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NEW SUBSTANCES:

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

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INTRODUCTION

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 multicompartment hemispheric transport model has been used. A multicompartment 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 (see Annex) 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.

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 per year 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.1.

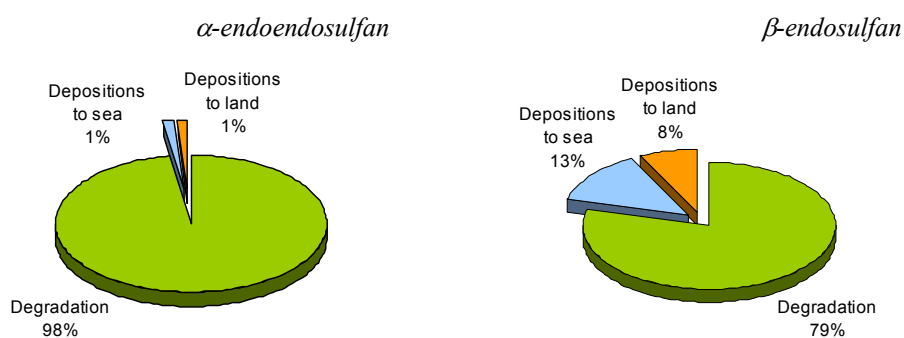


Fig.1. Calculated annual balances of endosulfan isomers removal from the atmosphere

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

| Isomer | <i>Half-life in air calc</i> $T_{1/2}^{air}$, 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 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 2 and 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.

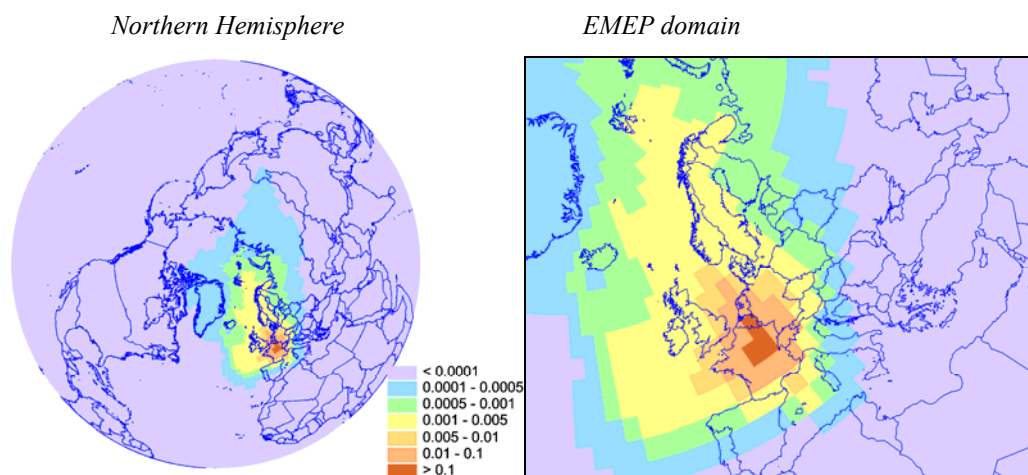


Fig. 2. Spatial distribution of α -endosulphan concentrations in the above-ground air in the Northern Hemisphere and in the EMEP domain (relative units)

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.

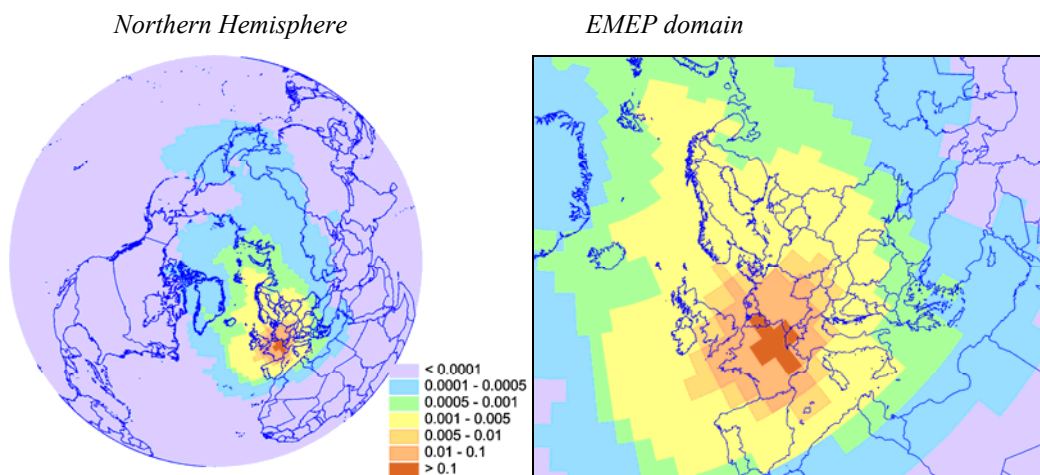


Fig. 3. Spatial distribution of β -endosulphan concentrations in the above-ground air in the Northern Hemisphere and in the EMEP domain (relative units)

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.

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; 2001; Beyer and Matthies, 2001; Leip and Lammel, 2004, etc]. For example, among such characteristics are spatial range, spatial scale, transport distance, characteristic travel distance, and so on. In the present assessment an additional characteristic demonstrating LRTP of the endosulfan isomers provided by the model is their *Transport Distance (TD)*. Numerical values of *TD* are determined with the help of Eq. 1 as an average distance from the point source at which the annual mean atmospheric concentration of a chemical in question is diminished 1000 times compared with the concentration near the source (see Fig.4):

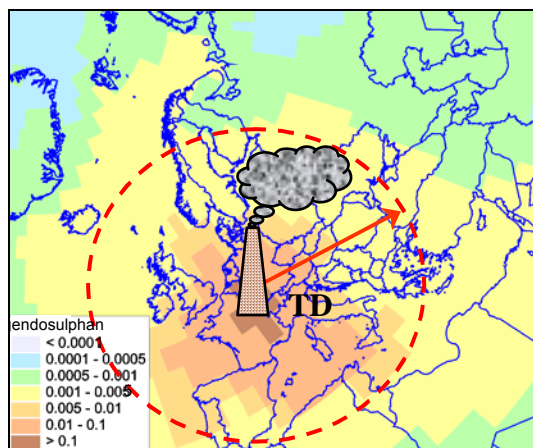


Fig.4. Definition of the transport distance

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

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

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

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 2.

Table 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.

2. PERSISTENCE IN THE ENVIRONMENT

The behaviour of a substance in the environment to a large extent is determined by its persistence not only in the atmosphere but also in water and soil. Its redistribution between the air and other media such as 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. To obtain half-lives either special laboratory research is conducted or measurements made under field conditions of specific land or water ecosystems are analyzed. Modeling allows numerical experiments to be made taking into account numerous factors dictating redistribution trends and determining the overall persistence of a substance.

In compliance with the Executive Body Decision 1998/2 the persistence of new substances in terms of their potential 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 also be greater than six months. In addition to these parameters describing the persistence in particular media, multimedia model calculations allow characteristics of persistence to be estimated for the environment as a whole, i.e. allow the overall residence time or overall environmental persistence to be determined [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 congeners on the basis of their atmospheric transport calculated by the model taking into account deposition processes, degradation and exchange of a pollutant between main environmental media.

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

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

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

Thus, the 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.5.

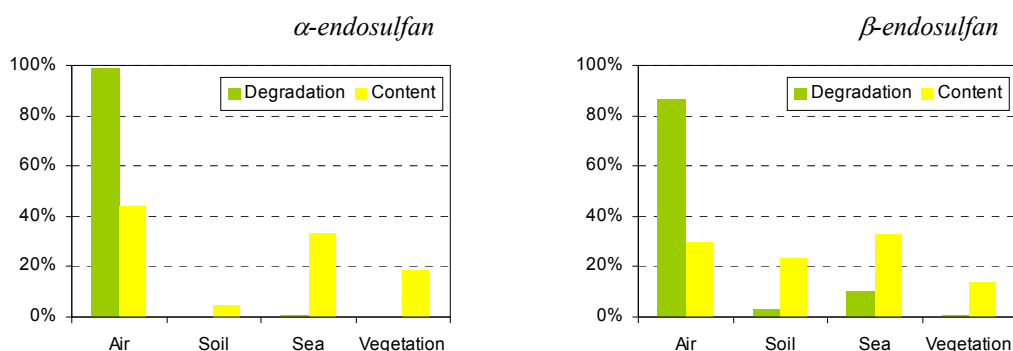


Fig.5. Annual degradation and media balances for endosulfan isomers

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 3 together with half-lives in specific media used in calculations. References to data sources on half-lives in specific media are given in the Annex, Table A2.

Table 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 4. Therefore for model calculations average values of data given in literature are used.

Table 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 | |

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 modeling 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. 6).

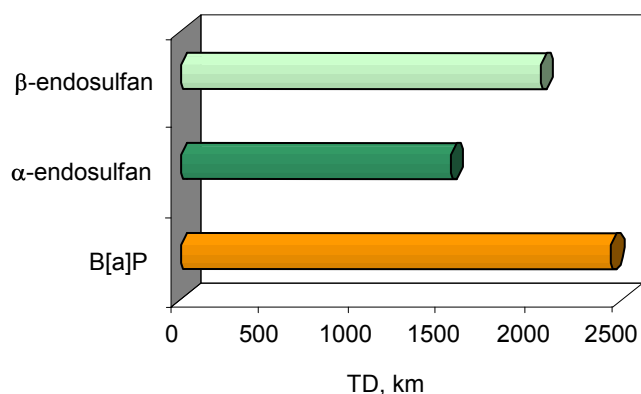


Fig. 6. Comparison of long-range potential of endosulfan isomers and B[a]P

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.

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 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 Annex (Tables A1 and A2).

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 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.

Table 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 | <100 0 | 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 |

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]

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.

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Annex A

Key physical-chemical properties of endosulfan isomers presented in [Herrmann, 2004] are shown in Table A1.

Table A1. 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

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It should be noted that values of these physical-chemical properties of endosulfan isomers different from those presented in [Herrmann, 2004] were selected for modeling 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 A2. 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 A2. Parameters of endosulfan isomers for modeling 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> |