in [Peltola and Ylä-Mononen, 2001] and obtained by modelling in relation to the indicative criteria outlined in the Executive Body Decision 1998/2

Criterion	Criterion values	Meets the criterion (Yes/No)	Characteristics of PentaBDE		Remarks
			BDE-47	BDE-99	
Potential for Long-Range Transboundary Atmospheric Transport					
Vapour pressure, Pa	< 1000	Yes	$1.45 \cdot 10^{-5}$	$7.76 \cdot 10^{-6}$	Presented in <i>Peltola and Ylä-Mononen, 2001</i>
Half-life in air, days	>2	Yes	11	10-20	
Half-life in air _{calc} , days		Yes	7	11	
Persistence					
Half-life in water, months	> 2	Yes	5	5	Presented in <i>Peltola and Ylä-Mononen, 2001</i>
Half-life in soil, months	>6	No	5	5	
Half-life in sediment, months	>6	Yes	20	20	
Half-life in the environment, months	-	-	5.5	6	$T_{1/2}^{env}$ calculated by MSC-E

II.5. Physical-chemical properties used for modelling

The key physical-chemical properties of the major components of PentaBDE presented in [Peltola and Ylä-Mononen, 2001] are shown in Table II.5.

Table II.5. Physical-chemical properties of BDE congeners presented in [Peltola and Ylä-Mononen, 2001]

Physical chemical properties	Numerical values	
	BDE-47	BDE-99
	<i>Peltola and Ylä-Mononen, 2001</i>	
Vapour pressure, Pa	$1.45 \cdot 10^{-5}$ [1]	$7.76 \cdot 10^{-6}$ [1]
Henry's Law constant, Pa·m ³ /mol	0.86* [2]	0.36 [2]
Octanol-water partition coefficient (log <i>K</i> _{OW})	5.87-6.16* [3]	6.46-6.97* [3]
Half-life, days		
Air	11 [4]	13 [2] 20 [4] 10 [5]
Water	150 [6]	150 [6]
Soil	150 [6]	150 [6]
Sediment	600 [6]	600 [6]

*- data are given for the particular homological group as a whole;

References: 1- Tittlemier and Tomy, 2000; 2- COM, 2000; 3- Watanabe and Tatsukawa, 1990; 4- Palm, 2001; 5- Danish EPA, 2001; 6- Estimated by Palm, 2001 with the help of Syracuse Corporation's EPIWIN program.

It should be noted that values of these physical-chemical properties of BDE-47 and BDE-99 different from those presented in [Peltola and Ylä-Mononen, 2001] were selected for modelling mostly on the basis of the literature sources available after 2001. Besides, in the case of selecting such parameters as Henry's law constant and subcooled liquid-vapour pressure their temperature dependencies were used in the calculations. The full set of physical-chemical properties of BDE-47 and BDE-99 used in the model parameterization is presented in Table II.6. Temperature dependences of some physical-chemical characteristics (Henry's law constant, subcooled liquid-vapour pressure, octanol-air partition coefficient) are given for the considered congeners at reference temperature equal to 283.15 K.

Table II.6. Physical-chemical properties of BDE congeners used for modelling

Physical-chemical properties	Numerical values		References
	BDE-47	BDE-99	
Henry's law constant for fresh and sea water, Pa·m ³ /mol	0.053	0.034	Estimated with the use of <i>K_{oa}</i> temperature dependence from <i>Harner and Shoeib</i> , 2002 and <i>K_{ow}</i> taken from <i>Braekevelt et al.</i> , 2003
Coefficient of Henry's constant temperature dependences, K	11685	10958	
Washout ratio	100 000	100 000	Selected values
Subcooled liquid-vapour pressure, Pa	2.53·10 ⁻⁵	1.793·10 ⁻⁶	<i>Titlemier et al.</i> , 2002
Coefficient of subcooled liquid –vapour pressure temperature dependences, K	11375	12959	
Degradation rate constant in air, s ⁻¹ (due to reaction with OH radical)	7.52·10 ⁻⁷	4.12·10 ⁻⁷	<i>Gouin and Harner</i> , 2003
Half-life in air, days	10.7	19.5	
Degradation rate constant in water, s ⁻¹	9.63·10 ⁻⁹	9.63·10 ⁻⁹	
Half-life in water, months	27.8	27.8	
Degradation rate constant in soil, s ⁻¹	9.63·10 ⁻⁹	9.63·10 ⁻⁹	
Half-life in soil, months	27.8	27.8	
Molar volume, cm ³ /mol	294.2	317.5	Calculated on the basis of <i>Palm et al.</i> , 2002
«Octanol-water» partition coefficient	6456500	20893000	<i>Braekevelt et al.</i> , 2003
«Octanol-air» partition coefficient	2.75·10 ¹¹	1.46·10 ¹²	<i>Harner and Shoeib</i> , 2002
Coefficient of <i>K_{OA}</i> temperature dependences, K	11685	10958	
Molecular diffusion coefficients, m ² /s:			Calculated with the help of equations from <i>Swarzenbach et al.</i> , 1993
in water	5.30·10 ⁻¹⁰	5.06·10 ⁻¹⁰	
in air	4.66·10 ⁻⁶	4.47·10 ⁻⁶	
“Organic carbon-water” partition coefficient, m ³ /kg	2647	8566	Calculated with the help of relationship between <i>K_{OC}</i> and <i>K_{OW}</i> given in <i>Karickhoff</i> , 1981

III. ENDOSULFAN

Endosulfan is used as a wide-range pesticide with acaricide properties against a variety of insects and some mites. It is used to disinfect seeds and to kill pests on potato, vegetable, fruit, tea, tobacco and cotton crops. It can also be used in flower cultivation and wood preservation. Thiodan (a commercial name of endosulfan) began to be widely used in agriculture in the mid-1950s. Endosulfan and endosulfan-bearing products were used and are still used in many European countries [*European Directory of Agrochemical Products*, N330]. The most detailed information on the use of endosulfan in agriculture of European countries is given in [*Herrmann, 2004*].

Endosulfan 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*].

A preliminary risk profile of endosulfan prepared by the national expert [*Herrmann, 2004*] testifies that its characteristics meet the criteria outlined in the Executive Body Decision 1998/2 and it may be a candidate for the inclusion into the UN-ECE Protocol on POPs. Additional information on the evaluation of this product in accordance with the two criteria: potential for long-range transboundary atmospheric transport (LRTP) and persistence can be provided by the model assessment.

Endosulfan is a mixture of two stereoisomers - α -endosulfan и β -endosulfan. The proportion of α - and β -isomers in the technical endosulfan is reported as either 4:1 [*Melnikov et al., 1995*] or 2:1 and 7:3 [*Herrmann, 2004*]. The purity of the technical product does not exceed 94%, it also contains 2% of endosulfan alcohol and 1% of endosulfan ether as admixtures.

To evaluate the potential of endosulfan isomers for the long-range transboundary atmospheric transport and persistence in the environment, the EMEP/MSCE-POP multicompartiment hemispheric transport model has been used. A multicompartiment approach is conditioned by the ability of POPs to be accumulated in soil, seawater and vegetation with subsequent re-emission. To model atmospheric transport of the considered substances the information on their physical-chemical properties as well as meteorological and geophysical data has been used. More detailed information on the structure of the model and parameterisation of the media processes can be found in the EMEP/MSCE-E reports [*Shatalov et al., 2003; Dutchak et al., 2004*] and on the Internet (<http://www.msceast.org>).

To estimate LRTP and persistence of endosulfan isomers with the help of the EMEP/MSCE-POP model calculations of their transport from a conventional point emission source located in Europe (France) were made for a one-year period.

III.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 the indicative numerical values of their vapor pressure and atmospheric half-life, which should be greater than two days. The residence time in the atmosphere - (*Half-life in air*_{calc} ($T_{1/2}^{air}$)) can be estimated on the basis of model calculations of their atmospheric transport.

To estimate the letter characteristic for “new substances” such processes as degradation in the atmosphere, partitioning between particulate and gas phases, dry and wet deposition of particles and gas exchange with various underlying surfaces are taken into account. When “new substances” under

consideration have isomers it is of interest to identify differences in their environmental fate. With the help of the MSCE-POP model annual atmospheric balances of endosulfan α -and β -isomers have been calculated at the hemispheric level provided that a conventional point emission source emitting 1t/y is located in France. The main process of endosulfan isomers removal from the atmosphere is degradation. Balances of endosulfan isomers removal from the atmosphere are given in Fig.III.1.



Fig. III.1. Calculated annual balances of endosulfan isomers removal from the atmosphere

Assessments obtained by the model clearly show the difference between endosulfan isomers in terms of their behaviour in the air and rank the processes by their impact on removal of α -and β -endosulfan from the atmosphere. For α -endosulfan deposition on sea and land underlying surfaces does not exceed 2%, 98% are removed from the air through degradation. The rate of substance degradation in the atmosphere depends on the substance – OH-radical interaction rate constant (K_{OH}). For β -endosulfan is it lower almost by an order of magnitude compared to α -endosulfan. So, it means that β -endosulfan “manages” to be involved in the processes of dry and wet deposition as well as gas exchange with sea (13%) and land (8%) surfaces.

Values of $T_{1/2}^{air}$ calculated for both of endosulfan isomers differ considerably (see Table III.1). The results are based on the values of half-life in the air calculated for the endosulfan isomers gas phase–OH-radical interaction and with regard to the removal processes. K_{OH} s of endosulfan isomers differed by an order of magnitude, i.e. the hydroxyl radical reaction rate constant of α -endosulfan amounted to $8.25 \cdot 10^{-11} \text{ cm}^3/\text{molec}\cdot\text{s}$, and that of a β -endosulfan – to $7.59 \cdot 10^{-12} \text{ cm}^3/\text{molec}\cdot\text{s}$. OH rate constants were calculated with the SRC’s AOP[®] software using a fragment constant method [Howard and Meylan, 1997]. Therefore, when only degradation is taken into account, half-lives in the air for both isomers amount to <2 days.

Table III.1. Characteristic of LRTP (Half-life in air calc) calculated for endosulfan isomers

Isomer	Half-life in air _{calc} $T_{1/2}^{air}$, days
α -endosulfan	1
β -endosulfan	5

Calculations made it clear that *Half-life in air_{calc}* of β -endosulfan meets the LRTP selection criteria for POPs, but that of α -endosulfan does not meet them. However, on evidence of data available in the Hazard Substances Data Bank [HSDB, 2001] the degradation rate of endosulfan considered as a sum of isomers amounts to $8.2 \cdot 10^{-12} \text{ cm}^3/\text{molec}\cdot\text{s}$. In this case $T_{1/2}^{air}$ will be close to that of β -endosulfan

(See Table III.1) exceeding the established LRTP criterion. In addition, Dossier Endosulfan 2003 and 2004 give the unpublished data of half-life in the air obtained by indirect measurements. They exceed the established criteria too. It was found that half-life of α -endosulfan is > 2.7 days and that of β -endosulfan is > 15 days [Herrmann, 2003; 2004].

Additional information on LRTP of the considered isomers is provided by the spatial distribution of air pollution. In this case wind transport directions (meteorology), relief and types of underlying surface, distribution of vegetation cover currently actual for the region under consideration are used. In Figs III.2 and III.3 concentration fields of α -endosulfan and β -endosulfan in the Northern Hemisphere and EMEP domain are given. Relative values of concentrations, i.e. ratios of the concentration calculated in the point under consideration to the concentration near a source.

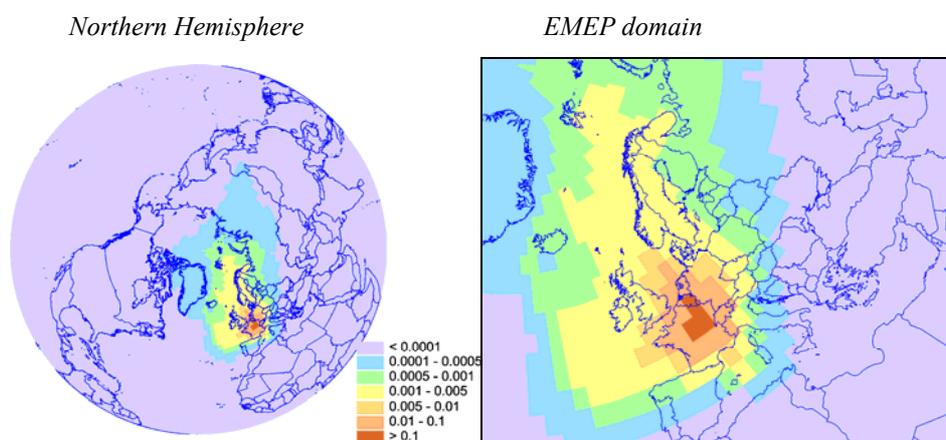


Fig. III.2. Spatial distribution of α -endosulphan concentrations in the above-ground air in the Northern Hemisphere and in the EMEP domain (relative units)

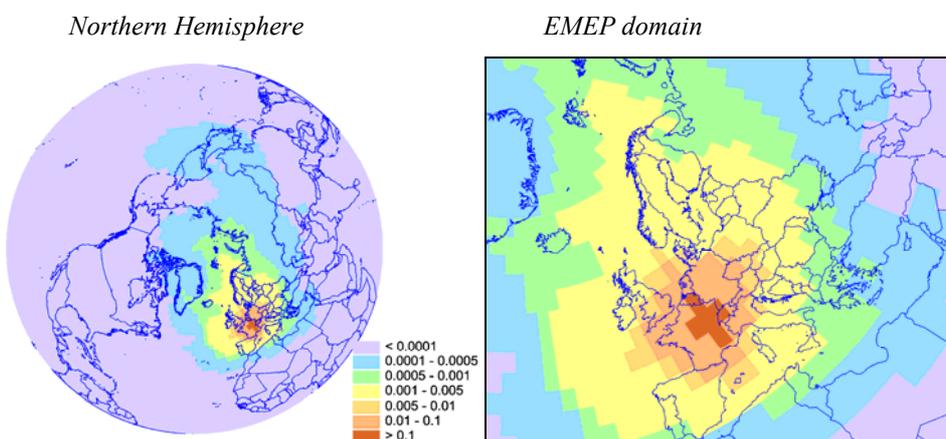


Fig. III.3. Spatial distribution of β -endosulphan concentrations in the above-ground air in the Northern Hemisphere and in the EMEP domain (relative units)

With a source of emissions in Europe (France), the area of atmospheric air contamination by α -endosulfan having concentration 1000 times lower than the initial concentration, covers the entire Central Europe, Scandinavia and approaches Greenland. In case of β -endosulfan the source affects even larger area.

The differences in physical-chemical properties of the considered isomers lead to the larger area of possible air contamination by β -endosulfan compared to α -endosulfan with the emissions being equal. However, in thiodan the proportion of α - and β - isomers is 7:3. This may explain the fact that the concentrations of α -endosulfan in remote regions exceed those of β -endosulfan.

The value of TD obtained by calculations depends on the processes removing the pollutant from the atmosphere. These are deposition to the underlying surface (land, sea) and atmospheric degradation.

Transport distance (TD) is the second qualitative characteristic of LRTP obtained by model calculations. It is evident that the difference in degradation rates of endosulfan isomers mainly determines the difference in the calculated TDs. Besides, β -endosulfan has higher ability to accumulation in soil and seawater compared with α -endosulfan.

The calculated values of TD as well as numerical values of $T_{1/2}^{air}$ are given in Table III.2.

Table III.2. Characteristics of LRTP (Half-life in air_{calc} and Transport Distance) calculated for endosulfan isomers

Isomer	Half-life in air_{calc} $T_{1/2}^{air}$, days	TD, km
α -endosulfan	1	1621
β -endosulfan	5	2041

LRTP quantitative characteristics of endosulfan isomers - *Half-life in air_{calc}* and Transport Distance clearly show how the difference between α - and β -endosulfan in structure and physical-chemical properties is reflected in their long-range transport potential. Values of both characteristics obtained by calculations for β -endosulfan exceed those obtained for α -endosulfan. This makes it possible to conclude that LRTP of β -endosulfan is higher than that of α -endosulfan.

III.2. Persistence in the environment

The values of $T_{1/2}^{env}$ depend on the distribution of the total environmental content of the considered endosulfan isomers between main environmental media (air, soil, water, sediment and vegetation) and the values of their half-life in each particular medium determined by the degradation process. For the endosulfan isomers under consideration the distribution of their total content in the environment between main environmental media (annual media balance) and relative fractions of these pollutants degraded in each media during a year (annual degradation balance) were obtained on the basis of simulations for a one-year period. It should be noted that seawater includes the pollutant content in sediments, and only degradation in forest litter is considered as degradation in vegetation.

The amount of a substance in various media is determined by the degradation/accumulation ratio. For endosulfan isomers the model assessments are given in Fig. III.4.

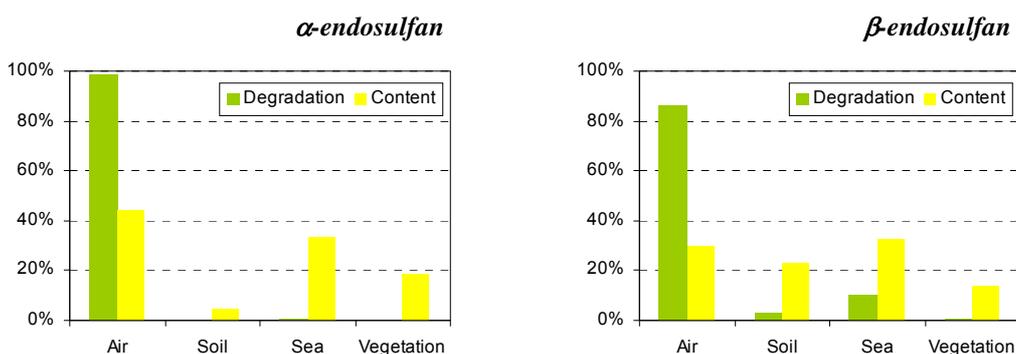


Fig. II.4. Annual degradation and media balances for endosulfan isomers

Best of all both isomers degrade in the atmosphere. α -endosulfan is accumulated for the most part also in the atmosphere (44%). The rest of the accumulated α -endosulfan is distributed in the following way: seawater – 33%, vegetation – 18% and soil – 5%. Accumulation of α -endosulfan in soil is very low due to its rapid degradation in the atmosphere and intensive exchange at the soil-atmosphere boundary. For β -endosulfan the main accumulator is seawater (33%), 30% remain in the air, 23% are accumulated by soil and 14% - by vegetation. The contribution of seawater to β -endosulfan degradation is also fairly high amounting to 10%, degradation in soil and vegetation is slightly higher than 3% of the overall degradation in the environment. Therefore the model assessments give an idea of the annual cycle of endosulfan isomers in the environment and help to identify both the environmental media capable to accumulate endosulfan and the environmental media that need special attention under future observation programmes. Measurement data on concentrations of endosulfan isomers in water and soil currently available in publications are inadequate. The available data do not always give information on both isomers. Measurements of endosulfan in atmospheric precipitation made under the IADN Programme in the region of the Great Lakes show that concentrations of β -endosulfan are always higher than those of α -endosulfan, despite the fact that the ratio between air concentrations measured by the same stations is exactly the opposite.

The overall persistence of endosulfan isomers in the environment - Half-life in the environment - $T_{1/2}^{env}$ was calculated in modelling of their distribution. The calculated values of $T_{1/2}^{env}$ for endosulfan isomers are given in Table III.3 together with half-lives in specific media used in calculations. References to data sources on half-lives in specific media are given in Table III.6.

Table III.3. Characteristics of Persistence (Half-life in environment) and half-life of endosulfan isomers in different environmental media used for modelling of atmospheric transport

Isomer	$T_{1/2}^{env}$		Half-life, days		
	Days	Months	air	water	soil
α -endosulfan	0.43	0.01	0.11	35.4	50
β -endosulfan	4.7	0.16	1.2	37.5	60

The obtained values $T_{1/2}^{env}$ show that persistence of endosulfan isomers in the environment is relatively low. Also it should be noted that values of $T_{1/2}^{env}$ are lower than those of half-life in water and soil. The latter are based on physical-chemical properties of substances and at that only the processes of degradation in each particular medium are taken into account. The data obtained confirm that properties of the media to which the pollutant arrives and features of the territory over which it is transported are of importance. These include type of the underlying surface (land or sea), orography of the region, peculiarities of soil and vegetation cover.

Half-life of endosulfan in water depends upon hydrolysis as well as on life activity of organisms and intensity of ultraviolet radiation. There are no data on the rate of endosulfan photolysis in water. Hydrolysis is expected to be an important fate process based on hydrolysis half-lives. At pH 7 for α - and β -endosulfan they amount to 35.4 и 37.5 days respectively. With pH decreasing to 5.5 half-life increases to 150.5 days for α - endosulfan and to 187.3 days for β -endosulfan. Half-life of endosulfan isomers is much shorter when there are ferric hydroxides in water. In addition to hydrolysis oxidation may occur in the water medium. Data of Spectrum Laboratories (<http://www.speclab.com/compound/c3321365.html>): Chemical Fact Sheet, testify that at pH 7 oxidation half-life for α - и β -endosulfan amounts to 66.6 и 71.4 days respectively. With pH decreasing to 5 oxidation half-life increases to 83.5 days for α - endosulfan and to 70 days for β -endosulfan.

Persistence of endosulfan in soil depends upon specific conditions. In aerobic conditions endosulfan isomers degrades more rapidly, than in anaerobic conditions *HSDB* [2001]. Half-life of a substance in soil depends also on the organic carbon content, soil moisture and temperature and other factors.

The information on half-life of endosulfan and endosulfan isomers in soil available from different sources is quite contradictory, see Table III.4. Therefore for model calculations average values of data given in literature are used.

Table III.4. Half-life of endosulfan isomers in soil

Substance	Half-life, days	References
α -endosulfan	28	<i>Bürkle et al.</i> , 2003
	27	<i>Beyer and Matthies</i> , 2001
	35	<i>Regional report. Indian Ocean</i> , 2002
	26.4 – loam soil	<i>HSDB</i> , 2001
	57	<i>Report Aventis Record No.B002953</i> , 2000
	60	<i>Endosulfan in the environment</i> , <i>FAO</i>
	19-33 – aerobic conditions	<i>Herrmann</i> , 2004
β -endosulfan	157	<i>Bürkle et al.</i> , 2003
	27	<i>Beyer and Matthies</i> , 2001
	150	<i>Regional report. Indian Ocean</i> , 2002
	52.8 – loam soil	<i>HSDB</i> , 2001
	208	<i>Report Aventis Record No.B002953</i> , 2000
	800	<i>Endosulfan in the environment</i> , <i>FAO</i>
	45-58 – aerobic conditions	<i>Herrmann</i> , 2004
endosulfan	40-160	<i>Herrmann</i> , 2003
	50	<i>Hornsby et al.</i> , 1996
	30-70	<i>Mackay et al.</i> , 1997, v.V
	120	

III.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” substance. This approach suggests that modelling 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.

The comparison of LRTP and persistence characteristics calculated for the considered endosulfan isomers against those obtained for benchmark pollutants is presented in this subsection. All calculations were performed for a one-year period and conventional point source with the same location (France) and the same emission intensity.

Benzo[a]pyrene (B[a]P) is used as a benchmark substance in this assessment. Characteristics of its behavior in the environment are well studied and clearly meet the UN ECE criteria. It is already included in the Protocol on POPs and is considered as pollutant of regional concern. Due to peculiarities of its physical-chemical properties this substance occurs in the atmosphere mainly in the particulate phase. Thus, for B[a]P it is dry and wet deposition of the particulate phase that for the most part determines its ability to the long-range transport. According to the model calculations the main medium-accumulator for B[a]P is soil.

Endosulfan isomers being discussed and B[a]P have been ranked in the ascending order according to the values of their *Transport Distance* (Fig. III.5).

It is evident that TD values of endosulfan isomers are close to those of B[a]P, though somewhat lower. Persistence of endosulfan isomer in the environment is lower than that of B[a]P (74 days). Values of $T_{1/2}^{env}$ differ by more than an order of magnitude.

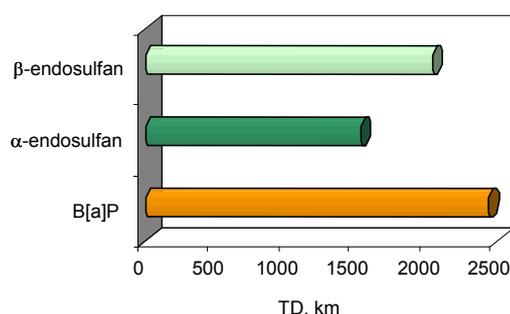


Fig. III.5. Comparison of long-range potential of endosulfan isomers and B[a]P

III.4. LRTP and persistence characteristics of endosulfan isomers in relation to the indicative criteria outlined in Executive Body Decision 1998/2

Before modelling the atmospheric transport of endosulfan isomers their physical-chemical properties were analyzed. In Table III.5 endosulfan properties are compared to criteria of *Executive Body Decision 1998/2* on the basis of available data [Herrmann, 2004] and the *MSCE-POP model* outputs. Data on physical-chemical properties of endosulfan isomers available in [Herrmann, 2004] and used in the model calculations are given in the Tables III.6 and III.7.

Physical-chemical properties of endosulfan given in the dossier [Herrmann, 2004] make it possible to conclude that these pollutants have the long-range atmospheric transport potential. As is seen in Table III.5 both isomers have vapour pressure and half-life values meeting the criteria of Executive Body Decision 1998/2. Assessments of their half-life in the atmosphere with due consideration of not only degradation resulted from interaction with OH-radical, but also deposition to different types of underlying surfaces show that β -endosulfan has higher LRTP than α -endosulfan.

Data on persistence of endosulfan isomers in water show that acid-base conditions are of importance. For instance, with water acidification half-life of both isomers exceed the POP selection requirements significantly. But β -endosulfan is more persistent than α -endosulfan.

Half-life in air and environment of endosulfan isomers calculated by the MSCE-POP model show that both LRTP and persistence of β -endosulfan are higher than those of α -endosulfan. This conclusion is consistent with data of [Herrmann, 2004].

Table III.5. Comparison of properties of endosulfan isomers and criteria of **Executive Body Decision 1998/2** based on data [Herrmann, 2004] and MSC-E calculations

Criterion	Criterion values	Meets the criterion (Yes/No)	Characteristics of endosulfan isomers		Remarks
			α -endosulfan	β -endosulfan	
Potential for Long-range Transboundary Atmospheric transport					
Vapour pressure, Pa	<1000	Yes	1.9×10^{-3}	9.2×10^{-5}	Presented in Herrmann, 2004
Half-life in air, days	>2	Yes	>2.7	>15	
Half-life in air _{calc.} , days		No/Yes	1	5	$T_{1/2}^{air}$ calculated by MSC-E
Persistence					
Half-life in water, months	>2	No/Yes	19 days at pH 7; >200 days at pH 5	10.7 days at pH 7; >200 days at pH 5	Presented in Herrmann, 2004
Half-life in soil, months	>6	No	< 1 under aerobic conditions	<6 under anaerobic conditions	
Half-life in sediments, months	>6	No	< 6	<6	
Half-life in the environment, months	-	-	0.01	0.2	$T_{1/2}^{env}$ calculated by MSC-E

The results of the study indicate that endosulfan isomers are organic pollutants having the long-range atmospheric transport potential and relatively low persistence. Therefore, the use of this pesticide in many countries results in contamination of environment and food, not only in places of its use but also within considerable distances from them. But timely measures aimed at reducing its emissions can reduce its impact harmful on the ecosystem and people beings within a short period of time.

III.5. Physical-chemical properties used for modelling

Key physical-chemical properties of endosulfan isomers presented in [Herrmann, 2004] are shown in Table III.6.

Table III.6. Physical-chemical properties of endosulfan isomers presented in [Herrmann, 2004]

Physical chemical properties	Numerical values	
	α -endosulfan	β -endosulfan
	[Herrmann, 2004]	
Vapour pressure, Pa	$1.9 \cdot 10^{-3}$ [1]	$9.2 \cdot 10^{-5}$ [1]
Henry's Law constant, Pa·m ³ /mol	0.7 – 12.9 [1]; 7.95 [2] 0.071 [3]; 1.9 [4]	0.04 – 2.12 [1] 0.039 [3]
Octanol-water partition coefficient (log K_{OW})	4.63 – 4.74 [1]	4.34 -4.79 [1]
Half-life, days		
Air	>2.7[5]	> 15 [6]
Water	19 at pH=7 [7]; >200 at pH=5 [7]	10.7 at pH=7 [7]; > 200 at pH=5 [7]
Soil	19-33* [8]; 25.5* [9]	42-58* [8]; 157*[9]
Sediment	8.3** [10]	22** [10]

*- aerobic conditions; **-seawater/sediment

References: 1- Ngabe B., T.F.Bidleman, 2001; 2- Rice et al., 1997; 3- Altschuh et al., 1999; 4- Coham W.E. and T.F.Bidleman, 1991; 5- Kloeppfer W., 1992, a; 6- Kloeppfer W., 1992, b; 7-European Commission, Peer Review Programme – Endosulfan, 1998; 8-Stumpf et al., 1988; 9- Stumpf et al., 1989; 10- Coham W.E. and T.F.Bidleman, 1989.

It should be noted that values of these physical-chemical properties of endosulfan isomers different from those presented in [Herrmann, 2004] were selected for modelling mostly on the basis of the available published data. Values half-life in water and soil for endosulfan isomers were estimated as averages of data found in publication and available in data bases, Hazardous Substances Data Bank (HSDB) first of all. At that data for neutral conditions (pH=7) were used. Besides, in selecting such parameters as Henry's law constant and subcooled liquid-vapour pressure their temperature dependencies were used in the calculations. The full set of physical-chemical properties of endosulfan isomers used in the model parameterization is presented in Table III.7. Temperature dependences of some physical-chemical characteristics (Henry's law constant, subcooled liquid-vapour pressure, octanol-air partition coefficient) are given for the considered congeners at reference temperature equal to 283.15 K

Table III.7. Parameters of endosulfan isomers for modelling of atmospheric transport

Parameter Base values at 10 °C	Numerical value		References
	α -endosulfan	β -endosulfan	
Henry's law constant for freshwater, Pa m ³ /mol	5.30	0.307	<i>Rice et al., 1997; IADN Results, 2000</i>
Henry's law constant for seawater, Pa m ³ /mol	10.12	0.743	
Henry's law constant temperature coefficient, K	2288.2	8136.7	
Washout ratio	20 000	20 000	Selected value
Supercooled liquid saturated vapour pressure, Pa	0.00108	0.000746	<i>Hinckley et al., 1990</i>
Coefficient of subcooled liquid – vapor pressure temperature dependences, K	9581	9820	
Rate constants for reaction of endosulfan isomers and OH-radical, cm ³ /molecule·s	$8.25 \cdot 10^{-11}$	$7.59 \cdot 10^{-12}$	<i>Howard and Meylan, 1997</i>
Half-life in air, days	0.1	1.2	<i>Calc with the use of OH-distribution, mean in Europe [OH] = 8.8×10^5 molecule/cm³. Estimated on the basis of [OH] distribution.</i>
Degradation in water constant, s ⁻¹	$2.27 \cdot 10^{-7}$	$2.14 \cdot 10^{-7}$	<i>HSDB, 2001</i>
Half-life in water, days	35	37.5	
Degradation in soil constant, s ⁻¹	$1.6 \cdot 10^{-7}$	$1.34 \cdot 10^{-7}$	estimated
Half-life in soil, days	50	60	
Molar volume, cm ³ /mol	312.8	312.8	<i>Mackay et al., 1997, v.V</i>
"Octanol-water" coefficient	3981.1	6760.8	
"Octanol-air" coefficient	$1.77 \cdot 10^6$	$5.18 \cdot 10^7$	estimated
Temperature coefficient of K_{OA} coefficient, K	2017.1	7865.6	
Molecular diffusion coefficient, m ² /s			Calculated with the help of equations from <i>Schwarzenbach et al., 1993</i>
in water	$4.496 \cdot 10^{-10}$	$4.496 \cdot 10^{-10}$	
in the air	$4.549 \cdot 10^{-6}$	$4.549 \cdot 10^{-6}$	
"Organic carbon-water" partition coefficient, m ³ /kg	1.632	2.772	Calculated with the help of relationship between K_{OC} and K_{OW} given in <i>Karickhoff, 1981</i>

IV. DICOFOL

Dicofol is an organochlorine pesticide of widespread occurrence. Chemicals with different trade names (Kelthane, Hifol, Milbol et al.) and different content of dicofol were used in agriculture. In addition mixtures of dicofol with other pesticides were used. Dicofol is a miticide and broad-spectrum non-systematic acaricide with little insecticidal activity. It is used on terrestrial food crops and non-food sites [RED Dicofol, 1998].

Dicofol is included into the OSPAR List of Chemicals for Priority Action (Update 2004) [Meeting of the OSPAR Commission (OSPAR), 2004]. As a potential candidate for the inclusion into the UN-ECE Protocol on POPs this chemical was addressed by the Ad Hoc Expert Group on POPs [Lerche et al., 2002]. This year the Netherlands has re-submitted the dossier on dicofol [van de Plassche and Rasenberg, 2003] for technical review by the Task Force on POPs. Additional information for the evaluation of dicofol 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.

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 dicofol, the model calculation of its atmospheric transport from a conventional emission source located in Europe is made for one-year period. Since dicofol is a pesticide its emissions to the atmosphere occur as a result of its application on crop areas. In this connection, a conventional diffusive emission source covered the use area of approximately 200 by 200 km is considered. Of note, in this model assessment dicofol was treated not as one compound - p,p'-isomer but as the technical product - a mixture of two isomers (p,p'- and o,p'-dicofol).

To illustrate LRTP of dicofol, 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 dicofol is provided by the spatial distribution of air pollution caused by the considered conventional diffusive source.

Persistence in the environment is evaluated by *Half-life in the environment* ($T_{1/2}^{env}$) estimated for dicofol 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 dicofol with the help of the model dependent *TD* and $T_{1/2}^{env}$, a comparison of their numerical values against those obtained for adequately studied "benchmark substance" B[a]P is presented.

In conclusion, the calculated numerical characteristics of LRTP and persistence of dicofol 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/MSCE-E reports [Gusev et al., 2005] and on the Internet (<http://www.msceast.org>).

IV.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 dicofol with the help of above-mentioned characteristics obtained on the basis of the EMEP/MSCE-POP model calculations performed at the hemispheric level.

IV.1.1. Residence time in the atmosphere

To estimate the residence time in the atmosphere, the model calculation of atmospheric transport of dicofol 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 dicofol to the atmosphere are assumed to be 1 tonne per year from a conventional diffusive emission source with the use area of approximately 200 by 200 km and located in Europe (with centre in 10°E; 47.5°N). On the basis of this calculation annual atmospheric balance of the removal of dicofol from the atmosphere is estimated. The calculated balance of dicofol removal from the atmosphere is given in Fig. IV.1.

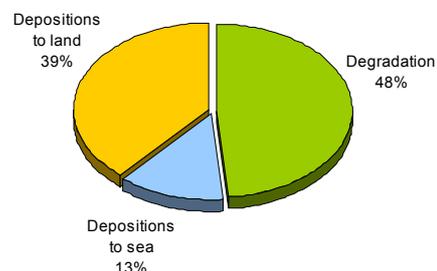


Fig. IV.1. Calculated annual balance of dicofol removal from the atmosphere

According to the model assessment, processes of degradation and depositions to different types of underlying surfaces contribute almost equally to the removal of dicofol from the atmosphere and produce equal effect on the calculated value of $T_{1/2}^{air}$. The character of 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 and some meteorological parameters. As seen from the balance, dicofol removal from the atmosphere due to deposition processes to soil is three times more intensive and affects LRTP of this pollutant to a greater extent than deposition to the sea surface.

In this model assessment degradation process of dicofol in the atmosphere is considered as the gas-phase interaction with photochemically – produced hydroxyl radicals and all other reactions are neglected. In the literature the half-life for this reaction is estimated to be 3.1 [Syracuse database, 2000 cited by van de Plassche and Rasenberg, 2003] and 4.7 days [HSDB, 2001]. For the model calculation of $T_{1/2}^{air}$, literary data on second-order degradation rate constant for the gas-phase of dicofol equal to $3.43 \cdot 10^{-12} \text{ cm}^3/\text{molec}\cdot\text{s}$ and derived using a structure estimation method [Howard and Meylan, 1997; HSDB, 2001] are used. The residence time of dicofol in the atmosphere ($T_{1/2}^{air}$) estimated on the basis of model calculations of its atmospheric transport totals to three days. The numerical value of this characteristic of LRTP for this compound fully meets the existing criterion for POPs (atmospheric half-life is greater than two days).

IV.1.2. Spatial distribution of pollution from conventional emission source

Additional information on LRTP of dicofol is provided by the spatial distribution of its air pollution obtained also on the basis of simulation of its atmospheric transport from conventional diffusive emission source and calculated atmospheric balance. In Fig. IV.2 concentration fields of dicofol 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.

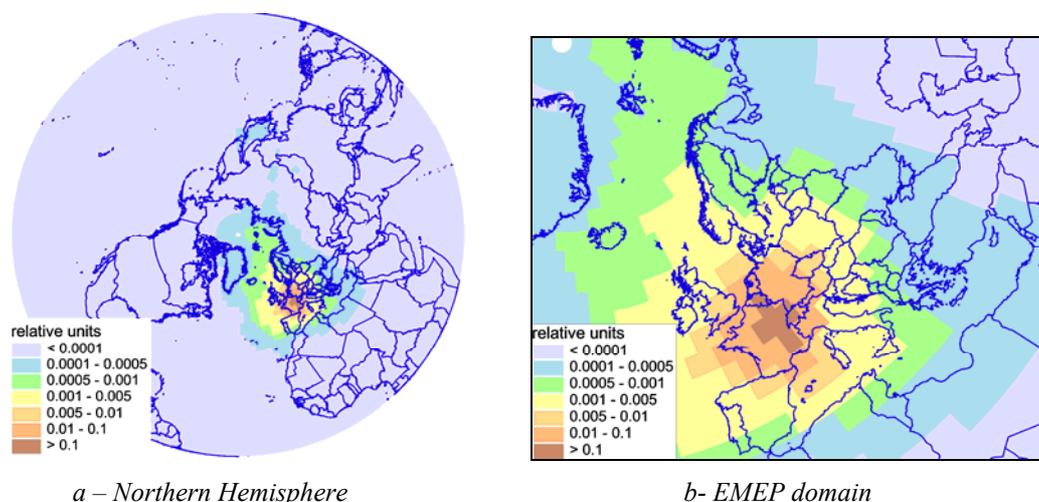


Fig. IV.2. Spatial distribution of dicofol concentrations in the above-ground air in the Northern Hemisphere and in the EMEP domain

With a conventional diffusive source of emissions located in Europe, the area of atmospheric air concentration of dicofol, which is 1000 times lower than the concentration near the source, is located over the most part of the Central Europe and the UK, includes Mediterranean Sea and Eastern Europe and reaches southern part of the Scandinavian Peninsula, northern Africa and middle-Atlantic. Considering the influence of the emission source on the EMEP domain in more detail (see Fig. IV.2b) shows that the most intensive air pollution by dicofol is characteristic of territories of France and its neighbouring countries - Switzerland and Belgium. The area with concentrations 100 times less than that near the source spreads also over the Netherlands, Austria and covers the considerable part of Germany, Italy and the Czech Republic.

IV.1.3. Transport Distance

Transport distance is the second numerical characteristic of LRTP obtained by the model calculations. The value of *TD* obtained by calculations depends on the processes removing the pollutant from the atmosphere. These are deposition to the underlying surface (land, sea) and atmospheric degradation. The calculated value of *TD* for dicofol occurs to be **1650 km**.

Both characteristics of LRTP obtained for dicofol with the help of model calculations are presented in Table IV.1.

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

Substance	$T_{1/2}^{air}$, days	<i>TD</i> , km
Dicofol	3	1650

The presented quantitative characteristics of dicofol LRTP meet the LRTP criteria of Executive Body Decision 1998/2.

IV.2. Persistence in the environment

Hydrolysis is expected to be an important fate process for dicofol with half-life value, which at pH 7 amounts less than 3 days. With decrease of pH up to 5 the value of hydrolysis half-life for the considered pollutant rises steeply up to 85 days [HSDB, 2001]. According to the data of Spray Material Half-life Chart 2005 the half-life of dicofol at pH 7 totals to 5 days; at pH 5 – 20 days. Thus, dicofol may be substantially more persistent in some acidic water, particularly in those with relative long hydrological residence times and low microbiological populations [RED Dicofol, 1998]. Data on acidity of surface water in the European and US countries available at present testify that water bodies are not acidic with pH values typically around 7- 8. However, there are sensitive, ecologically valuable water bodies in some regions in many countries with lower, more acidic pH values [van de Plassche and Rasenberg, 2003]. That is why, for the sake of model parameterisation half-life of dicofol in water was taken as an average value between available data for the interval of pH from 5 to 7, i.e. 30 days. Besides, the half-life of dicofol in water depends not only upon the above-mentioned hydrolysis but also on the life activity of organisms and intensity of ultraviolet radiation. For soluble dicofol, photolysis may be important degradation pathway. The half-life for this reaction is 37 days.

The different estimates of dicofol persistence in soil can be found in various literary sources. The scattering of data on half-life of dicofol in soil available in the literature is reflected in Table IV.2.

Laboratory and field studies indicate that dicofol has a short to intermediate half-life and is moderately persistent in the environment as a result of normal label use [HSDB, 2001]. Since substances classified as moderately persistent have half-life values amounting from 30 to 100 days, half-life of dicofol in soil equal to 60 days was taken for model parameterisation. Besides, of note, the technical product for the most part contains p,p'-dicofol (80%), which is more persistent in soil than o,p'-isomer.

Table IV.2. Dicofol half-life in soil and bottom sediment

Half-life, days	Notes	References
45		<i>Pesticide Properties in the Environment</i> , [1996]
66.4	Aerobic soil	<i>PAN Pesticides Database - Chemicals</i>
203		<i>ARS pesticide properties</i> , at pH=7.8
15.9	Anaerobic soil	<i>PAN Pesticides Database - Chemicals</i>
16		<i>ARS pesticide properties</i> , at pH=7.8
60		<i>EXTOXNET</i>
15.9	Anaerobic soil condition	
30	Silty loam, photodegradation	
58	California cotton fields, irrigated soil	
113	Florida, citrus groves	<i>HSDB</i> , 2001
90	New York, apple orchards	
43	Silty loam, biodegradation	
194 – 345	Bottom sediment and soil at aerobic conditions	
30	Bottom sediment and soil at anaerobic conditions	

For dicofol 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 dicofol in comparison with its annual degradation balance is shown in Fig. IV.4.

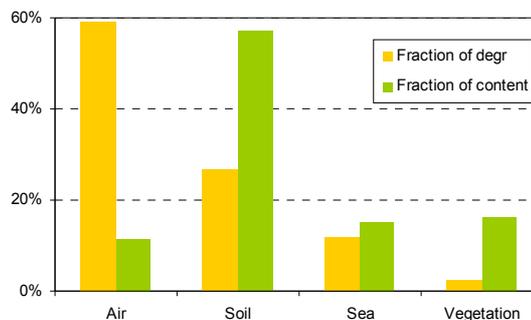


Fig. IV.4. Annual degradation and media balances for dicofol

By the end of a year 1 tonne of dicofol emitted to the atmosphere has degraded in this medium more than by half. At that the degradation of dicofol amount appeared to be in soil due to intermedia exchange processes between the atmosphere and soil is equal to almost 30%. The contribution of vegetation to dicofol degradation is practically negligible amounting to 2%, the relative fraction of the pollutant degraded in sea is somewhat higher totalling to 12%. At that more than a half of overall dicofol content in the environment is accumulated in soil, 10% remain in the air, the rest part of the pollutant is distributed in the following way: seawater – 15%, and vegetation – 16%. Thus, model calculations allow us to demonstrate the re-distribution of dicofol between main environmental media defining among them the media capable to accumulate the most part of the considered pollutant as well as those characterized by the most intensive degradation of the substance.

Calculated value of Half-life in the environment for dicofol is equal to 20 days (or 0.7 month). The obtained estimate of $T_{1/2}^{env}$ together with values of half-life in the separate environmental media used for modelling are presented in Table IV.3.

Table IV.3. Characteristics of Persistence (Half-life in environment) and half-life of dicofol in different environmental media used for modelling of atmospheric transport

Substance	$T_{1/2}^{env}$		Half-life, days		
	days	months	air	water	soil
Dicofol	20	0.7	3	30	60

The obtained value of $T_{1/2}^{env}$ shows that persistence of dicofol in the environment is relatively not high. Also it should be noted that value of $T_{1/2}^{env}$ is lower than those of half-life in water and soil, which take into account degradation processes only.

IV.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 chemical ranking and classification approach are described by Matthies *et al.* 1999], Beyer *et al.* [2000] 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 dicofol against those obtained for a benchmark pollutant is presented in this subsection. Benzo[a]pyrene (B[a]P) is used as a benchmark substance in this assessment. Characteristics of its behaviour in the environment are well studied and clearly meet UN ECE criteria. 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 diffusive source with one and the same location in Europe and one and the same emissions intensity.

The considered dicofol and B[a]P have been ranked in ascending order according to their values of *Half-life in the environment* (Fig. IV.4a) and *Transport Distance* (Fig. IV.4b).

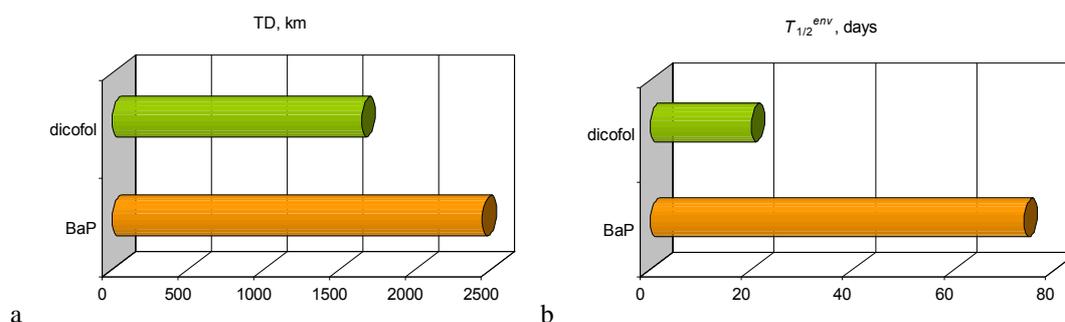


Fig. IV.4. Half-life in the environment and Transport distance calculated for dicofol and B[a]P

The ranking of dicofol and B[a]P with respect to $T_{1/2}^{env}$ shows that dicofol is less persistent than B[a]P. According to the model calculations of *TD*, LRTP of dicofol is slightly less than that of B[a]P.

Thus, according to the results of the present investigation, dicofol meets the LRTP criteria for POPs.

IV.4. Characteristics of dicofol LRTP and persistence in relation to the indicative criteria outlined in Executive Body Decision 1998/2

In Table IV.4 dicofol properties presented in [van de Plassche and Rasenberg, 2003] are compared to criteria of Executive Body Decision 1998/2 with additions of the MSCE-POP model outputs.

Table III.4. Comparison of properties of dicofol and criteria of Executive Body Decision 1998/2 based on data [van de Plassche and Rasenberg, 2003] and with additions of MSCE-POP model outputs

Criterion	Criterion values	Meets the criterion (Yes/No)	Characteristics of dicofol	Remarks
Potential for Long-range Transboundary Atmospheric transport				
Vapour pressure, Pa	<1000	Yes	5.3×10^{-5}	Presented in van de Plassche and Rasenberg, 2003
Half-life in air, days	>2	Yes	3.1 – gas phase; 3.5 – 10 - particles	
Half-life in aircalc, days		Yes	3	$T_{1/2}^{air}$ calculated by MSC-E
Persistence				
Half-life in water, months	>2	Yes	Half-life o,p'-isomer: 47; 0.3 and <0.1 days for pH 5, 7, and 9. Half-life p,p'-isomer: 85, 4 and <0.1 days for pH 5, 7 and 9.	Presented in van de Plassche and Rasenberg, 2003
Half-life in soil, months	>6	No	Half-life o,p'-isomer: 8-35 days. Half-life p,p'-isomer; 21-60 days.	
Half-life in sediments, months	>6	No	Half-life < 1 day for p,p'-isomer and p,p'-isomer (pH water phase 7.6-7.8).	
Half-life in the environment, months	-	-	0.7 months (20 days)	$T_{1/2}^{env}$ calculated by MSC-E

The results of the model assessment demonstrate the considerable long-range atmospheric transport potential and relatively low persistence of dicofol in the environment. This conclusion is also confirmed by the comparison of calculated numerical characteristics of LRTP and persistence of dicofol against those obtained for typical POP of regional concern – B[a]P. However, it should be noted that in this model assessment the behaviour of dicofol in the environment was studied as for the mixture of two isomers. Besides, due to the lack of available data on dicofol isomers in the literature, the model estimates are obtained not taking into account temperature dependence of their key physical-chemical properties such as subcooled liquid-vapour pressure, the Henry's law constant, and partition coefficients. In this connection the obtained model results should be considered as preliminary.

IV.5. Physical-chemical properties of dicofol used for modelling

In industry dicofol manufacture begins with DDT dehydrochlorination and the received product is sequentially chlorinated and treated with hydrochloric acid. As a result a mixture of p,p'-dicofol (~80%) and o,p'-dicofol (~20%) is produced. In addition the technical product always has admixtures such as metabolites of DDT and its derivatives as well as other compounds. 18 species in all have been identified [Clark, 1990]. Modern manufacturing processes can produce technical grade dicofol which contains less than 0.1% DDT [EXTOXNET]. In this model assessment dicofol was treated not as one compound - p,p'-isomer but as the technical product - a mixture of two isomers. Obviously presence of admixtures in the preparation, first of all of o,p'-isomer, should influence its physical-chemical properties. At present in the literature, values of saturated vapour pressure, solubility etc. are given for the technical product. Therefore, for further understanding of the behaviour of the substance in the environment more detail investigation of key physical-chemical properties of the dicofol isomers is needed.

Key physical-chemical properties of dicofol presented in [van de Plassche and Rasenberg, 2003] are shown in Table IV.5.

Table IV.5. Physical-chemical properties of dicofol presented in [van de Plassche and Rasenberg, 2003]

Physical chemical properties	Numerical values
Vapour pressure, Pa	5.3· 10 ⁻⁵ [1]
Henry's law constant, Pa·m ³ /mol	-
Octanol-water partition coefficient (log K _{OW})	4.08 – 5.02 – various sources
Half-life, days	
Air	3.1 [2]
Water	Hydrolysis half-life o,p'-isomer: 47; 0.3 and <0.1 days for pH 5; 7; and 9. Hydrolysis half-life p,p'-isomer: 85; 4 and <0.1 days for pH 5; 7 and 9. Photodegradation half-life o,p'-isomer – 1.5 and 14.8 days for sensitised and non-sensitised conditions. Photodegradation half-life p,p'-isomer - 4 and 92.5 days, respectively [3].
Soil	On silt loam soil irradiated with artificial light half-life o,p'-isomer- 30 days, half-life p,p'-isomer-21-30 days [4]. In a silt loam half-life p,p'-isomer of 43 days, in anaerobic conditions – 30 days [5]. O,p'-dicofol degraded in aerobic soil with a half-life of 8 days in a loam soil. Under anaerobic condition o,p'-dicofol degraded with a half-life of 6 days from a flooded silt loam soil [4]. Field dissipation studies total parent – t _{1/2} = 62 days at pH 8.4-8.9 (Kelthan 35); t _{1/2} = 3.7 days at pH 6.3-7.2 (Kelthan MF). p,p'-dicofol - t _{1/2} = 50-60 days and o,p'-dicofol - t _{1/2} = 30-35 days at pH 7 (Kelthan APS NEW) [3].
Sediment	Half-life o,p'-isomer: 0.31-54 days. Half-life p,p'-isomer: 0.05-0.06 days

Reference: 1 - Pesticide Manual; 2 - Syracuse Database; 3 - IUCLID dataset; 4 - EPA RED; 5 - MRID 41050701

Since the temperature dependences of all physical-chemical properties and degradation rates of dicofol were not found in the literature, the analysis of available data did not allow us to prepare the “traditional” model parameterisation as it is made in MSCE-POP model usually. The set of dicofol properties used for the model assessment is presented in Table IV.6.

Table IV.6. Physical-chemical properties of dicofol used for modelling of its atmospheric transport

Physical-chemical properties	Values at 25 °C	References
Henry' s law constant for fresh water, Pa m ³ /mol	0.0244	<i>HSDB</i> , 2001
Henry' s law constant for marine water, Pa m ³ /mol	0.0244	
Coefficient of Henry's law constant temperature dependences, K	-	
Washout ratio	20 000	Selected value correspond Washout ratio for p,p'-DDT
Subcooled liquid-vapour pressure, Pa	$3.07 \cdot 10^{-4}$	Estimated on Ps at 25 °C <i>Mackay et al.</i> [1997], vol.V
Coefficient of subcooled liquid-vapour pressure temperature dependences, K	-	
Rate constant of the reaction with OH-radical in air, cm ³ /c	$3.43 \cdot 10^{-12}$	<i>Howard and Meylan</i> , 1997
Half-life in air, days	3	Calc with the use of average value of OH- spatial distribution used in the model: [OH] = 8.8×10^5 molecule/cm ³
Degradation rate constant in water, c ⁻¹	$2.14 \cdot 10^{-7}$	Selected value on data from <i>HSDB</i> , 2001
Half-life in water, months	1	
Degradation rate constant in soil, c ⁻¹	$1.34 \cdot 10^{-7}$	
Half-life in soil, months	2	
Molar volume, cm ³ /моль	333.5	Molar volume for p,p'-DDT, <i>Mackay et al.</i> [1997], vol.V
«Octanol-water» partition coefficient	19100	<i>HSDB</i> , 2001
«Octanol-air» partition coefficient	$1.95 \cdot 10^9$	Estimated
Coefficient of «octanol-air» partition coefficient temperature dependence, K	-	
Molecular diffusion coefficients, m ² /s:		Calculated with the help of equations from <i>Schwarzenbach et al.</i> , 1993
in water	$4.92 \cdot 10^{-10}$	
in air	$4.49 \cdot 10^{-6}$	
“Organic carbon-water” partition coefficient, m ³ /kg	7.812	Calculated with the help of relationship between <i>K_{OC}</i> and <i>K_{OW}</i> given in <i>Karickhoff</i> [1981]

V. HEXACHLOROBUTADIENE (HCBD)

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.

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 multicompartiment 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.

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.

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/MSCE-E reports [Gusev *et al.*, 2005] and on the Internet (<http://www.msceast.org>).

V.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.

V.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 t/y 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. V.1.

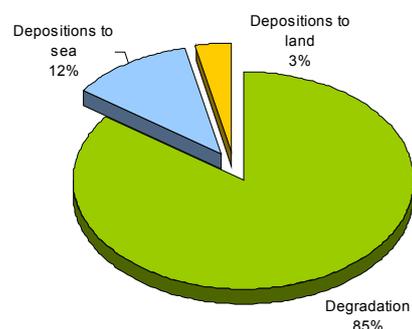


Fig. V.1. Calculated annual balance of HCBd removal from the atmosphere

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 $2.24 \cdot 10^{-14}$ cm³/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/cm³), 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).

V.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. V.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.

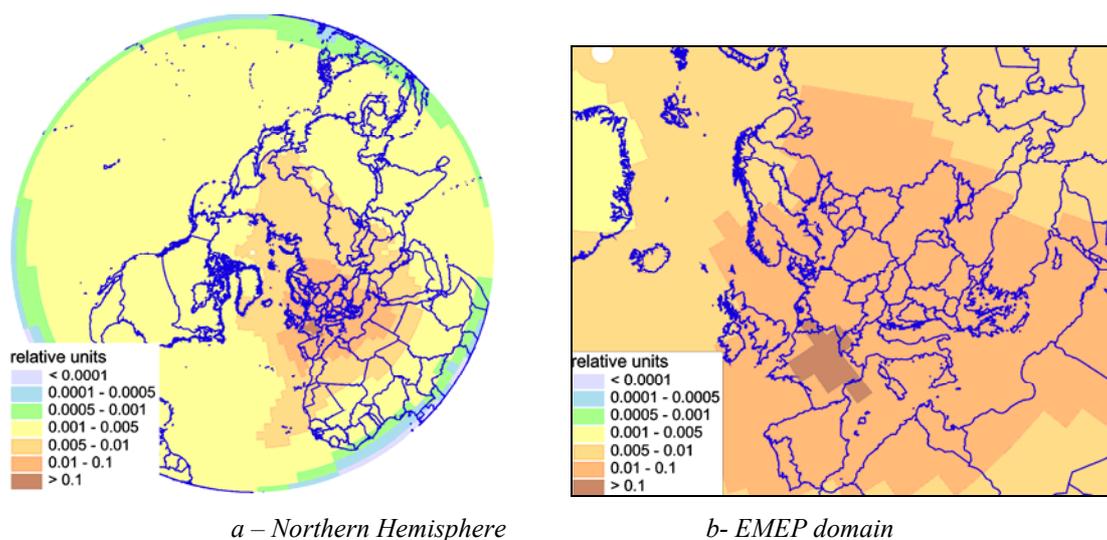


Fig. V.2. Spatial distribution of HCBd concentrations in the above-ground air in the Northern Hemisphere and in the EMEP domain

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 V.1.

Table V.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 ± 0.58 ng/m³ and this concentration estimated for the Southern Hemisphere - 0.81 ± 0.35 нг/м³ [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/m³ or 100 ng/m³. 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/m³ [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/m³ and in atmospheric deposition (0.042 ng/m²/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/m³.

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.

V.1.3. 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 V.2.

Table V.2. Characteristics of LRTP (Half-life in air_{calc} and Transport Distance) calculated for HCBd

Substance	$T_{1/2}^{air}$, days	<i>TD</i> , km
HCBd	118	8784

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

V.2. Persistence in the environment

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 V.3.

Table V.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. <i>et al.</i> , 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 Howard *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. V.3.

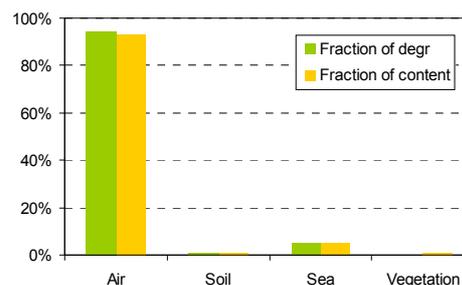


Fig. V.3. Annual degradation and media balances for HCBd

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 are presented in Table V.4.

Table V.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

The obtained value of *Half-life in the environment* shows that HCBd possesses 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 takes into account degradation processes only, and considerably exceeds those for degradation in water and soil.

V.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 HCB and 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. V.4a) and *Half-life in the environment* (Fig. V.4b).

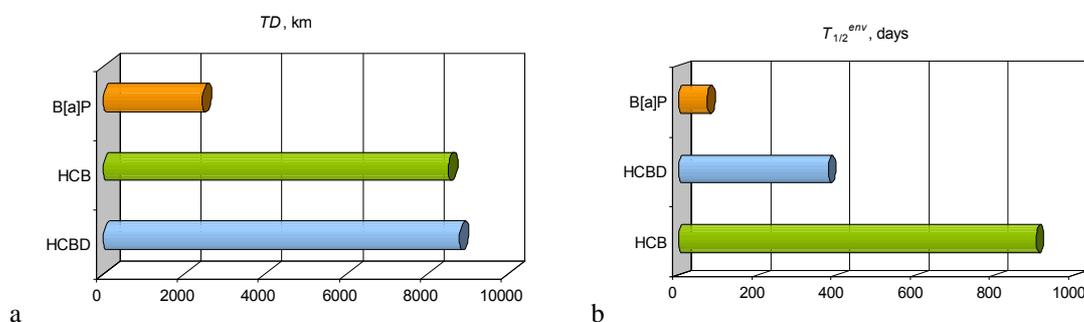


Fig. V.4. *Transport distance and Half-life in the environment calculated for HCBd, B[a]P and HCB*

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.

V.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 Schwegler, 2005] are given in Table V.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.

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

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 <i>van de Plassche and Schwegler</i> [2005]
Half-life in air, days	>2	Yes	200-350 days	
Half-life in air _{calc.} , days		Yes	118 days	
Persistence				
Half-life in water, months	>2	Yes	Based on scarce and sometimes conflicting information	Presented in <i>van de Plassche and Schwegler</i> [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.

V.5. Physical-chemical properties of hexachlorobutadiene used for modelling

Key physical-chemical properties and degradation rates of HCBD presented in [van de Plassche and Schwegler, 2005] are shown in Table V.6.

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 V.7.

Table V.6. 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]
Henry's Law constant, Pa·m ³ /mol	1044 – 2604 [Mackay et al., 1998]
Octanol-water partition coefficient (log <i>K</i> _{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	-

Table V.7. Physical-chemical properties of HCBd used for modelling

Physical-chemical properties	Values	References
Henry's law constant for fresh water at 10 °C, Pa m ³ /mol	443	HSDB, NIST [2001]
Henry's law constant for marine water at 10 °C, Pa m ³ /mol	443	
Coefficient of Henry's constant temperature dependences, K	4700	
Subcooled liquid-vapour pressure at 10°C, 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 · 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 · 10 ⁵ molec/cm ³
Degradation rate constant in water, s ⁻¹	8.02 · 10 ⁻⁸	Estimated
Half-life in water, days	100	
Degradation rate constant in soil, s ⁻¹	4.58 · 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 °C	60256	Howard and Meylan [1997]
«Octanol-air» partition coefficient at 10 °C	3.2 · 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 · 10 ⁻¹⁰	
in air	6.18 · 10 ⁻⁶	
“Organic carbon-water” partition coefficient, m ³ /kg	24.705	Calculated with the help of relationship between <i>K</i> _{OC} and <i>K</i> _{OW} given in Karickhoff [1981]

VI. PENTACHLOROBENZENE (PECB)

Pentachlorobenzene (PeCB) is a widespread organochlorine compound. PeCB is always present in all chlorinated benzenes, which in their turn are widely known as:

- intermediate products at the production of many organic species;
- solvents in stain manufacturing;
- additions to transformer oils and lubricants.

Besides, there is information about the presence of chlorinated benzenes in emissions (flue gases) from pulp and paper mills. PeCB concentrations in pulp and paper mills in Finland are from 0.2 to 0.9 $\mu\text{g}/\text{m}^3$ [HSDB, 2001]. This substance is also present as an admixture to pentachlorophenol, other chlorinated phenols and hexachlorobenzene therefore it can be found in places of their application. PeCB like others chlorinated aromatic compounds with one and more benzene rings are identified at different stages of solid domestic waste incineration [Wilkström and Marklund, 2000]. PeCB can be formed "de novo" at the combustion of ethane, ethylene and acetylene at the presence of hydrogen chloride and catalysts which are silicon, aluminium and copper oxides and flue soot particles [Fröse and Hutzinger, 1996a,b]. PeCB was the original reagent for the manufacturing the fungicide **quintozene** or pentachloronitrobenzene (PCNB). Mainly PCNB is used as a fungicide against agents of diseases of cotton, grain-crops, vegetables and decorative cultures.

PeCB is within a scope of interest of the Task Force on POPs as a potential candidate for the inclusion into the Protocol on POPs. 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 preliminary dossier on PeCB prepared by national experts [van de Plassche et al., 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 PeCB 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.

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 multicompartiment hemispheric transport model is used. To estimate the considered parameters for PeCB, 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 PeCB used for modelling is included in Annex A.

To illustrate LRTP of PeCB, two numerical characteristics are calculated. The first one is residence time in the atmosphere (*Half-life in air*_{calc} ($T_{1/2}^{\text{air}}$)) 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 PeCB is provided by the spatial distribution of air pollution caused by the considered conventional point source.

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

To diminish uncertainties in evaluating LRTP and persistence of PeCB with the help of the model dependent TD and $T_{1/2}^{env}$, a comparison of their numerical values calculated for the considered chemical 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 PeCB 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/MSCE reports [Gusev *et al.*, 2005] and on the Internet (<http://www.msceast.org>).

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

VI.1.1. Residence time in the atmosphere

To estimate the residence time in the atmosphere, the model calculation of atmospheric transport of PeCB 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 PeCB to the atmosphere are assumed to be 1 tonne per year from a conventional point source located in Europe (10°E; 47.5°N). On the basis of this calculation annual atmospheric balance of PeCB emitted to the atmosphere is estimated. The calculated balance for the processes of PeCB removal from the atmosphere is given in Fig.VI.1.

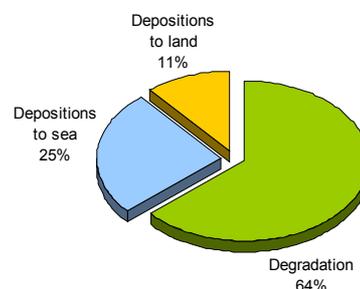


Fig. VI.1. Calculated annual balance of PeCB removal from the atmosphere

The calculated balance reveals that the most significant process affecting LRTP of PeCB in the atmosphere is degradation. It was found that approximately 64% of this pollutant are removed from the air through degradation, whereas depositions to sea and land underlying surfaces amount to 25 and 11%, respectively.

The character of the calculated balance for PeCB is determined for the most part by such key physical-chemical properties as subcooled liquid-vapour pressure, Henry's law constant and degradation rate constant. Being characterized by relatively high value of subcooled liquid-vapour pressure, PeCB occurs in the atmosphere mostly in the gaseous phase. Based on the second-order degradation rate constant for the PeCB gas-phase equal to $5.90 \cdot 10^{-14} \text{ cm}^3/\text{molec}\cdot\text{s}$ [Howard and Meylan, 1997] and the average value of OH radical spatial distribution implemented in the model ($8.8 \cdot 10^5 \text{ molec}/\text{cm}^3$), the atmospheric half-life of PeCB due to the degradation process only is estimated to be 155 days.

According to the model assessment of PeCB atmospheric transport performed taking into account not only degradation in the atmosphere, but also dry and wet deposition and gaseous exchange with various underlying surfaces, its residence time in the atmosphere ($T_{1/2}^{\text{air}}$) totals to 65 days or approximately 2.2 months. This calculated numerical value characterising LRTP of PeCB fully meets the existing criterion for POPs (atmospheric half-life is greater than two days).

VI.1.2. Spatial distribution of pollution from conventional emission source

To illustrate the relatively high ability of PeCB to the atmospheric transport, an additional characteristic of LRTP for this pollutant can be provided by the spatial distribution of its air pollution obtained with the help of the model simulation. The calculated fields of PeCB air pollution in the Northern Hemisphere and EMEP domain caused by the considered conventional emission source located in Europe are given in Fig. VI.2a,b. For convenience, we present air concentrations of PeCB in the relative units so that the maximum value equals 1 near the source (basic value).

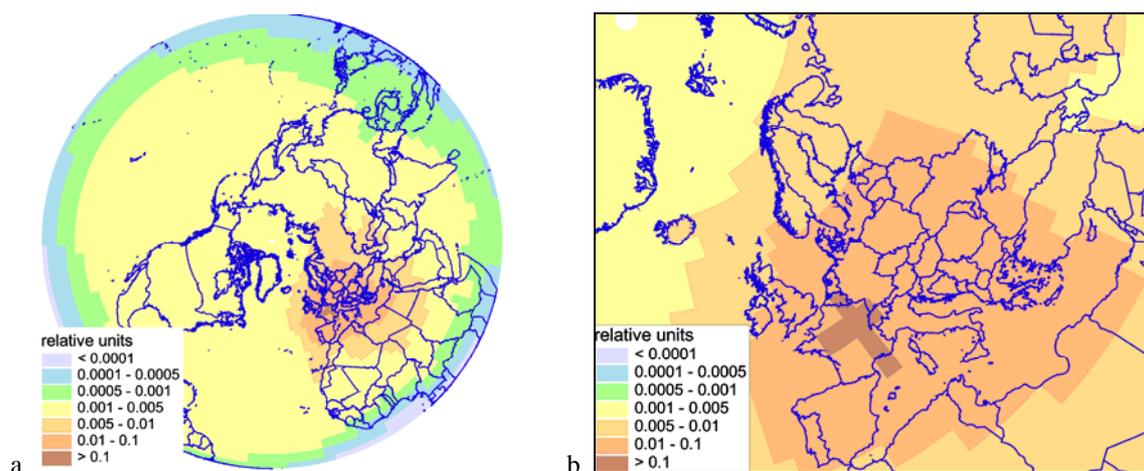


Fig. VI.2. Spatial distribution of PeCB concentrations in the above-ground air in the Northern Hemisphere and in the EMEP domain

According to the model assessment, the area where air concentrations of PeCB drop down less than 1000 times covers the whole territory of Europe, as well as that of the Americas, Asia and of the considerable part of Africa. Large pollution field with relatively high levels of PeCB air concentrations (0.005 – 0.01 of the concentration near a source) is located over the northern Africa, the entire Central Asia, the territory of Russian Federation together with its Arctic part, the Atlantic Ocean and approaches Greenland. The levels of air concentrations over the major part of European countries are considerably higher varying from 0.01 to 0.1 of the basic value.

A reasonable amount of monitoring data is available for PeCB [van de Plassche et al., 2005]. Some additional data on measurements of air concentrations carried out in 1980s in the different regions of the Northern Hemisphere (Arctic, Great Lakes, Germany, etc.) are given in Table VI.1. Mean values of PeCB air concentrations recorded at stations of European (see the table) and Canadian Arctic (31 – 135 pg/m³ at Ellesmere Island, see [van de Plassche et al., 2005]) are close and kept mostly within the same order of magnitude.

Table 1. Measured values of PeCB concentrations in air

Sampling site	Date	Number of samples	PeCB air concentration, pg/m ³		Reference
			Range	Mean value	
European Arctic					
Bear Island	1980, September	n = 5	3.3 - 6.2	4.5	Oeme and Manø [1984]
	1981, February	n = 5	7.0- 31	18	
Lillestroem	1981, May	n = 5	30 - 78	43	
Spitzbergen	1980, September	n = 4	5.1 - 23	11	
	1981, February	n = 5	6 - 37	22	
Great Lakes					
Egbert, ON	1988, July 1989, September	n = 143	0.04 - 78	>54	Hoff et al. [1992]
Southern Ontario	-	-	8		HSDB [2001]
USA					
Niagara Falls	-	-	17		HSDB [2001]
State Michigan			35 – 69		
American Samoa			9		
Germany					
Hamburg	1986 – 1987			920	Bruckmann and Kersten [1988]
Bavaria			100 – 190		HSDB, 2001
Other regions					
Enewetak atoll			16		HSDB [2001]
Peruvian coast			24		
New Zeland			16		

In the framework of measurement study of hexachlorobutadiene carried out at the background sites Råö and Pallas in 2003 [Kaj and Palm, 2004] a number of samples have been also screened for PeCB. It was found that measured air concentrations of this pollutant varied in the range from 16 to 57 pg/m³. Of note, air concentrations of HCB also measured within this study were equal to 12 - 86 pg/m³ at the same sites. Atmospheric depositions of PeCB and HCB at Råö were 85 and 140 pg/m²/day, respectively.

VI.1.3. 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 PeCB the contribution of degradation process to its removal from the atmosphere is more significant than that of deposition. The calculated value of TD for PeCB is amounted to 8256 km. Both characteristics of LRTP obtained for PeCB with the help of model calculations are presented in Table VI.2.

Table 2. Characteristics of LRTP (Half-life in air_{calc} and Transport Distance) calculated for PeCB

	$T_{1/2}^{air}$, days	TD , km
PeCB	65	8256

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

V.2. Persistence

The distribution of PeCB 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 annual media balance of PeCB in comparison with its annual degradation balance is shown in Fig. VI.3.

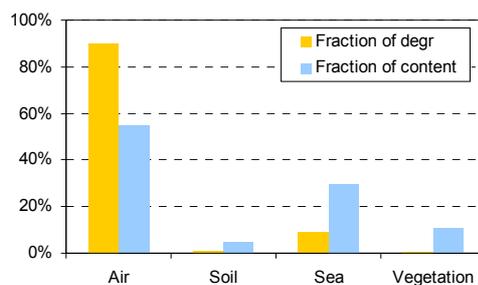


Fig. VI. 3. Annual degradation and media balances for PeCB

According to the model assessment, the most part of PeCB total content in the environment (more than 50%) by the end of the year occurs in the atmosphere. Seawater accumulates approximately 30% of PeCB environmental content. Its content in soil and vegetation equals 5 and 11%, respectively. This testifies that the value of the PeCB 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 PeCB and the values of its half-life in each of the considered environmental media, the obtained value of Half-life in the environment for PeCB is equal to 188 days or approximately 6.3 months. The calculated estimate of $T_{1/2}^{env}$ together with values of half-life in the particular environmental media used for modelling are presented in Table VI.3.

Table VI.3. Characteristics of Persistence (Half-life in environment) and half-life of PeCB in different environmental media used for modelling of atmospheric transport

Substance	$T_{1/2}^{env}$, months	Half-life, months		
		air	water	soil
PeCB	6.3	5.2	11.6	11.6

According to the model value of *Half-life in the environment*, persistence of PeCB in the environment can be characterised as high enough. At that the obtained value of $T_{1/2}^{env}$ is considerably lower than those of half-life due to degradation process in soil and seawater and higher than that for degradation in the atmosphere only.

VI.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 P_{ov} 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 PeCB 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 behaviour 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 PeCB, B[a]P and HCB have been ranked in ascending order according to their values of *Transport Distance* (Fig. VI.4a) and *Half-life in the environment* (Fig. VI.4b).

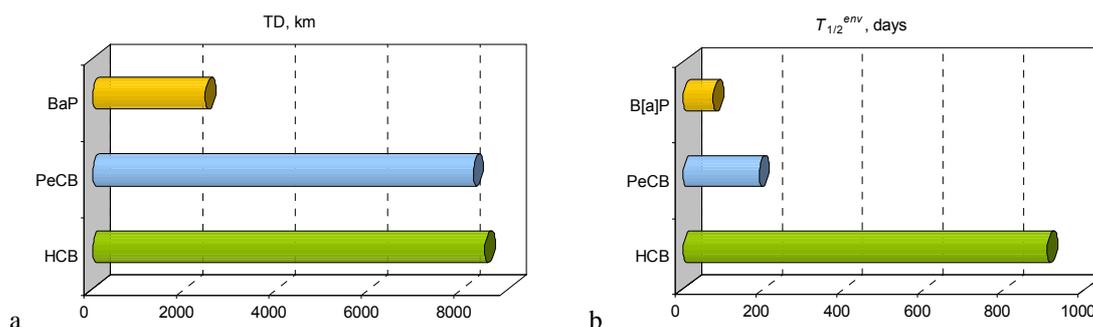


Fig. VI.5. Transport distance and Half-life in the environment calculated for PeCB, B[a]P and HCB

According to the model calculations of TD , LRTP of PeCB is considerably higher than that of B[a]P and close to that of HCB. Like the latter pollutant of the global concern PeCB also can be transported over long distances. Therefore, environmental pollution by PeCB should be viewed at hemispheric or global scale. The ranking of PeCB, B[a]P and HCB with respect to $T_{1/2}^{env}$ values shows that PeCB are found to be more persistent in the environment than B[a]P but less than HCB.

Thus, according to the results on ranking the considered substances, numerical characteristics of LRTP and persistence obtained by modelling for PeCB is comparable with those calculated for the adequately studied “benchmark” pollutants already included into the Protocol on POPs. It can be noted that PeCB meets both the LRTP and persistence criteria for POPs.

VI.4. PeCB characteristics of LRTP and persistence in relation to the indicative criteria outlined in Executive Body decision 1998/2

Characteristics of LRTP and persistence of PeCB presented in [van de Plassche et al., 2005] and obtained by the model calculations are given in Table 4 in relation to the indicative criteria outlined in the Executive Body Decision 1998/2.

Table VI.4. Characteristics of LRTP and persistence of PeCB presented in [van de Plassche et al., 2005] and obtained by modelling in relation to the indicative criteria outlined in the Executive Body Decision 1998/2

Criterion	Criterion values	Meets the criterion (Yes/No)	Characteristics of PeCB	Remarks
<i>Potential for Long-Range Transboundary Atmospheric Transport</i>				
Vapour pressure, Pa	< 1000	Yes	2.2 at 25 °C	Presented in van de Plassche et al., 2005
Half-life in air, days	>2	Yes	277	
Half-life in air _{calc} , days		Yes	65	
<i>Persistence</i>				
Half-life in water, months	> 2	Yes	6.5 – 46.0	Presented in van de Plassche et al., 2005
Half-life in soil, months	>6	Yes	3.4 -11.5	
Half-life in sediment, months	>6	Yes	3.4 -11.5	
Half-life in the environment, months	-	-	6.3	

Thus, the model results on *Half-life in air_{calc}* and *Half-life in the environment* show that PeCB fully meets the criterion for Potential for Long-Range Transboundary Atmospheric Transport and Persistent in the environment with criterion values of half-life outlined in the Executive Body Decision 1998/2. Besides, it can be also confirmed by the comparison of calculated numerical characteristics of LRTP and persistence of PeCB against those obtained for B[a]P and HCB as well-studied pollutants already included into the Protocol on POPs.

VI.5. Physical-chemical properties of pentachlorobenzene used for modelling

The key physical-chemical properties and degradation rates of PeCB presented in [van de Plassche et al., 2005] are shown in Table VI.5.

Table VI.5. *Physical-chemical properties and degradation rates of PeCB presented in [van de Plassche et al., 2005]*

Physical chemical properties	Numerical values
Vapour pressure, Pa	2.2 at 25 °C
Solubility in water, mg/L	0.56 at 20 °C
Henry's Law constant, Pa·m ³ /mol	-
Octanol-water partition coefficient (log <i>K_{OW}</i>)	4.8 – 5.18
Half-life, days	
Air	277 [Syracuse database] 45 – 467 [CEPA, 1993]
Water	194 – 1250 – surface water [CEPA, 1993] 776 – 1380 – anaerobic biodegradation in deeper water [CEPA, 1993]
Soil	194-345 [Beck and Hansen, 1974] 109-219 – sewage sludge-amended soil [Min-Jian Wang et al., 1994]
Sediment	7 years – sediment cores, native anaerobic microflora [Beurskens et al., 1994] 7 – special mixed culture of anaerobic species [Beurskens et al., 1994]

The full set of physical-chemical properties and degradation rates of PeCB selected for the model parameterisation on the basis of data available in literature is presented in Table VI.6.. Temperature dependences of some physical-chemical characteristics (Henry's law constant, subcooled liquid-vapour pressure, octanol-air partition coefficient) are given at reference temperature equal to 283.15 K.

Table VI.6. Physical-chemical properties and degradation rates of PeCB used for modelling

	Numerical values	References
Henry's law constant for fresh and sea water at 10 °C, Pa·m ³ /mol	32.6	Estimated with the use of temperature dependence p_{OL} and S_{WL} from <i>Beyer and Matthies</i> [2001]
Coefficient of Henry's law constant temperature dependences, K	5638	
Subcooled liquid-vapour pressure at 10 °C, Pa	0.19	<i>Beyer and Matthies</i> [2001]
Coefficient of subcooled liquid – vapour pressure temperature dependences, K	7832	
Rate constant of the reaction with OH-radical in air, cm ³ /molec·s	$5.90 \cdot 10^{-14}$	<i>Howard and Meylan</i> [1997]
Half-life in air, days	155	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	$2.3 \cdot 10^{-8}$	<i>HSDB</i> [2002]
Half-life in water, days	349	
Degradation rate constant in soil, s ⁻¹	$2.3 \cdot 10^{-8}$	<i>HSDB</i> [2002]
Half-life in soil, days	349	
Molar volume, cm ³ /mol	153.9	<i>Ruelle and Kesselring</i> [1997]
«Octanol-water» partition coefficient at 25 °C	69500	<i>Beyer and Matthies</i> [2001]
«Octanol-air» partition coefficient at 10 °C	$8.81 \cdot 10^6$	<i>Harner and Mackay</i> [1995]
Coefficient of K_{OA} temperature dependences, K	8489	
Molecular diffusion coefficients, m ² /s:		Calculated with the help of equations from <i>Schwarzenbach et al.</i> [1993]
in water	$7.76 \cdot 10^{-10}$	
in air	$6.43 \cdot 10^{-6}$	
“Organic carbon-water” partition coefficient, m ³ /kg	28.504	Calculated with the help of relationship between K_{OC} and K_{OW} given in <i>Karickhoff</i> [1981]

VII. POLYCHLORINATED NAPHTHALENES (PCNs)

Polychlorinated naphthalenes (PCNs) are a group of compounds composed of two fused benzene rings with one to eight chlorine substitutions. Their molecular structures are similar to those of PCDD/Fs and PCBs. Several of the higher chlorinated congeners are found to elicit biochemical responses similar to the toxic 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) [Lundgren *et al.*, 2003]. A quantitative assessment of dioxin-like potential of PCN congeners has been performed in several studies [Hanberg *et al.*, 1990, Blankenship *et al.*, 1999; Villeneuve *et al.*, 2000; Blankenship *et al.*, 2000, etc].

Due to chemical and thermal stability, good electrical insulation properties, excellent weather resistance and low flammability, PCNs were manufactured as several different technical formulations and widely used in electrical and electronic equipment [Järnberg *et al.*, 1997]. Besides, several emission sources of PCNs in the environment have been suggested apart from those associated with the production and continued use of these formulations. In particular, PCNs are usually common impurities found in technical PCB mixtures and they are formed in thermal (e.g. combustion, roasting, metal reclamation) and other processes (e.g. chloro-alkali industry) in the presence of chlorine [Falandysz, 1998].

PCNs are included into the OSPAR List of Chemicals for Priority Action (Update 2004) [Meeting of the OSPAR Commission (OSPAR), 2004]. As potential candidates for the inclusion into the UN ECE Protocol on POPs this group of compounds 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 PCNs. 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 PCNs prepared by national experts [van de Plassche and Schwegler, 2002] 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 PCNs as potential new POPs in accordance with the two criteria: potential for long-range transboundary atmospheric transport (LRTP) and persistence can be provided by modelling.

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 PCNs, EMEP/MSCE-POP multicompartiment hemispheric transport model is used. Taking into account that PCN group includes 75 possible congeners; this model assessment is carried out for PCN-47. This congener was selected as a representative of the most widespread group of tetra-chlorinated naphthalenes (tetra-CNs) in PCN congener profiles of environmental and source related samples. The homological group of tetra-CNs was detected in most types of samples in prevalent quantities. To estimate LRTP and persistence for PCN-47, 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.

To illustrate LRTP of the considered congener of tetra-CNs, 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 PCN-47 is provided by the spatial distribution of air pollution caused by the considered conventional point source.

Persistence in the environment is evaluated by *Half-life in the environment* ($T_{1/2}^{env}$) estimated for PCN-47 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 the considered congener of PCNs 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 as an adequately studied “benchmark substance” is presented.

In conclusion, the calculated numerical characteristics of LRTP and persistence of PCN-47 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/MSCE reports [Gusev *et al.*, 2005] and on the Internet (<http://www.msceast.org>).

VII.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 PCN-47 with the help of above-mentioned characteristics obtained on the basis of the EMEP/MSCE-POP model calculations performed at the hemispheric level.

VII.1.1. Residence time in the atmosphere

To estimate the residence time in the atmosphere, the model calculation of PCN atmospheric transport 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 PCN-47 to the atmosphere are assumed to be 1 t/y from a conventional point emission source located in Europe (10°E; 47.5°N). On the basis of this calculation annual atmospheric balance of the considered congener of PCNs emitted to the atmosphere is estimated. The calculated balance for the processes of PCN-47 removal from the atmosphere is given in Fig. VII.1.

model calculation of PCN atmospheric

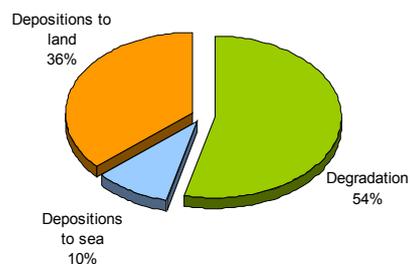


Fig. VII.1. Calculated annual balance of PCN-47 removal from the atmosphere

As seen from the calculated balance, the removal of this PCN congener from the atmosphere is determined approximately to the same extent by degradation and deposition processes. Within a year 54% of PCN-47 are degraded in the atmosphere and 46% are deposited to the different types of underlying surface. Here, the most part of deposited pollutant (36%) is accumulated in soil and the rest (10%) is in seawater. So, the character of the presented balance can be explained 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 and some meteorological parameters.

The considered congener of tetra-CNs exists in the atmosphere both in the gas and particulate phases with considerable predominance of the gaseous phase. Its degradation in the atmosphere is governed by the second-order rate constant equal to $9.11 \cdot 10^{-13} \text{ cm}^3/\text{molec}\cdot\text{s}$ estimated for its gas-phase interaction with OH radical [Howard and Meylan, 1997]. Taking into account the degradation process only, the atmospheric half-life of PCN-47 obtained with the use of average value of OH radical spatial distribution used in the model ($8.8 \cdot 10^5 \text{ molecule}/\text{cm}^3$) is 10 days.

The residence time of PCN-47 in the atmosphere ($T_{1/2}^{\text{air}}$) estimated on the basis of model calculations of its atmospheric transport is amounted to 7 days. So, for this pollutant the numerical characteristic of LRTP obtained by modelling meets the existing criterion for POPs (atmospheric half-life is greater than two days).

VI.1.2. Spatial distribution of pollution from conventional emission source

Additional information on LRTP of the considered chemical is provided by the spatial distribution of PCN air pollution estimated by modelling on the basis of its atmospheric transport from the conventional point emission source and atmospheric balance. In Fig. VII.2a,b concentration fields of PCN-47 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.

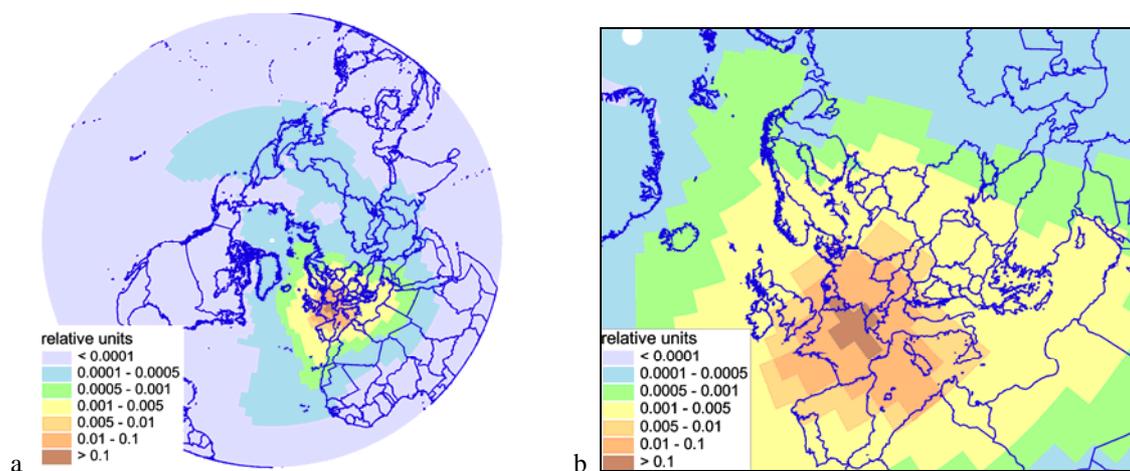


Fig. VII.2. Spatial distribution of PCN-47 concentrations in the above-ground air in the Northern Hemisphere and in the EMEP domain

According to the model assessment, the area of air pollution with PCN-47 from the conventional point source, where air concentration is 1000 times lower than that near the source, is located over the most part of Europe, includes Mediterranean Sea, and some part of the Atlantic ocean and reaches the Arctic region and northern Africa. The levels of air concentrations over most European countries vary from 0.001 to 0.1 of the basic value.

The model assessment demonstrates that PCNs emitted from a conventional European source of such intensity are capable to cause air pollution over the considerable areas including remote regions located far from the source. Available data on measurements of PCN air concentrations in different region of the Northern Hemisphere also testify that this group of pollutants is ubiquitous. Measured air concentrations of PCNs available from the literature along with data on congener profiles in the screened samples are presented in Table VII.1.

According to the data presented, the range of measured PCN air concentrations is wide varying from 0.8 (Dunai Island, Russia) to 175 $\mu\text{g}/\text{m}^3$ (Chicago, USA). Values of total toxicity given in ΣTEQ do not exceed 3.6 fg/m^3 . Homological groups of tri- and tetra-CNs are detected in prevalent quantities in all analysed air samples in comparison with other CN groups.

Table VII.1. Measured air concentrations of PCNs

Sampling site	Sampling date	Concentrations Σ PCN		Congener profile, %	References
		pg/m ³	Σ TEQ, fg/m ³		
Germany					
Ausburg	VI. 1992-II. 1993	60		Tri-CNs – 76.5; Tetra-CNs – 19.3; Penta-CNs – 2.9.	<i>Dörr et al., 1996</i>
Background station near Ausburg	VI. 1992-II. 1993	24		Tri-CNs – 76.4; Tetra-CNs – 17.0; Penta-CNs – 4.5.	
UK					
Lancaster (Hazellrig)	1994	66			<i>Harner et al., 2000</i>
Lancaster	1995	152	3.6	Tri-CNs – 44; Tetra-CNs – 51.5; Penta-CNs – 3.4.	<i>Lee et al., 2000</i>
Hazellrig	1998-1999	38.5			<i>Harner et al., 2000</i>
High Muffles	1998-1999	26.5			
Stoke Ferry	1998-1999	31			
Manchester	1998-1999	<u>138-160</u> 149			
Sweden					
Hoburgen	1990-1991	5.07		Tri-CNs	<i>Egebäck et al., 2004</i>
Ammarnäs	1990-1991	1.55			
USA					
Chicago, IL	II–III, 1995	<u>24-175</u> 68		PCN-24 – 40; PCN-33 – 10; PCN- 38 - >9.	<i>Harner and Bidleman, 1997</i>
Canada					
Lake Superior	VIII 1996	3.25*			<i>Helm et al., 2003</i>
	V 1997	1.82*			
Lake Ontario	VII, IX 1998	4.27*			
	VI 2000	12.3		Tri-CNs – 54.4; Tetra-CNs – 36.3; Penta-CNs – 8.2.	
Cornwall	II 1999	6.38		Tri-CNs – 46.4; Tetra-CNs – 41.8; Penta-CNs – 9.7.	
Downview, near Toronto	III, 1995	<u>12-22</u> 17			<i>Harner and Bidleman, 1997</i>
Totonto, UT	2000-2001	<u>31-78</u> 51.1	<u>0.5-2.2</u> 1.4	Tri-CNs – 32; Tetra-CNs – 49; Penta-CNs – 17.	<i>Helm and Bidleman, 2003</i>
Toronto, MSC	2000-2001	<u>7-84</u> 28	<u>0.08-0.53</u> 0.30	Tri-CNs – 47; Tetra-CNs – 41; Penta-CNs – 9.	
Polar regions					
Barents Sea	1996	40	0.99	Tri-CNs – 42; Tetra-CNs – 47; Penta-CNs – 8.	<i>Harner et al., 1998</i>
Norwegian Sea	1996	7.1	0.36	Tri-CNs – 46; Tetra-CNs – 39; Penta-CNs – 10.	
E. Arctic Ocean	1996	12	0.55	Tri-CNs – 48; Tetra-CNs – 37; Penta-CNs – 9.	
Alert, Canada	1993-1994	3.5	0.076	Tri-CNs – 69.5; Tetra-CNs – 19.8; Penta-CNs – 2.7.	
Dunai Island, Russia	1993	0.8	0.092	Tri-CNs – 54.2; Tetra-CNs – 37.6; Penta-CNs – 5.3.	

* - summa tetra- hexa-CNs; Tri-CNs – tetra-chlorinated naphthalenes; Tetra-CNs - tetra-chlorinated naphthalenes; Penta-CNs - penta-chlorinated naphthalenes; Hexa-CNs - hexa-chlorinated naphthalenes.

VII.1.3. 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 PCN-47 processes of degradation and depositions to different types of underlying surfaces contribute almost equally to its removal from the atmosphere and produce equal effect on the calculated value of *TD*. The calculated value of *TD* for PCN-47 is amounted to 2271 km. Both characteristics of LRTP obtained for PCN-47 with the help of model calculations are presented in Table VII.2.

Table VII.2. Characteristics of LRTP (*Half-life in air_{calc}* and *Transport Distance*) calculated for PCN-47

Substance	$T_{1/2}^{air}$, days	<i>TD</i> , km
PCN-47	7	2271

The presented numerical characteristics of LRTP for PCN-47 fully meet the LRTP criteria of Executive Body Decision 1998/2.

VI.2. Persistence

The distribution of PCN 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 annual media balance of PCN-47 in comparison with its annual degradation balance is shown in Fig. VII.3.

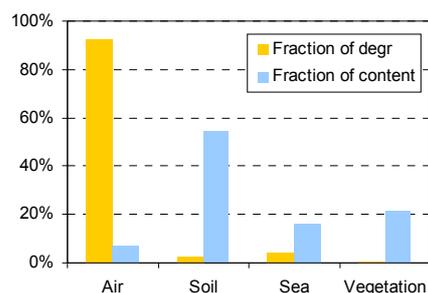


Fig. VII.3. Annual degradation and media balances for PCN-47

Degradation of this pollutant in the atmosphere is substantially more rapid than that in other environmental media coming to approximately 92% of PCN-47 amount degraded in the environment by the end of a year. Relative fractions of the pollutant degraded in each other media are the following: approximately 4% for seawater; 3% for soil and 0.5 for vegetation. At that, due to deposition processes within a one-year period more than a half of overall PCN-47 content in the environment (~55%) is accumulated in soil and only 7% remain in the atmosphere. Its content in seawater and vegetation equals 16 and 22%, respectively. Soil is appeared to be the main medium accumulating this pollutant.

The value of *Half-life in the environment* for PCN-47 calculated on the basis of annual media and degradation balances totals to 95 days or approximately 3.2 months. The calculated estimate of $T_{1/2}^{env}$ together with values of half-life in the particular environmental media used for modelling [HSDB, 2002] is presented in Table VII.3.

Table VII.3. Characteristics of Persistence (*Half-life in environment*) and half-life of PCN-47 in different environmental media used for modelling of atmospheric transport

Substance	$T_{1/2}^{env}$, months	Half-life, months		
		air	water	soil
PCN-47	3.2	0.3	12	57

According to the calculated value of *Half-life in the environment*, persistence of PCN-47 in the environment can be characterised as moderate. At that the obtained value of $T_{1/2}^{env}$ is considerably lower than those of half-life due to degradation process in soil and seawater and higher than that for degradation in the atmosphere only. Due to relatively high ability of PCN-47 to accumulate in soil, this pollutant may course long-term adverse affect through this medium.

VII.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 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 [ENV/JM/MONO(2004)5, 2004].

The comparison of calculated characteristics of LRTP and persistence for PCN-47 against those obtained for a benchmark pollutant is presented in this subsection. Benzo[a]pyrene (B[a]P) is used as a benchmark substance in this assessment. Characteristics of its behaviour in the environment are well studied and clearly meet 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 emissions intensity.

The considered PCN-47 and B[a]P have been ranked in ascending order according to their values of *Transport Distance* (Fig. VII.4a) and *Half-life in the environment* (Fig. VII.4b).

According to the model calculations of *TD*, LRTP of the considered congener of tetra-CNs is close to that of B[a]P, though slightly lower. Persistence of PCN-47 in the environment is somewhat higher than that of B[a]P (95 days compared to 74 days for B[a]P).

Thus, according to the results on ranking the considered substances, the numerical characteristics of LRTP and persistence of PCN-47 are comparable with those of the adequately studied “benchmark” pollutant already included into the Protocol on POPs.

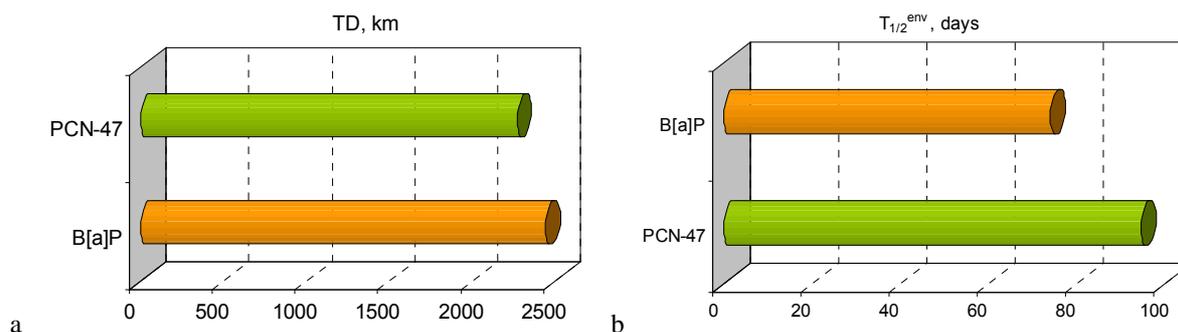


Fig. VII.4. Transport distance and Half-life in the environment calculated for PCN-47 and B[a]P

VII.4. Characteristics of PCN LRTP and persistence in relation to the indicative criteria outlined in Executive Body decision 1998/2

As it was stated above this model assessment was carried out for PCN-47 chosen as a representative of all possible congeners of PCNs. This assumption was made since the considered congener belongs to the homological group of tetra-CNs, which are detected in the most part of emission source samples and samples taken from remote sites. In this connection, physical-chemical properties of tetra-CNs presented in [van de Plassche and Schwegler, 2002] are given in Table VII.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.

Table VII.5. Comparison of LRTP and persistence of tetra-CNs and criteria of Executive Body Decision 1998/2 based on data [van de Plassche and Schwegler, 2002] and with additions of MSCE-POP model estimates

Criterion	Criterion values	Meets the criterion (Yes/No)	Characteristics of TetraCN	Remarks
<i>Potential for Long-Range Transboundary Atmospheric Transport</i>				
Vapour pressure, Pa	< 1000	Yes	0.048 at 25 °C	Presented in <i>van de Plassche and Schwegler, 2002</i>
Half-life in air, days	>2	Yes	18	
Half-life in air _{calc} , days		Yes	7	
<i>Persistence</i>				
Half-life in water, months	> 2	Yes		Presented in <i>van de Plassche and Schwegler, 2002</i>
Half-life in soil, months	>6	Yes		
Half-life in sediment, months	>6	Yes		
Half-life in the environment, months	-	-	3.2	$T_{1/2}^{env}$ calculated by MSC-E

The results of the model assessment demonstrate the considerable long-range atmospheric transport potential and persistence of PCN-47 in the environment. This conclusion is also confirmed by the comparison of calculated numerical characteristics of LRTP and persistence of dicofol against those obtained for typical POP of regional concern – B[a]P. However, since in this model assessment the

behaviour of PCNs in the environment was studied on the example of one selected homological group, further detailed analysis of model results on LRTP and persistence of other groups is required.

VII.5. Congener profiles and levels of PCNs measured in emission and environmental samples

The model assessment of LRTP and persistence of PCNs is carried out for PCN-47. This congener was selected as a representative of the homological group of tetra-chlorinated naphthalenes, which is prevalent in PCN congener profiles of most types of environmental and source related samples analysed. The choice of the considered congener is based on the available data on PCN congener profiles, patterns and levels detected in different types of emission sources and concentrations in the main environmental media. The analysed data are presented briefly in this section.

Emission sources of PCNs in the environment

Waste incineration along with other thermal processes is one of the most important pathways of PCN entry to the environment. Content and congener profiles of PCNs identified in emission samples collected from different types of waste incinerators have been investigated within several studies [Sakai *et al.*, 1996; Schneider *et al.*, 1998; Abad *et al.*, 1999]. Homologue mass distribution of the considered pollutants in fly ash of municipal solid waste incinerators, cement kilns, medical waste incinerator and iron sintering plant was compared in the study of Helm and Bidleman [2003]. PCN congener profile in the flue gas of aluminium smelter plant was identified by Aitolla *et al.* [1996]. Comparison of homological profiles of PCNs detected in samples collected from different emission sources is presented in Fig. VII.5.

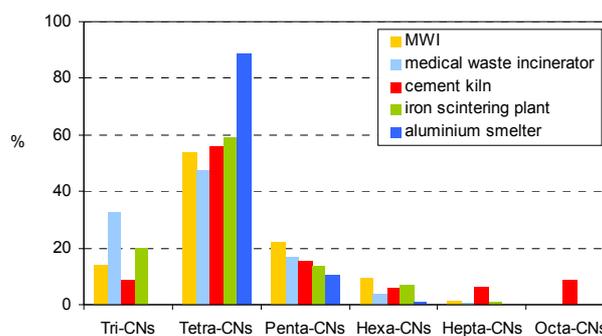


Fig. VII.5. Comparison of homological profiles of PCNs identified in samples collected from different emission sources

According to the data presented, the contribution of homological group of tetra-CNs to the total PCN emissions from different types of thermal sources is the most substantial as compared with other groups. Besides, it was found that in the most emission samples analyzed considerable variations in PCN concentrations were observed. In particular, PCN concentration in the flue gases of aluminium smelter amounted to 2981 ng/m³, whereas in the flue gases of MWI it was in the range from 1 to 21 ng/m³. The highest level of these pollutants was measured in the fly ash from medical waste incinerators up to 5439 ng/m³.

Pyrolysis of polyvinylchloride (pvc) is reported to be another important emission source of PCNs [HSDB, 2002]. During this process tetra-CNs are formed in the prevalent quantities (94.5-104 mg/kg/g) in comparison with other homological groups.

Air concentrations

Air concentration levels of PCNs have been monitored in different regions including those located far from emission sources such as the Arctic region (see Table VII.2 in Section VII.1.2). PCN congener profiles detected in air samples taken in different remote and background regions are demonstrated in Fig. VII.6.

It can be noted that for all considered sampling sites the groups of lighter congeners – tri- and tetra-CNs are found to be detected in the larger quantities than other groups. Several studies of PCN air pollution in the Central Europe and in the Great Lakes region demonstrated the similar homologue distribution.

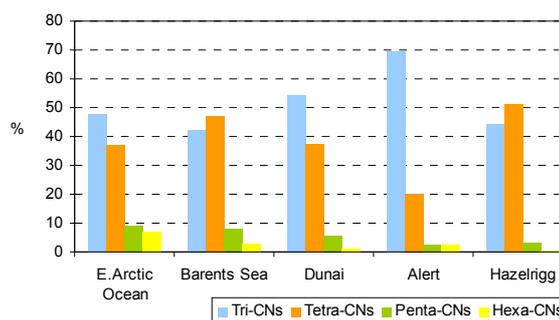


Fig. VII.6. Congener profile of PCNs in the air concentrations

Soil concentrations

The distribution of PCNs in soil samples collected at different region of the Northern Hemisphere can be illustrated with the help of monitoring data available in the literature (see Table VI.6).

The influence of industrial sources on homologue distribution of PCNs in soils is shown in Fig. VII.7. The data on soil pollution measured near by different productions were taken for this diagram from the following studies: chlor-alkali plant - *Kannan et al.* [1998]; chemical industry and petrochemical industry - *Schumacher et al.* [2004]; industrial - *Krauss and Wilcke* [2003]. In soil samples collected near industrial sources of northern Bavaria, Germany tetra- and penta- CNs are prevalent among other homological groups.

Main features of PCN distribution in rural soils of Bavaria have been investigated in the study of *Krauss and Wilcke* [2003] (see Fig. VII.8). Here, tetra- and penta-CNs are detected also in the larger quantities than other groups.

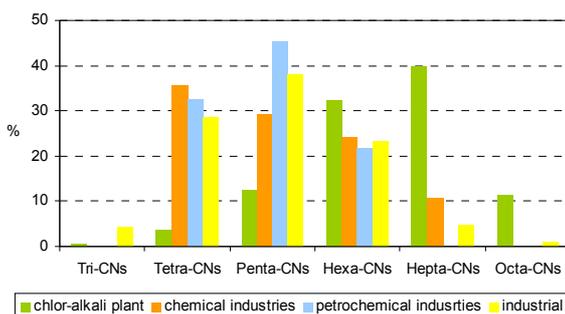


Fig. VII.7. Homological profile of PCNs in industrial soils

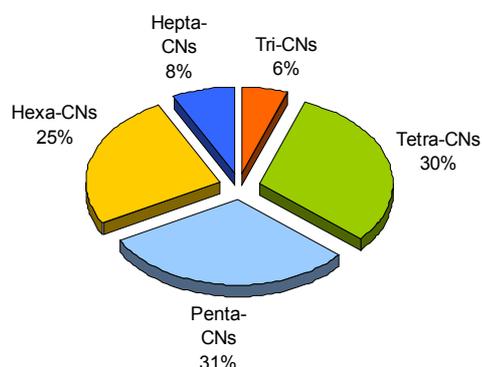


Fig. VII.8. Homological profile of PCNs in soils of rural area in northern Bavaria

Table VII.6. PCN soil concentrations

Sampling site	Sampling date	Soil concentrations of Σ PCN		Congener profile, %	References
		ng/g	Σ TEQ, pg/g dw		
UK					
Rothamsted station, 42 km north of London (archived soil)	1986	0.32	0.008	Tri-CNs – 44.6 Tetra-CNs – 42.5 Penta-CNs – 3.1 Hexa-CNs – 2.3 Hepta-CNs – 1.5	<i>Meijer et al., 2001</i>
Ludington 30 km south of Birmingham (archived soil)	1990	0.42	0.012		
Contemporary soils, southwest of the U.K collected at several sites across the U.K	1993	0.35			<i>Harner et al., 1999</i>
Germany, Bayreuth, northern Bavaria					
urban area	Before 2003	Nd – 15, 4			<i>Krauss and Wilcke, 2003</i>
industrial		0.67 – 15.0		Tri-CNs – 4.5 Tetra-CNs – 28.4 Penta-CNs – 38.2 Hexa-CNs – 23.2 Hepta-CNs – 4.7	
agricultural		n.d – 0.51			
rural sites		Nd – 0.82		Tri-CNs – 5.5 Tetra-CNs – 30.6 Penta-CNs – 30.9 Hexa-CNs – 25.5 Hepta-CNs – 7.5	
Spain, Tarragona County					
Chemical industries	2002	0.12		Tetra-CNs – 34.4 Penta-CNs – 28.2 Hexa-CNs – 23.2 Hepta-CNs – 10.2 *Cl ₈ N – 4.1	<i>Schumacher et al., 2004</i>
Oil refinery and petrochemical industries		0.07		Tetra-CNs – 16.2 Penta-CNs – 22.5 Hexa-CNs – 10.8 * Hepta-CNs – 4.1 * Octa-CNs – 4.1	
Residential (urban)		0.18		Tetra-CNs – 34.6 Penta-CNs – 42.4 Hexa-CNs – 15.3 Hepta-CNs – 4.9 * Octa-CNs – 2.8	
unpolluted		0.03		Tetra-CNs – 31.9 Penta-CNs – 21.8 * Hexa-CNs – 15.8 * Hepta-CNs – 15.8 * Octa-CNs – 15.8	
USA, Brunswick, GA					
southern coastal Georgia near chlor-alkali plant	II, 1996	17900	5330	Tri-CNs – 0.5 Tetra-CNs – 3.6 Penta-CNs – 12.4 Hexa-CNs – 32.4 Hepta-CNs – 39.8 Octa-CNs – 11.3	<i>Kannan et al., 1998</i>

* Hepta-CNs – 4.1 - sum PCN was calculated assuming that when in a group of homologues the sum was below the limit of detection (10 ng/g), this sum was equal to one-half of this limit;

Tri-CNs – tetra-chlorinated naphthalenes;

Hexa-CNs - hexa-chlorinated naphthalenes;

Tetra-CNs - tetra-chlorinated naphthalenes;

Hepta-CNs - hepta-chlorinated naphthalenes;

Penta-CNs - penta-chlorinated naphthalenes;

Octa-CNs - octa-chlorinated naphthalenes.

Water concentrations

Available data on monitoring of water pollution by PCNs are very scarce in the literature. In particular, there are data on levels of water concentrations in the lake Ontario, Canada [Helm *et al.*, 2003] and in a lake and river polluted by PCBs in Scandinavia [Järnberg *et al.*, 1997].

In the samples collected from the surface water of the lake Ontario the analysis was made for the high volume of water (100 L) and for the dissolved phase of pollutants. At that, only tri- and tetra- CNs were identified there. Observed levels of water concentrations were within the range from 16.35 to 24.48 pg/L. In all samples concentrations of tri-CN homologous group were from 1.7 to 3.5 times higher than that of tetra-CN.

Measured levels of water concentrations in the river Emån and the lake Järnsjön, polluted with PCBs, considerably exceed those in the lake Ontario amounting to 890 pg/L. Tetra-, penta-, hexa- and hepta-homologous group were detected in the analysed samples. In this region contribution of tetra-CN to the total content of PCNs was dominated and come to 1.6 times.

Concentration in vegetation

Limited number of monitoring data on PCN concentrations in vegetation was found in the literature. Total PCN concentrations in grasses sampled in semi-rural field station site in the northwest of England were measured in the study of Harner *et al.* [1999]. Total concentration of PCNs in this region amounted to 2.12 ng/g of dry weight. This study revealed also that the groups of lighter congeners – tri- and tetra-CN prevailed over other groups.

The concentration of PCNs have been determined in wild chard samples collected in an area of Tarragona County (Catalonia, Spain) with an important number of chemical and petrochemical industries [Schumacher *et al.*, 2004]. Samples were also collected in urban/residential zones, as well as in presumably unpolluted sites. There were insignificant differences among collecting zones in the levels of PCNs found in chard. PCN concentration detected at the industrial sampling sites was equal to 214 ng/kg of dry weight; at the urban sites – 172 ng/kg of dry weight, and at the unpolluted sites – 146 ng/kg of dry weight. Homologue distribution of PCNs in samples of vegetation presented in [Schumacher *et al.*, 2004] is shown in Fig. VII.9.

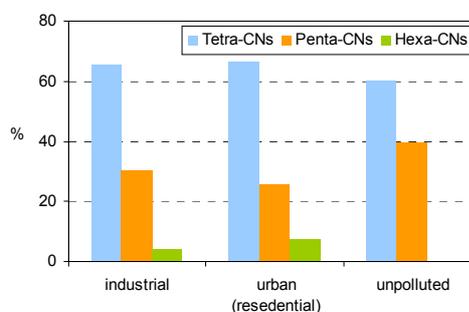


Fig. VII.9. Homologue distribution of PCNs in vegetation samples collected in Catalonia, Spain

As seen from the data presented, in all analyzed samples of wild chard the group of tetra-CN was found to be in predominant quantities as compared with other groups. Its fraction amounted to more than a half (not less than 60%) of the total PCN content measured in all the samples.

Thus, for the sake of model assessment of LRTP and persistence for PCNs, homologous group of tetra-CN, which prevails over other groups in the most part of source-related samples and samples taken from main environmental media, was chosen on the basis of available measurement data on

PCN congener profiles. PCN-47 was selected among other tetra-CNs because of availability of all physical-chemical properties and degradation rates required for modelling.

VI.6. Physical-chemical properties of polychlorinated naphthalenes used for modelling

The key physical-chemical properties and degradation rates of tetra-CNs presented in [van Plassche and Schwegler, 2002] are shown in Table VII.7.

Table VII.7. Physical-chemical properties of tetra-CNs presented in [Plassche and Schwegler, 2002]

Physical chemical properties	Numerical values
Vapour pressure, Pa	0.048 at 25 °C
Solubility in water, mg/L	0.004
Henry's Law constant, Pa·m ³ /mol	16.06
Octanol-water partition coefficient (log <i>K_{ow}</i>)	6.19
Half-life, days	
Air	18
Water	
Soil	
Sediment	

References: Crookes and Howe, 1993; Syracuse in HSDB, 2000

The full set of physical-chemical properties and degradation rates of PCN-47 selected for the model parameterisation on the basis of data available in literature is presented in Table VII.8. Temperature dependences of some physical-chemical characteristics (Henry's law constant, subcooled liquid-vapour pressure, octanol-air partition coefficient) are given at reference temperature equal to 283.15 K.

Table VII.8. Physical-chemical properties of PCN-47 used for modelling

Physical-chemical properties	Numerical values	References
Henry's law constant for fresh and sea water at 10 °C, Pa·m ³ /mol	2.91	Estimated on the basis of temperature dependence of K_{OA} given in <i>Harner and Bidleman</i> , 1998
Coefficient of Henry's constant temperature dependences, K	9617	
Subcooled liquid-vapour pressure at 10 °C, Pa	$5.88 \cdot 10^{-3}$	<i>Lei et al.</i> , 1999
Coefficient of subcooled liquid – vapour pressure temperature dependences, K	8666	
Rate constant of reaction with OH radical in air, cm ³ /(molec·sec)	$9.11 \cdot 10^{-13}$	<i>Howard and Meylan</i> , 1997
Degradation rate constant in air, s ⁻¹	$8.02 \cdot 10^{-7}$	Calculated with the use of average value of OH-spatial distribution used in the model: [OH] = $8.8 \cdot 10^5$ molec/cm ³
Half-life in air, days	10	
Degradation rate constant in water, s ⁻¹	$2.19 \cdot 10^{-8}$	Estimated
Half-life in water, days	366	<i>HSDB</i> , 2001
Degradation rate constant in soil, s ⁻¹	$4.72 \cdot 10^{-9}$	Estimated
Half-life in soil, months	1700	<i>Hazardous Substances Databank - HSDB</i> , 2002
Molar volume, cm ³ /mol	228	<i>Lei et al.</i> , 1999
«Octanol-water» partition coefficient at 25 °C	$8.65 \cdot 10^5$	Estimated with the use of K_{OA} taken from <i>Harner and Bidleman</i> , 1998
«Octanol-air» partition coefficient at 10 °C	$7.00 \cdot 10^8$	<i>Harner and Bidleman</i> , 1998
Coefficient of K_{OA} temperature dependences, K	9257	
Molecular diffusion coefficients, m ² /s:		Calculated with the help of equations from <i>Swarzenbach et al.</i> , 1993
in water	$6.15 \cdot 10^{-10}$	
in air	$5.37 \cdot 10^{-6}$	
“Organic carbon-water” partition coefficient, m ³ /kg	354	Calculated with the help of relationship between K_{OC} and K_{OW} given in <i>Karickhoff</i> , 1981

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