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Model assessment of potential for long-range transboundary atmospheric transport and persistence of Chlordecone

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CONTENTS

INTRODUCTION

Chlordecone is an organochlorine compound, which has been used under different trade names (Kepone, Curlone, Kelevan, etc.) as an insecticide, fungicide, and miticide in agriculture in various part of the world. From 1951 to 1975 1600 tonnes of chlordecone was produced in the USA and mostly exported to Europe, Asia, Latin America, and Africa [*Chlordecone Draft Risk Profile*, 2006]. Later it was synthesized also in Brazil [*Chlordecone Draft Risk Profile*, 2006]. According to the Carcinogen Rating of IARC chlordecone refers to group 2B of possible carcinogens for human based on sufficient evidence of carcinogenecity in experimental animals [*IARC 1979, 1987 cited by Substance Profiles, Report on Carcinogens, Eleventh Edition*]. This substance also indicates high toxicity as a developmental and reproductive toxin and is suspected to be an endocrine disruptor [*PAN Pesticides Data Base*].

In accordance with the screening criteria outlined in the Executive Body Decision 1998/2 of the Convention on Long-Range Transboundary Air Pollution (hereinafter CLRTAP) chlordecone has been identified as a persistent organic pollutant and included in the UN ECE 1998 Aarhus Protocol on Persistent Organic Pollutants (hereinafter UN ECE Protocol on POPs). It is also included as a substance of possible concern in the OSPAR Convention. Besides, this compound is a ketone analog and degradation product of the insecticide mirex, which is also included into Annex A of the Stockholm Convention and Annex 1 of the UN ECE Protocol on POPs. Technical grade mirex contains 2.58 mg/kg chlordecone as a contaminant [*Great Lakes Pesticide Report, 2000*].

Chlordecone is proposed as a potential POP candidate for possible inclusion in the Stockholm Convention (hereinafter the Convention). Chlordecone Draft Risk Profile prepared by the ad hoc working group under the Persistent Organic Pollutant Review Committee of the Convention [*UNEP/POPS/POPRC.2/8*] testifies that characteristics of this substance meets all the screening criteria laid down in Annex D of the Convention and it should be considered as a POP warranting global action. In addition information for the evaluation of chlodecone 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 UN ECE Protocol on POPs as well as in the Convention and some potential new POPs [*Shatalov et al.*, 2003; *Dutchak et al.*, 2004; *Mantseva et al.*, 2004; *Vulykh et al.*, 2004, 2005 a, b, c, d, e, 2006] is accumulated in the Meteorological Synthesizing Centre-East of the Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (hereinafter EMEP). For the evaluation of LRTP and persistence of pollutants, EMEP/MSCE-POP multicompartment hemispheric transport model with spatial resolution 2.5º × 2.5º is used. This choice was conditioned by the fact that this version of the model is more applicable for evaluation of substances with high LRTP (for example such as pentachlorobenzene, hexachlorobenzene, hexachlorobutadiene, and others) than the regional one with finer spatial resolution (50 × 50km). For the sake of comparability with model estimates obtained previously for other new substances (see *Vulykh et al.*, 2004, 2005 a, b, c, d, e, 2006), the model evaluation of the considered parameters for chlordecone is also performed with the help of hemispheric version of the model. To estimate LRTP and persistence for this pesticide, the model calculation of its atmospheric transport from a conventional diffusive emission source located in Europe (10°E; 47.5°N) and covering the area of approximately 200 × 200 km is made for one-year period. Information on physical-chemical properties and degradation rates of chlordecone used for modelling is included in Annex.

Persistence in the environment is evaluated by *Half-life in the environment* ($T_{1/2}^{env}$) estimated for chlordecone 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 illustrate LRTP of chlordecone in the atmosphere 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. LRTP of chlordecone is also characterised by the spatial distribution of its air pollution caused by the considered conventional emission source acting permanently within one year.

Additional information on chlordecone long-range transport potential in the atmosphere can be obtained from the model simulation of the transport of a plum originated from a conventional single emission pulse. Such type of model runs allows revealing the influence of real meteorological and geophysical conditions on spatial distribution of air pollution caused by an accidental release occurred to the air from some conventional manufacturing site. For more precise analysis, calculations are performed by the regional version of EMEP/MSCE-POP model with resolution 50km × 50 km. The location of initial emission pulse is chosen in the Netherlands on sea cost with non-trivial meteorological situation. In calculations meteorological data of 2000 are used.

To diminish uncertainties in evaluating LRTP and persistence, the model dependent numerical characteristics of these parameters (*TD* and $T_{1/2}^{env}$) calculated for chlordecone are compared with those obtained for a number of other substances. The latter includes pollutants both already included in the CLRTAP and/or Stockholm Convention and new POPs candidates.

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. PERSISTENCE IN THE ENVIRONMENT

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

In compliance with indicative criteria values (Executive Body Decision 1998/2, Annex D of the Stockholm Convention) for the persistence of "new substances" their half-life in water, should be greater than two months, or half-life in soil should be greater than six months, or half-life in sediments 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 chlordecone is demonstrated by the numerical value of $T_{1/2}^{env}$ calculated with the help of Eq.1 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:

$$T_{1/2}^{env} = \ln2 / \sum k_i \cdot f_i \qquad (1)$$

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 chlordecone 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.

1.1. Persistence in main environmental media

Available information reported on the investigation of chlordecone degradation in environmental media is quite limited. It is reported that half-life of chlordecone in air is very high. Table 1 presents numerical data on chlordecone half-life in the atmosphere together with corresponding degradation rate constant available in the literature.

Table 1. *Chlordecone half-life in air*

Half-life, Ys	Degradation rate constant, s-1
50-200 [1]	1.10×10^{-10} - 4.40×10^{-10} [1]
>30 [2]	< 8.02×10^{-9} [2]
-	0 [3]

1. *Mackay et al*., v.V., 1997
2. *Scheringer et al*., 2006
3. *Howard&Meylan*, 1997 and *Chlordecone Draft Risk Profile*, 2006

In the model calculations the value of half-life in the atmosphere equal to 150 years is used which corresponds to the value of degradation constant of $1.47 \cdot 10^{-10}$ s^{-1}.

Available literature data on half-life of chlordecone in water together with the corresponding degradation rate constants are presented in Table 2.

Table 2. *Chlordecone half-life in water*

Half-life, days	Degradation rate constant, s-1
312 – 720 [1]	$2{,}57 \times 10^{-8}$ - 1.11×10^{-8} [1]
730 [2]	1.10×10^{-8} [2]

1. *Mackay et al.*, v.V., 1997
2. *Scheringer et al.*, 2006

The presented values of half-life demonstrating persistence of chlordecone in water vary from about 300 days to approximately 2 years. For model parameterisation the value of chlordecone half-life in water of 730 days (2 years) used in [*Scheringer et al.,* 2006] is taken.

Chlordecone being a degradation product of mirex is similar to that in structure and is also highly persistent in soils and sediments because of its resistance to biodegradation [*Toxicological profile for mirex and chlordecone*, 1995]. Hence, under the lack of literature data (first of all experimental) on half-life of chlordecone in soils for evaluation of this parameter comparative data on persistence of mirex and chlordecone are used (Table 3).

**Table 3.** *Data on mirex and chlordecone half-lifes in soil*

Degradation half-life, Y		Degradation rate constant in soil, s-1	
Mirex	Chlordecone	Mirex	Chlordecone
6 [1]	<1 – 2 [1]	3.5×10^{-9} [1]	2.57×10^{-8} - 1.11×10^{-8} [1]
12 [2]	2 [3]	1.80×10^{-9} [2]	1.10×10^{-8} [3]
8 [4]	10 [5]	2.67×10^{-9} [4]	2.2×10^{-9} [5]

1. *Mackay et al.*, v.V., 1997
2. *Scheringer*, 1997
3. *Scheringer et al.*, 2006
4. *Hornsby et al.*, 1995
5. *Toxicological profile for mirex and chlordecone*, 1995

As it is seen from the data given above, half-life of mirex in soil varies from 6 years according to [*Mackay et al.,* 1997] to 12 years according to [*Scheringer,* 1997]. For chlordecone the presented values vary from less than one year to 10 years. For the model calculations the maximum estimate of half-life of chlordecone in soil equal to 10 years is selected. It corresponds to the value of degradation constant of $2.2 \cdot 10^{-9}$ s^{-1}.

1.2. Persistence in the environment (model evaluation)

The distribution of total chlordecone 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) obtained on the basis of simulations for one-year period are shown in Figs. 1 a and b, respectively. It should be noted that seawater includes pollutant content in sediments, and only degradation in forest litter is considered as degradation in vegetation.
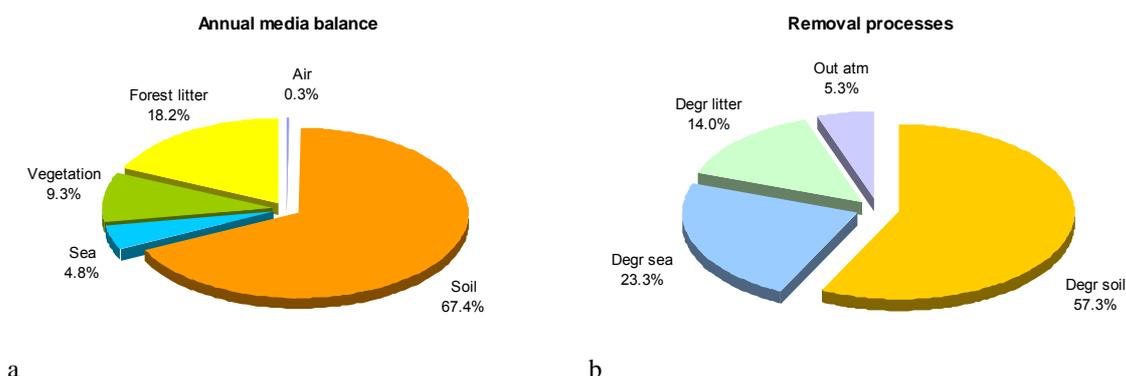
Fig. 1. *Calculated media balance (a) and contributions of different processes to the removal of chlordecone from the environment (b)*

As obtained by calculations, main process determining chlordecone removal from the environment is degradation in soil. This is natural since about two thirds of chlordecone environmental content is contained in soil. In spite of the fact that the fraction of environmental content in seawater is small (about 5%) degradation in seawater is considerable accounting to about one fourth of overall degradation in the environment. This is due to higher degradation rate of chlordecone in this medium than in others. Then follow degradation in forest litter and transport outside the Northern Hemisphere. Degradation in the atmosphere is not shown in the diagram since its contribution is negligible.

Calculation results for chlordecone persistence in the environment (environmental half-life) together with half-lives in main media used for calculations are presented in Table 4.

Table 4. *Half-life in the environment and half-lives in main environmental compartments for chlordecone*

Half-lives in main environmental media, years			Half-life in the environment, years
Air	Soil	Seawater	
150	10	2	**9**

Evaluated value of overall environmental half-life for chlordecone (**9** years) is much more than for all earlier considered substances. For example, environmental half-life for hexachlorobenzene is about **2.7** years. Thus, the obtained value of *Half-life in the environment* shows that chlordecone posses very high persistence in the environment.

2.   LONG-RANGE TRANSPORT POTENTIAL

In accordance with Annex D of the Stockholm Convention the information on model results demonstrating that the chemical has a potential for long-range environmental transport through air with the potential for transfer to a receiving environment in locations distant from the source of its release is considered together with monitoring data during the evaluation of new substances as a potential candidate for the inclusion into the Convention. Besides, as in the Executive Body Decision 1998/2 LRTP of the chemical can also be characterized by an indicative numerical value of its atmospheric half-life, which should be greater than two days.

There are two numerical characteristics of long-range transport potential of chlordecone obtained on the basis of the model simulation of its atmospheric transport. The first one is residence time in the atmosphere (*Half-life in air$_{calc}$* ($T_{1/2}{}^{air}$)) due to all removal processes (degradation, deposition and gaseous exchange). 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 the second numerical characteristic - *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. Model evaluation of these characteristics of LRTP for chrordecone is presented below.

2.1.   Residence time in the atmosphere

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 such as dry and wet deposition and gaseous exchange with underlying surface. Advantages of modelling approach are contained in possibility to distinguish the most important processes affecting LRTP of a particular considered pollutant in the atmosphere.

According to the model calculations, half-life of chlordecone in the atmosphere due to all removal processes is about 1 day. Relative contributions of various removal processes to total removal of chlordecone from the atmosphere are plotted in Fig. 2.

It is seen that the process of dry deposition to land (gaseous exchange with soil) is a most important process for chlordecone removal from the atmosphere. The rest is accounted for wet deposition process. The contribution of degradation in the atmosphere and gaseous exchange with seawater are not included into the diagram since these contributions are negligible.

High value of gaseous flux to soil can be explained by peculiarities of physical-chemical properties of chlordecone. First, it is relatively high solubility leading to low value of Henry's law constant in comparison with other well-known pollutants. Its value is one order less than for lindane and four orders less than for HCB. Second, octanol/water partitioning coefficient for chlordecone is comparable with that for HCB and is two orders higher than for lindane. Such values of the
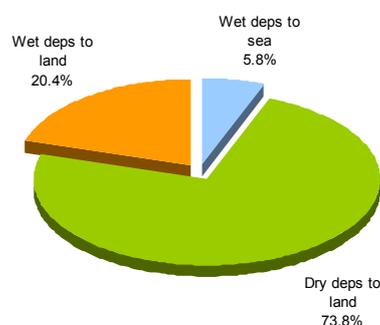

Fig. 2. *Contributions of different processes to chlordecone removal from the atmosphere*

two partitioning coefficients shift the equilibrium between liquid, gaseous and solid fractions of chlordecone in soil to very low concentrations of clordecone in the soil air. The difference between chlordecone concentrations in the atmospheric air and soil air leads to high values of the flux directed from the atmosphere to soil. Calculations show that, due to the above reasons, equilibrium partition coefficient between soil and air concentrations for chlordecone is more than three orders of magnitude higher than for HCB and about 50 times higher than for lindane. Mass transfer coefficient for air/soil exchange for chlordecone is comparable with that for lindane and is higher by an order of magnitude than that for HCB. All this leads to the fact that calculated value of gaseous flux to soil for chlordecone is higher than for earlier considered pollutants.

2.2. Spatial distribution of pollution from conventional emission source

LRTP of chlordecone can be also characterised by the spatial distribution of its air pollution obtained with the help of the model simulation. At present there exist different approaches to model assessment of LRTP. These approaches use different types of POP models (from simple box models to sophisticated spatially resolved models) and different metrics for evaluation of LRTP. The advantage of box models in evaluation of LRTP is their minimum requirements for input information and computational resources, so that these models could be used for screening a large number of substances at the first step of evaluation. At the same time spatially resolved models provide additional information concerning spatial distribution of contamination originated from a point or diffusive emission source of a given location taking into account peculiarities of land use, meteorology, etc. These models can be used at further stages of evaluation of new substances. The comparison of ranking of pollutants by models of different types can be found in [*Shatalov et al.*, 2007 in preparation].

We begin with a short description of model approach to evaluation of LRTP by hemispheric EMEP/MSCE-POP model. To evaluate the pollution originated by conventional diffusive source acting continuously during the whole year the model calculates the transport of each part of the emitted pollutant and sums the results. Fig. 3 shows the results of calculations for the conventional source of the power of 1 t/y located in France in 1996.

| a) January | b) May | c) Annual |
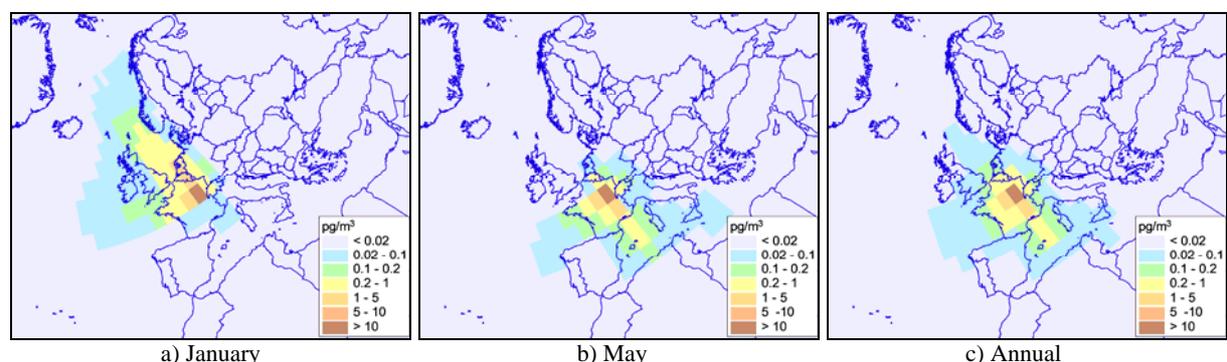
Fig. 3. *Monthly and annual averages of air concentrations caused by a conventional point source in Europe*

Fig. 3a shows average concentrations caused by the source in January. Due to the fact that prevailing wind direction in January is to the north, chlordecone from the considered source is transported mainly in north direction reaching wide areas in the North Atlantic and partly northern part of the Scandinavian Peninsula.

On the opposite, average concentrations of chlordecone in May (Fig. 3b) are located mainly to the South and Southeast from the source according to the wind directions characteristic of this month.

To obtain a picture of annual contamination annual averages of calculated air concentrations can be used (Fig. 3c). The map of contamination shows that the pollution from the considered source is noticeable in most neighboring countries and reaches the Mediterranean Sea and eastern part of the Atlantic Ocean.

There exist two types of model calculations illustrating long-range transport potential of a pollutant. First, it is calculations of pollution caused by a source constantly acting during long time period (a year in our case). The second is based on the calculations of the transport of a parcel of the pollutant emitted momentarily to the atmosphere. Both these types of calculations are used in different models for obtaining numerical evaluation of long-range transport potential of a substance. The results of evaluation of transport distance based on a first of these two approaches are presented below (Section 2.3). In Section 2.4 we illustrate how the second approach can be realized on the basis of calculations made by a spatially resolved model.
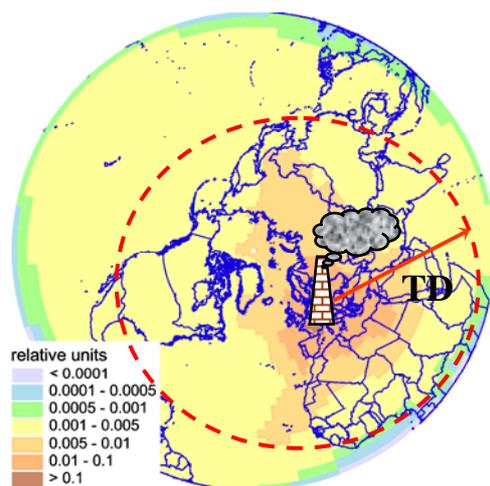
2.3. Transport distance (TD)

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 atmospheric residence time of chlordecone, 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. 2 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.6):

$$TD_{0.001} = \sqrt{\frac{S_{0.001}}{\pi}} \qquad (2)$$

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. 4. *Definition of the transport distance*

The results of evaluation transport distance for chlordecone for particular months and based on annual averages of air concentrations are presented in Table 5.

Table 5. *Calculated transport distance for chlordecone (on the basis of monthly and annual averages of air concentrations)*

|	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual
Transport distance	1436	1316	1265	1271	1265	1146	1503	1091	1396	1148	1085	1130	**1290**

The calculated *TD* for chlordecone (**1290** km) is almost twice less than for B[a]P (about **2500** km) and is similar to that for BDE-28.

2.4. Alternative approach to the determination of TD

Here alternative approach to the determination of transport distance based on calculations of chlordecone transport from a single emission pulse is illustrated. To check the robustness of the model evaluation of LRTP for this pollutant, the location of the source, meteorological data and model used are changed. Namely, the transport from initial emission pulse located in the Netherlands on sea cost with non-trivial meteorological situation in the beginning of January 2000 is calculated by means of the regional version of EMEP/MSCE-POP model. On the basis of these calculations transport distance for chlordecone is evaluated.

Such type of model runs allows revealing the influence of real meteorological and geophysical conditions on spatial distribution of air pollution caused by an accidental release of chlordecone occurred to the air from some conventional manufacturing site.

Fig. 5 shows spatial distribution of pollution originated by single emission pulse after 12, 24, 36 and 48 hours of transport as calculated by the model. It is not reasonable to consider longer period of time since, as it was shown above (Section 2.1), the half-life in the atmosphere due to all removal processes is about 1 day. For the comparison trajectories of air masses for first four model layers during these two days (January 1 and 2) are given. The heights of these trajectories are approximately 50, 100, 200 and 400 m above sea level.

12 hours   **24 hours**

36 hours   **48 hours**
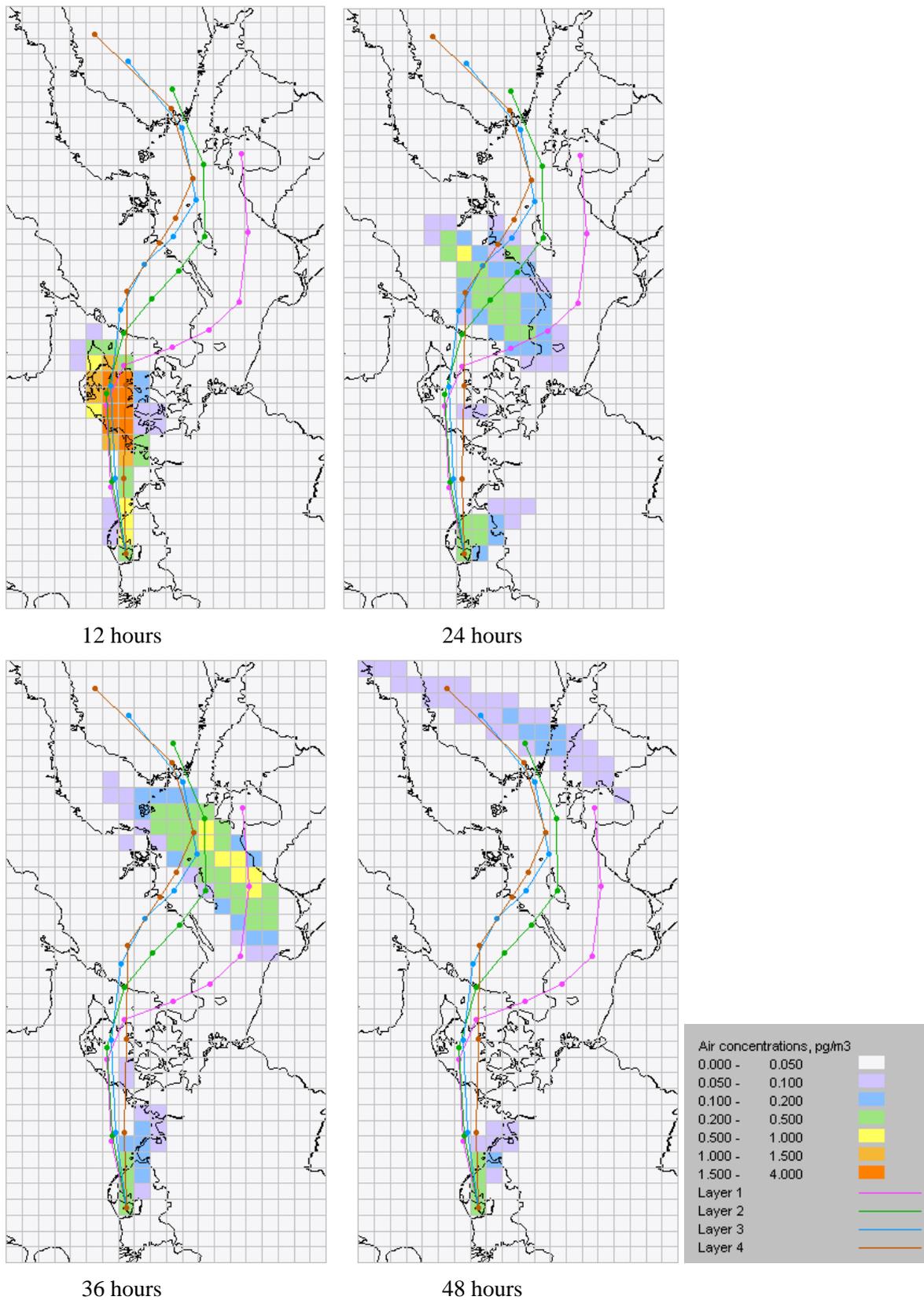
Fig. 5. *Atmospheric transport of a plum initiated by single emission pulse in the beginning of the year after 12, 24, 36 and 48 hours and trajectories of air masses. The movement of center of mass of concentration distribution is given in red*

It is seen that during first 12 hours the contamination originated in the Netherlands is transported to the central part of Denmark. Then, turning to the east, the contamination is moved to southern Sweden after 24 hours and to southeastern part of the Baltic Sea after 36 hours. Then again turning to the north according to the wind direction, the contamination is transported to southern part of Finland up to the end of second day.

The maps show also comparably high contamination in the vicinity of the location of initial emission pulse. This contamination is formed by some amount of pollutant accumulated by soil in the beginning of the transport when air concentrations at this location were high enough. After removing air pollution from this location due to atmospheric transport, air contamination is supported by re-volatilization of clordecone from soil. Model calculations show relatively high values of re-emission flux at this location. The re-emission from soil with subsequent atmospheric transport determines also "secondary plum" along trajectories with concentrations much lower than in the center of primary plum.

On the basis of these calculations it is possible to evaluate transport distance for chlordecone. To do that, the distance from the location of initial pulse to the center of the plum after each 6 hours is calculated. Under the assumptions that concentration is decreasing exponentially with the distance, the dependence of values of concentrations at the center of the plum on the distance from the location of initial pulse is

$$c = c_0 e^{-kr},$$

(3)

so that the dependence of $\ln(c_0/c)$ on r should be linear with coefficient k. Then transport distance TD, that is, the distance at which concentrations drop 1000 times can be calculated from this coefficient by
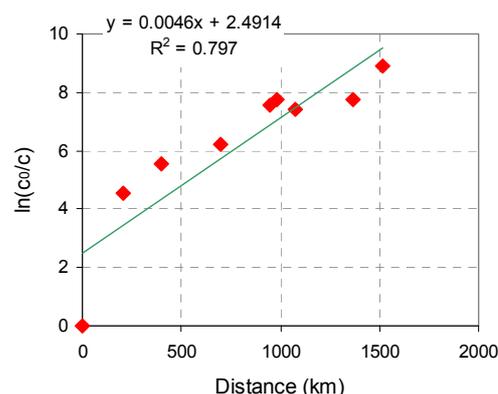
$$TD = \frac{\ln(1000)}{k},$$

(4)

The plot of the dependence of $\ln(c/c_0)$ on r is presented in Fig. 6.

It is seen that these dependence is approximately linear except for the first point. The discrepancies between calculated dependency and linear one are explained by variability of meteorological conditions, properties of the underlying surface, etc. The exceptional character of the first point is explained by the fact that for this point the plum transported from the initial point is overlapped with the result of re-emission from soil at the initial location of the plum.

Fig. 6. *Calculated dependence of c_0/c on r*

Fig. 6 also contains linear approximation of the plot with its equation. Transport distance calculated from the values of coefficients of this equation equals about **1500 km.**

Below two numerical characteristics of LRTP - residence time in the atmosphere (*Half-life in air$_{calc}$* ($T_{1/2}{}^{air}$)) and transport distance obtained for chlordecone on the basis of the model simulation of its atmospheric transport from the conventional emission source acting permanently within one year as

well as of the transport of a parcel of the pollutant emitted momentarily to the atmosphere are brought together in Table 6.

Table 6. Characteristics of LRTP (Half-life in air$_{calc}$ and TD) calculated for chlordecone

Substance	$T_{1/2}^{air}$, days	TD, km
Permanently acting emission source	1	1290
Pulse emission release	-	1500

Residence time in the atmosphere of chlordecone does not meet an indicative numerical value of the atmospheric half-life, which should be greater than two days in accordance with LRTP screening criterion for POPs.

Calculations made it clear that having been emitted from the diffusive or point emission source this substance has a potential for transfer to a receiving environment in locations distant from the source of its release approximately within the distance of 1290 - 1500 km. It should be also concluded that value of transport distance calculated on the basis of pulse emission release is quite close to that obtained by the approach of permanently acting source.

3. COMPARISON WITH OTHER SUBSTANCES

In this Section a comparison of numerical characteristics of LRTP and persistence in the environment (*TD* and $T_{1/2}^{env}$) calculated for chlordecone with those obtained for a number of other substances is performed. Among them there are pollutants already included in the CLRTAP and Stockholm Convention: aldrin, hexachlorobenzene (HCB), and three congeners of polychlorinated biphenyls (PCB-28, PCB-153 and PCB-180). Besides, benzo(a)pyrene (B[a]P) and α-hexachlorocyclohexane (α-HCH as one of stereo isomers of technical HCH) as POPs included into the UN ECE Protocol on POPs are also added. New POPs candidates, which are (or were previously) considered under these Conventions, are also included into this comparison. They are hexachlorobutadiene (HCBD), pentachlorobenzene (PeCB), polychlorinated naphthalenes (PCN-47), dicofol, three congeners of polybrominated diphenyl ethers (BDE-28, BDE-47 and BDE-99, the latter two being the major components of commercial PentaBDE), pentachlorophenol (PCP) and two isomers of endosulfan (α- and β-).

To ensure the comparability of the results, calculations of *TD* and $T_{1/2}^{env}$ for the all these substances are performed by the hemispheric version of EMEP/MSCE–POP model for 1996 with one and the same location of conventional emission source [*Vulykh et al.*, 2004, 2005 a, b, c, d, e, 2006; *Shatalov et al.*, 2007 in preparation].

The values of transport distance and persistence in the environment of these substances are compared on the plots in Fig. 7.
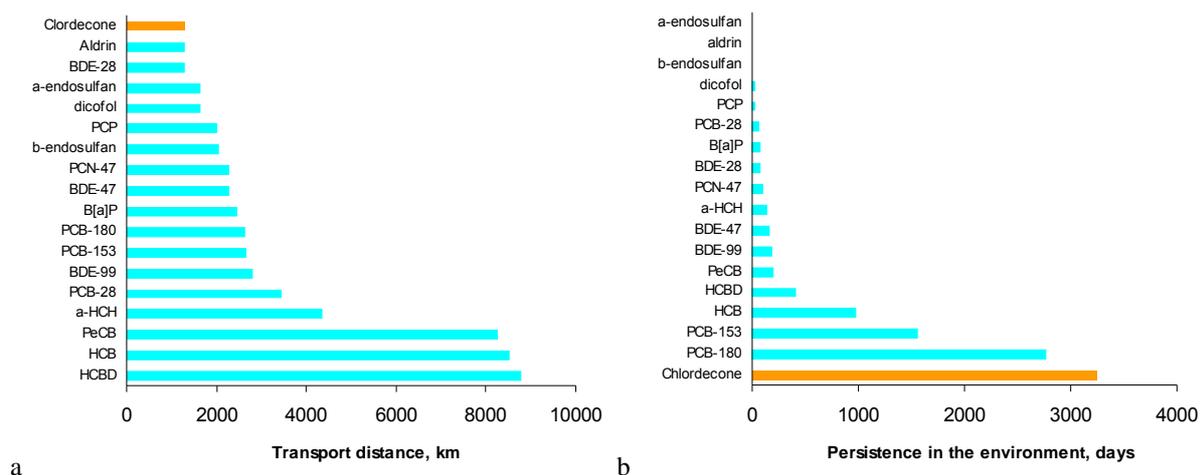
Fig. 7. *Comparison of transport distance (a) and persistence in the environment (b) for chlordecone with that for other substances*

According to the comparison it could be concluded that chlordecone has the lowest LRTP and the highest persistence in the environment among other considered pollutants. The comparison of *TD* of chlordecone with that for other substances shows that this pollutant has rather low long-range transport potential comparable with that of aldrin, α-endosulfan, BDE-28 and dicofol. It should be noted that aldrin is already included into Annex A of the Stockholm Convention and Annex 1 of the UN ECE Protocol on POPs. From the other hand, according to the model calculations of $T_{1/2}^{env}$, persistence of chlordecone in the environment is very high and considerably exceeds that for HCB and long-living PCB congeners. These pollutants are POPs listed in the Stockholm Convention and UN ECE Protocol on POPs.

4.   CONCLUDING REMARKS

The results of the model assessment demonstrate relatively low long-range atmospheric transport potential and very high persistence of chlordecone in the environment. This conclusion is also confirmed by the comparison of calculated numerical characteristics of LRTP and persistence of chlordecone in the environment against those obtained for a number of typical POPs and new POPs candidates. At that, it should be noted that the model evaluation demonstrates a certain potential of this chemical for transfer to a receiving environment in locations distant from the source of its release to the air. Its LRTP is similar to that of such substances as aldrin, BDE-28 and dicofol, which are already included or considered as a new POP candidates under the CLRTAP and the Stockholm Convention.

The comparison of determined values of transport distance obtained with the help of different approaches, different locations of the initial source and different meteorology shows that this characteristic of LRTP is robust enough to be used for characterization of the ability of substances to be transported far from the location of initial emissions. Besides, model calculations with the help of spatially resolved models provide additional information such as spatial distribution of pollution originated from a point or diffusive source taking into account the peculiarities of meteorological situation and properties of underlying surface.

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REFERENCES

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

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

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

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

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

Bocquene G. and A.Franco [2005] Pesticide contamination of the coastline of Martinique, Marine Pollution Bulletin, vol.51, pp. 612-619.

Chemical Fact Sheet – http://www.speclab.com/compound/c143500.htm

Chlordecone. Draft Risk Profile [2006] This draft risk profile is based on the draft prepared by Milieu/DHI Water&Environment Consortium foe the European Commission, DG Environment, 24 p.

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

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

Eisenreich S.J., Looney B.B., Thornton J.D. [1981] Airborne organic contaminants in the Great Lakes ecosystem, *Environ.Sci.Technol.,* vol.15, No.1, pp.30-38.

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.

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

Great Lakes Pesticide Report [2000] Final, Part 3.0 Review of Domestic use status by pesticide, pp.3.1-3.17

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.

Hornsby A.G., Wauchope R.D., A.E.Herner [1995] Pesticide properties in the environment, Springer, 227 p.

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

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

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.

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

Mackay D., Shiu W.-Y., Ma K.-C. [1997] Illustrated handbook of Physical-chemical Properties and Environmental fate for Organic Chemicals, vol.V, Pesticide Chemicals, pp. 431 – 434, 562, 568.

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.

PAN Pesticides Data Base – Pesticide Registration Status - http://www.pesticideinfo.org/Detail_ChemReg.jsp?Rec_Id=PC35101.

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.

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.

Scheringer M., MacLeod M., Wegmann F. [2006] Analysis of Four Current POP Candidates with the OECD P_{OV} and LRTP Screening Tool, pp.1-10.

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

Shatalov V. et al., [2007] "POP Model Intercomparison Study. Stage III. Comparison of calculated overall environmental persistence and long-range transport potential for evaluation of new substances ", EMEP/MSC-E Technical Report _/2007 DRAFT.

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

Substance profiles. Report on Carcinogens, Kepone (Chlordecone) CAS No.143-50-0, Eleventh Edition.

Toxicological profile for mirex and chlordecone [1995] http://www.astdr.cdc.gov/toxprofiles/t66.html.

UNEP/POPS/POPRC.1/4 Format for submitting pursuant to Article 8 of the Stockholm Convention the information specified in Annex E (Information on chlordecone)of the Convention, pp.1-9.

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

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 [2005a] "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.

Vulykh N., E. Mantseva, V. Shatalov [2005b] "EMEP Contrubution 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 Dicofol" EMEP/MSC-E Information Note 13/2005.

Vulykh N., E. Mantseva, V. Shatalov [2005c] "EMEP Contrubution to the Preparatory Work for the Review of the CLRTAP Protocol on POPs. New Substances: Model Assessment of Potential for Long-range Transboundary Atmospheric Transport and Persistence of Hexachlorobutadiene". EMEP/MSC-E Information Note 14/2005.

Vulykh N., E. Mantseva, V. Shatalov [2005d] "EMEP Contrubution 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 Pentachlorobenzene" EMEP/MSC-E Information Note 15/2005.

Vulykh N., E. Mantseva, V. Shatalov [2005e] "EMEP Contrubution 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 Polychlorinated Naphthalenes". EMEP/MSC-E Information Note 16/2005.

Vulykh N., S. Dutchak, E. Mantseva, V. Shatalov [2006] "EMEP contrubution 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, Endosulfan, Dicifol, HCBD, PeCB, PCN" EMEP/MSC-E Technical Report 1/2006.

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.

Annex A. Physical-chemical properties of chlordecone used for modeling

The data set of physical-chemical properties and degradation rates of chlordecone selected for the model parameterization on the basis of data available in literature is presented in Table A1.

Table A1. *Physical-chemical properties and degradation rates of chlordecone used for modelling*

Physical-chemical properties	Selected values	Comments	References
Henry's law constant for fresh and sea water, Pa·m^3/mol	$5.45 \cdot 10^{-3}$	Calculated from vapour pressure and water solubility	in Chlordecone Draft Risk Profile, May 2006 quoted from http://esc.syrres.com/interkow/webprop.exe; SRC PhysProp database; HSDB
Subcooled liquid-vapour pressure, Pa	$4.92 \cdot 10^{-2}$	Recalculated from vapour pressure value of the solid phase at 25 ºC (p_S)	p_S value taken from *Kilzer et al.*, 1979 cited in *Mackay et al.*, v.V, 1997; Chlordecone Draft Risk Profile, May 2006;
Degradation rate constant in air, s^{-1}	$1.47 \cdot 10^{-10}$	Estimated by MSC-E	-
Half-life in air, years	149		
Degradation rate constant in water, s^{-1}	$1.1 \cdot 10^{-8}$	-	*Scheringer et al.,* 2006
Half-life in water, years	2		
Degradation rate constant in soil, s^{-1}	$2.2 \cdot 10^{-9}$	-	Toxicological profile for mirex and chlordecone, 1995
Half-life in soil, years	10		
Molar volume, cm^3/mol	369.9		*Mackay et al.,* v. V, 1997
«Octanol-water» partition coefficient	$2.57 \cdot 10^5$		*Hansch et al.,* 1995 cited in Chlordecone Draft Risk Profile, May 2006; SRC PhysProp database
«Octanol-air» partition coefficient	$1.17 \cdot 10^{11}$	Calculated from selected K_{OW} and K_{AW}	-
Molecular diffusion coefficients, m^2/s:		Calculated	*Schwarzenbach et al.,* 1993
in water	$4.63 \cdot 10^{-10}$		
in air	$4.17 \cdot 10^{-6}$		
"Organic carbon-water" partition coefficient, m^3/kg	$1.05 \cdot 10^2$	Calculated with the help of relationship: $K_{OC} = 0.41 \cdot K_{OW}$ from [*Karikhoff,* 1981]	-

Due to the lack of available data in the literature the model estimates for chlordecone are obtained without 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.