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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 Pentachlorobenzene

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INTRODUCTION

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 $\mu g/m^3$ [*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 multicompartment 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***$_{calc}$ ($T_{1/2}^{air}$)) 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/MSC-E reports [*Gusev et al*., 2005] and on the Internet (http://www.msceast.org).

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

1.1. Residence time in the atmosphere

To estimate the residence time in the atmosphere, the model calculation of atmospheric transport of 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.1.

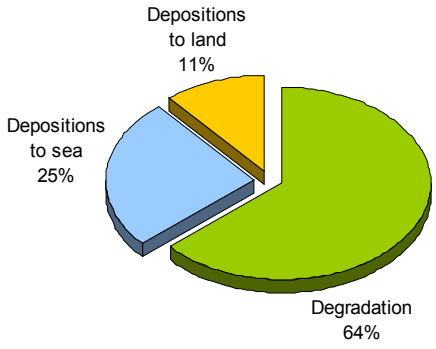

Fig.1. *Calculated annual balance of PeCB removal from the atmosphere*

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 charaterized 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 $5.90 \cdot 10^{-14}$ cm^3/molec·s [*Howard and Meylan*, 1997] and the average value of OH radical spatial distribution implemented in the model ($8.8 \cdot 10^5$ molec/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 ($T_{1/2}^{air}$) 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).

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.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).

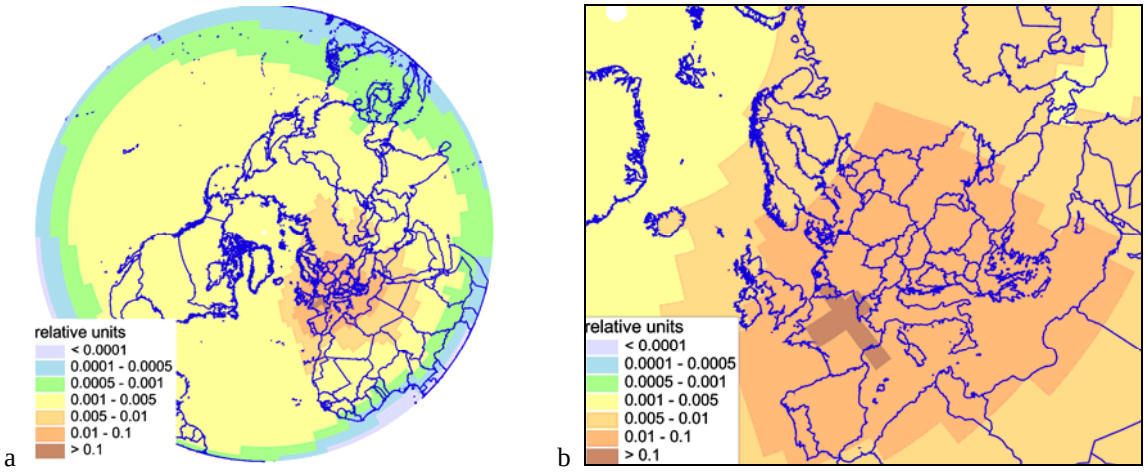

Fig. 2. *Spatial distribution of PeCB concentrations in the above-ground air in the Northern Hemisphere and in the EMEP domain*

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 1. Mean values of PeCB air concentrations recorded at stations of European (see the table) and Canadian Arctic (31 – 135 pg/m^3 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/m^3. Of note, air concentrations of HCB also measured within this study were equal to 12 - 86 pg/m^3 at the same sites. Atmospheric depositions of PeCB and HCB at Råö were 85 and 140 pg/m^2/day, respectively.

1.3. Transport Distance

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

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

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

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

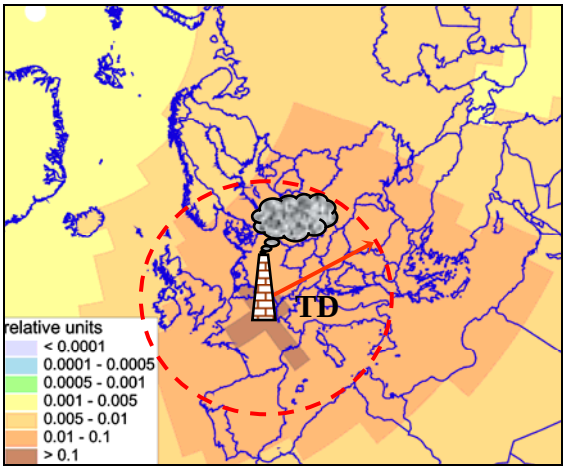

Fig. 3. *Definition of the transport distance*

The value of *TD* depends on all of the processes removing the pollutant from the atmosphere such as deposition to the underlying surface (land, sea) and atmospheric degradation. It was found that for 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 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.

2. PERSISTENCE

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

In compliance with the Executive Body Decision 1998/2 the persistence of "new substances" in terms of their possible inclusion into the Protocol on POPs is demonstrated by indicative numerical values of their half-life in water, which should be greater than two months, or half-life in soil, which should be greater than six months, or half-life in sediments, which should be greater than six months also. In addition to these parameters characterizing the persistence for particular media, multimedia model calculations allow estimating complementary characteristics of persistence in the whole environment - overall residence time or overall environmental persistence [*Scheringer*, 1996; *Webster et al*., 1998; *Gouin et al*., 2000, etc]. In this assessment such characteristic as *Half-life in the environment* ($T_{1/2}^{env}$) is estimated for the considered pollutant on the basis of the model calculations of its atmospheric transport taking into account deposition processes, degradation and gaseous exchange between main environmental media.

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

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

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

Thus, the value of *Half-life in the environment* is affected by the distribution of the total environmental content of PeCB between main environmental media (air, soil, water, sediment and vegetation) and the values of its half-life in each particular medium due to degradation process.

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.4.

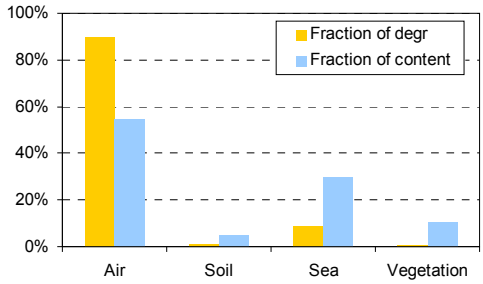

Fig.4. *Annual degradation and media balances for PeCB*

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 (for references please see Annex A) are presented in Table 3.

Table 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.

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. 5a) and *Half-life in the environment* (Fig. 5b).

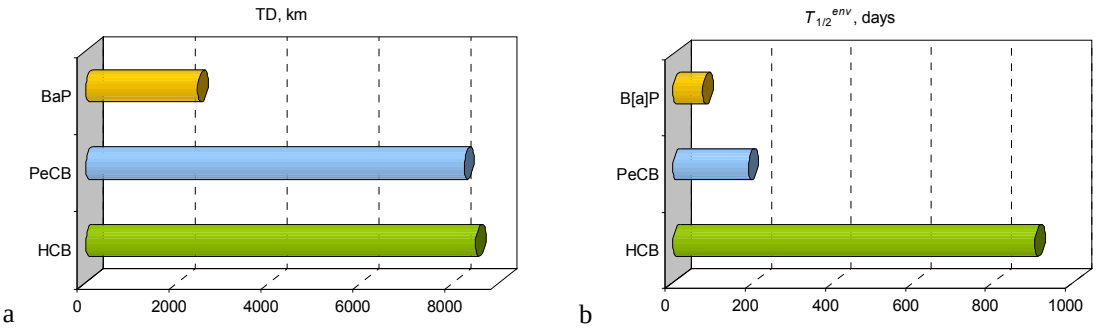

Fig. 5. *Transport distance and Half-life in the environment calculated for PeCB, B[a]P and HCB*

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 $\boldsymbol{T_{1/2}^{env}}$ 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.

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. Data on physical-chemical properties of PeCB available in [*van de Plassche et al.*, 2005] and used in the model calculations are given in the Annex A (Tables A1 and A2).

Table 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
Potential for Long-Range Transboundary Atmospheric Transport				
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	$T_{1/2}^{air}$ calculated by MSC-E
Persistence				
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	$T_{1/2}^{env}$ calculated by MSC-E

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.

REFERENCES

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

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

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

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

Bruckmann P. and Kersten W. [1988] The occurrence of chlorinated and other organic trace compounds in urban air, *Chemosphere*, vol.17, No.12, pp.2363-2380.

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

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

Fröse K. L. and O. Hutzinger [1996a] Polychlorinated Benzene, Phenol, Dibenzo-p-dioxin, and Dibenzofuran in heterogeneous combustion reactions of acetylene. *Environ. Sci. Technol*., vol. 30, N. 3, pp. 998-1008.

Fröse K. L. and O. Hutzinger [1996b] Polychlorinated Benzene and Polychlorinated Phenol in heterogeneous combustion reactions of ethylene and ethane. *Environ. Sci. Technol*., vol. 30, N. 3, pp. 1009-1013.

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

Harner T. and Mackay D., [1995], Measurement of octanol-air partition coefficients for chlorobenzenes, PCB, and DDT, *Environ. Sci. Technol*., vol. 29, No.6, pp. 1599 - 1606.

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

Hoff R.M., D.C.G. Muir, N.P.Grift, [1992] Annual cycle of polychlorinated biphenyls and organohalogen pesticides in air Southern Ontario. 1. Air concentration data, *Environ. Sci. Technol*., vol. 26, N. 2, pp. 266-275.

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

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

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

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

Mackay D., Wan Ying Shiu and K.C. Ma [1992] Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals. vol.1, pp. 270-271.

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

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

Oeme M. and Manø S. [1984] The Long-Range transport of Organic pollutants to the Arctic, Fresenius, Z. Anal.Chem., Bd.319, S.141-146

van de Plassche E., A. Schwegler, M. Rasenberg, G. Schouten [2005] Pentachlorobenzene. Dossier. Royal Haskoning, The Netherlands, pp. 18.

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

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

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

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

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

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

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

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

Vulykh N., S. Dutchak, E. Mantseva, V. Shatalov [2004] "EMEP Contribution to the Preparatory Work for the Review of the CLRTAP Protocol on POPs: New Substances. Model Assessment of Potential for Long-range Transboundary Atmospheric Transport and Persistence of PentaBDE". EMEP/MSC-E Information Note 10/2004.

Vulykh N., E. Mantseva, V. Shatalov [2005] "EMEP Contribution to the Preparatory Work for the Review of the CLRTAP Protocol on POPs. New Substances: Model Assessment of Potential for Long-range Transboundary Atmospheric Transport and Persistence of Endosulfan". EMEP/MSC-E Information Note 10/2005.

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

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

Wikström E. and S. Marklund [2000] Secondary Formation of Chlorinated Dibenzo-p-dioxins, Dibenzofurans, Biphenyls, Benzene, and Phenols during MSW Combustion, *Environ. Sci. Technol*., vol. 34, No. 4, pp. 604 – 609.

Annex A

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 A1.

Table A1. *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
Henrys'Law constant, $Pa \cdot m^3/mol$	-
Octanol-water partition coefficient (log K_{OW})	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 A2. 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 A2. *Physical-chemical properties and degradation rates of PeCB 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	32.6	Estimated with the use of temperature dependence p_{OL} and S_{WL} from *Beyer and Matthies* [2001]
Coefficient of Henry's law constant temperature dependences, K	5638	
Subcooled liquid-vapour pressure at 10 °C, Pa	0.19	*Beyer and Matthies* [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	$5.90 \cdot 10^{-14}$	*Howard and Meylan* [1997]
Half-life in air, days	155	Calc with the use of average value of OH-spatial distribution used in the model: $[OH^{\cdot}] = 8.8 \cdot 10^5$ molec/cm^3
Degradation rate constant in water, s^{-1}	$2.3 \cdot 10^{-8}$	*HSDB* [2002]
Half-life in water, days	349	
Degradation rate constant in soil, s^{-1}	$2.3 \cdot 10^{-8}$	*HSDB* [2002]
Half-life in soil, days	349	
Molar volume, cm^3/mol	153.9	*Ruelle and Kesselring* [1997]
«Octanol-water» partition coefficient at 25 °C	69500	*Beyer and Matthies* [2001]
«Octanol-air» partition coefficient at 10 °C	$8.81 \cdot 10^6$	*Harner and Mackay* [1995]
Coefficient of K_{OA} temperature dependences, K	8489	
Molecular diffusion coefficients, m^2/s:		Calculated with the help of equations from *Schwarzenbach et al*. [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 *Karikhoff* [1981]