# Overall Persistence, Long-range Transport Potential and Global Distribution of Endosulfan and its Transformation Products

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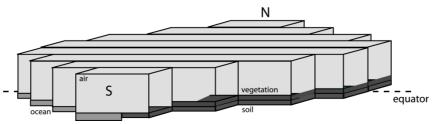
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### Summary

Overall persistence ( $P_{OV}$ ) and long-range transport potential (LRTP) of  $\alpha$ - and  $\beta$ endosulfan and two of their transformation products, endosulfan sulfate and endosulfan diol, are estimated with two multimedia box models, the OECD  $P_{OV}$  and LRTP Screening Tool and the global, latitudinally resolved model CliMoChem. The OECD Tool yields  $P_{OV}$  and LRTP for each compound separately, whereas the CliMoChem model calculates the environmental distribution of the parent compounds and the formation and distribution of the transformation products simultaneously. Results from the CliMoChem model show that  $P_{OV}$  and LRTP of the endosulfan substance family are similar to those of acknowledged Persistent Organic Pollutants, such as aldrin, DDT, and heptachlor. The results also show that  $P_{OV}$  and LRTP of the entire substance family, i.e. including the transformation products, are significantly higher than those of the parent compounds alone.

### 1 Introduction

In a first step, we use the OECD  $P_{OV}$  and LRTP Screening Tool (Wegmann et al. 2009) to estimate the  $P_{OV}$  and LRTP of  $\alpha$ - and  $\beta$ -endosulfan and two of its transformation products, endosulfan sulfate and endosulfan diol. The OECD Tool is a generic multimedia box model that yields estimates of  $P_{OV}$  and LRTP for screening purposes. In the context of endosulfan, a drawback of the OECD Tool is that it cannot cover parent compounds and transformation products in parallel, i.e. the dynamic formation of the transformation products out of the parent compound during the parent compound's environmental transport is neglected. Therefore, we also use the more complex global environmental fate model CliMoChem (Scheringer et al. 2000, see Figure 1) and calculate the phase partitioning and long-range transport of  $\alpha$ and  $\beta$ -endosulfan along with its conversion into endosulfan sulfate and endosulfan diol. In the CliMoChem model, we use 10 latitudinal zones and a single pulse release of the parent compound ( $\alpha$ - and  $\beta$ -endosulfan in a ratio of 7:3) to the air of the tropical region directly north of the equator (0-18 °N) and calculate the overall environmental persistence  $(P_{OV})$  of the parent compound and also that of the parent compound and the transformation products in combination (joint persistence, see Fenner et al. (2000), Schenker et al. (2007)). In addition, the model yields the spatial range as a metric of LRTP that is given in percent of the pole-to-pole distance, see section 2.4.a below.



*Figure 1:* Structure of the CliMoChem model (Scheringer et al. 2000). S, N: south and north pole.

We also present model calculations employing a scenario with realistic endosulfan emissions. In these calculations, we use 18 latitudinal zones and an emission inventory from 1955 to 2008 that reflects global endosulfan usage from its introduction until today. Results from these model calculations are concentrations of endosulfan and its transformation products that represent global background levels. A comparison between modeled concentrations and measured concentrations in the environment is used here to evaluate the model performance for endosulfan. Such a comparison has earlier been carried out for DDT with the CliMoChem model (Schenker et al. 2008a), and it has been found that the CliMoChem model is well suited to calculate the global fate of POPs.

### 2 Models and Methods

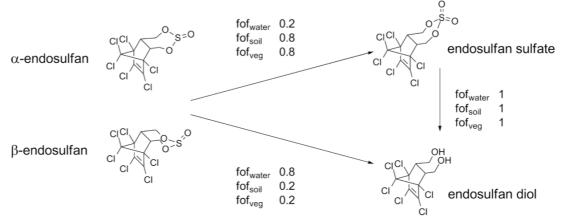
### 2.1 Models Used

The OECD  $P_{OV}$  and LRTP Screening Tool (The Tool) consists of a single box that reflects average properties of the global environment (Wegmann et al. 2009). The Tool cannot calculate the joint persistence and joint spatial range of parent compound and transformation products of endosulfan together but, as a simpler approach, calculates  $P_{OV}$  and LRTP for each compound individually. The Tool requires the chemical properties at 298 K as input and does not take into account lower temperatures in colder regions of the globe. The results for endosulfan and its transformation products are compared here with the  $P_{OV}$  and LRTP of several acknowledged POPs already regulated under the Stockholm convention, and a set of substances that are generally considered not to show POP-like characteristics. Chemical property data of the POPs (DDT, heptachlor, and dieldrin) were taken from Schenker et al. (2005) and will also be used with the CliMoChem model; property data of the non-POPs (*p*-cresol, biphenyl, and atrazine) were taken from Klasmeier et al. (2006).

The CliMoChem model (Scheringer et al. 2000, see Figure 1) consists of a sequence of latitudinal zones from the southern polar region to the northern polar region; each zone has its specific land-to-water surface ratio, temperature, organic matter content in soil, concentration of OH radicals in air, and precipitation rate. Each zone consists of up to seven environmental media: bare soil, ocean water, atmosphere, vegetation covered soil (further on designated as "soil"), vegetation, ice and snow. The model simulates diffusive and advective phase exchange processes within a zone, and describes interzonal transport with eddy-diffusion coefficients in ocean water and tropospheric air. In contrast to The Tool, CliMoChem makes it possible to calculate the distribution and degradation dynamics of parent compounds and transformation products simultaneously.

### 2.2 Transformation Scheme for endosulfan

The transformation scheme including  $\alpha$ - and  $\beta$ -endosulfan as well endosulfan sulfate and endosulfan diol that is used in the CliMoChem model is shown in Figure 2. The degradation pathways of endosulfan and known transformation products have been described in the literature (e.g. Martens 1977 for soil, Walse et al. 2002 for water; no information for air). For the description of the degradation pathways in the model, a fraction of formation (fof) is required for the processes that convert a parent compound into transformation products. The *fof* is the molar ratio of a given transformation product that is formed from the amount of the parent compound. Actual fof values are not available in the literature, but qualitative information is. In our scheme,  $\alpha$ - and  $\beta$ -endosulfan (emitted as a 7:3 mixture) are transformed in soil, water, and vegetation to endosulfan sulfate (main soil metabolite) and endosulfan diol (direct hydrolysis product in water). The sulfate itself is hydrolzed to the diol as well. Although further transformation products are known (endosulfan ether, hydroxy carboxylic acid, endosulfan ether and lactone), the diol is modeled here as the final product before mineralization. The data that are presently available do not allow inclusion of the other transformation products in the model. In air, the degradation of the parent compounds leads to direct mineralization as no information on transformation products is available. Finally, a possible conversion of  $\beta$ -endosulfan to  $\alpha$ -endosulfan has been reported, but no kinetic data for this process are available. Therefore, this conversion is not represented in our model setting.



*Figure 2:* Degradation pathway and fractions of formation (*fof*) for endosulfan in the soil, water, and vegetation compartments as used in the CliMoChem model.

### 2.3 Physicochemical properties and degradation rate constants

Information on the physicochemical properties of endosulfan and its transformation products was compiled from different sources. Reliable  $\alpha$ - and  $\beta$ -endosulfan partition coefficients could be taken from the compilation by Schenker et al. (2005); this data are based on an extensive literature search and have been harmonized to yield internally consistent values. Experimental partitioning data for the sulfate and the diol is scarce and, therefore, the partition coefficients of these two substances were obtained from QSAR software (EPISuite). Energies of phase transition ( $\Delta U_{OW}$  and  $\Delta U_{AW}$ , which describe the temperature dependence of the octanol-water and air-water partition coefficients) were estimated according to MacLeod et al. (2007) for all four substances. Degradation half-lives in air, water, and soil for the endosulfan compounds were compiled from a variety of sources and are summarized in Table 1, sources are given in the Appendix. Only experimentally derived values (except the OH reaction rate constant of endosulfan diol, derived with QSAR software) were taken to calculate the degradation rate constants that were used in the CliMoChem model. Experimental activation energies ( $E_a$ , which describe the temperature dependence of the degradation rate constants) where only available for hydrolysis (Hengpraprom and Lee 1998) and degradation in soil (Ghadiri and Rose 2001) of the parent compounds; other  $E_a$  values are not available and a standard value was selected (Scheringer et al. 2000).

*Table 1:* Degradation half-lives, activation energies, partition coefficients, and energies of phase transition of  $\alpha$ - and  $\beta$ -endosulfan and their transformation products, endosulfan sulfate and endosulfan diol.

|                                 | $\alpha$ -endosulfan | β-endosulfan | endosulfan sulfate | endosulfan diol |
|---------------------------------|----------------------|--------------|--------------------|-----------------|
| <i>t</i> <sub>1/2</sub> air [d] | 27                   | 15           | 2.7                | 1.9             |
| t <sub>1/2</sub> water [d]      | 28                   | 29           | 99                 | 30              |
| t <sub>1/2</sub> soil [d]       | 39                   | 195          | 139                | 146             |
| E <sub>a</sub> air [kJ/mol]     | 15.0                 | 15.0         | 15.0               | 15.0            |
| E <sub>a</sub> water[kJ/mol]    | 45.5                 | 54.5         | 30.0               | 30.0            |
| E <sub>a</sub> soil [kJ/mol]    | 15.2                 | 39.1         | 30.0               | 30.0            |
| log Kow [-]                     | 4.93                 | 4.78         | 3.71               | 3.69            |
| log K <sub>AW</sub> [–]         | -3.56                | -4.75        | -4.78              | -7.43           |
| ∆U <sub>OW</sub> [kJ/mol]       | -20.0                | -20.0        | -20.0              | -20.0           |
| $\Delta U_{AW}$ [kJ/mol]        | 68.1                 | 68.6         | 73.4               | 85.7            |

The CliMoChem model uses the data in Table 1 and the transformation scheme in Figure 2 to calculate the concentrations of all four compounds as a function of time in all environmental compartments.

### 2.4 Emission Scenarios

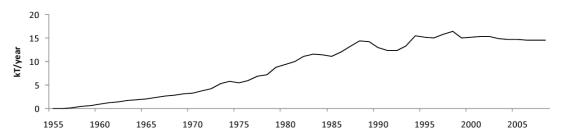
It is crucial to distinguish between two types of model calculations that are presented here: (a) a generic pulse release that can be used to calculate metrics of  $P_{OV}$  and LRTP (these metrics are independent of the amount of chemical released) and to compare  $P_{OV}$  and LRTP results for different chemicals; (b) calculations based on a historical emissions inventory that specifies the amounts of chemical released at different times in different latitudinal zones; this type of calculation yields realistic estimates of chemical concentrations in different geographical regions and environmental media, which can then be compared to concentrations measured in the field.

### a) Pulse release scenario

In the pulse release scenario, an arbitrarily chosen value of  $10^4$  tonnes is emitted at time t = 0. The calculated concentrations are then used as basis by the CliMoChem model to derive the  $P_{OV}$  of the parent compound and each transformation product individually as well as the joint persistence of the parent compound and the transformation products together (Fenner et al. 2000, Schenker et al. 2007). The joint persistence reflects the contribution of the transformation products to the total environmental levels caused by the entire substance family. The model also calculates the spatial range as a metric of LRTP. The spatial range is expressed in percent of the pole-to-pole distance; a chemical that is uniformly distributed over the globe has a spatial range of about 90% to 95% of the pole-to-pole distance (this is observed for chlorofluorocarbons, for example). Again, the CliMoChem model calculates the spatial range of the parent compound and each transformation product individually as well as the joint spatial range of parent compound and transformation products together. In the investigation of endosulfan presented here, we exactly apply the approach described in more detail by Schenker et al. (2007).

### b) Realistic emissions scenario

A spatially and temporally resolved endosulfan emission inventory has not yet been published and had, therefore, to be generated. Based on estimations of the temporal evolution of global endosulfan usage (Li and Macdonald 2005, Figure 4 therein; see Figure 3 below) and information on the spatial distribution of the cumulative endosulfan usage (Li and Li 2003), a temporally (1955-2008) and spatially resolved emission inventory was compiled that is adapted to the 18 latitudinal zones of the CliMoChem model: 1% of the cumulative endosulfan emissions was assigned to the Arctic region, 32% to the northern temperate region, 55% to the tropics, and 12% to the southern temperate region. We presumed that endosulfan is emitted in the summer half-year in the northern and southern temperate regions, and year-round in the tropics. Endosulfan is applied by different spraying methods (aerial and ground spray); we assumed that 80% of the pesticide enters into the atmospheric compartment and 20% into the soil compartment.



*Figure 3*: Temporal evolution of global endosulfan usage. Figure based on Figure 4 in Li and Macdonald (2005).

To estimate the error associated with the calculated concentrations, an uncertainty analysis was conducted for the realistic emissions scenario according to the way described by MacLeod et al. (2002). For that purpose, confidence factors were assigned to the various input parameters of the CliMoChem model, i.e. general environmental parameters (confidence factors taken from Schenker et al. 2009), degradation rate constants and partitioning coefficients (confidence factors derived from the property data compiled), the fraction of formation values (confidence factors assumed), emission scaling factor (confidence factors assumed), and the air-to-soil ratio of the emissions (confidence factors assumed). All confidence factors are given in Table A1 in the Appendix. Model sensitivity was derived by individual variation of each input parameters, the calculation of output confidence factors as a measure of uncertainty. By multiplication and division of calculated concentrations by the square root of the output confidence factors, one obtains the 68% interval of confidence for the log-normally distributed concentrations.

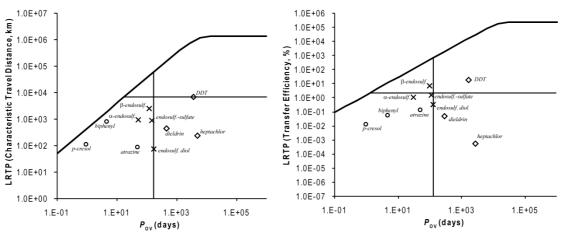
### 2.5 Field data

To compare calculated concentrations derived from the realistic emissions scenario with actual levels in the environment, we gathered measurement data from published studies (Table A2). Because concentrations calculated with the CliMoChem model are representative of background levels, only measurement sites distant from any emission source were included. The data points from the literature were evaluated,

selected, and aggregated to measurement series as described in Schenker et al. (2008a).

# 3 Results from the OECD Tool for overall persistence and long-range transport potential

Figure 4 presents results from the OECD Tool for the substance family of endosulfan (crosses), for acknowledged POPs (dieldrin, DDT, and heptachlor, diamonds), and for substances known not to show POP-like behavior (*p*-cresol, biphenyl, and atrazine, circles); chemicals are also indicated by their names in the graphs. Outputs of the OECD Tool are the  $P_{OV}$  and two LRTP metrics, the Characteristic Travel Distance, CTD (in km), and the Transfer Efficiency (TE, in %). For the definition and interpretation of these metrics, see Wegmann et al. (2009).



*Figure 4:* Results from the OECD Tool for  $P_{OV}$  and LRTP of the substance family of endosulfan (crosses), acknowledged POPs (diamonds), and non POP-like substances (circles). The left panel shows the Characteristic Travel Distance, CTD, vs.  $P_{OV}$ ; the right panel shows the Transfer Efficiency, TE, vs.  $P_{OV}$ . The horizontal and vertical lines represent reference points derived from acknowledged POPs (Klasmeier et al. 2006).

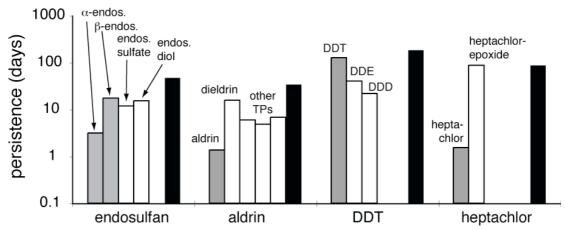
The results from the OECD Tool show that the LRTP of the endosulfan substance familiy is higher than that of dieldrin and heptachlor (with the exception of endosulfan diol, which has the lowest CTD but a TE exceeding that of heptachlor and dieldrin). The individual compounds of the endosulfan substance family exhibit lower persistences than the three POPs. It has to be kept in mind, however, that the persistences of individual compounds from the endosulfan substance family have to be summed-up, and that the joint persistence (as shown in section 4.1) will be comparable to that of acknowledged POPs.

Comparison of the compounds of the endosulfan substance family with the substances that are not known as POPs shows that endosulfan exhibits an overall persistence and a long-range transport potential that is clearly higher than that of non-POPs.

# 4 Results from the CliMoChem model for overall persistence and long-range transport potential

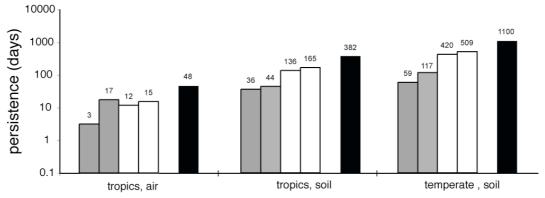
### 4.1 Overall persistence

 $P_{\rm OV}$  results for the endosulfan substance family are shown in Figure 5 and, for comparison, also results for the substance families of aldrin, DDT and heptachlor that were investigated by Schenker et al. (2007). The number of transformation products included (white bars in Figure 5) is different for the different substance families. For release to air, the individual persistences of  $\alpha$ - and  $\beta$ -endosulfan (gray bars) are 3 and 17 d, and those of the two transformation products are around 15 d. The joint persistence is the sum of the four individual persistences and has a value of approximately 50 d (black bar). This value is between the joint persistences of the aldrin substance family (35 d) and the heptachlor substance family (85 d).



*Figure 5:*  $P_{OV}$  of parent compounds and transformation products for the endosulfan substance familiy (calculated here) and the substance families of aldrin, DDT, and heptachlor (taken from Schenker et al. (2007)). Release is to air in the northern tropical zone (zone #5) of the CliMoChem model. Gray bars: parent compounds, white bars: transformation products, black bars: joint persistence.

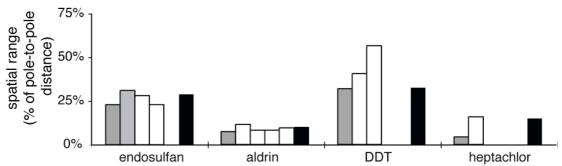
An important feature of the overall persistence is that, if the chemical's degradation half-lives are different in the different environmental media,  $P_{OV}$  is highly dependent on the release pathway of the chemical. In the case of endosulfan, the half-life is considerably longer in soil than in air (see Table 1), which implies that  $P_{OV}$  is also higher for release to soil than for release to air. Figure 6 shows  $P_{OV}$  values of the endosulfan substance family for release to air in zone #5 (northern tropical; same values as in Figure 5) and also for releases to soil in zone #5 (northern tropical) and soil in zone #3 (northern temperate). Release to soil leads to joint persistences of about 1 yr (zone #5) and about 3 years (zone #3; higher persistence because of lower temperatures and slower degradation).



*Figure 6:*  $P_{OV}$  values of the endosulfan substance family for the base case considered here, emission to air in the northern tropical zone (0–18° N) of the CliMoChem model (left), and for two additional cases, releases to soil in the northern tropical zone (middle) and to soil in the northern temperate zone (36 °N–54 °N) (right). Gray bars:  $\alpha$ - and  $\beta$ -endosulfan; white bars: endosulfan sulfate (left), endosulfan diol (right); black bars: joint persistence. Values above gray and white bars are  $P_{OV}$  values of individual chemicals, values above black bars values of joint persistence (all values in days).

### 4.2 Spatial range

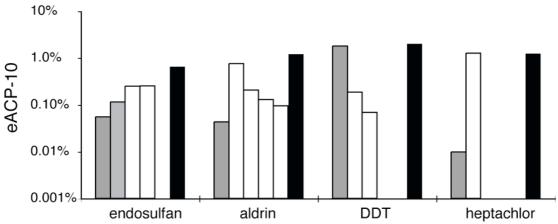
Figure 7 shows the spatial ranges of the endosulfan substance family in comparison to those of the substance families of aldrin, DDT and heptachlor (Schenker et al. 2007); the transformation products included are the same as in Figure 5. The individual spatial ranges of the four compounds are between 20% and 30%. The joint spatial range is not directly the sum of the individual spatial ranges but their mass-weighted average. The joint spatial range is 29%, which is higher than that of aldrin and heptachlor and close to the one of DDT (33%).



*Figure 7:* Spatial ranges of the parent compounds and the transformation products for the endosulfan substance familiy (calculated here) and the substance families of aldrin, DDT, and heptachlor (taken from Schenker et al. 2007). Release to air in zone #5 of the CliMoChem model (northern tropical). Gray bars: parent compounds, white bars: transformation products, black bars: joint spatial range. Same transformation products included as in Figure 3.

#### 4.3 Arctic contamination potential

Finally, Figure 8 shows the Arctic Contamination Potential after 10 years of continuous releases (Wania 2003), again results for the endosulfan substance family are given in comparison to results for aldrin, DDT and heptachlor. The joint eACP-10 of the endosulfan family is 0.67%, which is similar to that of the aldrin (1.23%) and heptachlor (1.27%) families.



*Figure 8:* Arctic contamination potential (eACP-10 (Wania 2003)) of parent compounds and transformation products for the endosulfan substance familiy (calculated here) and the substance families of aldrin, DDT, and heptachlor (taken from Schenker et al. (2007)). Gray bars: parent compounds, white bars: transformation products, black bars: joint eACP-10. Same transformation products included as in Figure 5.

### 4.4 Conclusion from CliMoChem results

Results from the CliMoChem model for  $P_{OV}$ , spatial range and eACP-10 indicate that the family of  $\alpha$ - and  $\beta$ -endosulfan and the two transformation products, endosulfan sulfate and endosulfan diol, has similar overall persistence and potential for longrange transport in the environment as the families of some acknowlegded POPs. The contribution of the two transformation products to joint persistence, joint spatial range and joint eACP-10 is significant, i.e. similar to or higher than that of the two parent compounds.

There are considerable uncertainties associated with the individual values of the chemical properties used and with the components of the transformation scheme shown in Figure 2. However, experience from other cases investigated with the CliMoChem model has shown that the model results are relatively robust against gradual changes of the transformation scheme (Schenker et al. 2008b). The uncertainty of the half-lives and the partition coefficient is around a factor of 10 (half-lives) and a factor of 5 (partition coefficients).

### 5 Results from the CliMoChem model for realistic emissions

To evaluate the performance of the CliMoChem model in the simulation of the global fate of the endosulfan substance family, we compared concentrations obtained from the model runs with the realistic emissions scenario with measured concentrations of endosulfan in the environment.

Modeled concentrations of  $\alpha$ - and  $\beta$ -endosulfan, endosulfan sulfate, and endosulfan diol in the atmosphere, ocean water, and soil in the northern temperate region (20–50° N), averaged for the period from 1995 to 1999 and corresponding measured values (where available) are given in Table 2. The model results are in good agreement with actual environmental measurements and differ by less than an order of magnitude from measured values, in several cases by less than a factor of 3. This indicates that the CliMoChem model captures the main features of the large-scale distribution of endosulfan and the two transformation products with sufficient accuracy. This, in turn, lends credibility to the results for overall persistence and LRTP presented in sections 4.1 to 4.3.

|                                  | α-endosulfan |       | β-endosu | lfan  | endosulfan sulfate endosulfan die |       | loi        |       |
|----------------------------------|--------------|-------|----------|-------|-----------------------------------|-------|------------|-------|
|                                  | model        | meas. | model    | meas. | model                             | meas. | model      | meas. |
| Ocean water (ng/m <sup>3</sup> ) | 1.1-7.5      | n.a.  | 0.7-4.4  | n.a.  | 1.2-10                            | n.a.  | 1.3-9      | n.a.  |
| Atmosphere (pg/m <sup>3</sup> )  | 21-86        | 31    | 4.8-16   | 3.4   | 0.2-4                             | 1.2   | 0.001-0.03 | n.a.  |
| Soil (microg/kg)                 | 0.003-0.1    | 0.04  | 0.08-0.4 | 0.16  | 0.1-0.8                           | 2.6   | 0.1-0.9    | n.a.  |

*Table 2:* Modeled concentrations ranges (68% confidence interval) and measured levels in the environment (median of measurement series) for the endosulfans in the northern temperate region for the period from 1995 to 1999 (n.a. = not available).

The main contributors to the output uncertainties are uncertainties of the substanceand media-specific degradation rate constants. With a few exceptions, only substance properties (degradation rate constants and partition coefficients and their temperature dependencies) contribute significantly to the total output uncertainty for a specific substance and environmental compartment. Uncertainties associated to the fractionof-formation values, the general parameters of the model environment, and the emissions (emission amount and the air-to-soil ratio of the emissions) generally contribute less than 10% to the output uncertainties.

### **Conclusions and Outlook**

Given the agreement between calculated and measured concentrations, we conclude that the model can generally reproduce the behavior of endosulfan in the environment. This finding supports the values calculated for overall persistence, spatial range, and arctic contamination potential. We are planning to present more detailed information on calculations with realistic endosulfan emissions in the near future.

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## Appendix

*Table A1:* Literature-derived values for the degradation half-lives  $(t_{1/2})$  in air, water, and soil. The geometric mean of the data sets were used for the calculations; given in parentheses are the confidence factors (cf) associated to a property that were used for the uncertainty estimations. Several original sources cited within some of the cited data compilations have not been published and could therefore not be accessed.

| Half-lives in air  | <i>t</i> <sub>1/2</sub> air [d] |   | Data source (original citation in brackets) |
|--------------------|---------------------------------|---|---|
| α-endosulfan       | 27                              | measured, 75 °C, [OH] = 5e5 cm <sup>-3</sup> (cf: 8)          | (UNEP p.7) Zetzsch 1992                     |
| β-endosulfan       | 15                              | indirect (CFC113) measurement of OH radical addition (cf: 8)  | (UNEP p.7) Kloepffer 1992                   |
| endosulfan sulfate | 2.7                             | indirect (CFC113) measurement of OH radical addition (cf: 10) | (UNEP p.7) Kloepffer 1992                   |
| endosulfan diol    | 1.9                             | AOPWIN (QSAR) (cf: 10)  |   |

| Half-lives in water | <i>t</i> <sub>1/2</sub> water [d] | Comments  | Data source (original citation in brackets) |  |
|---------------------|-----------------------------------|---|---|--|
| α-endosulfan        | 38                                | rhine surface water   | Zoeteman et al. 1980                        |  |
|                     | 5                                 | river water   | (Mackay) Eichelberger and Lichtenberg       |  |
|                     | 19                                | hydrolysis at pH 7  | (UNEP p.26) Görlitz and Rutz 1989           |  |
|                     | 22                                | hydrolysis at pH 7  | (NRA ECRP) Görlitz and<br>Klöckner 1982     |  |
|                     | 157                               | hydrolysis at pH 7  | (NRA ECRP) Guerin and<br>Kennedy 1992       |  |
|                     | 35.4                              | hydrolysis at pH 7 (rhine water?)                                 | (OSPAR) Greve and Witt 1971                 |  |
|                     | 27.5                              | hydrolysis at pH 7 (sterile buffer)                               | (OSPAR) Singh et al 1991                    |  |
|                     | 28.5                              | geometric mean (cf: 4)  |   |  |
| β -endosulfan       | 45                                | rhine surface water   | (Chemfate) Zoeteman et al.<br>1980          |  |
|                     | 10.7                              | hydrolysis at pH 7  | (UNEP p.26) Görlitz and Rutz 1989           |  |
|                     | 17                                | hydrolysis at pH 7  | (NRA ECRP) Görlitz and<br>Klöckner 1982     |  |
|                     | 37.5                              | hydrolysis at pH 7 (rhine water?)                                 | (OSPAR) Greve and Witt 1971                 |  |
|                     | 23.5                              | hydrolysis at pH 7 (sterile buffer)                               | (OSPAR) Singh et al 1991                    |  |
|                     | 29.4                              | geometric mean (cf: 4)  |   |  |
| endosulfan sulfate  | 184                               | extrapolated, hydrolysis at pH 7 (cont. small quantities of MeOH) | (NRA ECRP) Guerin and<br>Kennedy 1992       |  |
|                     | 53                                | water-sediment system, pH 7.2-8.2                                 | (FAO p.353) Hammel 2004                     |  |
|                     | 99                                | geometric mean (cf: 5.8)  |   |  |
| endosulfan diol     | 29.5                              | water-sediment system, pH 7.2-8.2 (cf: 5.8)                       | (FAO p.353) Hammel 2004                     |  |

| Half-lives in soil | <i>t</i> <sub>1/2</sub> soil [d] | Comments   | Data source (original citation in brackets) |
|--------------------|----------------------------------|--|---|
| α-endosulfan       | 50                               |  | (Mackay) Ryan et al 1988                    |
|                    | 50                               |  | (Mackay) Wauchope 1991                      |
|                    | 120                              |  | (Mackay) Pait et al 1992                    |
|                    | 46                               | geometric mean of reported range 30-70 d                 | (Mackay) Tomlin 1994                        |
|                    | 50                               |  | (Mackay) Halfon 1996                        |
|                    | 28                               | clay soil, 25°C, extrapolated for 15% soil water content | Ghadiri and Rose 2001                       |
|                    | 8                                | clay soil, 25°C, extrapolated for 25% soil water content | Ghadiri and Rose 2001                       |

|                     | 60    |  | (FAO) unknown               |  |
|---------------------|-------|--|-----------------------------|--|
|                     | 22    | laboratory conditions, geometric mean of 5 different soils                                   | (UNEP p. 22) Stumpf 1995    |  |
|                     | 38.8  |  |                             |  |
|                     |       | Half lives in acidic to neutral soil range from one to two months for $\alpha$ -endosulfan   | (US EPA)                    |  |
| $\beta$ -endosulfan | 376   | clay soil, 25°C, extrapolated for 15% soil water content                                     | GhadiriandRose 2001         |  |
|                     | 100   | clay soil, 25°C, extrapolated for 25% soil water content                                     | GhadiriandRose 2001         |  |
|                     | 800   |  | (FAO) (unknown)             |  |
|                     | 158   | sandy loam, laboratory conditions, 21 °C   | (UNEP p. 22) Stumpf 1995    |  |
|                     | 264   | loamy sand, laboratory conditions, 21 °C   | (UNEP p. 22) Stumpf 1995    |  |
|                     | 132   | silt loam, laboratory conditions, 21 °C  | (UNEP p. 22) Stumpf 1995    |  |
|                     | 108   | sandy loam, laboratory conditions, 21 °C   | (UNEP p. 22) Stumpf 1995    |  |
|                     | 115   | sandy loam, laboratory conditions, 21 °C   | (UNEP p. 22) Stumpf 1995    |  |
|                     | 194.6 | geometric mean (cf: 4)   |                             |  |
|                     |       | Half lives in acidic to neutral soil range from three to nine months for $\beta$ -endosulfan | (US EPA)                    |  |
| endosulfan sulfate  | 117   | sandy loam, laboratory conditions  | (UNEP p. 23) Buerkle        |  |
|                     | 138   | silty clay loam, laboratory conditions   | (UNEP p. 23) Buerkle        |  |
|                     | 412   | loam, laboratory conditions  | (UNEP p. 23) Buerkle        |  |
|                     | 134   | silt loam, laboratory conditions   | (UNEP p. 23) Buerkle        |  |
| 123                 |       | laboratory conditions  | (UNEP p. 23) Schnoeder 2002 |  |
|                     | 147   | laboratory conditions  | (UNEP p. 23) Schnoeder 2002 |  |
|                     | 134   | laboratory conditions  | (UNEP p. 23) Schnoeder 2002 |  |
|                     | 75.2  | loam, field conditions (Spain)   | (FAO p.350) Hardy 2001      |  |
|                     | 161   | loam, field conditions (Greece)  | (FAO p.350) Balluff 2001    |  |
|                     | 240   | laboratory conditions, sterile cotton farming soil   | Guerin 2005                 |  |
|                     | 60    | laboratory conditions, non-sterile cotton farming soil                                       | Guerin 2005                 |  |
|                     | 139   | geometric mean (cf: 5)   |                             |  |
| endosulfan diol     | 255   | laboratory conditions, sterile cotton farming soil   | Guerin 2005                 |  |
|                     | 83    | laboratory conditions, non-sterile cotton farming soil                                       | Guerin 2005                 |  |
|                     | 145.5 | geometric mean (cf: 5)   |                             |  |

*Table A2:* The sources used for the compilation of measurement series for background concentrations of endosulfan in the atmosphere, ocean water and soil. Measurements listed within a publication but measured elsewhere are not listed separately.

| Study                | media        | geographic<br>location | measurement period | substances           | meas.<br>series |
|----------------------|--------------|------------------------|--------------------|----------------------|-----------------|
| Shen et al. 2005     | atmos        | N-America              | 2000               | alpha, beta          | 6               |
| Hung et al. 2002     | atmos        | Arctic                 | 1993-1997          | alpha                | 5               |
| Hung et al. 2005     | atmos        | Arctic                 | 1993-1994          | alpha                | 1               |
| Su et al. 2008       | atmos        | Arctic                 | 2000               | alpha                | 5               |
| Daly at al. 2007     | atmos, soil  | Canada                 | 2003               | alpha, beta, sulfate | 3, 3            |
| van Drooge 2004      | atmos        | Europe                 | 2001               | alpha, beta          | 1               |
| Zhang et al.2008     | atmos        | India                  | 2006               | alpha, beta          | 1               |
| Pozo et al. 2009     | atmos        | Global                 | 2005               | alpha, beta, sulfate | 6               |
| Harner et al. 2006   | atmos        | Global                 | 2000-2001          | alpha                | 4               |
| Hargrave et al. 1997 | atmos, ocean | Arctic                 | 1993               | alpha                | 1               |
| Weber et al. 2006    | ocean        | Arctic                 | 1993-1997          | alpha                | 9               |
| Jantunen et al. 1998 | ocean        | Arctic                 | 1993-1994          | alpha, beta          | 3               |
| Loewen et al. 2005   | soil         | Himalaya               | 2000               | alpha                | 1               |