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# Final Report

# WP3A – Modelling Exercises

Cefic-LRI ECO52 project

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# Content

# Acronyms and Abbreviations

| | |
|---|---|
| BCF | Bioconcentration factor |
| DT50 | Dissipation time, half-life, the time required for a quantity to reduce to half of its initial value |
| FOCUS | FOrum for the Co-ordination of pesticide fate models and their Use |
| MUST | MUltimedia Stock pollution Tool |
| PBT | Persistent Bioaccumulative Toxic |
| POP | Persistent Organic Pollutant |
| STP | Sewage Treatment Plant |
| SSQ | Sum of SQuares |

| Term | Definition |
|---|---|
| Bioconcentration factor | ratio of the chemical concentration in an organism or biota to the concentration in water |
| Diffusion | Exchange of objects in region of higher concentration to a region of lower concentration |
| Disappearance | Mass leaving the system either due to degradation or due to export |
| residence time | the time during which water remains within a water body before continuing around the hydrological cycle |

# 1 Introduction and objectives

The existing persistence assessment framework is mainly based on knowledge related to the environmental fate of persistent organic pollutants obtained from test data. The models that have been designed and parameterized are useable for this suite of chemicals (i.e., neutral, non-polar organics) (Matthies et al. 2016; McLachlan 2018). However, challenges arise when attempting to assess the degradability of chemicals for which test systems are not suitable (ionizable organics, polymers, super hydrophobic organics, particles, UVCBs).

This modelling exercise will explore the use of overall persistence in persistence assessment of a range of substances including UVCBs, polymers and microplastics. The overall persistence will be reviewed as this is important since in the EU, current assessment of P and vP is based on a set of reaction half-lives in environmental media, obtained from standardized experimental test systems. However, these test results do not directly lead to an assessment of the continental/regional half-life as an indicator for the overall persistency of compounds. In the past several attempts have been made to use multimedia fate modelling for the estimation of overall persistence (e.g. Mackay and Peterson 1991, Wania and Mackay 1995, Klein 2001).

The aim is to establish a more comprehensive understanding of the potential environmental fate, including identification of physical and chemical properties most relevant for the prediction (modelling) of environmental partitioning and the compartment of concern. Based on that knowledge the overall persistence of these compounds could be much better assessed.

The modelling will focus on the calculation of the overall persistence for different kinds of test substances. As demonstrated by recent studies (e.g., McLachlan 2018) assessments based on overall persistence may result in more realistic decisions than those based on a compartment-by-compartment approach. In addition to general substances the modelling will also cover difficult substances, UVCBs and polymers.

Cousins, Ng et al. (2019) presented concentrations of model chemicals as function of time in the scenario with dynamic emissions. This exercise shows that the steady state concentration may be much higher and the time for recovery takes longer for substances with higher DegT50 values even if the logKow is similar. In this report these interesting results will be analysed further in order to find the dependencies which finally determine whether or not a substance should be assessed as persistent. This would also include the question to what extent a substance should be degraded in the region/continent before it is transported further into the global environment.

In order to address the above mentioned questions this review will

- analyse the actual clearance time of persistent substances in Europe or in the global environment dependent on their compartmental half lives
- discuss the meaningful trigger values when determining a substance as P or vP based on the overall persistence approach instead of compartmental half-lives
- address difficult substances, such as polymers, microplastic, and UVCBs (for different applications/uses)
- examine whether current persistence criteria still accomplish their protection goals for those difficult substances.

This report documents the methods and results of the modelling work (WP3A). It is the basis for a guidance document detailing how multimedia modelling and overall fate can be incorporated to improve the robustness of current persistence assessment methodologies (WP3B).

*The current persistence criterion is based on compartment specific degradation rates*

Within REACH regulation 253/2011 (Annex XIII) the criteria for the identification of persistent substances have been specified (Comission, 2011). The persistence criteria are based on the single DegT50 values for each compartment. The within REACH regulation considered criteria focus on compartment specific half-lives. Modelling enables the possibility to consider an overall persistence criterion, overall persistence, which the average mean of the single compartments. In addition to that, overall persistence is compared to alternative endpoints.

*Overall persistence as joint persistence criterion integrating several compartments*

Overall persistence is discussed as criterion for identifying persistent organic pollutants (POPs) and persistent bioaccumulative and toxic (PBT) substances in (Scheringer, Jones et al. 2009). Overall persistence is calculated as average mean of degradation rates of the single compartments as well as steady state distribution. Thus, for the calculation of overall persistence a level III model can be used. However, currently, it is not clear which compartments shall be considered in the calculation (e.g. only air, water, soil). Furthermore, overall persistence depends on the chosen emission scenario (e.g. 100% emission to air). OECD the tool, considers three different emission scenarios, and selects the maximum of the three calculated overall persistence value as worst case result.

*Sensitivity analysis is used to identify important model parameters with respect to overall persistence*

The sensitivity analysis investigates the effect of input parameters on output. For the analysis a systematic approach is chosen whereas only one parameter is systematically changed. The influence of both substance-specific and environmental/media specific parameters is investigated.

*The software MUST is analysed representatively for a regional/continental level III and level IV model*

MUST (multimedia stock pollution tool) is a user-friendly implementation calculating the stock pollution in the environment for the assessment of long term behaviour of chemicals. The basic fugacity model is based on Mackay III and Mackay IV (Mackay and Paterson 1982). Additionally emission entries can be modified using a sewage treatment plant (STP, SimpleTreat).

# 2 Material and Methods

## 2.1 Literature research

The state of the art of current EU persistence frame work considers half-lives for individual compartments rather than overall persistence. A literature review was conducted to check methodology, fields of application, output, and user friendliness as well as the validation status of the models. Furthermore, possible extensions of the model were discussed to enable the transport of microplastics in air and water. A literature research was conducted to recommend models to be used for persistence modelling.

## 2.2 Conceptual analysis of multimedia fate models

### 2.2.1 Multimedia models

*Multimedia Models describe environmental fate mechanistically*

Environment is described using a set of compartments that are homogeneous subsystems exchanging gas, water, solids, and chemical contaminants with other adjacent compartments (OECD 45). Multimedia models can be used for "benchmarking" known pollutants (OECD 46).

*Mackay models can be classified in four levels of complexity*

The first multimedia fate models were developed in 1970-1980 (e.g. Klöpffer 1978, Mackay and Paterson 1981, 1982). The existing models differ amongst others in their level of complexity and environmental scale. One distinguishes between four levels of complexity (Mackay 2001):

a) Level I: Closed System at Equilibrium
b) Level II: Open System at Equilibrium
c) Level III: Open System at Steady State and Non-equilibrium
d) Level IV: Dynamic Open System

Herein only level III or level IV models were considered.

#### *Must*

*The software MUST is analysed representatively for a regional/continental level III and level IV model*

MUST (multimedia stock pollution tool) is a user-friendly implementation calculating the stock pollution in the environment for the assessment of long term behaviour of chemicals. The basic fugacity model is based on Mackay III and Mackay IV (Mackay and Paterson 1982). Additionally emission entries can be modified using a sewage treatment plant (STP, SimpleTreat).

The software MUST was used in the analysis as representative for a level III and level IV model. Amongst the deterministic result, also the sensitivity analysis was performed using MUST.

#### *OECD 'the Tool'*

The OECD POV and LRTP Screening Tool is a three compartment (air, water, soil) level III multimedia fate model. The Tool is a Microsoft Excel file based on VBA (Visual Basic for Applications). The user has to activate the use of macros. ´The Tool´ was a result of an OECD/UNEP Workshop on The Use of Multimedia Models for Estimating Overall Environmental Persistence and Long-Range Transport in the Context of PBT/POPs Assessment that was held in Ottawa, Canada, in October 2001 (OECD 2002).

*Three different emission scenarios are considered*

In the EXCEL sheet, the same emission is assumed for all three compartments, namely constant emission of 100 mol/h. For each run, the calculation is performed three times: emission only to air, emission only to water, and emission only to water.

*Only 5 substance specific input parameter needed*

The substance specific input parameters are degradation half-lives in soil, water and air (in h), and partition coefficients between air and water and between octanol and water.

*Sensitivity analysis is included in the spreadsheet*

´The Tool´ also includes sensitivity and uncertainty analysis (Monte Carlo simulation). The analysis is restricted to the substance specific parameters. These can be changed using a lognormal distribution and dispersion factor for each parameter. The user cannot change the distribution. The environmental parameters cannot be changed. Correlation of input parameter is not considered.

In this report, OECD 'the Tool' was used as a representative for a *global* level III model.

*SimpleBox4.0-nano*

SimpleBox4.0-nano is a variant of the SimpleBox model. It is designed to simulate the specific environmental behaviour of nanomaterials.

"Main input parameters related to nanomaterial fate are the size and density of the nanomaterial, the size, density and concentration of natural particles and the transformation rates from emitted nanomaterial to the heteroagglomerate or dissolved species "(About SimpleBox 4.0-nano).

The model is a Microsoft Excel spreadsheet, supported by numerical computations in R. Four compartments are considered air, water, sediment and soil. Three environmental scenarios are considered: regional, continental and global scale are considered.

The model can be used to calculate the distribution, but it *can not* be used for the determination of persistence.

### 2.2.2 Release pattern (mode of entry)

In this report, four possible emission scenario were evaluated:

1. 100% emission to air
2. 100% emission to water
3. 100% emission to soil
4. Equal distribution to air, water and soil

For level III solution, constant emission was considered. In case of level IV, the result of 10 years constant emission followed by a 2 years recovery period was evaluated. For level IV, the emission was entered in kg. Thus, e.g. 100% air emission of 100 kg of a substance emitted per year during a time period of 10 years was followed by a clean recovery period of two years with zero emission. In the software MUST, the emission in kg is internally converted to hourly emission in mole based on the molecular weight of the substance.

Additionally, in the software MUST, the option is integrated to use a sewage treatment plant (STP) to model a more realistic emission. The STP has an influence on the emission to water and to soil. Thus, only the two emission scenarios 100% water and equal distribution were affected.

The average connection to STP was default set to 80%. Thus, 80% of the emission of water was changed. The sludge fraction is based on the substance specific parameters KOC and Henry's law constant whereas the KOC has the main influence.

$$E_{water} = \overline{E_{water}} - \overline{E_{water}} \cdot \frac{f_{STP}}{100} \cdot \frac{f_{sl}}{100},$$

$$E_{soil} = \overline{E_{soil}} + \overline{E_{water}} \cdot \frac{f_{STP}}{100} \cdot \frac{f_{sl}}{100},$$

| | |
|---|---|
| $f_{STP}$ | average connection fraction to sewage treatment plant (STP) (location specific) in % |
| $f_{sl}$ | Fraction of sludge (substance specific, calculated via SimpleTreat model) in % |
| $E_i$ | Emission in mole to compartment ($i = air, water, soil, \ldots$) |

The fraction of sludge is based on substance specific parameters KOC and Henry's law constant.

**Table 1: Fraction of sludge based on KOC and Henry's law constant for the use of sewage treatment plant (STP) in the software MUST**

| LOG KOC<br>LOG Henry | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|---|
| -4 | 0.02 | 0.21 | 2.02 | 17.12 | 66.64 | 91.65 | 94.83 | 95.15 |
| -3 | 0.02 | 0.21 | 2.02 | 17.12 | 66.64 | 91.66 | 94.83 | 95.15 |
| -2 | 0.02 | 0.21 | 2.02 | 17.11 | 66.63 | 91.66 | 94.83 | 95.15 |
| -1 | 0.03 | 0.21 | 2.02 | 17.1 | 66.6 | 91.65 | 94.83 | 95.15 |
| 0 | 0.02 | 0.2 | 2 | 16.95 | 66.32 | 91.58 | 94.82 | 95.15 |
| 1 | 0.01 | 0.19 | 1.84 | 15.75 | 63.91 | 90.94 | 94.75 | 95.14 |
| 2 | 0.02 | 0.15 | 1.43 | 12.44 | 55.55 | 88.15 | 94.41 | 95.1 |
| 3 | 0.02 | 0.12 | 1.24 | 10.89 | 50.33 | 85.63 | 94.06 | 95.07 |
| 4 | 0.01 | 0.12 | 1.21 | 10.69 | 49.52 | 84.76 | 93.96 | 95.06 |

### 2.2.3 Model parameters

The software MUST was analysed representatively for a regional/continental level III and level IV model. A detailed description of the model can be found in the MUST report (Klein & Klein 2020). The program MUST consists of three types of parameters:

1. Environmental specific parameters
2. Substance specific parameters
3. Default parameters (constants)

In the following, the parameters are specified in more detail. In the sensitivity analysis, only environmental and substance specific are considered.

*Environmental specific parameters*

In MUST, the user can choose between two environmental scenarios: EU continental water and EU regional. Main difference is the environmental area as well as residence time in air and water. Regional

scenario was considered instead of a global world because risk assessment is usually related to a certain region, not the whole world.

For a better comparison with SimpleBox the values for the environmental scenarios are set to the same values as in SimpleBox. The area of EU regional scenario is smaller than EU continental water as marine freshwater is not considered. The data was taken from Gabbert et al. 2018 (Annex 2 Table S2.4, and p.25). Due to this general principle MUST considers also the same fraction of biota in water as in EUSES (100 ppm) see the table below). Biota could have been set to zero since this compartment is generally not considered in the persistence assessment. However, as the respective fraction is very small and in order to keep the comparability to EUSES the default value wasn't changed in the sensitivity analysis. It was also not expected that biota is especially sensitive to overall persistence given the small fraction of 100 ppm in the water compartment.

**Table 2: Parameters of environmental scenarios.**

| Parameter | Unit | EU continental water | EU regional |
|---|---|---|---|
| Height of the atmosphere | km | 1 | 1 |
| Area | km² | 3560000 | 40400 |
| Water fraction | % | 3 | 4 |
| Water depth | m | 3 | 4.75 |
| Soil depth | cm | 10 | 10 |
| Sediment depth | cm | 3 | 3 |
| Fraction of suspended sediment | ppm | 15 | 15 |
| Fraction of biota | ppm | 100 | 100 |
| Soil density | kg/L | 1.7 | 1.7 |
| Soil org. carbon content | % | 2 | 2 |
| Sediment org. carbon content | % | 5 | 5 |
| Suspended sediment org. carbon content | % | 10 | 10 |
| Temperature | K | 285 | 285 |
| Residence time water (only due to transport) | d | 172 | 40 |
| Residence time air (only due to transport) | d | 9.05 | 0.7 |
| Average connection percentage to STP | % | 80 | 80 |

The residence time in air and water are used to include time of water in certain water body. The values differ within continental and regional scale. These parameter are used to calculated additional export coefficients for air, water and suspended sediment. Please note there is not sediment burial parameter and suspended sediment is not transformed to sediment during a calculation.

### *Substance specific parameters*

The substance specific parameter values were taken from the EU report "Approach for evaluation of PBTs subject to authorisation and restriction procedures in context of socio-economic analysis" (Gabbert et al. 2018 Annex 2 Table S1.1-S1.17).

Molar mass of substance is needed to convert from mole to mass (kg). Remaining substance specific parameters are LogKow, LogKaw, Henry's law constant, KOC, BCF as well as DT50 of all compartments (air, water, soil, sediment, suspended sediment, and biota). An Overview about the most important input parameters is given in the table below.

### *Default parameters*

The diffusion fluxes are constants that are independent of the chosen scenario and of the considered substance. The following diffusion fluxes are considered in the model:

- Air and water
- Air and soil
- Water and sediment
- Water and suspended Sediment
- Water and biota

Transfer coefficients simulate the interphase transfer and are used to calculate the diffusion matrix.

**Table 3: Transfer coefficients in 1/h used for the simulations of interphase transfer**

| Source compartment *i* | Target compartment *j* | $kt_{ij}$ |
|---|---|---|
| Air (i=1) | Water (j=2) | 10 |
| Water (i=2) | Air (j=1) | 0.05 |
| Air (i=1) | Soil (j=3) | 2 |
| Soil (i=3) | Air (j=1) | 0.01 |
| Water (i=2) | Sediment (j=4) | 0.001 |
| Sediment (i=4) | Water (j=2) | 0.0001 |
| Water (i=2) | Suspended Sediment (j=5) | 0.001 |
| Suspended Sediment (i=5) | Water (j=2) | 0.0001 |
| Suspended Sediment (i=5) | Water (j=2) | 0.0001 |
| Water (i=2) | Biota (j=6) | 0.01 |
| Biota (i=6) | Water (j=2) | 0.0001 |

### 2.2.4 Example substances

As case studies, five substances including important PBT were selected, namely HBCDD, D4, Bisphenol A, Dechlorane Plus and DecaBDE. The properties of the substances were taken from the EU report "Approach for evaluation of PBTs subject to authorisation and restriction procedures in context of socio-economic analysis" (Gabbert et al. 2018, Annex 2 Table S1.1-S1.17).

**Table 4: Key properties of the example substances**

| No | Substance | LogKow | LogKaw | BCF | DT50 (air) | DT50 (water) | DT50 (soil) | DT50 (sed.) |
|---|---|---|---|---|---|---|---|---|
| | | - | - | - | d | d | d | d |
| 1 | HBCDD | 5.63 | -3.6 | 18100 | 3.2 | 1.00E+06 | 120 | 214 |
| 2 | D4 | 6.49 | 2.69 | 11495 | 14 | 16.7 | 180 | 315 |
| 3 | Bisphenol A | 3.4 | -99 | 36 | 0.13 | 15 | 3 | 30 |
| 4 | Dechlorane Plus | 9 | 1.75 | 5500 | 0.7 | 1.00E+06 | 350000 | 1.00E+06 |
| 5 | DecaBDE | 6.27 | -1.75 | 2000 | 94 | 1.00E+06 | 360 | 1.00E+06 |

### 2.2.5 Endpoints of multimedia fate models

Within REACH regulation 253/2011 (Annex XIII) the criteria for the identification of persistent substances have been specified (Comission, 2011). The persistence criteria are based on the single DegT50 values for each compartment.

A substance fulfils the *persistence criterion (P)* in any of the following situations:

a) the degradation half-life in marine water is higher than 60 days;
b) the degradation half-life in fresh or estuarine water is higher than 40 days;
c) the degradation half-life in marine sediment is higher than 180 days;
d) the degradation half-life in fresh or estuarine water sediment is higher than 120 days;
e) the degradation half-life in soil is higher than 120 days.

A substance fulfils the *"very persistent" criterion (vP)* in any of the following situations:

a) the degradation half-life in marine, fresh or estuarine water is higher than 60 days;
b) the degradation half-life in marine, fresh or estuarine water sediment is higher than 180 days;
c) the degradation half-life in soil is higher than 180 days.

Thus within REACH regulation criteria for persistence focus on compartment specific half-lives. Multimedia Fate Modelling enables the possibility to consider further endpoints such as:

- Steady state distribution (%) in compartment
- Overall half-life - Regional/continental DT50
- Overall persistence
- Clearance time (a) in compartment
- Area under the curve in compartment
- Reduction (%) (maximum value divided by end value)

In the following section these parameters are explained in more detail.

#### *Steady State distribution (%)*

This parameter is a key result of level III modelling and regularly used in the PBT assessment. If substances reach steady state conditions fast the parameter gives essential information about the dominant compartment(s) where the substance will partition. However, if the time for reaching steady state concentration is very long it may not describe the actual distribution in the environment adequately. The steady state distribution is also the base for the calculation of the overall persistence (see below).

The steady state solution describes the distribution of substance to the compartment defined in the system assuming constant emission at steady state. Also known as Mackay III solution. Steady state distribution is calculated for each compartment separately. Steady state concentrations are calculated based on all processes

- emission into the system,
- transport out of the system,
- distribution between environmental compartments
- degradation in the different compartments

Together with the compartmental half-lives this distribution is the base calculation of overall half-lives or overall persistence. It is important to calculate the most realistic distribution in the system when the substance is used.

*Overall half-life (DT50)*

The overall half-life is an output of a level III calculation. It is based on all compartments defined in the model (e.g., air, water, soil, sediment, suspended sediment and biota but it can be calculated also based on a simpler scenario (e.g., without biota or suspended sediment). If an open system is defined (e.g., regional or continental scenarios) this endpoint includes advection (export). Regional and continental DT50 values give suitable information about the actual disappearance of PBT in a defined environment based on a level III calculation. The overall half-life gives an estimation for the overall concentration decline in an open environmental system when the emissions would stop. Of course, the decline may be primarily caused by transportation outside the system rather than degradation and concentrations outside the system could even accumulate.

An overall degradation rate per hour can be calculated as follows for a system with n compartments:

$$k_{regional} = \frac{\sum_{i=1}^{n} V_i \cdot f_i \cdot Z_i \cdot (k_i + k_i^*)}{\sum_{i=1}^{n} V_i \cdot f_i \cdot Z_i}.$$

| Parameter | Unit | Description |
|---|---|---|
| $f_i$ | Pa | Fugacity for each compartment $(i = 1, \cdots, 6)$ |
| $k_i$ | 1/h | Degradation constants for each compartment $(i = 1, \cdots, 6)$ |
| $k_i^*$ | 1/h | Additional transfer rates for air, water and susp. sediment $(i = 1,2,5)$ |
| $V_i$ | m³ | Volume of each compartment $(i = 1, \cdots, 6)$ |
| $Z_i$ | mol/(m³ Pa) | fugacity capacity for each compartment $(i = 1, \cdots, 6)$ |

This overall degradation rate can be translated into a half-live value in years

$$DT50_{regional} = \frac{\log(2)}{365 \cdot 24 \cdot k_{regional}}.$$

Regional/continental DT50 could be based on all six compartments, air, water, soil, sediment, suspended sediment and biota, but could be based also on simpler scenario definitions. However, it is always calculated as the weighted average of steady state solution and degradation rate including advection (export). Thus, this is one joint endpoint. As explained previously this parameter gives information about the actual decline in an open system (like Europe) after emissions have stopped. However, decline in a continental model does not necessarily mean degradation of the compound but it could be caused simply by transportation out of the system. These DT50 are therefore not suitable as persistence endpoint. It was nevertheless considered in the analysis for comparison with the overall persistence.

More information on the model procedure implemented in MUST can be found in the appendix.

*Overall persistence (Pov)*

Multimedia fate models are often used to calculate the overall persistence. Similar as the regional/continental half-lives the overall persistence is a result of a level III simulation.

It is calculated by dividing the total mass at steady-state by the sum of all degradation mass fluxes (Wegmann, Cavin et al. 2009). Simply speaking the overall persistence represents the mass weighted average mean of the individual degradation rates in various compartments. The overall persistence can be calculated only for closed system without export parameters (OECD 45). In closed system overall persistence and overall half-life are based on the same overall rate constant. However, the overall persistence is often expressed as life-time rather than half-life. In order to avoid

misinterpretation, it should be also mentioned whether the overall persistence is based on the DT50 or the life-time.

Overall persistence depends on the environmental release pattern, fate and transport and the degradation rates in specific media. As the overall persistence is based on the mass at steady-state, the overall persistence depends on the mode-of-entry (e.g., OECD 36).

The overall persistence is the perfect parameter to describe the persistence of compounds based on level III modelling. It sets individual degradation rates for sediment, soil and water into context by considering the distribution of the PBT at steady state conditions.

As mentioned above the overall persistence was originally calculated only by models which describe open systems. However, meanwhile equations were implemented also in models which describe open system e.g., RAIDAR (Arnot and Mackay 2006), MUST (Klein and Klein 2020). They are based on the definition that "*the overall persistence represents the mass weighted average mean of the individual degradation rates in the different compartments.*" Arnot and Mackay (2006) are also using the term "reaction residence time" for this overall persistence.

To clearly distinguish between the overall persistence in open and closed systems in this report the term "pseudo-overall persistence" is always used when open systems are evaluated whereas the term "overall-persistence" is used when closed systems are evaulated (see the sensitivity analysis.

### *Compartmental clearance time ($\tau$)*

The clearance time is a parameter obtained by level III modelling. It is only related to individual environmental compartments (e.g., soil) which receive direct emissions. Similar as the regional/continental half-lives it delivers information about the decline after emissions stopped. Although in this parameter transportation to other compartments or outside the system is included, the clearance time should not be confused with the environmental parameter residence time as used in SimpleBox. Clearance time is a substance specific parameter whereas residence time is not.

The clearance time was invented by Wegmann et al. as "residence time ", i.e., the ratio of the total mass at steady-state for the given mode of emission in hours divided by the emission mass flux entering the medium (Wegmann, Cavin et al. 2009). As the residence time is also an input parameter for MUST and SimpleBox which defines advection out of the air or water compartment it is called here "clearance time". This endpoint also depends on the mode-of-entry and the level III solution. It is only available for compartments having an emission greater than zero.

### *Area under the curve (AUC kg a)*

The area under the curve is a level IV parameter and describes the distribution of a substance under non-steady state conditions. It describes in principle a similar situation as the steady state concentrations but it gives also information about the variation of distribution with time. It was included in the sensitivity analysis to evaluate under which conditions the steady state concentrations significantly deviate from the area under the curve and the calculated steady state concentrations is questionable

Using the Mackay IV result, the change of mass in time for each compartment, the area under the curve (kg a) can be calculated. In MUST; the trapezoid rule is used for its calculation summing up the mass in the environment for each time point.

$$AUC_i = \sum_{l=1}^{n-1} 0.5 \cdot (t_{l+1} - t_l) \cdot (V_l \cdot f_l \cdot Z_l + V_{l+1} \cdot f_{l+1} \cdot Z_{l+1})$$

| Parameter | Unit | Description |
|---|---|---|
| $AUC_i$ | kg a | Area under the curve for compartment $(i = 1, \cdots, 6)$ |
| $f_i$ | Pa | Fugacity for each compartment $(i = 1, \cdots, 6)$ |
| $t$ | | time |
| $V_i$ | m³ | Volume of each compartment $(i = 1, \cdots, 6)$ |
| $Z_i$ | mol/(m³ Pa) | fugacity capacity for each compartment $(i = 1, \cdots, 6)$ |

This endpoint implies the accumulation potential of the substance. The endpoint is calculated for each compartment separately. As level IV simulation do not simply give distribution (in %) but also total masses the stock pollution in the different compartments can be calculated but also the aggregated value (total mass in the system) dependent on the total emission period but also dependent on the after the emission had stopped. More information on the model procedure implemented in MUST can be found in the appendix.

*Reduction potential (in %) for a given time period*

This is also a level IV parameter which is comparable to the "clearance time in a compartment" (level III output). However, here the actual reduction to a certain percentage after a fix time period without emission is calculated. This parameter was included in the sensitivity analysis to analyse how much the decline is affected when the emission scenario is dynamic.

The emission scenario is based on an emission period of 10 years and a 2 years recovery period. This time line should be seen as a pragmatic approach in line with common decision making in these type of regulations. Mathematically, dependent on the compound properties, it sometimes needs more than 1000 years or more to reach steady state conditions in a level IV model. The parameter describes the reduction at the end of the total period. Therefore, the value at the end of the period is divided by the maximum value obtained in the period. The endpoint is based on the level IV solution. This describes the clearance of the substance out of the system. The endpoint is calculated for each compartment separately. As mentioned previously similar as the level III parameter "clearance times" this parameter is also not suitable as a persistence criteria. However, as this parameter gives a prediction how long it may take until the pollution reaches a certain level when emissions are stopped it could be used as a supporting parameter in the decision making.

## 2.3 Sensitivity analysis

Sensitivity analysis was used to identify the most important parameters influencing the model output like overall persistence. According to OECD 36, it is sufficient to restrict the sensitivity analysis on the "key variables that would exert the greatest influence on the output." Herein, a more generic analysis was performed and all parameters, both, substance specific as well as environmental parameters, were inspected.

A sensitivity analysis describes the relative effect of different parameters values on the output. The analysis was performed to improve the understanding how important a certain parameter is in influencing the model output. In OECD 36, it is suggested to analyse the influence of both substance-specific and environmental/media specific parameters.

In general, there are two possibilities to change all parameters at a time (AAT) or only one parameter at time (OAT). Either the parameter value is changed in a systematic way in a range (e.g. ±5%) or randomly changed under a certain distribution (e.g. log normal distribution).

OECD 45 suggest to change only one parameter at time systematically. A sensitivity analysis depends on the considered substance as well as the chosen scenario (e.g. emission, temperature). However, the analysis can give additional insight in the model's performance.

A local sensitivity analysis around the environmental and substance specific parameter values was conducted, i.e., one parameter was systematically varied and the others were kept fixed (see EFSA PPR Panel 2014). Thus, in total not one analysis was conducted, but several, for each parameter one analysis. The parameters were changed in a range of 0.1 times the default parameter and 10 times the default parameter. In total, 500 scenarios for each parameter were conducted.

In this report, a local sensitivity analysis around the environmental and substance specific parameter values was conducted, i.e., one parameter was systematically varied and the others were kept fixed (see EFSA PPR Panel 2014).

As a result of the sensitivity analysis, the parameter values and the model output were normalized. This enables to show the results in one plot comparing the sensitivity behaviour of the different parameters.

*Visual result of sensitivity analysis is a plot showing the relative change in scaled parameter value to scaled endpoint*

The relative change of the endpoint was plotted over the relative change of the parameter. Due to this standardisation to relative changes, the point (1, 1) in the resulting graph corresponds to the default setting. Normalization was obtained by dividing the endpoint by the default value.

*Sensitivity coefficients were calculated based in a relative change of ±10%*

In addition, sensitivity coefficients were calculated as suggested by EFSA PPR Panel (2014). Therefore, the relative change of the endpoint if a parameter is changed by 10 % was divided by the 10 %. As the parameter can be changed in both directions, the mean of the two resulting coefficients was used. A sensitivity above one indicates that the model output reacts to a greater degree than the parameter has been changed, and vice versa. A negative sensitivity coefficient indicates the output reaction inverse to the parameter change. For example, a sensitivity coefficient of -0.5 indicates that an increase (decrease) of the analysed parameter by 10 % resulted in a decrease (increase) of the endpoint by 5 %. A parameter was considered to be insensitive if its sensitivity coefficient is close to 0.1 respectively -0.1.

Sensitivity analysis was used to identify the most important parameters influencing the model output like overall persistence. According to OECD 36, it is sufficient to restrict the sensitivity analysis on the "key variables that would exert the greatest influence on the output." Herein, a more generic analysis was performed and all parameters, both, substance specific as well as environmental parameters, were inspected.

A sensitivity analysis describes the relative effect of different parameters values on the output. The analysis was performed to improve the understanding how important a certain parameter is in influencing the model output. In OECD 36, it is suggested to analyse the influence of both substance-specific and environmental/media specific parameters.

In general, there are two possibilities to change all parameters at a time (AAT) or only one parameter at time (OAT). Either the parameter value is changed in a systematic way in a range (e.g. ±5%) or randomly changed under a certain distribution (e.g. log normal distribution).

OECD 45 suggest to change only one parameter at time systematically. A sensitivity analysis depends on the considered substance as well as the chosen scenario (e.g. emission, temperature). However, the analysis can give additional insight in the model's performance.

In this report, a local sensitivity analysis around the environmental and substance specific parameter values was conducted, i.e., one parameter was systematically varied and the others were kept fixed (see EFSA PPR Panel 2014).

A second analysis was performed which was restricted to the substance specific parameters: KOC, Kaw, DT50 in air, water and soil. The parameter KOC influences the fugacity capacity of the compartments soil, sediment and suspended sediment. The parameter Kaw is used to calculate the Henry's law constant which in fact influences the fugacity capacity of all compartments.

The parameters KOC, Kaw as well as half-life (DT50) in soil, air and water influence the steady state distribution. Persistence as endpoint is calculated based on the weighted average of the half-lives in the compartments as well as the steady state solution of the compartments.

| Parameter | Property | Variant 1 | Variant 2 | Variant 3 | Variant 4 |
|---|---|---|---|---|---|
| KOC | Variable | 100 | 1000 | 10000 | 100000 |
| LogKaw | Variable | -8 | -6 | -4 | -2 |
| DT50soil | Variable | 100 | 200 | 400 | 800 |
| DT50air | Variable | 10 | 20 | 40 | 80 |
| DT50water | Variable | 100 | 200 | 400 | 800 |
| DT50sediment | correlates with water | 200 | 400 | 800 | 1600 |

Only the equal distribution scenario was considered.

Due to the dependency of DT50 water and DT50 sediment not all possible combinations were considered. In total, 4^5 = 1040 different combinations were generated for the statistical analysis.

ANOVA (analysis of variance) was used to test whether there is a significant difference in means of the groups at each level of the independent variable. The null hypothesis (H0) of the ANOVA is that there is no difference in means. If the p-value smaller than the typical alpha value of 0.05, the null hypothesis is false. Thus, the mean of groups is not equal. Thus, the alternative hypothesis is true. Thus, there is a difference in means of the considered groups. However, ANOVA is only indicating that there is a difference among the different groups. However, it is not possible to distinguishes between which group there is a significant difference.

Performing a Post-Hoc-Test as Tukey HSD helps to understand which single groups are different. In a Post-Hoc-Test every group is compared to each other. In the result table the difference in means of both considered groups is displayed as well as a corresponding adjusted p-value. In case of a p-value smaller than 0.05, the difference between the two considered groups is significant. The significant groupwise differences are anywhere the 95% confidence interval doesn't include zero. This is another way of saying that the p-value for these pairwise differences is < 0.05.

For the analysis the R build-in functions aov() and TukeyHSD() were used.

## 2.4 Difficult substances, UVCBV and nanoparticles

Two types of difficult substances are considered in this analysis, UVCBs and nano particles.

UBCBs are considered *difficult* as the different components in this mixture behaviour differently in fate models like MUST. The consequence is that once released into the environment they may split and accumulate in various compartments because of different sorption constants. As the components could also degrade differently, the composition will change with time even though the sorption constants may be quite similar. This situation is the reason why UVCBs are called *difficult substances*.

A traditional political solution was to test (and also to simulate) all constituents separately. However, this is somewhat an extreme view especially when the substance behaves similarly with regard to portioning and degradation. The idea of this analysis is therefore to explore some boundaries under which physical chemical properties are sufficiently similar that they would expect to partition similarly and therefore could be tested together (as either whole substances, fractions or composed mixtures).

In order to achieve that goal a composition with five hypothetical substances was defined. In the table below the key parameters are summarised. As environmental scenario, EU regional was considered. Furthermore, as emission scenario equal distribution scenario was chosen. Sewage treatment plant was used. Ranges of 2000 L/kg to 25 000 L/kg and 25 d to 3000 d were considered for the sorption constant KOC and the DT50 in soil, respectively.

**Table 5: Key properties of hypothetical difficult substance**

| Zustande | LogKow | LogKaw | KOC | BCF | DT50 (air) | DT50 (water) | DT50 (soil) | DT50 (sed.) |
|---|---|---|---|---|---|---|---|---|
| | - | - | L/kg | - | d | d | d | d |
| Substance A | 6.1 | -4.7 | 3600 | 50000 | 0.3 | 71 | 710 | 2300 |
| Substance B | 4.5 | -7.8 | 17200 | 1100 | 1.2 | 50 | 25 | 250 |
| Substance C | 5.0 | -2.7 | 22350 | 140 | 1.4 | 15 | 3000 | 300 |
| Substance D | 4.0 | -6.9 | 2085 | 2400 | 2.4 | 4 | 25 | 10 |
| Substance E | 3.5 | -1.2 | 1800 | 2000 | 1.5 | 15 | 3000 | 300 |

# 3 Results and discussion

Several aspects of multimedia models are evaluated in this section.

- First result of the preliminary literature research is presented.
- Result of a typical model (MUST) are analysed based on for four PBT substances HBCDD, D4, Bisphenol A, Dechlorane Plus and Decade. Level III as well as level IV solution are included. The standard scenarios of MUST include export parameters (open systems). Consequently, instead of the overall persistence the dependency of the pseudo-overall persistence has to be evaluated instead of the overall persistence. The evaluation includes several aspects, namely, a comparison of the pseudo-overall persistence with regional half-lives, the influence of using a sewage treatment plant, the difference of regional and continental scenario, as well as the effect of export.
- The same substances are also analysed using the *global* model OECD ´the Tool´ aiming at the overall persistence. The Tool is a closed system without export parameters.

- The result of the sensitivity analysis is presented to identify key parameters parameter of multimedia models. This analysis is also included difficult substances, polymer microplastics, nano plastics as well as UVCB.
- Finally, the effect of parameters KOC, Kaw, DT50 in air, water and soil on steady state as well as overall persistence are analysed in more detail.

## 3.1 Literature research

In the literature database PubMed several search terms were entered. Entering only the term "modelling OR modelling OR model" yields more than 2 million counts. Adding the search term "degradation OR persistence" reduced the number of references to 12 thousand hits. The count number was further reduced with the search term "transport AND environment" to 5585. Finally, adding "polymers OR UvCB OR microplastics OR POP" reduced it to 349 (Figure 1).

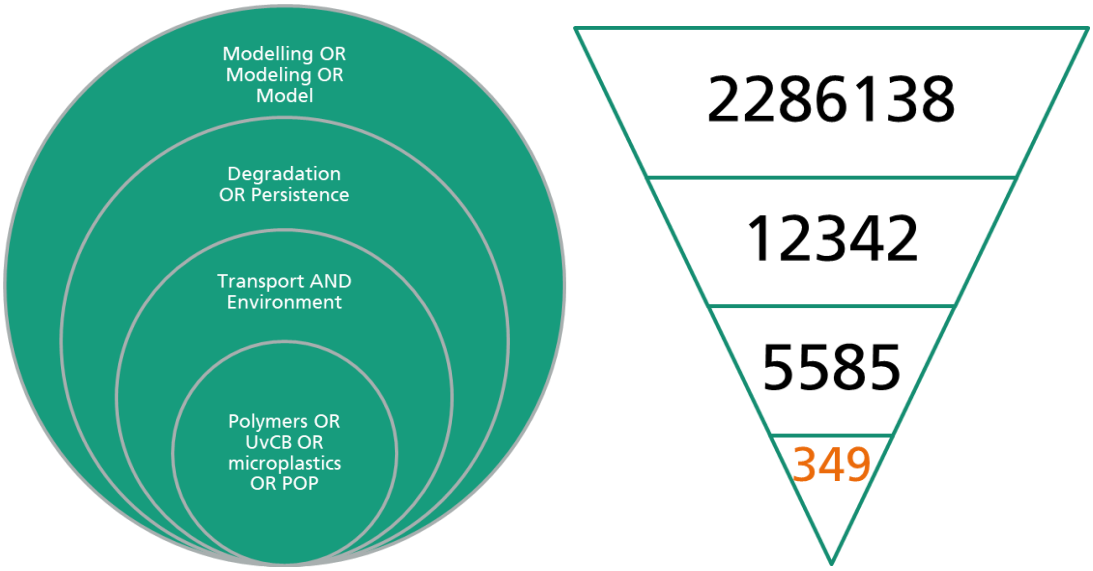



**Figure 1: Search terms entered in PubMed (left) as well as resulting counts (right)**

These references were further reduced by adding "NOT blood", "NOT cell", "NOT corona", "NOT virus", "NOT membrane", "NOT bone ", "NOT genomic", "NOT protein" to 194 counts. These 194 counts were analysed in more detail. Finally, 94 not relevant references, 47 possibly relevant and 53 relevant references were identified (Figure 1).

Filtering the found references, almost 60 models were identified whereas 7 models were applied with regard to research question and only one in regulation. The main part of the model was based on regional (17) or global scale (16). Less continental (6) and local (5) model exists (Figure 2). For the remaining models the scale was unspecified. At least a regional scale is needed to calculate overall persistence.

The models found in literature differed in complexity. The complexity level III is sufficient to calculate overall persistence. The relation of Mackay III (18) to Mackay IV (18) models was even (Figure 2). For very persistent chemicals steady-state distribution may be unrealistic because it takes a long time until steady state is reached. One advantages of a Level IV model is that it enables the use of variable emission data. Thus, it is possible to test different policy scenarios as e.g. 10 years emission followed by a clean period of 2 years.

The substance to be modelled influences the selection of the model as the choice of model is substance specific. In general, the models were suitable for organic substance and were designed for single substance not for mixtures (Figure 2).

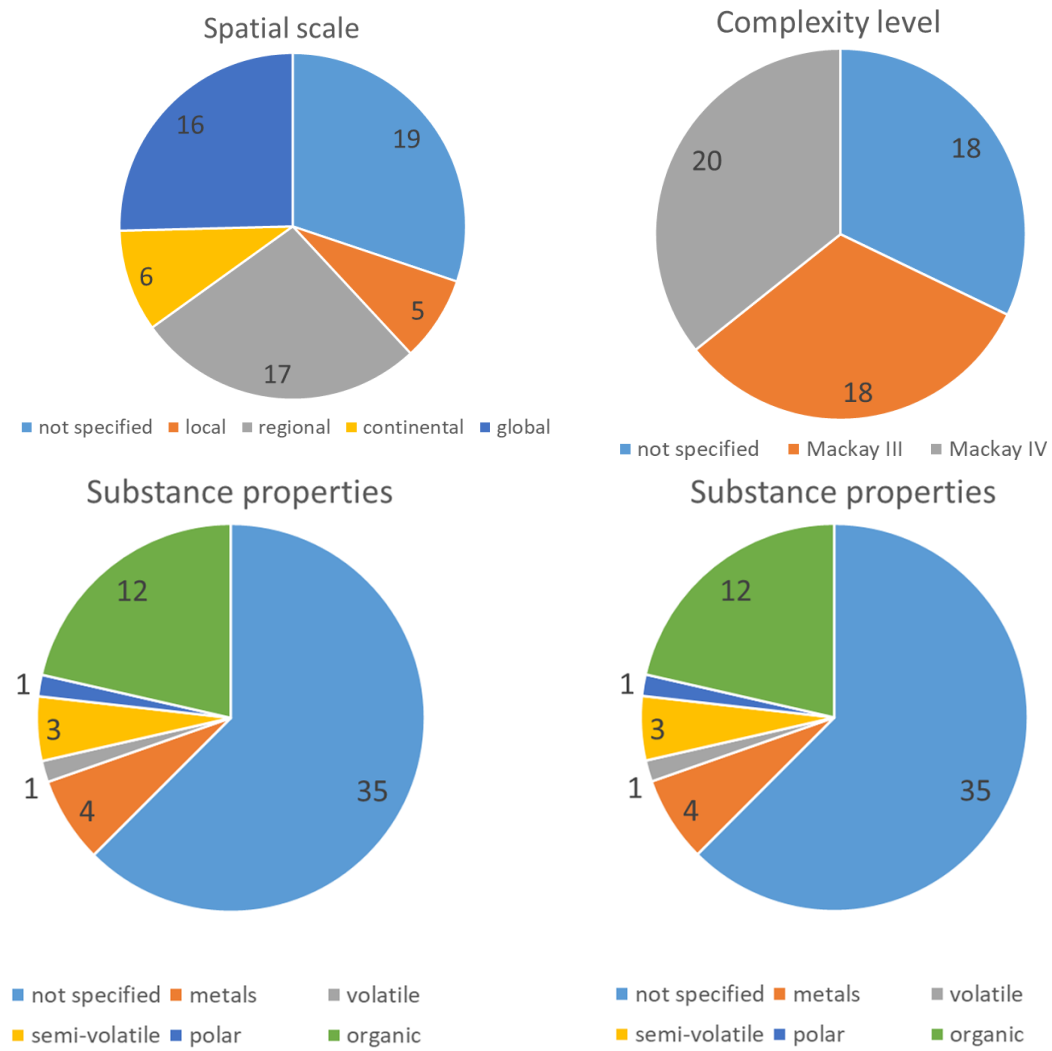



**Figure 2: Overview of results of literature review**

## 3.2 Conceptual analysis

In the following, the deterministic result using the default values for the substances for the four chosen emission scenarios is shown. Therefore, the level III and level IV solutions of the software MUST were considered. Furthermore, the endpoint regional DT50 and overall persistence within all emission scenarios and substances were compared.

The result of the level III solution is based on constant emission. For level IV, the emission was entered in kg. Thus, e.g., 100% air emission is 100 kg of substance was emitted per year during a time period of 10 years followed by a clean recovery period of two years with zero emission. In the software, the emission in kg is internally converted to hourly emission in mole based on the molecular weight of the substance.

### 3.2.1 Relative size of compartments

Usually, it is assumed that model results significantly depend on the multimedia model they are based on. However, results differ between models because of the definition and the dimension of their scenarios rather than because of the models themselves. Table 6 shows how extremely different model scenarios are defined in common multi-media models. For this reason, it is not surprising that the calculated overall persistence usually depends on the chosen model.

**Table 6: Comparison of different models and their compartmental dimensions**

| | MUST<br>Regional | Episuite<br>EQC | EUSES<br>Continental | OECD<br>The Tool |
|---|---|---|---|---|
| ratio water/soil | 2 | 11 | 2063 | 2448 |
| ratio water/sediment | 158 | 400 | 6475 | - |
| ratio air/water | 5263 | 500 | 10 | 85 |

Especially MUST and 'OECD the tool' are based on different scenarios (see e.g., ratio water/soil in Table 6). Background of these differences are their scale: MUST is a regional model with only low water content whereas the Tool is designed as global model with a much bigger water compartment. Furthermore, in the tool only three compartments (air, water, soil) are defined without a sediment phase and also without a sewage treatment plant. Finally, in ´the Tool´ only three emission scenarios can be considered (100% emission to air, 100% emission to water or 100% emission to soil) whereas MUST allows defining individual release pattern (e.g., equal distribution). Due to their extreme different design MUST and The Tool were considered for the comparison. The results are presented in Table 7. For comparison reasons, the percentages of biota, sediment and suspended sediment are added to the percentage of water. For MUST, the continental scenario, closed system (no export), without STP is considered.

Considering the 100% emission to water scenario, OECD ´the Tool` predicts main distribution to water for all substances. For the 100% soil scenario, the main distribution is to soil for all substances except D4, which tends to distribute mainly to air (78%). When assuming 100% of the release to air, for the three substances D4, Dechlorane Plus and DecaDBE, OECD ´the Tool` concludes a mainly distribution in air. However, for HBCDD and Bisphenol A, the most distribution is found in water.

For 100% emission to air and 100% emission to water, the program MUST predicts a higher distribution in soil. For the remaining emission scenario, 100% emission to soil, for all chosen substances, similar results for both tools are obtained. Especially, the compartment with the highest distribution is similar.

Considering the dominant compartments, the compartment with the highest distribution, OECD ´the Tool´ identifies the water compartment (seven times) whereas MUST identifies soil (eight times). With regard to the air compartment, both tools identify air four times as dominant compartment. This observation is based on the five chosen substances covering a broad range of properties.

**Table 7: Steady state distribution using the global model OECD ´the Tool´ in comparison to regional scenario of MUST**

| Substance | Emission | Model | Air (%) | Water (%)* | Soil (%) |
|---|---|---|---|---|---|
| HBCDD | 100% air | ´the Tool´ | 2 | 97 | 1 |
| | | MUST | 10 | 12 | 78 |
| | 100% soil | ´the Tool´ | 0 | 1 | 99 |
| | | MUST | 0 | 0 | 100 |
| | 100% water | ´the Tool´ | 0 | 99 | 0 |
| | | MUST | 0 | 26 | 73 |
| D4 | 100% air | ´the Tool´ | 100 | 0 | 0 |
| | | MUST | 99 | 0 | 1 |
| | 100% soil | ´the Tool´ | 78 | 0 | 22 |
| | | MUST | 96 | 0 | 4 |
| | 100% water | ´the Tool´ | 11 | 89 | 0 |
| | | MUST | 78 | 20 | 2 |
| Bisphenol A | 100% air | ´the Tool´ | 0 | 92 | 8 |
| | | MUST | 73 | 12 | 15 |
| | 100% soil | ´the Tool´ | 0 | 1 | 99 |
| | | MUST | 0 | 0 | 100 |
| | 100% water | ´the Tool´ | 0 | 100 | 0 |
| | | MUST | 0 | 97 | 3 |
| Dechlorane Plus | 100% air | ´the Tool´ | 60 | 0 | 40 |
| | | MUST | 14 | 0 | 86 |
| | 100% soil | ´the Tool´ | 0 | 0 | 100 |
| | | MUST | 1 | 0 | 99 |
| | 100% water | ´the Tool´ | 0 | 100 | 0 |
| | | MUST | 0 | 98 | 2 |
| DecaDBE | 100% air | ´the Tool´ | 52 | 34 | 14 |
| | | MUST | 3 | 20 | 76 |
| | 100% soil | ´the Tool´ | 2 | 1 | 97 |
| | | MUST | 0 | 2 | 98 |
| | 100% water | ´the Tool´ | 30 | 61 | 8 |
| | | MUST | 0 | 66 | 34 |

* including percentages for biota, sediment and suspended sediment

### 3.2.2 The scenario

In MUST, the user can choose between two environmental scenarios: EU continental water and EU regional. Main difference is the environmental area as well as residence time in air and water. Regional scenario is considered instead of a global world because risk assessment is usually related to a certain region, not the whole world. In this comparison, STP is not considered.

The environmental scenario influences the result of steady state distribution and thus also regional/continental DT50 and pseudo-overall persistence (Table 8). However, in most cases, the difference in level III solution comparing regional and continental environment remains neglectable.

**Table 8: Comparison of steady state distribution, regional/continental DT50 and pseudo-overall persistence (P) of regional/continental scenario (without STP)**

| | Emission | Environment | Air (%) | Water (%) | Soil (%) | Sediment (%) | Suspended Sediment (%) | Biota (%) | DT50 (d) | P* (d) |
|---|---|---|---|---|---|---|---|---|---|---|
| HBCDD | 100% air | regional | 10 | 2 | 82 | 3 | 1 | 3 | 4 | 26 |
| | | continental | 10 | 2 | 80 | 4 | 1 | 3 | 18 | 26 |
| | 100% soil | regional | 0 | 0 | 100 | 0 | 0 | 0 | 120 | 120 |
| | | continental | 0 | 0 | 100 | 0 | 0 | 0 | 120 | 120 |
| | 100% water | regional | 0 | 21 | 1 | 33 | 6 | 38 | 62 | 449 |
| | | continental | 1 | 16 | 8 | 39 | 6 | 29 | 110 | 175 |
| D4 | 100% air | regional | 99 | 0 | 1 | 0 | 0 | 0 | 0.5 | 14 |
| | | continental | 99 | 0 | 1 | 0 | 0 | 0 | 4 | 15 |
| | 100% soil | regional | 53 | 0 | 47 | 0 | 0 | 0 | 1 | 25 |
| | | continental | 91 | 0 | 9 | 0 | 0 | 0 | 4 | 15 |
| | 100% water | regional | 3 | 19 | 0 | 43 | 13 | 22 | 11 | 66 |
| | | continental | 25 | 10 | 0 | 36 | 17 | 11 | 15 | 40 |
| Bisphenol A | 100% air | regional | 74 | 10 | 15 | 1 | 0 | 0 | 0.1 | 0.2 |
| | | continental | 74 | 9 | 15 | 2 | 0 | 0 | 0.2 | 0.2 |
| | 100% soil | regional | 0 | 0 | 100 | 0 | 0 | 0 | 4 | 4 |
| | | continental | 0 | 0 | 100 | 0 | 0 | 0 | 4 | 4 |
| | 100% water | regional | 0 | 88 | 0 | 12 | 0 | 0 | 11 | 15 |
| | | continental | 0 | 82 | 0 | 17 | 0 | 0 | 15 | 18 |
| Dechlorane Plus | 100% air | regional | 14 | 0 | 85 | 0 | 0 | 0 | 4 | 4 |
| | | continental | 14 | 0 | 86 | 0 | 0 | 0 | 4 | 4 |
| | 100% soil | regional | 0 | 0 | 100 | 0 | 0 | 0 | 91 | 223 |
| | | continental | 1 | 0 | 99 | 0 | 0 | 0 | 95 | 106 |
| | 100% water | regional | 0 | 0 | 0 | 100 | 0 | 0 | 14662 | 41263 |
| | | continental | 0 | 0 | 0 | 100 | 0 | 0 | 16239 | 19214 |
| DecaDBE | 100% air | regional | 3 | 0 | 75 | 22 | 0 | 0 | 15 | 409 |
| | | continental | 3 | 0 | 77 | 19 | 0 | 0 | 124 | 398 |
| | 100% soil | regional | 0 | 0 | 100 | 0 | 0 | 0 | 332 | 361 |
| | | continental | 0 | 0 | 99 | 1 | 0 | 0 | 343 | 361 |
| | 100% water | regional | 0 | 0 | 0 | 99 | 0 | 0 | 2201 | 73748 |
| | | continental | 0 | 0 | 3 | 96 | 0 | 0 | 2643 | 8859 |

* Pseudo-overall persistence

### 3.2.3 Relevant/realistic release pattern

Typically, the default situation is assumption of an environmental release pattern with equal release to air, surface water and soil (ECHA, 2017). If a more relevant respectively a more realistic release pattern than equal emission rate to air, water and soil can be assumed based on knowledge about use of the substance, the model should be run with an appropriately changed release pattern (ECHA, 2017).It is relevant, but depending on the use profile of the substance, to run such models assuming the default environmental risk assessment emission pattern, e.g., release to water only. Another option is to consider comparing the results of the modelling with the normally employed environmental exposure assessment where emission normally takes place via emission to STP (ECHA 2017).

MUST uses a sewage treatment plant (STP) to model a more realistic emission scenario when the substance is released into water. The release into water is then automatically corrected and a fraction of the release into water is moved to soil. Thus, only the two emission scenarios, 100% water and equal distribution, are affected. In this subsection, the effect of this STP on the overall persistence is evaluated. Please notice, MUST does not consider any additional degradation in the sewage treatment plant or any releases into air.

*The resulting emission scenario differed within the substances*

The effect was analysed based on the default substances. If the release is originally completely to water the actual release in MUST will be corrected resulting only about 25% to water, but about 75% to soil and for all substances except bisphenol. The difference is caused by the relatively low sorption constant of bisphenol A had compared to other substances. The same outcome was found for the equal distribution scenario. Here approximately 8% was emitted to water, whereas 58% was emitted to soil. Again for bisphenol A the situation was different: 29 % to water, 37% to soil (Table 9).

**Table 9: Emission scenario after the use of sewage treatment plant (STP)**

| Scenario | Substance | Air (%) | Water (%) | Soil (%) |
|---|---|---|---|---|
| 100% water | HBCDD | 0 | 26 | 74 |
| | D4 | 0 | 25 | 75 |
| | Bisphenol A | 0 | 88 | 12 |
| | Dechlorane Plus | 0 | 24 | 76 |
| | DecaDBE | 0 | 24 | 76 |
| Equal distribution | HBCDD | 33 | 9 | 58 |
| | D4 | 33 | 8 | 58 |
| | Bisphenol A | 33 | 29 | 38 |
| | Dechlorane Plus | 33 | 8 | 59 |
| | DecaDBE | 33 | 8 | 59 |

The emission influences the steady state distribution and thus different level III scenarios were obtained comparing the solution with and without STP. The steady state distribution of both variants, with and without STP, are presented in Table 10. The environmental scenario EU regional including export was used for the comparison.

**Table 10: Comparison of steady state distribution with STP and without STP**

| | Scenario | STP | Air (%) | Water (%) | Soil (%) | Sediment (%) | Suspended Sediment (%) | Biota (%) |
|---|---|---|---|---|---|---|---|---|
| HBCDD | 100% water | Yes | 0 | 3 | 85 | 5 | 1 | 6 |
| | | No | 0 | 21 | 1 | 33 | 6 | 38 |
| | Equal distribution | Yes | 0 | 2 | 93 | 2 | 0 | 3 |
| | | No | 0 | 7 | 66 | 11 | 2 | 13 |
| D4 | 100% water | Yes | 13 | 15 | 9 | 35 | 10 | 17 |
| | | No | 3 | 19 | 0 | 43 | 13 | 22 |
| | Equal distribution | Yes | 29 | 11 | 16 | 25 | 7 | 12 |
| | | No | 11 | 17 | 3 | 38 | 11 | 19 |
| Bisphenol A | 100% water | Yes | 0 | 85 | 4 | 11 | 0 | 0 |
| | | No | 0 | 88 | 0 | 12 | 0 | 0 |
| | Equal distribution | Yes | 33 | 29 | 38 | 0 | 0 | 0 |
| | | No | 1 | 68 | 22 | 9 | 0 | 0 |
| Dechlorane Plus | 100% water | Yes | 0 | 0 | 2 | 98 | 0 | 0 |
| | | No | 0 | 0 | 0 | 100 | 0 | 0 |
| | Equal distribution | Yes | 0 | 0 | 4 | 96 | 0 | 0 |
| | | No | 0 | 0 | 1 | 99 | 0 | 0 |
| DecaDBE | 100% water | Yes | 0 | 0 | 32 | 68 | 0 | 0 |
| | | No | 0 | 0 | 0 | 99 | 0 | 0 |
| | Equal distribution | Yes | 0 | 0 | 53 | 47 | 0 | 0 |
| | | No | 0 | 0 | 14 | 86 | 0 | 0 |

As the resulting emission using a STP is substance specific, also the resulting steady state distribution with and without STP are substance specific and thus, no clear trend considering all substances was observable. However, using the sewage treatment plant leads to higher distribution in soil and lower distribution in sediment. This yields for both relevant emission scenarios, 100% water and equal distribution. The extent of this effect depends on the substance dependent sorption coefficient.

In Table 11, the resulting regional DT50 and pseudo-overall persistence values in days is given. Again, the endpoint persistence was generally more conservative as the regional DT50 as the export processes (advection) is not considered. For HBCDD; in both emission scenarios, the no STP scenario yielded a lower persistence value than using a STP. For the other substances, a higher overall persistence using no STP was obtained. Especially for Dechlorane Plus and DecaDBE, the persistence value for the 100% emission to water scenario was very high (Table 11).

**Table 11: Comparison of regional DT50 and overall persistence using STP and without STP**

| Substance | Scenario | STP | Regional DT50 (d) | Pseudo-overall persistence (d) |
|---|---|---|---|---|
| HBCDD | 100% water | yes | 106 | 135 |
| | | no | 62 | 449 |
| | Equal distribution | yes | 77 | 117 |
| | | no | 62 | 142 |
| D4 | 100% water | yes | 4 | 51 |
| | | no | 11 | 66 |
| | Equal distribution | yes | 2 | 34 |
| | | no | 4 | 51 |
| Bisphenol A | 100% water | yes | 11 | 15 |
| | | no | 11 | 15 |
| | Equal distribution | yes | 4 | 4 |
| | | no | 4 | 7 |
| Dechlorane Plus | 100% water | yes | 3581 | 9030 |
| | | no | 14662 | 41263 |
| | Equal distribution | yes | 1226 | 3022 |
| | | no | 4917 | 12567 |
| DecaDBE | 100% water | yes | 788 | 1113 |
| | | no | 2201 | 73748 |
| | Equal distribution | yes | 376 | 683 |
| | | no | 849 | 2581 |

### 3.2.4 Advection out of the system (export)

Overall persistence which is most relevant in the context of persistence assessment is estimated based on degradation processes only without any advection and other losses out of the system. It is calculated using a multimedia model and does usually not include any transportation (losses) outside the system borders. However, as mentioned above in open system the pseudo-overall persistence as defined in section 2.3.5 is a comparable endpoint

In closed systems overall half-life and overall persistence do not differ. In open systems there is a difference between both parameters since the overall persistence is based only degradation rates whereas for the regional DT50 export is added to the degradation rate.

All comparisons are done with MUST using the regional scenario and assuming steady state conditions (level III). An overview about the regional DT50 in comparison to the pseudo-overall persistence is shown in Table 12 for all evaluated substances and emission scenarios using STP (1$^{st}$ comparison). All endpoints are given in days.

**Table 12: Regional DT50 and overall persistence of all emission scenarios and substances (export and STP)**

| Substance | Emission | Regional DT50 (d) | Pseudo-overall persistence (d) |
|---|---|---|---|
| HBCDD | 100% air | 4 | 26 |
| | 100% soil | 120 | 120 |
| | 100% water | 106 | 135 |
| | Equal distribution | 77 | 117 |
| D4 | 100% air | 0.5 | 14 |
| | 100% soil | 1 | 25 |
| | 100% water | 4 | 51 |
| | Equal distribution | 2 | 34 |
| Bisphenol A | 100% air | 0.1 | 0.2 |
| | 100% soil | 4 | 4 |
| | 100% water | 11 | 15 |
| | Equal distribution | 4 | 4 |
| Dechlorane Plus | 100% air | 4 | 4 |
| | 100% soil | 91 | 223 |
| | 100% water | 3581 | 9030 |
| | Equal distribution | 1226 | 3022 |
| DecaDBE | 100% air | 15 | 409 |
| | 100% soil | 333 | 360 |
| | 100% water | 788 | 1113 |
| | Equal distribution | 376 | 683 |

The regional DT50 and pseudo-overall persistence differ within the various substances and the different emission scenarios. The highest pseudo-overall persistence value was obtained for Dechlorane Plus when released into water. Generally, the persistence value was higher than the regional DT50 value. This was expected as only degradation rates were included and thus, pseudo-overall persistence is a more conservative endpoint.

Both, the pseudo-overall persistence and the persistence are defined as the mass weighted average degradation rate in the system. In closed systems the overall half-life and the overall persistence (expressed as a half-life) are identical. In open system they differ because of the export parameters included in the scenario. This is shown in the following table.

So far the pseudo-overall persistence was compared with overall half-lives in open system. In the following table advection out of the system was set to zero to analyse whether overall persistence (closed system) and pseudo-overall persistence (open system) are comparable. Four emission scenarios, 100% emission into air, 100% emission into soil, 100% emission into water as well as the equal distribution scenario were taken into consideration. The sewage treatment plant was switched off for this comparison. Furthermore, the exercise was based on the regional scenario of MUST.

The result of the comparison is presented in Table 13.

**Table 13: Comparison of steady state distribution, overall DT50, overall and pseudo-overall persistence (P) without STP**

| | Release | type | Air (%) | Water (%) | Soil (%) | Sed. (%) | Susp.Sed. (%) | Biota (%) | Overall DT50 (d) | P or P* (d) |
|---|---|---|---|---|---|---|---|---|---|---|
| HBCDD | 100% air | open | 10 | 2 | 82 | 3 | 1 | 3 | 4 | 26 |
| | | closed | 10 | 2 | 78 | 5 | 1 | 4 | 26 | 26 |
| | 100% soil | open | 0 | 0 | 100 | 0 | 0 | 0 | 120 | 120 |
| | | closed | 0 | 0 | 100 | 0 | 0 | 0 | 120 | 120 |
| | 100% water | open | 0 | 21 | 1 | 33 | 6 | 38 | 62 | 449 |
| | | closed | 0 | 5 | 73 | 11 | 2 | 8 | 128 | 128 |
| D4 | 100% air | open | 99 | 0 | 1 | 0 | 0 | 0 | 0.5 | 14 |
| | | closed | 99 | 0 | 1 | 0 | 0 | 0 | 15 | 15 |
| | 100% soil | open | 53 | 0 | 47 | 0 | 0 | 0 | 1 | 25 |
| | | closed | 96 | 0 | 4 | 0 | 0 | 0 | 15 | 15 |
| | 100% water | open | 3 | 19 | 0 | 43 | 13 | 22 | 11 | 66 |
| | | closed | 78 | 2 | 2 | 8 | 7 | 3 | 18 | 18 |
| Bisphenol A | 100% air | open | 74 | 10 | 15 | 1 | 0 | 0 | 4 | 4 |
| | | closed | 73 | 10 | 15 | 2 | 0 | 0 | 0 | 0 |
| | 100% soil | open | 0 | 0 | 100 | 0 | 0 | 0 | 0.1 | 0.2 |
| | | closed | 0 | 0 | 100 | 0 | 0 | 0 | 4 | 4 |
| | 100% water | open | 0 | 88 | 0 | 12 | 0 | 0 | 11 | 15 |
| | | closed | 0 | 80 | 3 | 17 | 0 | 0 | 15 | 15 |
| Dechlorane Plus | 100% air | open | 14 | 0 | 85 | 0 | 0 | 0 | 4 | 4 |
| | | closed | 14 | 0 | 86 | 0 | 0 | 0 | 4 | 4 |
| | 100% soil | open | 0 | 0 | 100 | 0 | 0 | 0 | 91 | 223 |
| | | closed | 1 | 0 | 99 | 0 | 0 | 0 | 95 | 95 |
| | 100% water | open | 0 | 0 | 0 | 100 | 0 | 0 | 14662 | 41263 |
| | | closed | 0 | 0 | 2 | 96 | 2 | 0 | 4322 | 4322 |
| DecaBDE | 100% air | open | 3 | 0 | 75 | 22 | 0 | 0 | 15 | 409 |
| | | closed | 3 | 0 | 76 | 20 | 0 | 0 | 402 | 402 |
| | 100% soil | open | 0 | 0 | 100 | 0 | 0 | 0 | 332 | 361 |
| | | closed | 0 | 0 | 98 | 2 | 0 | 0 | 365 | 365 |
| | 100% water | open | 0 | 0 | 0 | 99 | 0 | 0 | 2201 | 73748 |
| | | closed | 0 | 0 | 34 | 66 | 0 | 0 | 1018 | 1018 |

* Pseudo overall persistence Overall persistence expressed as half-life

For the 100% emission to soil scenario, the open system leads to higher distribution into water. The reason is the fast export of the substance via water respectively air. However, for the 100% emission to water scenario, the open system yields a lower percentage in soil compared to the closed system. The fast export process prevents the distribution to soil. The changes in the distribution are responsible for the changes in overall half-lives (overall DT50 as well as overall persistence and overall pseudo persistence). The extent of the effect is substance specific and depends on the degradation rates.

For DecaDBE the higher distribution to sediment (99%) leads to a significantly higher pseudo overall persistence for the open system (73748 d) compared to the overall persistence in closed systems (1018 d). Degradation is much slower in sediment ($10^6$ d) compared to degradation in soil (360 days).

For the emission to air scenario no significant difference between open and closed system can be observed. One reason is that degradation in air is generally fast compared to the other compartments.

### 3.2.5 Simulation level III versus level IV

The following simulations were performed with MUST considering an open system, the EU regional scenario and using a STP. For level III solution, constant emission was considered. In case of level IV, the result of 10 years constant emission followed by a 2 years recovery period was evaluated. For level IV, the emission was entered in kg. Thus, e.g. 100% air emission of 100 kg of a substance emitted per year during a time period of 10 years was followed by a clean recovery period of two years with zero emission. In the software MUST, the emission in kg is internally converted to hourly emission in mole based on the molecular weight of the substance. The steady state solution differs to the distribution after 10 years in cases where steady state is not reached in 10 years.

For HBCDD, steady state is reached for all compartments except for biota. HBCDD mainly distributes to soil. Furthermore, HBBCD degrades fast during the two years recovery (Figure 3).

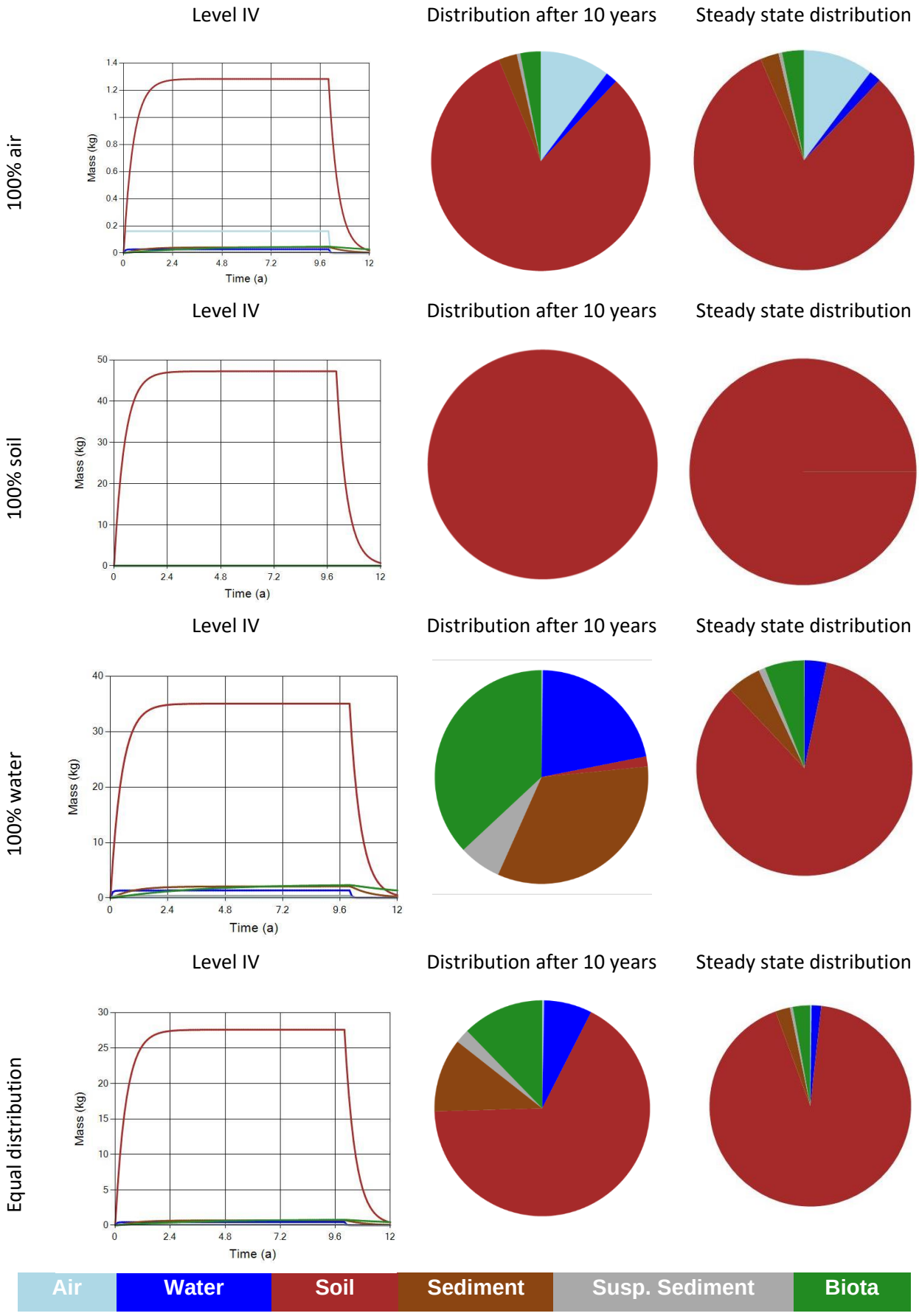



**Figure 3: HBCDD Level III and level IV solution**

In Figure 4, the steady state solution (level III) and mass in time during the observation period (level IV solution) is presented. For D4, the recovery time of two years is not sufficient for a complete clean environment in all emission scenarios. The importance of compartments differs within the different emission scenarios. For 100% air, D4 mainly stays in air (99%). Also for 100 % soil scenario, the main distribution is found in air (54%), the rest is distributed in soil. For 100% water and equal distribution, D4 is distributed in all compartments. For 100%, D4 is mainly distributed in sediment (35%) whereas equal distribution, D4 is mainly distributed in air (29%). Comparing D4 with HBCDD shows a much higher mass accumulation of HBCDD than D4 though the emission is exactly the same in the calculation. This is typical for substances like HBCDD which are mainly distributed to soil. In contrast, much higher fractions of D4 are distributed to air and water. As MUST is defined as an open system with permanent export via these two phases (air and water) accumulation is permanently reduced by transportation outside the system. That does not mean that D4 is also degraded it just not accumulates in an open system. A second surprising outcome of the simulation is the fast recovery time of D4 in soil compared to sediment though the related half-lives are not that different. A similar explanation can be given here: Due to the high vapour pressure of D4 there is fast partitioning from soil to air. But the air compartment is much more dynamic than the water compartment with regard to export out of the system. Consequently, the decline in the soil compartment is also faster than in the sediment compartment. Figure 4 shows significant amounts of the substances distributed to biota when releases into water are considered. It is a usual procedure to assume “no degradation” when no data is available. However, the figure elucidates the disadvantage of this formal definition: In a level III simulation the accumulation in biota becomes especially high and the decline at the end of a respective level IV simulations (after the releases stopped) is minimum and caused only by distribution to the water compartment. This shows that parameter setting should be done carefully in order to calculate a realistic scenario of the fate of compounds. With regard to overall persistence biota should be either completely neglected or the degradation rate set to a more realistic value (e.g., set to the degradation in sediment).

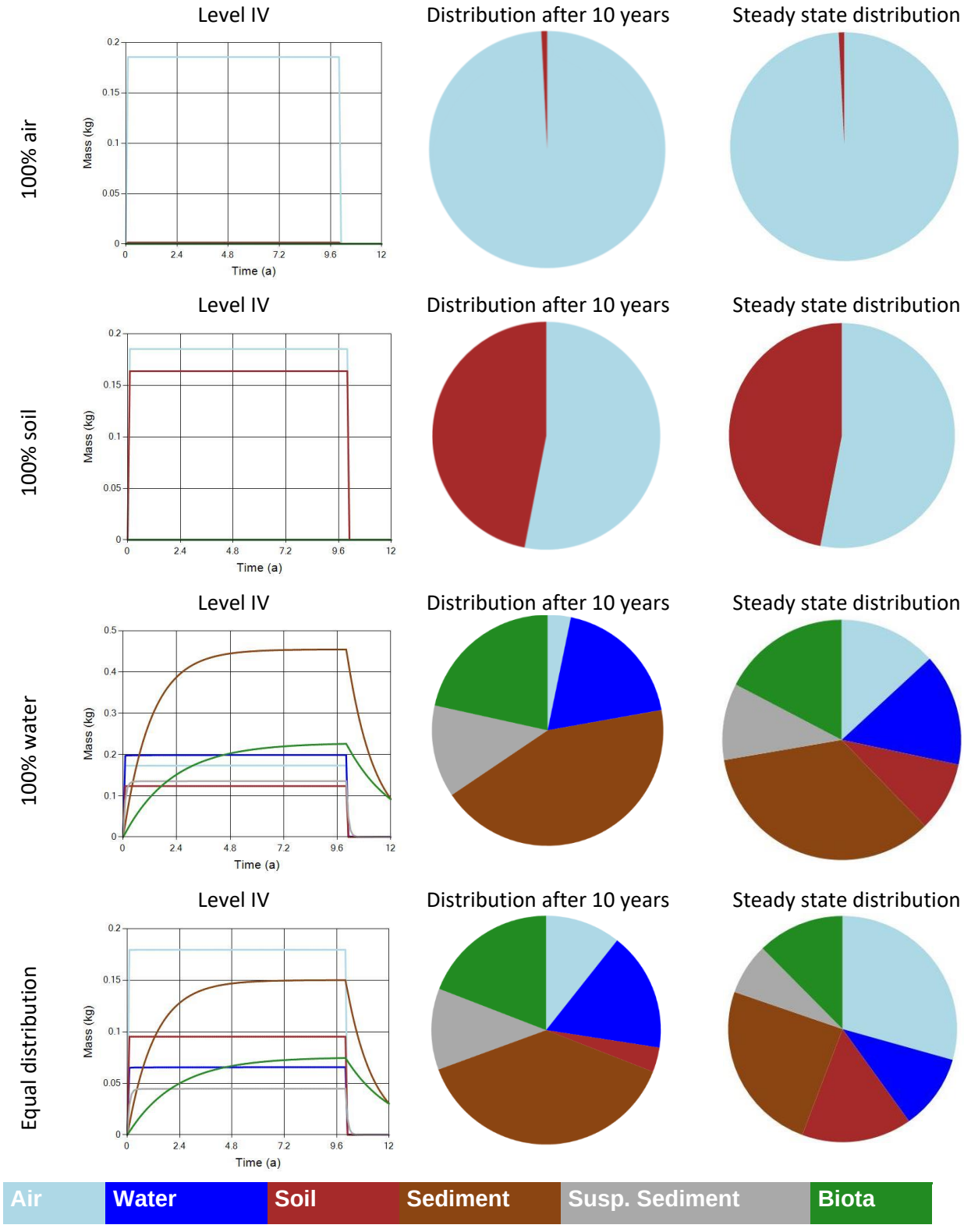



**Figure 4: D4 Level III and level IV solution**

In Figure 5, the results for Bisphenol A are presented. For Bisphenol A, the substance stays mainly in the environmental compartment to which it is emitted. For example, 100% emission to soil leads to 100% distribution of Bisphenol A. For 100% air the main part of the substance is distributed in air

(approx. 75%), followed by soil (approx. 15%) and water (approx. 10%) (Compare Table 14). The same yields for the 100% water scenario: approximately 85% of the substances is distributed in water, followed by approximately 10% in sediment and 4% in soil. For the equal distribution scenario, the main part of the substance distributes in water (approx. 64%), soil (approx. 27%) and sediment (8%).

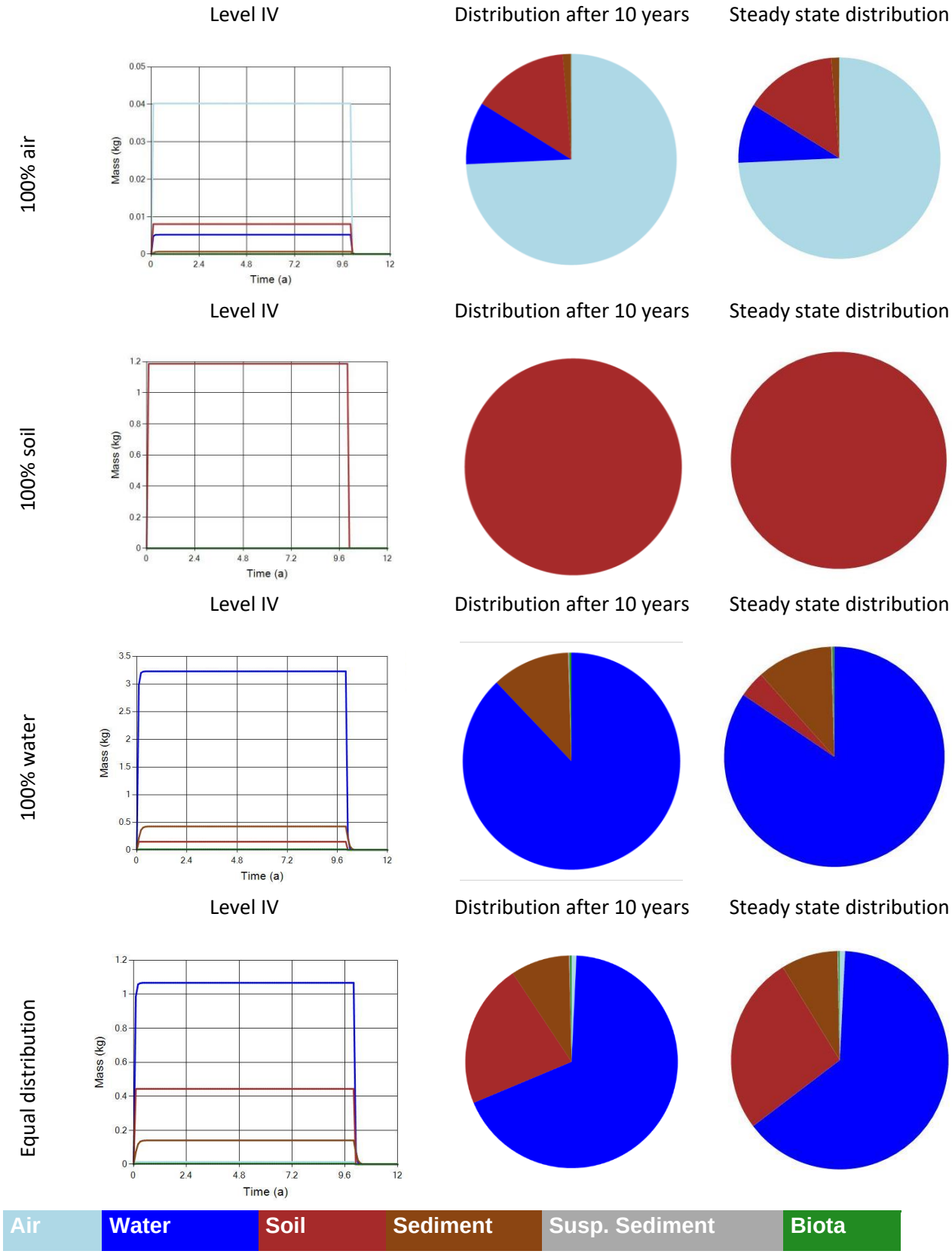



**Figure 5: Bisphenol A Level III and level IV solution**

Figure 6 presents the level III and IV solution for all four emission scenarios for Dechlorane. The substance is mainly distributed in soil and sediment within the different emission scenarios. Equal distribution and 100% soil results in main distribution in sediment (>95%), whereas for 100% air and 100% water Dechlorane Plus is mainly distributed to soil (>85%). The decline from soil is rather rapid though the very high half-live of 350 000 days because the model assumes a fast partitioning to air followed by a fast degradation (DT50 air: 0.7 d) or transportation out of the system. The situation is completely different when the Dechlorane plus is released to water. The steady state concentrations shows that after infinite time the substance should be mainly accumulate in sediment and only a small fraction in soil. However, the level IV simulation result in the opposite: most of the compounds is expected in the soil compartment and only a small (but growing) fraction is expected to partition to sediment. The problem here is the time until steady state is reached in the level IV simulation. There is a linear increase of the masses in sediment which will surely overrun the constant amount in soil. The situation is far from equilibrium after 10 years. As there is no degradation considered for Dechlorane plus in sediment there is also no recovery for the compound in this compartment.

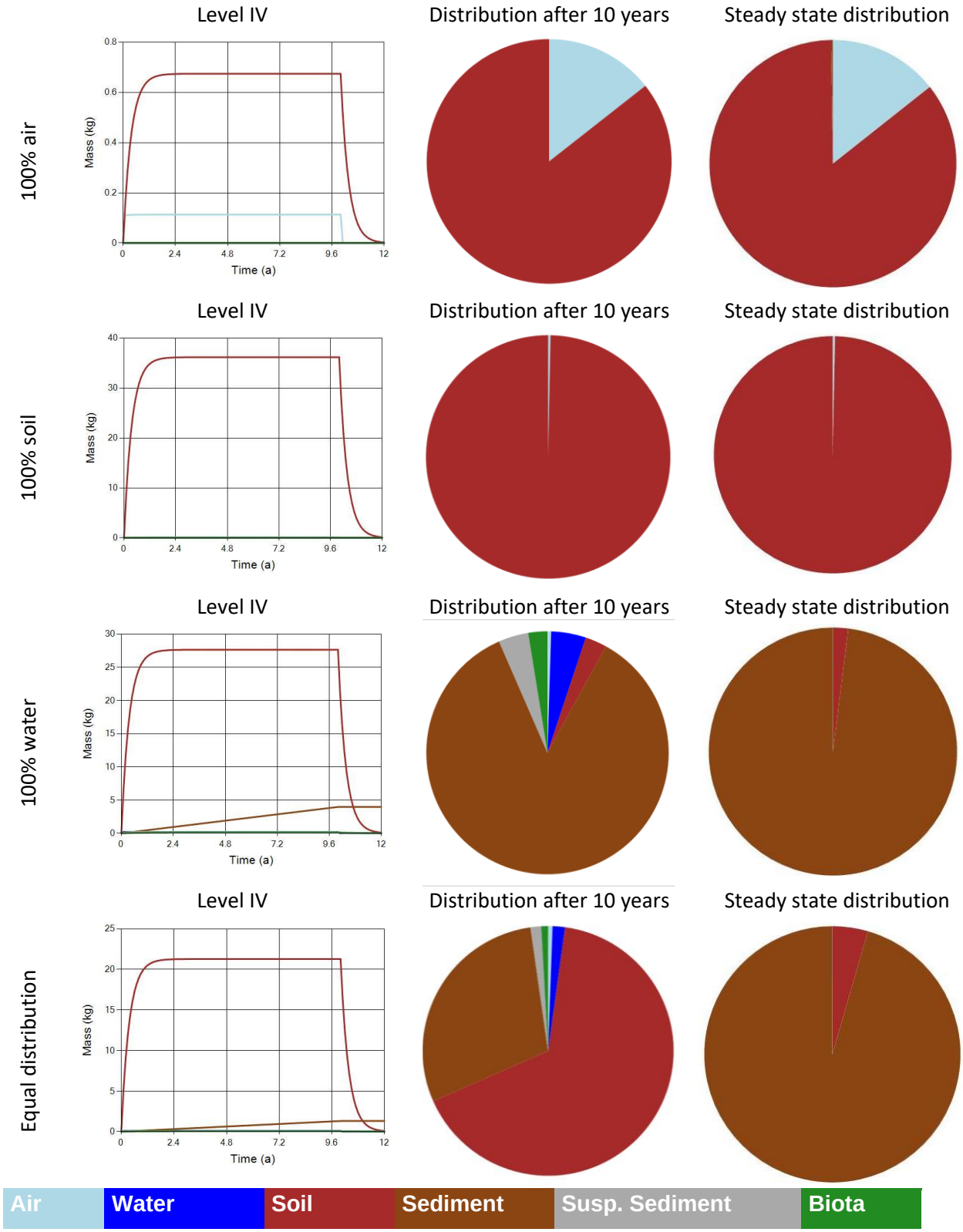



**Figure 6: Dechlorane Plus Level III and level IV solution**

In Figure 6, the steady state distribution (level III) and mass in time in the different compartments for DecaDBE is shown. Emission into 100% water leads to 99% distribution in soil. For the other emission

scenarios, DecaBDE is mainly distributed in soil and sediment: 100% air 74% in soil, 21% in sediment; 100% soil: 32 % soil, 67 % sediment; equal distribution: 53% in soil, 47 % in sediment. Similar as for dechlorane plus also for DecaDBE the steady state distribution at level III does not correspond to the results of the level IV simulation when emissions are put into the water compartment. Again simply steady state is not reached in the level IV simulation after 10 years and mass in sediment is still increasing. As long as the concentrations are time dependent the figure in the right is not in agreement with the distribution in the left.

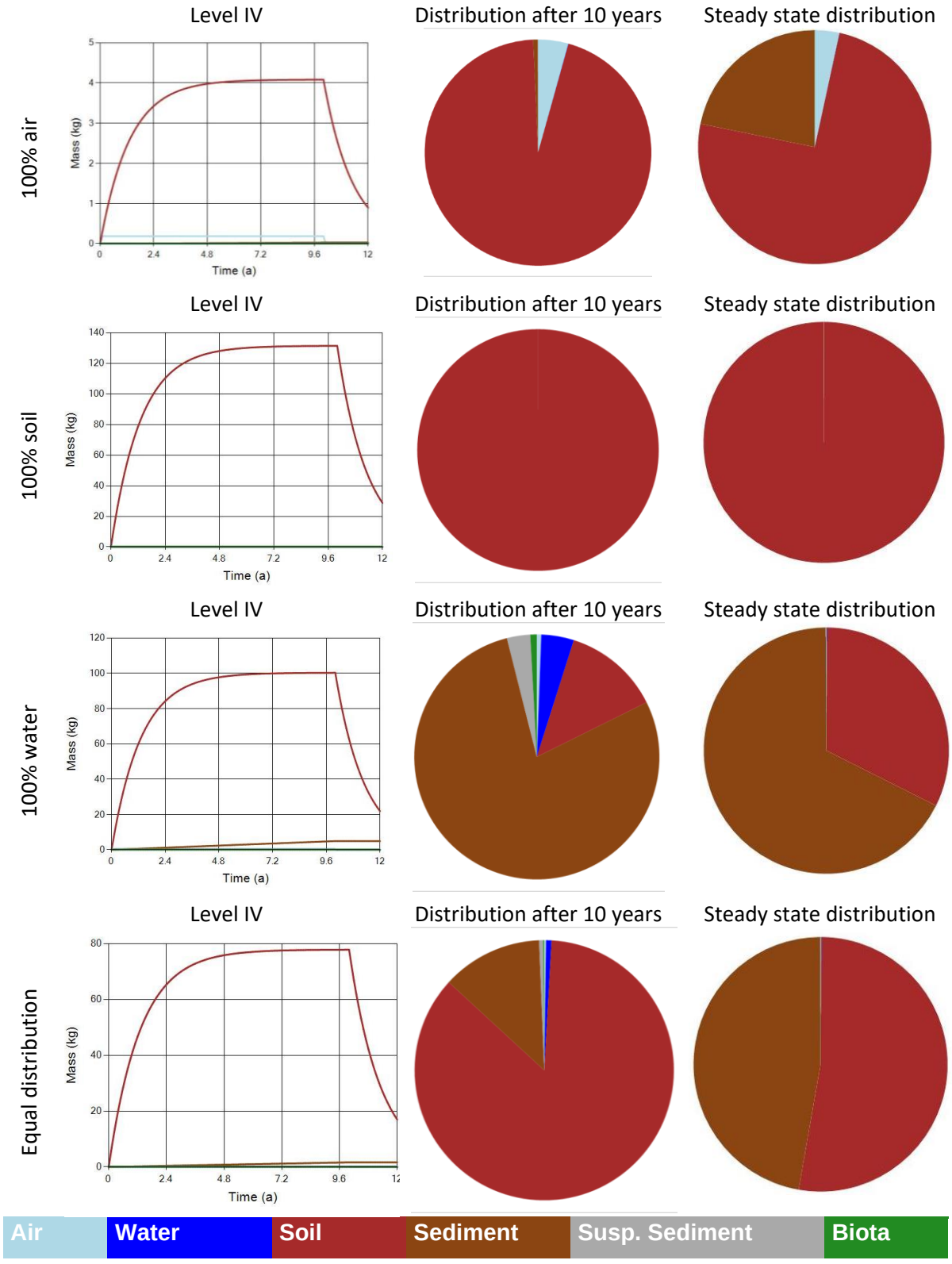



**Figure 7: DecaDBE Level III and level IV solution**

The calculated steady state distributions (level III solutions) for all substances are presented in Table 14.

**Table 14: Steady State distribution (level III solution) of all selected substances**

| Substance | Scenario | Air (%) | Water (%) | Soil (%) | Sediment (%) | Suspended Sediment (%) | Biota (%) |
|---|---|---|---|---|---|---|---|
| HBCDD | 100% air | 10 | 2 | 82 | 3 | 1 | 3 |
| | 100% soil | 0 | 0 | 100 | 0 | 0 | 0 |
| | 100% water | 0 | 3 | 85 | 5 | 1 | 6 |
| | Equal distribution | 0 | 2 | 93 | 2 | 0 | 3 |
| D4 | 100% air | 99 | 0 | 1 | 0 | 0 | 0 |
| | 100% soil | 53 | 0 | 47 | 0 | 0 | 0 |
| | 100% water | 13 | 15 | 9 | 35 | 10 | 17 |
| | Equal distribution | 29 | 11 | 16 | 25 | 7 | 12 |
| Bisphenol A | 100% air | 74 | 10 | 15 | 1 | 0 | 0 |
| | 100% soil | 0 | 0 | 100 | 0 | 0 | 0 |
| | 100% water | 0 | 85 | 4 | 11 | 0 | 0 |
| | Equal distribution | 1 | 64 | 27 | 8 | 0 | 0 |
| Dechlorane Plus | 100% air | 14 | 0 | 85 | 0 | 0 | 0 |
| | 100% soil | 0 | 0 | 100 | 0 | 0 | 0 |
| | 100% water | 0 | 0 | 2 | 98 | 0 | 0 |
| | Equal distribution | 0 | 0 | 4 | 96 | 0 | 0 |
| DecaDBE | 100% air | 3 | 0 | 75 | 22 | 0 | 0 |
| | 100% soil | 0 | 0 | 100 | 0 | 0 | 0 |
| | 100% water | 0 | 0 | 32 | 68 | 0 | 0 |
| | Equal distribution | 0 | 0 | 53 | 47 | 0 | 0 |

### 3.2.6 Overall persistence over time Pov(t)

It is possible to calculate the overall persistence not only based on steady state (level III) but also on the dynamic distribution (level IV). Thus, also overall persistence becomes a function in time, here, in days. In Figure 8, for all emission scenarios and substances the “level IV” overall persistence is calculated.

The dynamic (pseudo-)overall persistence depends on the chosen dynamic emission profile, here, 10 years with constant emission are considered. Export is included and a sewage treatment plant is considered for the fraction released to water.

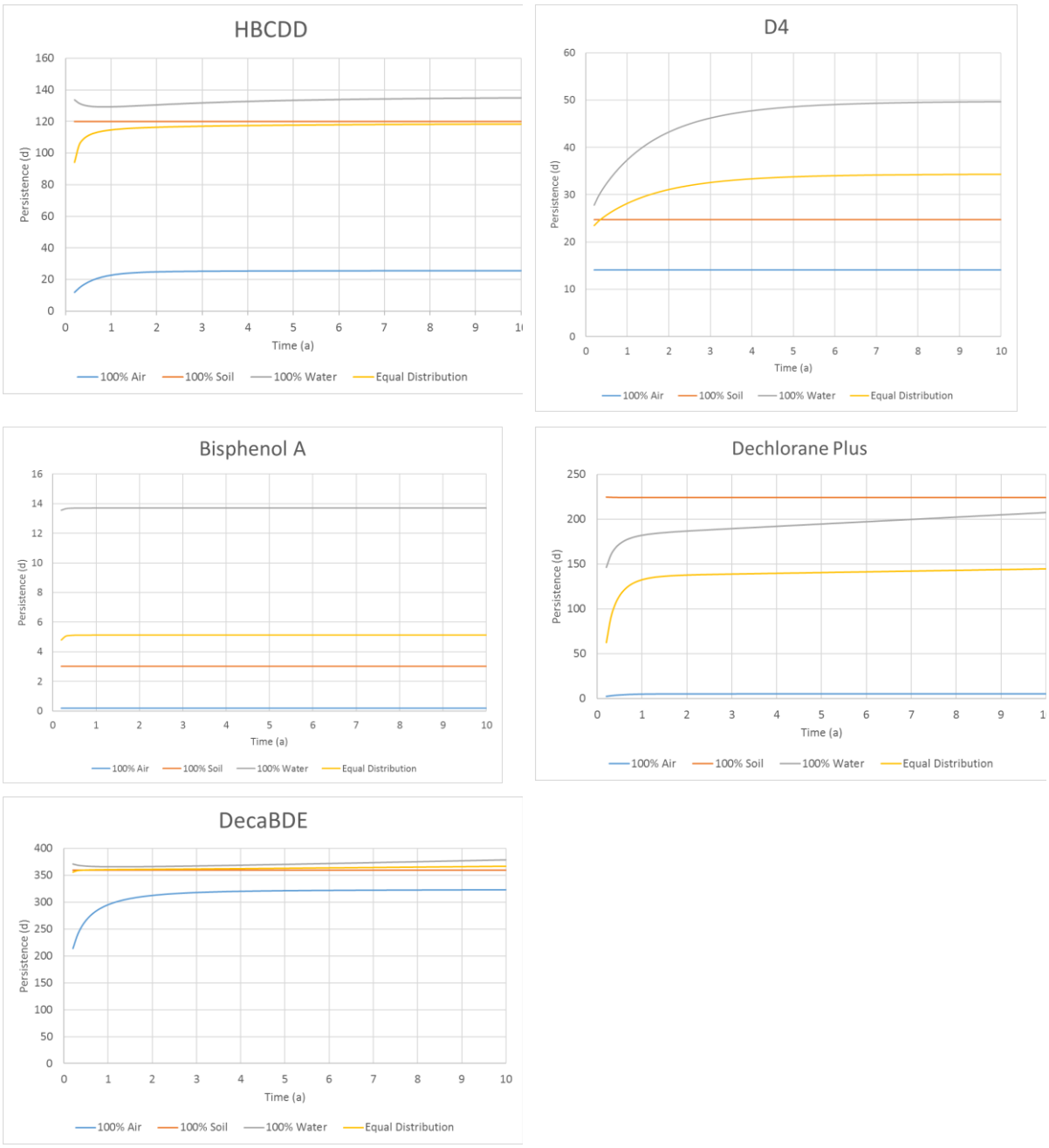



**Figure 8: ´Dynamic´ pseudo-overall persistence in time of all five chosen substance for all four emission scenarios**

The change of 'dynamic' overall persistence depends on substance's properties and on the release pattern. The substance influence becomes obvious when comparing the different charts in the figure. Dependent on the distribution and the degradation parameters steady state conditions can be reached fast (e.g., Bisphenol A) or only after several years (e.g., D4). The dependency of the release pattern on the overall persistence is demonstrated when looking at a certain figure. For Dechlorane plus steady state is fast reached when the substance is released into air or soil whereas steady state is not reached when the same substance is released into water. Usually, the overall persistence increases over time before it reaches steady state conditions, at least for a constant release. That means the level III simulation can be considered a conservative assumption for dynamic persistencies (level IV).

Further conclusions are:

- For all substances, the 100% soil scenario yields to an almost constant pseudo-overall persistence over time. The emission to soil, here, leads to a main distribution in soil.
- For all considered substances, the equal release into the environmental compartments leads to an average pseudo- overall persistence.

## 3.3 Sensitivity analysis

The sensitivity of parameter depends on the release pattern, the substance properties and the considered endpoints. Here, the EU regional scenario in open system (including export) and considering an STP to correct the initial emissions is evaluated.

Following endpoints are discussed:

- Steady state distribution in air, water, soil, sediment, susp. sediment and biota
- Overall DT50 and pseudo overall persistence
- Residence time in air, water, soil, sediment, susp. sediment and biota
- Area under the curve in air, water, soil, sediment, susp. sediment and biota
- Reduction in air, water, soil, sediment, susp. sediment and biota

At first all the analysis considers all endpoints, of multi-media models but only a single substance (D4). In the following steps the focus is led on the most relevant output (overall persistence and clearance time) are analysed including other substances

### 3.3.1 Most sensitive input parameters (substance D4, all endpoints)

The analysis focuses on the substance D4, as it is distributed in several environmental compartments. When equal emissions to the compartments air, water and soil is assumed D4 is distributed to several environmental compartments, namely in air (29 %), sediment (25%), soil (16%), biota (12%), water (11%) and suspended sediment (7%). The three most sensitive parameter are environmental parameters: Average connection of percentage to STP, fraction of biota and water depth.

The sum of squares of the sensitivity coefficients of all endpoints is calculated to identify the most relevant parameter considering all chosen endpoints: steady state of the compartments, regional DT50, persistence, clearance time in air, water and soil, area under the curve of all compartments and the reduction after the emission period in all compartments.

According to this procedure, in this scenario, the most important parameter is the parameter average connection percentage to STP (sum of squares 77.89). As the equal distribution scenario is considered, the emission of water and soil is influenced. Instead of a 33% emission to both compartments, using the STP yields to 8.2% emission to water and 58.4% emission to soil in the default scenario.

Thus, STP connection parameter influences mainly the reduction in soil (-3.48) as reduction of water is relatively fast. The higher the STP value, the higher the emission to soil, the lower is the reduction in soil. The parameter is also sensitive to the level IV solutions of the system. The area under the curve for water, sediment, suspended sediment and biota is smaller with higher STP connection value (sensitivity coefficient -3.04). For the area under the curve for soil, as higher STP value lead to a higher emission is soil, it also leads to higher area under the curve. However, it is less sensitive compared to the other AUC for water, sediment, suspended sediment and biota (0.42).

Level III solution is influenced as well, as a different emission pattern leads to a different steady state solution. Highest sensitivity is obtained for the compartments with increasing distribution: soil (2.03) and air (1.67). Same sensitivity is obtained for the compartments' group with lower distribution: water, sediment, suspended sediment and biota (-1.47).

Higher STP values leads to lower regional DT50 (-1.59) and persistence (-0.89).

Another important parameter considering all endpoints, is the fraction of biota (sum of squares 5.83). However, the total sum of squares is much smaller than for the average connection percentage to STP. The fraction of biota determines the volume of the compartment biota. The higher the fraction, the bigger the volume of the compartment. The higher fraction of biota, the higher the distribution in biota (level III, 0.88) and the area under the curve of biota (level IV, 1). Furthermore, the fraction of biota is slightly sensitive with respect to the steady state solution of the other compartments (-0.12). The higher fraction, the lower the steady state distribution in the other compartments. For regional DT50 and pseudo-overall persistence, fraction of biota is similar sensitive (0.12). In addition to that biota influences equally the reduction in air, water soil and suspended sediment (1).

In addition to fraction of biota and STP, water depth is an important parameter (sum of squares 5.35). Highest sensitivity is obtained for clearance time in water (0.76), area under the curve for water (0.76), suspended sediment (0.76) and biota (0.75), as well as the reduction of D4 in water (0.76) and suspended sediment (0.76). A higher water depth increases the volume of water.

For the other parameters, the total sum of squares of sensitivity is smaller 22.73. Average sum of squares of the remaining parameter is 1.3.

For 100% air and 100% soil the same most sensitive parameter with similar SSQ values are obtained, namely, the parameters height of atmosphere, Henry's law constant, and temperature.

The total sum of squares are much smaller than for the 100% and equal distribution scenario. For 100% water the same important parameter identified as for the equal distribution scenario.

**Table 15: Sum of squares of sensitivity coefficients for D4 considering all endpoints for all four emission scenarios**

| Scenario | Rank 1 | Rank 2 | Rank 3 |
|---|---|---|---|
| 100% air | Height of the atmosphere (SSQ 12.38) | Henry's law constant (SSQ 12.34) | Temperature (SSQ 11.89) |
| 100% soil | Height of the atmosphere (SSQ 13.55) | Henry's law constant (SSQ 11.49) | Temperature (SSQ 11.04) |
| 100% water | Average connection percentage to STP (SSQ 91.29) | Fraction of biota (SSQ 5.84) | Water depth (SSQ 5.33) |
| Equal distribution | Average connection percentage to STP (SSQ 77.89) | Fraction of biota (SSQ 5.83) | Water depth (SSQ 5.35) |

Temperature is used to calculate the proportionality constant, the "fugacity capacity" for air. Z quantifies the capacity of a phase to dissolve or sorb a chemical. If fugacity is low, then the escaping tendency is high. The default temperature value is set to 285 K, thus approximately 12°C. The higher the temperature value, the lower is the fugacity, and the higher the escaping tendency.

Furthermore, temperature is used to determine the Henry's law constant from logKaw, if no value for the Henry's law constant is available.

Henry's law constant is used to calculate the fugacity for water: the higher the Henry's law constant, the lower the fugacity. Furthermore, Henry's law constant is used to determine the substance specific sludge fraction for the STP though the sludge fraction is mainly influenced by KOC.

The environmental parameter height of atmosphere is default set to 1 km. It is used to calculate the volume of air, the higher the value, the higher is the volume of the compartment.

To summarize, the parameters identified as important are mainly environmental parameters influencing volume of the compartments.

### 3.3.2 Most sensitive input parameters (focusing only on the pseudo-overall persistence)

In the previous chapter several endpoints of multi-media were analysed. Now, the pseudo-overall persistence us evaluated in more detail since it is most relevant in the political discussion. The choice of endpoints, of course, also influence the resulting most sensitive input parameters. Again, sum of squares is considered as indicator.

In this section the most sensitive parameters are identified considering the pseudo-overall persistence as endpoint only. A parameter is considered to be insensitive if its sensitivity coefficient is close to 0.1 respectively -0.1.

For HBCDD, the most sensitive parameter is DT50 soil, which has the highest absolute sensitivity coefficient for the scenarios 100% soil, 100% water and equal distribution. For 100% air, DT50 air is most sensitive (0.82), but DT50 soil is similar sensitive (0.81). Additionally, considering all emission scenarios, the environmental parameters height of atmosphere (100% air, -0.73) and average connection percentage to STP (100% water, equal distribution) are sensitive for HBCDD. The latter is more sensitive for the 100% water scenario (-0.42) than for the equal distribution scenario (-0.15). The remaining parameters are insensitive (absolute value of sensitivity coefficient is smaller than 0.1).

For D4, the most sensitive parameters are DT50 air (mean sensitivity coefficient 0.77 over all scenarios). For 100% air, DT50 air is even the only sensitive parameter. Again average connection percentage to STP is sensitive for 100% water and equal distribution scenario. In addition to that soil depth (0.41) and residence time air (-0.39) are sensitive for 100% soil, DT50 water (0.48) for 100% water and residence time air (-0.42) for equal distribution.

For Bisphenol A, again DT50 air is sensitive for the 100% air scenario (0.99) followed by the environmental parameter height of the atmosphere (-0.25) and the substance specific DT50 soil (0.15). For 100% soil, DT50 soil is the only sensitive parameter (1). For 100% water, DT50 water (0.86) is sensitive and the average connection percentage to STP (-0.16). However, the latter is much less sensitive. Also for equal distribution, DT50 water (0.53) is most sensitive, followed by DT50 soil (0.27) and residence time water (0.17).

For Dechlorane Plus, for 100% air amongst DT50 air (1), the height of atmosphere (-0.88) also the substance specific Henry's law constant is sensitive (-0.87). The Henry's law constant is also most sensitive (-1.01) for the 100% soil scenario additionally to the soil related parameter soil depth (1) and soil organic carbon content (0.99). For 100% water and equal distribution the same parameter are sensitive in a similar range, average connection to STP, ST50 sediment and residence time air.

For DecaDBE, for 100% air (0.75) and 100% soil (1), the substance specific DT50 soil is most sensitive, whereas average connection percentage to STP is most sensitive for 100% water (-2.81) and equal distribution (-1.66). For 100% air, water fraction (0.22) and Henry's law constant (-0.21) are similar sensitive. For 100% soil, DT50 soil is the only sensitive parameter. For 100% water and equal distribution, DT50 soil and sediment depth are sensitive.

An overview over the sensitivity coefficients for the three most sensitive parameters for all considered substances and emission scenarios can be seen in Table 16.

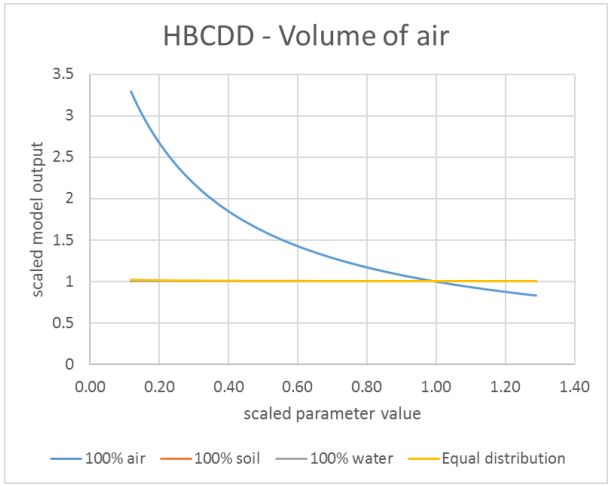
**Table 16: Sensitivity coefficients for all substance considering only overall persistence for all four emission scenarios**

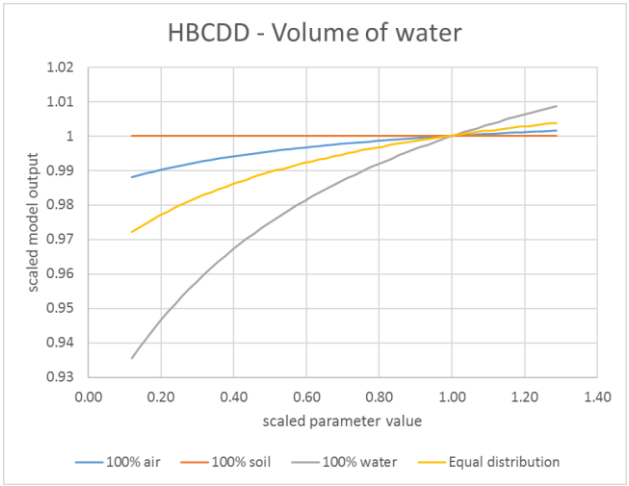
| Substance | Scenario | Rank 1 | Rank 2 | Rank 3 |
|---|---|---|---|---|
| HBCDD | 100% air | DT50 air (0.82) | DT50 soil (0.81) | Height of the atmosphere (-0.73) |
| | 100% soil | DT50 soil (1) | | |
| | 100% water | DT50 soil (0.84) | Average connection percentage to STP (-0.42) | Residence time water (0.07) |
| | Equal distribution | DT50 soil (0.92) | Average connection percentage to STP (-0.15) | DT50 air (0.06) |
| D4 | 100% air | DT50 air (1) | KOC (0.01) | Soil depth (0.01) |
| | 100% soil | DT50 air (0.92) | Soil depth (0.41) | Residence time air (-0.39) |
| | 100% water | Average connection percentage to STP (-0.83) | DT50 water (0.48) | DT50 air (0.46) |
| | Equal distribution | Average connection percentage to STP (-0.89) | DT50 air (0.71) | Residence time air (-0.42) |
| Bisphenol A | 100% air | DT50 air (0.99) | Height of the atmosphere (-0.25) | DT50 soil (0.15) |
| | 100% soil | DT50 soil (1) | | |
| | 100% water | DT50 water (0.86) | Average connection percentage to STP (-0.16) | DT50 sed (0.1) |
| | Equal distribution | DT50 water (0.53) | DT50 soil (0.27) | Residence time water (0.17) |
| Dechlorane Plus | 100% air | DT50 air (1) | Height of the atmosphere (-0.88) | Henry's law constant (-0.87) |
| | 100% soil | Henry's law constant (-1.01) | Soil depth (1) | Soil org. carbon content (0.99) |
| | 100% water | Average connection percentage to STP (-3.2) | DT50 sed (0.87) | Residence time air (-0.59) |
| | Equal distribution | Average connection percentage to STP (-3.05) | DT50 sed (0.84) | Residence time air (-0.6) |
| DecaDBE | 100% air | DT50 soil (0.75) | Water fraction (0.22) | Henry's law constant (-0.21) |
| | 100% soil | DT50 soil (1) | | |
| | 100% water | Average connection percentage to STP (-2.81) | Sediment depth (0.6) | |
| | Equal distribution | Average connection percentage to STP (-1.66) | DT50 soil (0.56) | Sediment depth (0.42) |

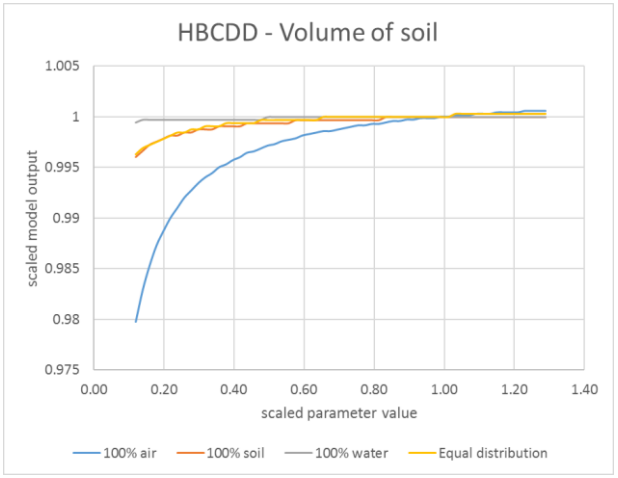
### 3.3.3 Sensitivity of volume of air, water, soil for all substances and scenarios

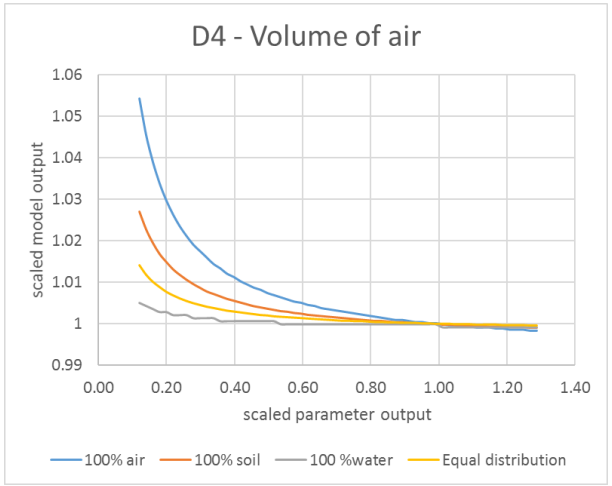
As shown discussed the environmental parameters can be very sensitive with respect to overall persistence. In this section the influence of the volumes of the main compartments air, water and soil on the overall persistence is analysed. The analysis was done using the model MUST (level III).

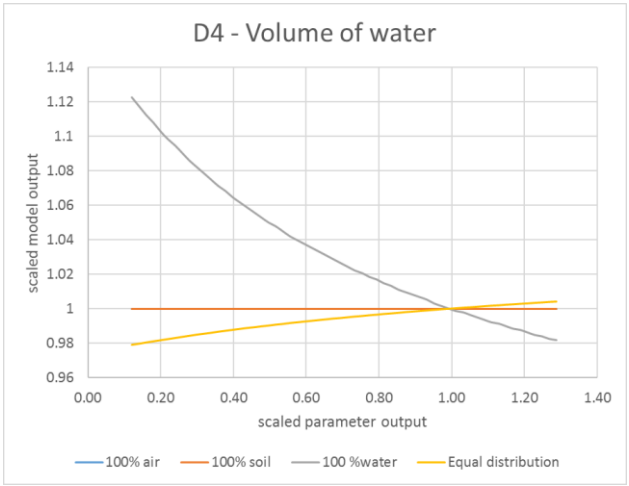
In Figure 9, for the five standard substances and all emission scenarios the sensitivity is presented with respect to overall persistence. The volumes in the x-axes and the overall persistence in the y-axes are normalised: A value of 2 means doubling of the standard volume (x-ax) and the persistence (y-ax) means double volume or double persistence compared to the standard conditions. The intersection point always corresponds to the default parameter values.

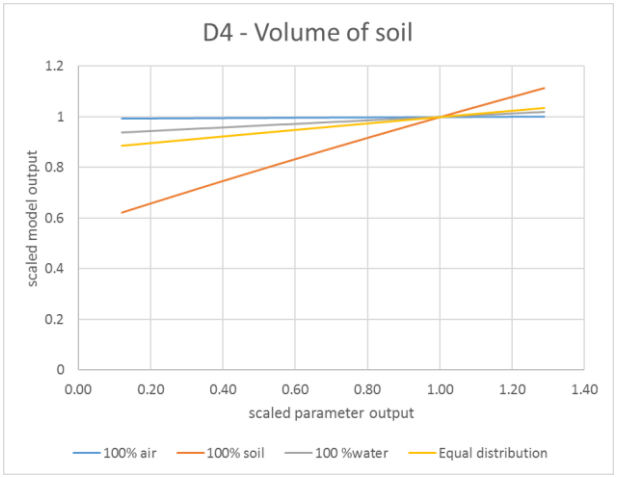

HBCDD - Volume of air
scaled model output
scaled parameter value
100% air
100% soil
100% water
Equal distribution

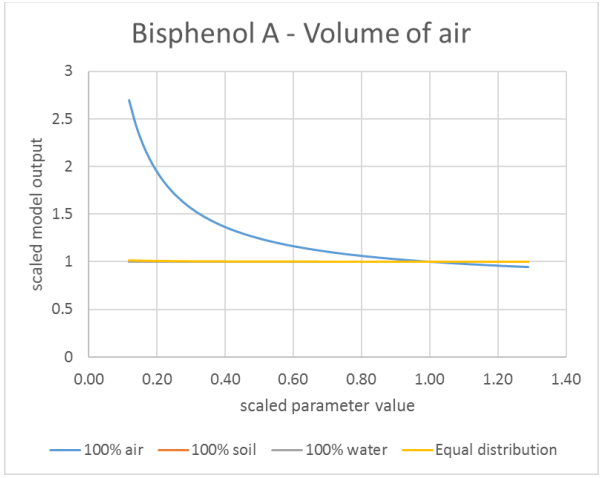

HBCDD - Volume of water
scaled model output
scaled parameter value
100% air
100% soil
100% water
Equal distribution

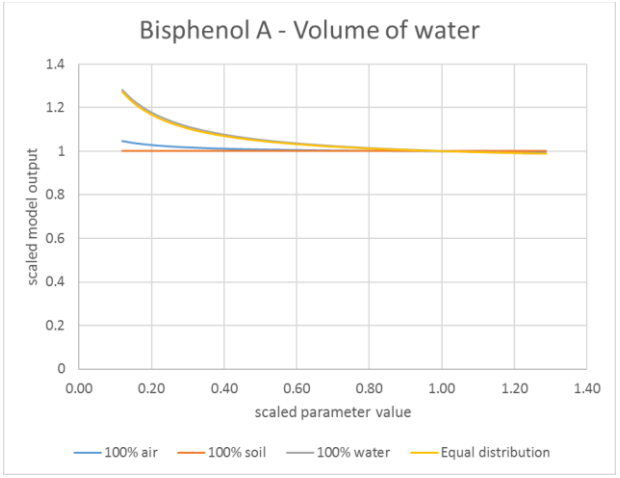

HBCDD - Volume of soil
scaled model output
scaled parameter value
100% air
100% soil
100% water
Equal distribution

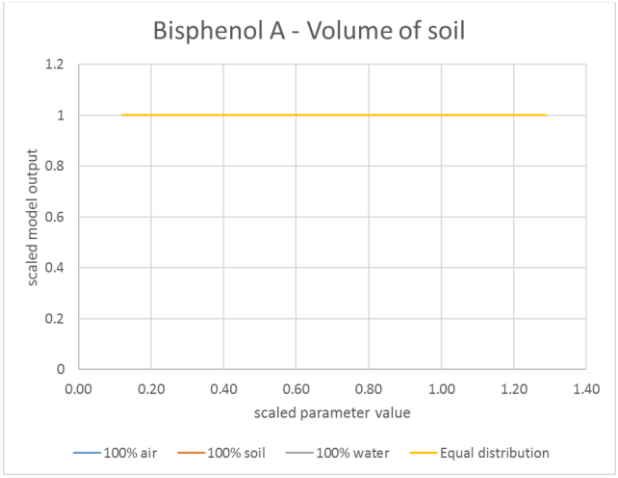

D4 - Volume of air
scaled model output
scaled parameter output
100% air
100% soil
100 %water
Equal distribution

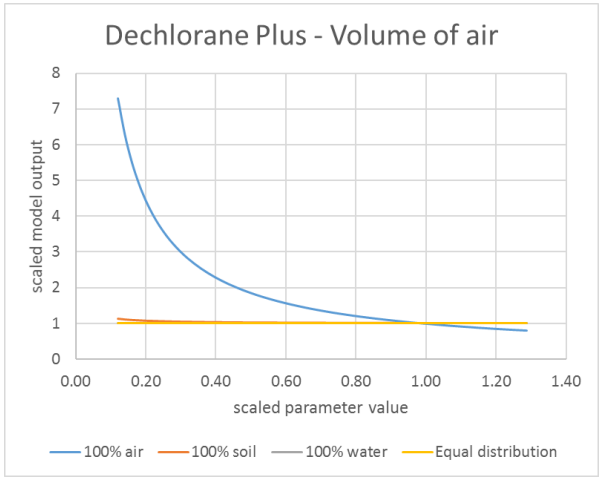

D4 - Volume of water
scaled model output
scaled parameter output
100% air
100% soil
100 %water
Equal distribution

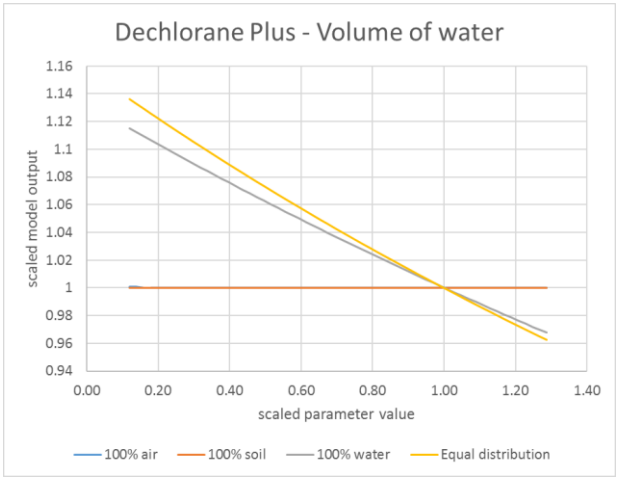

D4 - Volume of soil
scaled model output
scaled parameter output
100% air
100% soil
100 %water
Equal distribution

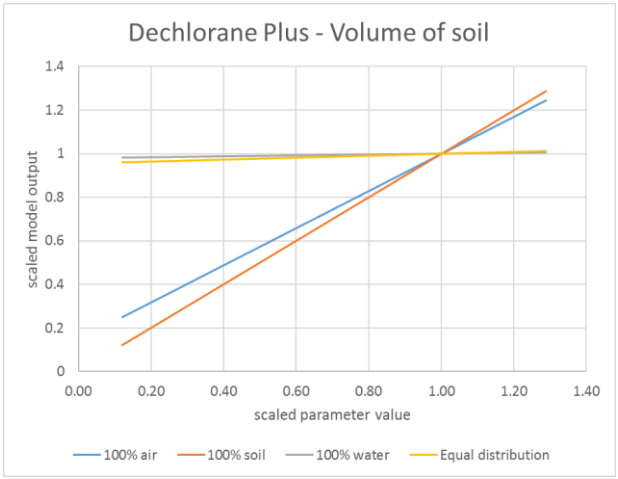

Bisphenol A - Volume of air
scaled model output
scaled parameter value
100% air
100% soil
100% water
Equal distribution

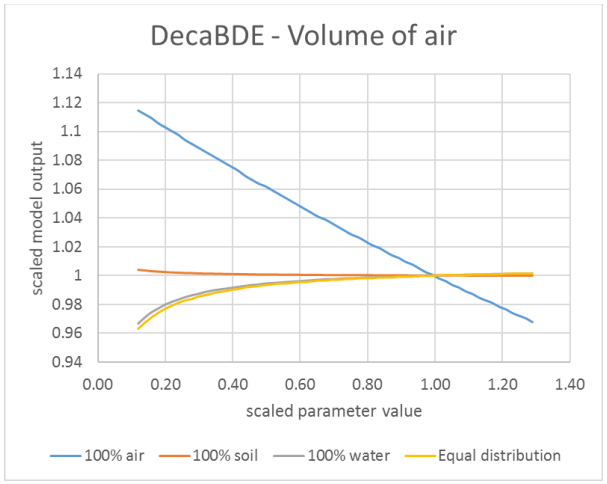

Bisphenol A - Volume of water
scaled model output
scaled parameter value
100% air
100% soil
100% water
Equal distribution

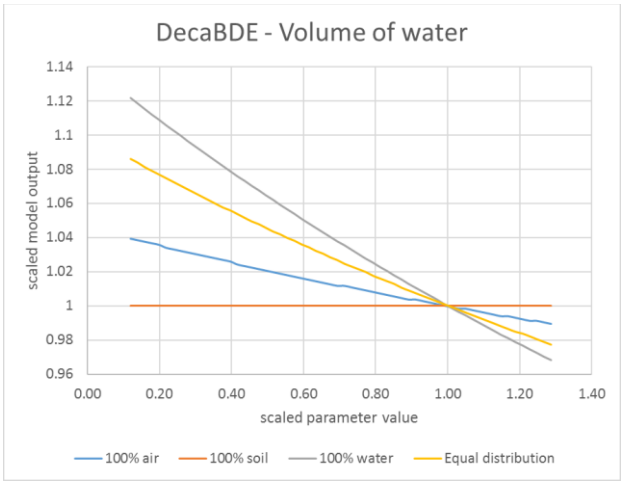

Bisphenol A - Volume of soil
scaled model output
scaled parameter value
100% air
100% soil
100% water
Equal distribution


Dechlorane Plus - Volume of air
scaled model output
scaled parameter value
100% air
100% soil
100% water
Equal distribution


Dechlorane Plus - Volume of water
scaled model output
scaled parameter value
100% air
100% soil
100% water
Equal distribution


Dechlorane Plus - Volume of soil
scaled model output
scaled parameter value
100% air
100% soil
100% water
Equal distribution



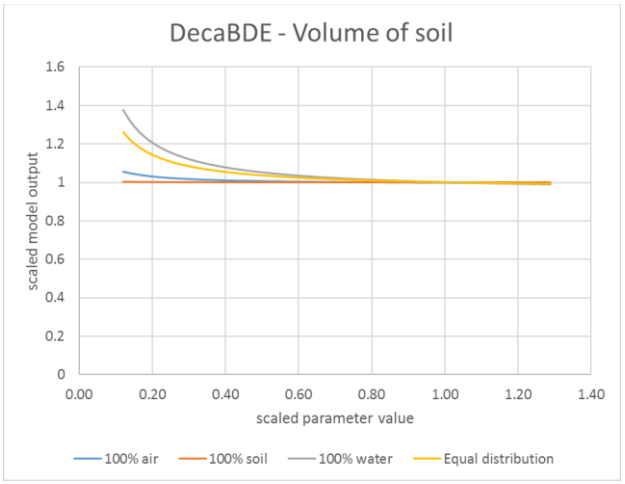




**Figure 9: Sensitivity of the volume of the compartments air, water and soil for the five chosen substances with respect to overall persistence**

The dimension of the volume is sensitive because changing the volume will change the ratio between the compartments and thus, the distribution of the substance in the system and finally also the overall persistence. Furthermore, the effect on the overall persistence is substance specific.

Following further conclusions could be drawn from the analysis:

- Assumed the substances is released into the air compartment the overall persistence is reduced when the volume of air is increased independent on the substance. This is caused by the fact that in that situation more substance amounts will partition to air and the half-lives in air are generally shorter than in the other environmental compartments.
- If the water volume is increased the situation is not that simple (e.g., increasing the volume of water will lead to a reduction of the overall persistence for HBCDD, but to an increase for dechlorane PLUS). The direction of the effect is driven by the ratio of half-lives of the compound in water compared to other compartments.
- The opposite dependency was found for the soil compartment. This can be explained by the fact that an increase of the soil volume automatically leads to a decrease of the water volume.

### 3.3.4 Analysis considering a matrix of hypothetical substances

The analysis was restricted to the substance specific parameters: KOC, Kaw, DT50 in air, water and soil. The parameter KOC influences the fugacity capacity of the compartments soil, sediment and suspended sediment. The parameter Kaw is used to calculate the Henry's law constant which in fact influences the fugacity capacity of all compartments.

The parameters KOC, Kaw as well as half-life (DT50) in soil, air, water influence the steady state distribution. Persistence as endpoint is calculated based on the weighted average of the half-lives in the compartments as well as the steady state solution of the compartments.

In Figure 10 , the different parameter values are shown as box plots with respect to overall persistence. Especially, the DT50 in soil yielded to a difference in overall persistence.

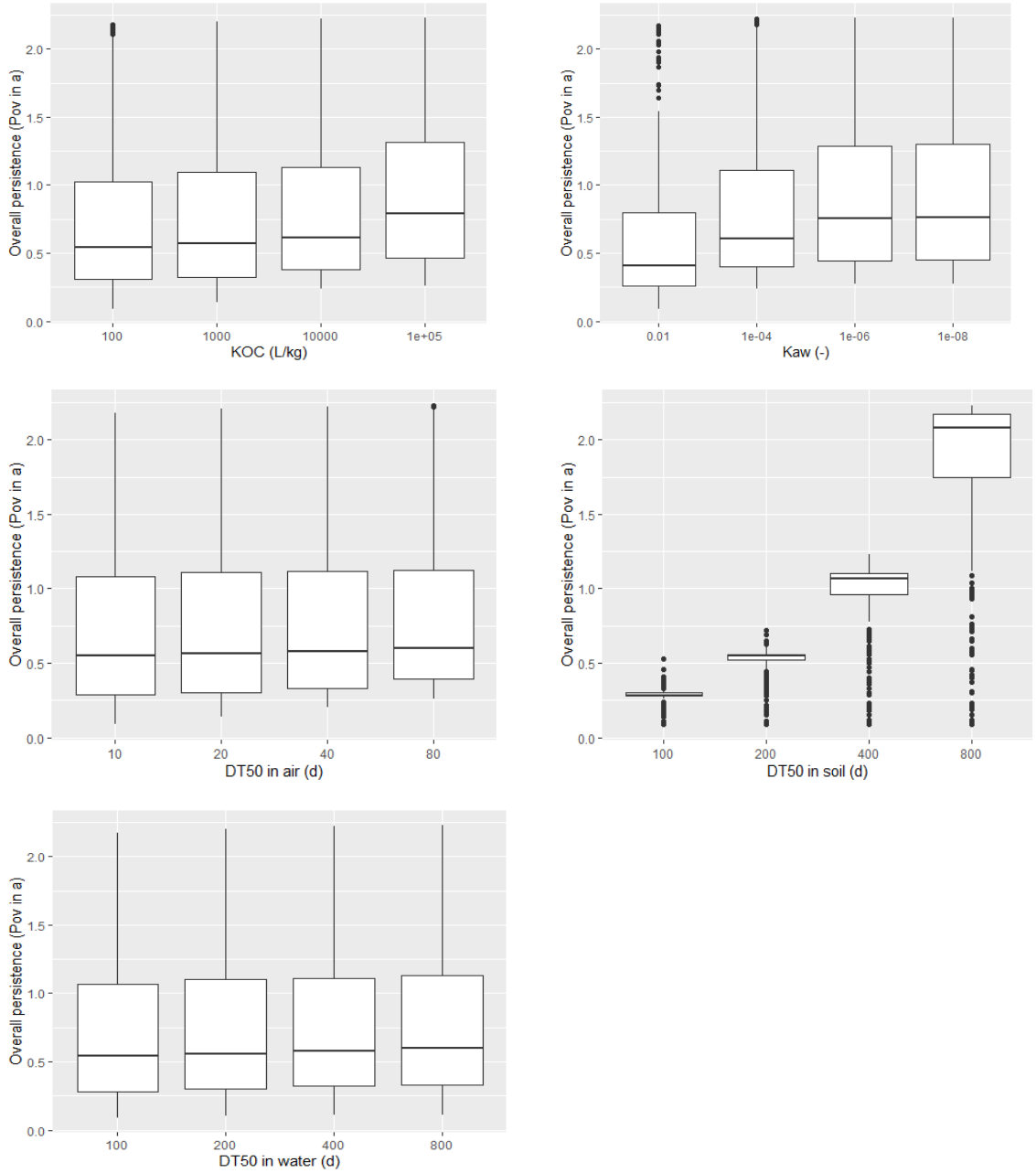



**Figure 10: Box plots of all chosen parameters in relation to overall persistence**

We found a statistically-significant difference in average overall persistence by KOC (f=10.27, p < 0.001), by Kaw (f=22.68, p<0.001) and by DT50 soil (f = 952.9, p< 0.001). No statistically-significant difference in DT50 air and DT50 water was found in average overall persistence was found.

A Tukey post-hoc test revealed that for KOC only the comparison in average overall persistence between a value of 100 (mean = 0.7275) to groups of 1000 (mean = 0.8277), 10000 (mean = 0.9603), and 100000 (mean =1.0182) are statistically-significant. For Kaw, only the comparison of average mean of groups of 0.01 (mean = 0.6029) to 1e-04 (mean = 0.9198), 1e-06 (mean = 1.0043) and 1e-06 (mean = 1.007) is statistically-significant.

As overall persistence is the average mean of steady state distribution and DT50 values in the compartments, we regard the steady state distribution in the main compartments in more detail.

In Figure 11, the difference in steady state in air, water, soil with respect to different groups of KOC as well as Kaw is represented.

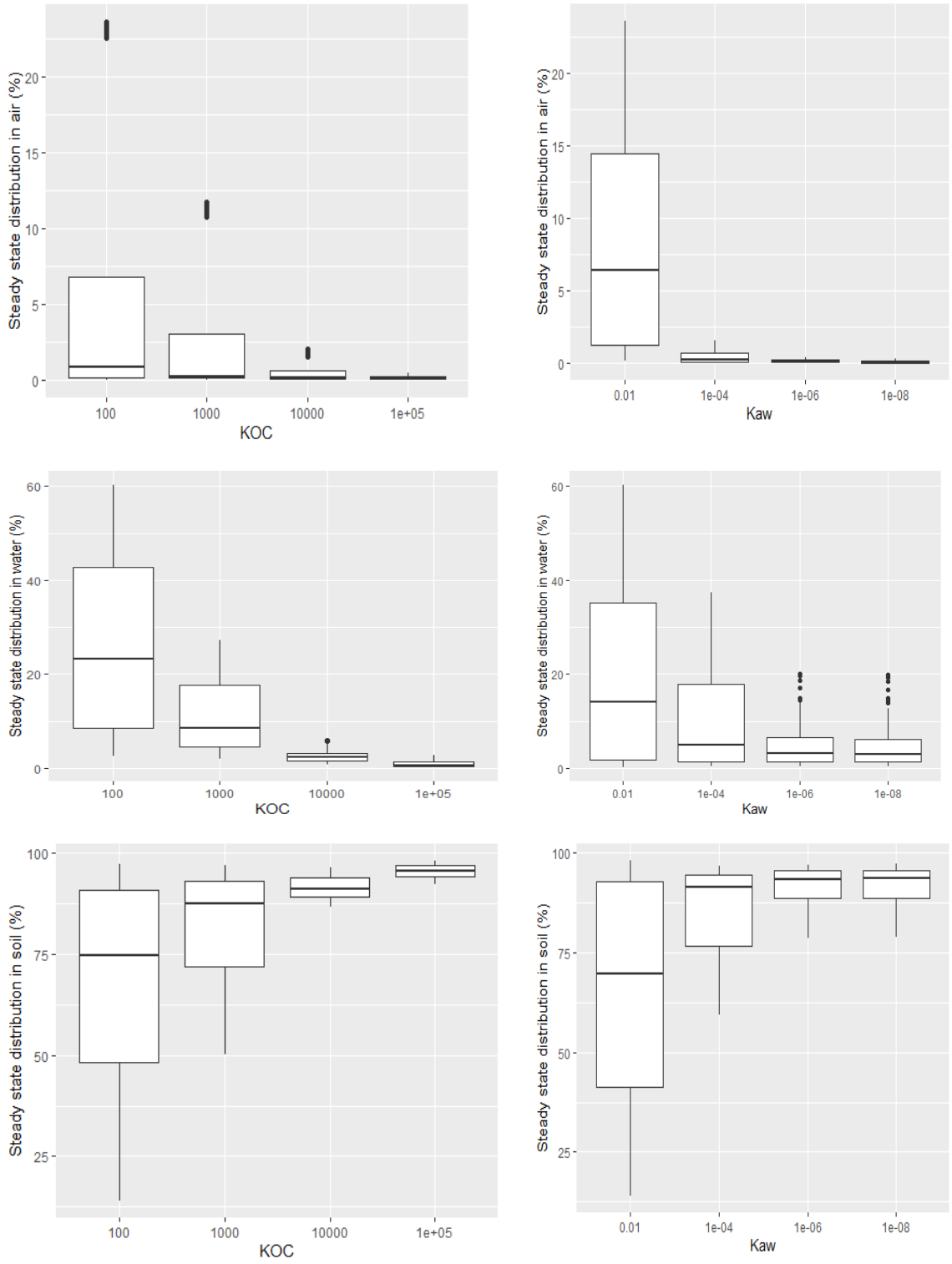



**Figure 11: Box plots of all chosen parameters in relation to steady state distribution**

We found a statistically-significant difference ($p < 0.001$) by KOC in average steady state distribution in air ($f=66.86$), water ($f=287.5$), and soil ($f=151.8$).

A Tukey post-hoc test showed that only the comparison between a KOC of 10000 and 100000 is not significant for the steady state distribution in air, water and soil.

For Kaw, there is also a statistically-significant difference ($p< 0.001$) in average steady state distribution of air ($f= 239.8$), water ($f = 84.44$) and soil ($f = 140.4$).

For average state distribution in air, no statistically-significant difference in the means of Kaw of 1e-08, 1e-06 and 1e-04 was found. For the steady state distribution in water and soil, there is no statistically-significant difference among the groups of Kaw of 1e-08 and 1e-06.

## 3.4 Difficult substances

For the analysis of difficult substances, a hypothetic difficult substance based on five single substances was used. As environmental scenario, EU regional was considered. Furthermore, as emission scenario equal distribution scenario was chosen. As it was assumed that 80% of the release to water is passing a sewage treatment the actual emission to water was reduced by all components of the difficult substance according to the sorption constant of the respective component.

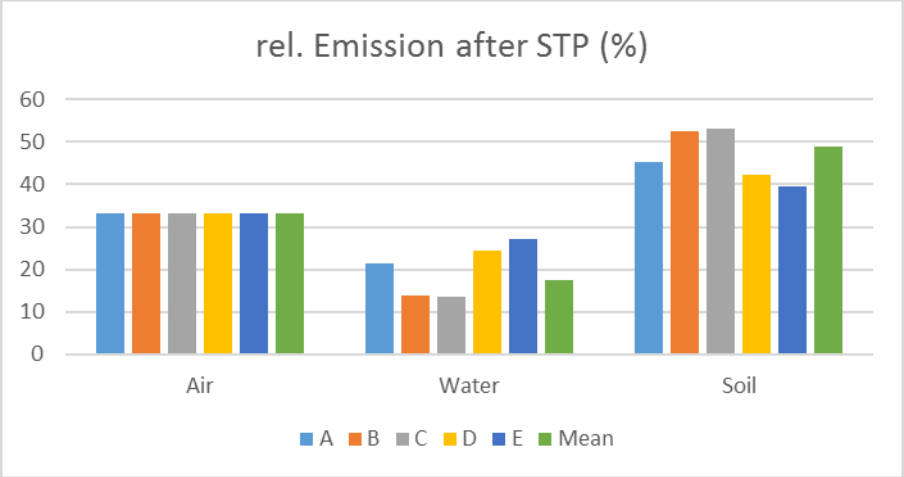



**Figure 12: Rel. emission (%) after the use of sewage treatment plant (STP) for the hypothetical single substances as well as of a mean representative of all substances**

For all five hypothetical substances, the emission to water was reduced (13% - 27%) and the emission to soil was increased accordingly (39% - 53%).

Due to the properties of the components of the mixture, the level III steady state distribution differs within the individual substances. However, all substances as well as the mean representative mainly distribute to soil (33% -99%).

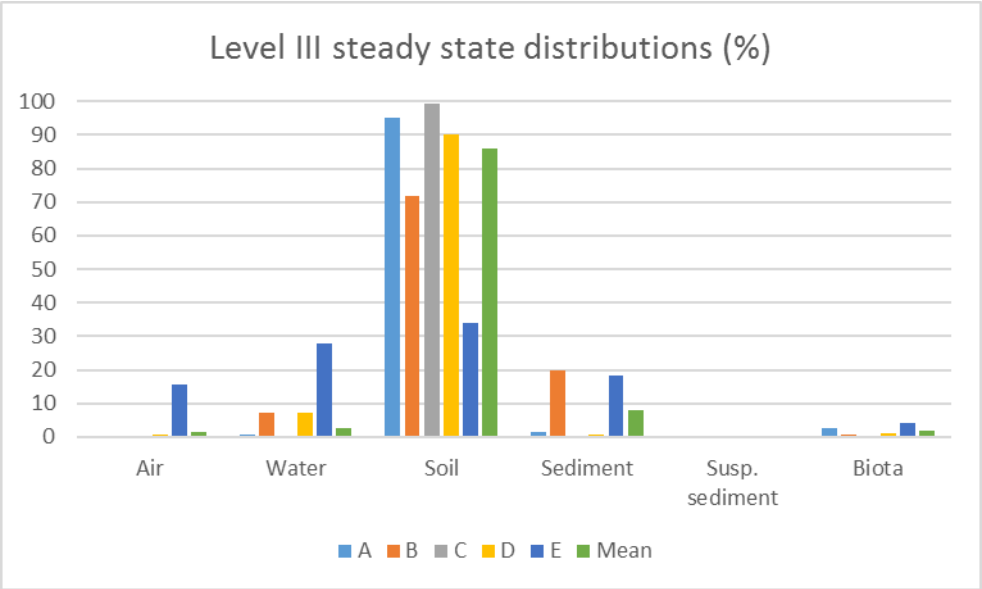



**Figure 13: Level III steady state distribution for all six compartments (%) for the hypothetical single substances as well as of a mean representative of all substances**

The resulting overall persistence based on all six compartments for all single substances and the mean substance was in a range of around 8 days for substance E as well as 2.5 years for substance A.

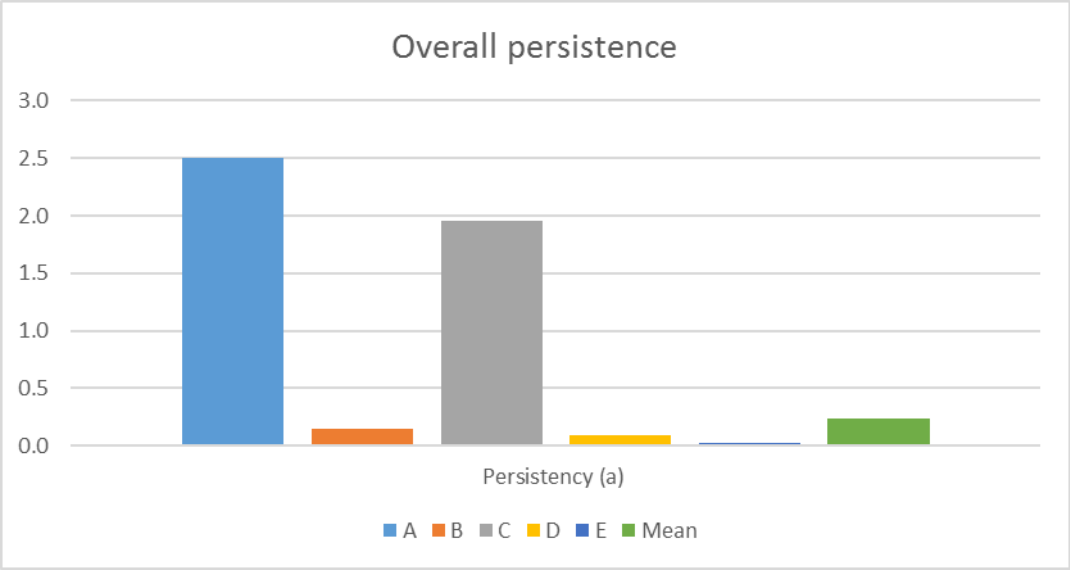



**Figure 14: Overall persistence for all six compartments (a) for the hypothetical single substances as well as of a mean representative of all substances**

*Two years recovery period is not sufficient to clear all compartments for all hypothetical single substances*

In Figure 15, the level IV solution for the hypothetical single substances can be seen. The figure is split into the six compartments. Due to the single properties, the single substances behave accumulate and

degrade differently. Not for all substances the 2 years recovery period after the 10 year emission period is sufficient to degrade completely.

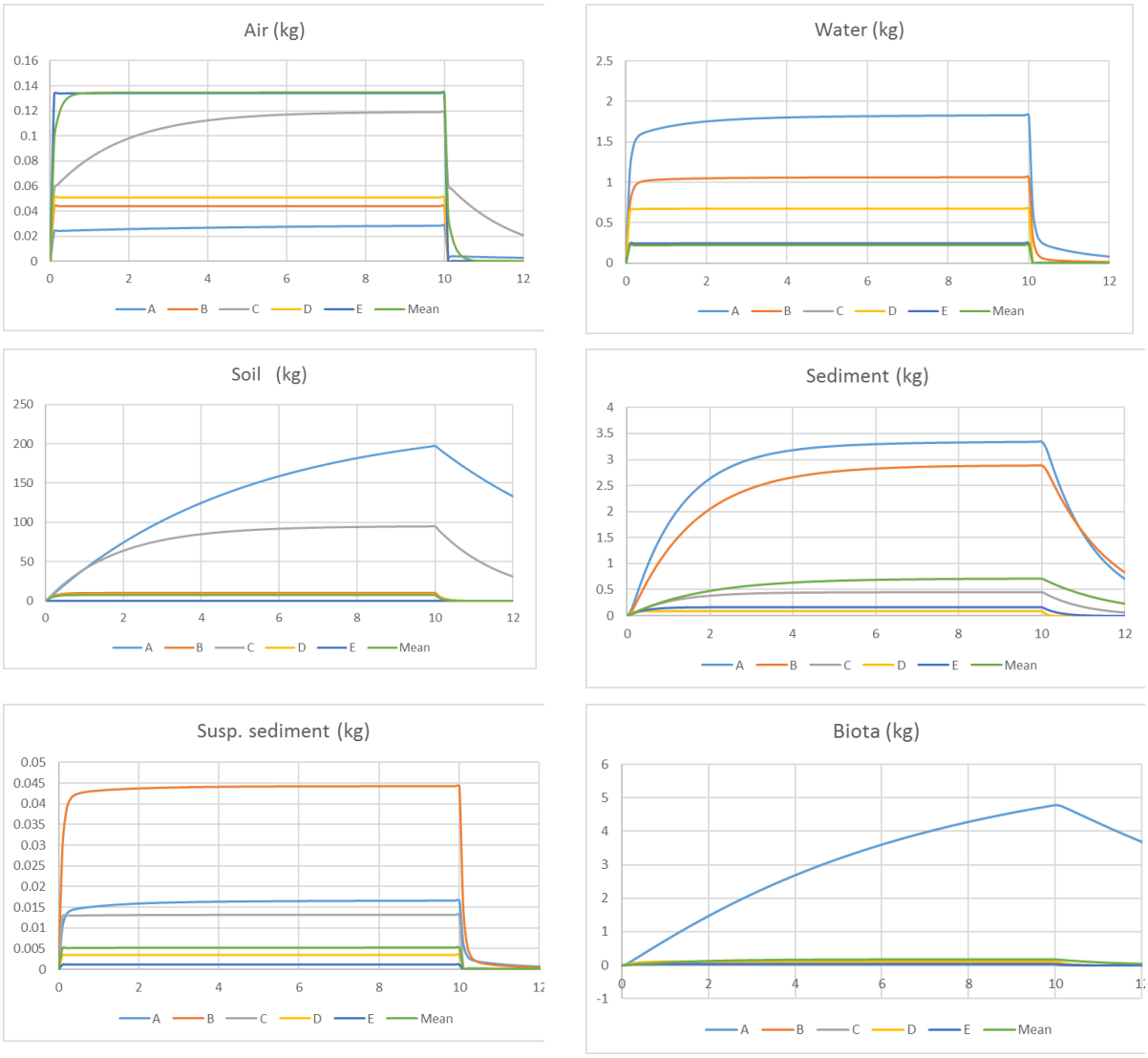



**Figure 15: Level IV solution, change of mass in time (kg), in all compartments for the hypothetical single substances as well as of a mean representative of all substances**

# 4 Conclusions

In this report several endpoints of multi-media fate modelling were available with regard to their role in persistence assessment. The results showed that most relevant are the steady-state distribution and overall persistence. Further alternative endpoints who can be helpful in the assessment are the lifetime and the clearance time. Especially when the half-lives in environmental compartment are long level IV simulations may be useful as well such as the area under the curve the reduction potential (reduction in percentage for a given time period).

The models themselves differ in environmental scale (e.g., regional, continental and global). However, model assumptions and model's philosophy are similar. Mostly, the models are level III models and

deliver only the steady state distribution and not the dynamic behaviour of the substance in the different compartments. However, level III simulations for most of the compounds are sufficient because as shown by level IV simulations steady state is reached fast within a couple of months. After this period the results of level III and level IV wouldn't differ assumed the same (constant) emission scenario is used. However, steady state will not be reached within a manageable number of time (e.g., 10 years) if the half-lives of the compound are extremely low. It is demonstrated that a level IV simulation over 10 years significantly differs from respective level III results for dechlorane plus with assumed DegT50 of 106 days in water and sediment and 350 000 days in soil.

Not only the substance, but also the emission scenario influences the steady state distribution and thus, the overall persistence.

The overall aim of this report was to perform model exercise to develop ideas in the support of persistence assessment (modelling guidance report). Thus, various model exercises as well as analyses were performed. Following conclusions could be drawn from the evaluation:

Model dimension

Especially the absence of model compartments (e.g., sediment) and differences in compartment dimensions (e.g., depth of the water compartment, land-to-water surface ratio, open/closed scenarios) lead to significant differences of the overall persistency. Because of that the model and its scenario will have a significant influence on the overall persistence.

Mode of entry

The mode of entry (e.g., water, soil) has no influence when level I or level II simulation are performed since equilibrium conditions are assumed. However, it is a key parameter in level III and level IV simulations (non-equilibrium). The evaluation showed that equal distribution represents average conditions compared to release into a single compartment (e.g., 100% soil or 100% water). The properties of the simulated substance especially the compartment specific half-lives control which single compartment represents the worst case.

Simulation level

Overall, steady state will not be reached within a manageable number of time (e.g. 10 years) if the half-lives of the compound are extremely long. However, this seems to be not relevant for persistence assessment as this is not the case for if the half-lives of the compound are lower or near the trigger values of persistence (40 d, 120 d, 180 d). In this case, steady state is reached fast within 1-2 years. After this period the results of level III and level IV wouldn't differ assumed the same (constant) release pattern is used, and the benefit of level IV simulation for persistence assessment is limited. However, it can give a better understanding of the processes to be considered in the persistence assessment.

Sewage treatment plant in the simulation

Using a sewage treatment plant (STP) to model a more realistic emission only has an influence when the substance is released to water. It is included in multi-media models to improve the fate calculation. The effect will be an increase of the emission to soil because of sludge applications. Whether this calculation leads to more conservative overall persistence depends on the half-life in soil and water. It will be more conservative if degradation is soil is lower than in the water/sediment compartment.

Model selection

The evaluation showed that model definition as the number of compartments or their dimension very much vary between models e.g.m OECD ´the Tool´ describes the global environment using three compartments whereas MUST or SimpleBox are based on six compartments. Consequently, the model selection has a significant influence on the result. For transparency the overall persistence should be

always connected with the model (and its scenario) which was used to calculate the persistence. Though models sometimes include a biota compartment it should be either completely neglected or the degradation rate set to realistic value (e.g., set to the degradation in sediment) for the calculation of overall persistence.

Sensitive substance parameters

Most sensitive parameters were dependent on the type of substance. For substances with high Pow (e.g., HBCDD) the degradation in soil was most relevant as long as the emission scenario was not extreme (e.g., emission 100% to air). The overall persistence was then found relatively stable against changes of the environmental scenario and always dominated by the degradation in soil. Other compounds remain in the environmental compartment to which they were emitted. The overall persistence of these type of compounds is dominated by the degradation rate in the initial compartment. In contrast, the overall persistence of compounds, which are distributing to all environmental compartments, is dominated by the scenario definition (e.g, soil depth, connection percentage to waste water treatment plants).

Additionally results of the sensitivity analysis with MUST with regard to the steady state distribution

- KOC influences average steady state distribution in air, water and soil significantly for KOC value of 100 and 1000
- No difference in average steady state distribution in air, water and soil comparing KOC of 10000 and 100000
- Kaw influences average steady state distribution in air, water and soil significantly for Kaw value of 0.01 and 1e-04
- No difference in average steady state distribution in air, water and soil comparing Kaw of 1e-06 and 1e-08
- No difference in average steady state distribution in air comparing1e-04, 1e-06 and 1e-08

With regard to the overall persistence following results were obtained (again MUST)

- No statistically-significant difference for DT50 air and DT50 water was found in average overall persistence was found
- For KOC only the comparison in average overall persistence between a value of 100 (mean = 0.7275) to groups of 1000 (mean = 0.8277), 10000 (mean = 0.9603), and 100000 (mean =1.0182) are statistically-significant
- For Kaw, only the comparison of average mean of groups of 0.01 (mean = 0.6029) to 1e-04 (mean = 0.9198), 1e-06 (mean = 1.0043) and 1e-06 (mean = 1.007) is statistically-significant
- However, the sensitivity analysis revealed that not only substance specific parameters are important but also environmental parameters play a major role. Thus, it is important to agree on the environmental parameters. In particular, the parameters describing the volume of the compartment are important as they influence directly the steady state distribution and thus, the overall persistence.

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# Annex A:

## 5.1 Properties of the substances considered for the sensitivity analysis

| No | Substance | Molar mass | Log Kow | Log Kaw | Henry's law constant | KOC | BCF | DT50 (air) | DT50 (water) | DT50 (soil) | DT50 (sed.) | DT50 (suspended Sed.) | DT50 (biota) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | g/mol | - | - | Pa m³/mol | L/kg | - | d | d | d | d | d | d |
| 1 | HBCDD | 641.7 | 5.63 | -3.6 | 0.75 | 175000 | 18100 | 3.2 | 1.00E+06 | 120 | 214 | 1.00E+06 | 1.00E+06 |
| 2 | D4 | 296.62 | 6.49 | 2.69 | 1.21E+06 | 1270000 | 11495 | 14 | 16.7 | 180 | 315 | 1.00E+06 | 1.00E+06 |
| 3 | Bisphenol A | 228.29 | 3.4 | -99 | 3.12E-07 | 796 | 36 | 0.13 | 15 | 3 | 30 | 1.00E+06 | 1.00E+06 |
| 4 | Dechlorane Plus | 653.73 | 9 | 1.75 | 1.30E+05 | 1.00E+08 | 55000 | 0.7 | 1.00E+06 | 350000 | 1.00E+06 | 1.00E+06 | 1.00E+06 |
| 5 | DecaBDE | 959.2 | 6.27 | -1.75 | 44 | 1590000 | 2000 | 94 | 1.00E+06 | 360 | 1.00E+06 | 1.00E+06 | 1.00E+06 |

## 5.2 Properties of hypothetical difficult substance

| Substance | Molar mass | LogKow | LogKaw (estimated from Henry) | Henry's law constant | KOC | BCF | DT50 (air) | DT50 (water) | DT50 (soil) | DT50 (sed.) | DT50 (susp. sed.) | DT50 (biota) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | g/mol | - | - | Pa m³/mol | L/kg | - | d | d | d | d | d | d |
| A | 250 | 6.1 | -4.7 | 0.0500000 | 3600 | 50000 | 0.3 | 71 | 710 | 2300 | 2300 | 2300 |
| B | 150 | 4.5 | -7.8 | 0.00004 | 17200 | 1100 | 1.2 | 50 | 25 | 250 | 250 | 250 |
| C | 140 | 5.0 | -2.7 | 5.0 | 22350 | 140 | 1.4 | 15 | 3000 | 300 | 300 | 300 |
| D | 150 | 4.0 | -6.9 | 0.0003 | 2085 | 2400 | 2.4 | 4 | 25 | 10 | 10 | 10 |
| E | 130 | 3.5 | -1.2 | 138 | 1800 | 2000 | 1.5 | 15 | 3000 | 300 | 300 | 300 |

## 5.3 Input for OECD the tool

| Chemical Name | Molar Mass (g/mol) | Log $K_{AW}$ | Log $K_{OW}$ | Half-life in air (hours) | Half-life in water (hours) | Half-life in soil (hours) |
|---|---|---|---|---|---|---|
| Bisphenol A | 228.29 | 9.881* | 3.4 | 3.12 | 360 | 72 |
| D4 | 296.62 | 2.69 | 6.49 | 336 | 400.8 | 4320 |
| DecaBDE | 959.2 | -1.75 | 6.27 | 2256 | 24000000 | 8640 |
| Dechlorane Plus | 653.73 | 1.75 | 9 | 16.8 | 24000000 | 8400000 |
| HBCDD | 641.7 | -3.6 | 5.63 | 76.8 | 24000000 | 2880 |

* estimated here from the Henry's law constant (3.12E-07 Pa m³/mol)

## 5.4 Model procedure implemented in MUST

The following procedure is implemented in MUST for the calculation of the mass/concentration in environmental media and biota. The index $i = 1, \cdots, 6$ corresponds to the considered environmental compartment: air ($i = 1$), water ($i = 2$), soil ($i = 3$), sediment ($i = 4$), suspended sediment ($i = 5$) and biota ($i = 6$).

1. Load the environmental data, the properties of the substance as well as the emission profile
2. Transform emission profile from kg per year to mole per hour
3. Set constants (transfer coefficients)
4. Calculate degradation constants in per hour for each compartment

$$k_i = \frac{1}{24} \cdot \frac{\log(2)}{DT50_i} \text{ for } i = 1, \cdots, 6$$

$k_i$ Degradation constants in 1/h for each compartment ($i = 1, \cdots, 6$)

$DT50_i$ Degradation half-life in d for each compartment ($i = 1, \cdots, 6$) (substance specific)

5. Calculate additional transfer rates for air, water and suspended sediment $k_i^*$, $i = 1,2,5$, based on residence time $\tau_i$ in 1/h

$$k_i^* = \frac{1}{\tau_i \cdot 24} \text{ for } i = 1,2,5$$

$k_i^*$ additional transfer rates in 1/h for air, water and susp. sediment ($i = 1,2,5$)

$\tau_i$ residence time in 1/h

6. Calculate the "fugacity capacity" $Z$ in mol/(m³ Pa) (quantifies the capacity of a phase to dissolve or sorb a chemical):

$$Z_1 = \frac{1}{R \cdot T},$$
$$Z_2 = \frac{1}{H},$$
$$Z_i = Z_2 \cdot K_{oc} \cdot \frac{f_{oc_i}}{100} \cdot \rho_i \text{ for } i = 3,4,5\ ,$$
$$Z_6 = Z_2 \cdot BCF \cdot \rho_6$$

$Z_i$ fugacity capacity in mol/(m³ Pa) for each compartment ($i = 1, \cdots, 6$)

$R$ Gas constant 8.314 J/(mol*K)

$H$ Henry constant (substance specific)

$K_{oc}$ organic carbon to water partition coefficient (substance specific)

$f_{oc_i}$ fraction of organic carbon in soil ($i = 3$), sediment ($i = 4$), susp. sediment ($i = 5$) in %

$\rho_i$ Density in kg/L of soil ($i = 3$), sediment ($i = 4$), susp. sediment ($i = 5$) and biota ($i = 6$)

$BCF$ Bioconcentration factor (substance specific)

7. Calculate of the volume $V$ of compartments in m³ (quantifies the capacity of a phase to dissolve or sorb a chemical):

$$V_1 = 1000000 \cdot A \cdot h \cdot 1000, V_2 = 1000000 \cdot A \cdot d_2 \cdot \frac{p_2}{100},$$
$$V_3 = 1000000 \cdot A \cdot \frac{d_3}{100} \cdot \left(\frac{100 - p_2}{100}\right),$$
$$V_4 = 1000000 \cdot A \cdot \frac{d_4}{100} \cdot \frac{p_2}{100}$$

$$V_i = V_2 \cdot \frac{p_i}{1000000} \text{for } i = 5{,}6$$

| | |
|---|---|
| $V_i$ | Volume in m³ of each compartment ($i = 1, \cdots, 6$) |
| $A$ | Area in km² (location specific) |
| $H$ | Height of atmosphere in km |
| $d_i$ | Depth of water in m ($i = 2$), soil in cm ($i = 3$), sediment in cm ($i = 4$) |
| $p_i$ | Fraction of water ($i = 2$), susp. sediment ($i = 5$) and biota ($i = 6$) in % |

8. Calculate of areas between compartments in m²

| | | |
|---|---|---|
| a) | Air and water | $A_{12} = A_{21} = 1000000 \cdot A \cdot \frac{p_2}{100}$ |
| b) | Air and soil | $A_{13} = A_{31} = 1000000 \cdot A \cdot \left(\frac{100-p_2}{100}\right)$ |
| c) | Water and sediment | $A_{24} = A_{42} = 1000000 \cdot A \cdot \frac{p_2}{100}$ |
| d) | Water and susp. sediment (assumed diameter of susp. particle: 0.1 mm) | $A_{25} = A_{52} = 6 \cdot \frac{V_5}{0.0001}$ |
| e) | Water and biota (assumed diameter of biota: 1 cm) | $A_{26} = A_{62} = 6 \cdot \frac{V_5}{0.01}$ |

| | |
|---|---|
| $V_i$ | Volume in m³ of each compartment ($i = 1, \cdots, 6$) |
| $A$ | Area in km² (location specific) |
| $p_i$ | Fraction of water ($i = 2$), susp. sediment ($i = 5$) and biota ($i = 6$) in % |

9. Interpolate linearly the emission for each time point and for each compartment
10. Calculate modified emission values for water and soil (sewage treatment plant)

$$E_2(t) = \overline{E_2}(t) - E_2(t) \cdot \frac{f_{STP}}{100} \cdot \frac{f_{sl}}{100},$$

$$E_3(t) = \overline{E_3}(t) + E_2(t) \cdot \frac{f_{STP}}{100} \cdot \frac{f_{sl}}{100},$$

| | |
|---|---|
| $t$ | Time (hour) |
| $f_{STP}$ | average connection fraction to sewage treatment plant (STP) (location specific) in % |
| $f_{sl}$ | Fraction of sludge (substance specific, calculated via SimpleTreat model) in % |
| $E_i(t)$ | Emission in mole per hour to compartment ($i = 1, \cdots, 6$) |

11. Calculate diffusion coefficients in matrix D in mol /(h Pa), $i, j = 1, \cdots, 6$

$$D_{ij} = \frac{A_{ij}}{\frac{1}{kt_{ij}Z_i} + \frac{1}{kt_{ij}Z_j}}$$

Structure of matrix $D = \begin{pmatrix} x & * & * & 0 & 0 & 0 \\ * & x & 0 & * & * & * \\ * & 0 & x & 0 & 0 & 0 \\ 0 & * & 0 & x & 0 & 0 \\ 0 & * & 0 & 0 & x & 0 \\ 0 & * & 0 & 0 & 0 & x \end{pmatrix}$

12. Calculate Mackay III (steady state solution) by solving the linear equation system $D \cdot f = E$
13. Calculate Mackay IV (solving for each compartment the following differential equation)

$$\frac{d}{dt}(V_i \cdot Z_i \cdot f_i) = E_i(t) + \sum_j f_j \cdot D_{ji} - \sum_j f_i \cdot D_{ij} - f_i \cdot \sum_i D_i$$

14. Retransform results from mole to kg
15. Transform result

| | |
|---|---|
| $C_i = f_i \cdot Z_i$ | Concentration in (kg/m³) in each compartment ($i = 1, \cdots, 6$) |
| $M_i = C_i \cdot V_i$ | Mass in kg in each compartment ($i = 1, \cdots, 6$) |
| $Dis_i = V_i \cdot C_i \cdot \left(k_i + k_{export_i}\right)$ | Disappearance in kg of each compartment ($i = 1, \cdots, 6$) |
| $Deg_i = V_i \cdot C_i \cdot k_i$ | Degradation in kg of each compartment ($i = 1, \cdots, 6$) |
| $Exp_i = V_i \cdot C_i \cdot k_{export_i}$ | Export in kg of each compartment ($i = 1, \cdots, 6$) |

In **Table 17**, and overview of the model parameters and constants is given. It contains a description of parameter/constant is given.

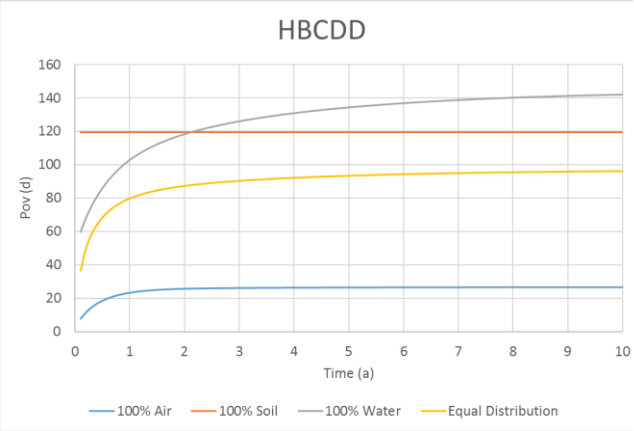
**Table 17: Overview of the model parameters and description**

| Parameter | Unit | Description |
|---|---|---|
| $A$ | km² | Area (location specific) |
| $BCF$ | - | Bioconcentration factor (substance specific) |
| $d_i$ | m resp. cm | Depth of water in m ($i = 2$), soil in cm ($i = 3$), sediment in cm ($i = 4$) |
| $DT50_i$ | d | Degradation half-life for each compartment ($i = 1, \cdots, 6$) (substance specific) |
| $E_i(t)$ | Kg | Emission in time to compartment ($i = 1, \cdots, 6$) |
| $f_i$ | Pa | Fugacity for each compartment ($i = 1, \cdots, 6$) |
| $f_{STP}$ | % | Average connection fraction to sewage treatment plant (STP) (location specific) |
| $f_{sl}$ | % | Fraction of sludge (substance specific, calculated via SimpleTreat model) |
| $f_{oc_i}$ | % | Fraction of organic carbon in soil ($i = 3$), sediment ($i = 4$), susp. sediment ($i = 5$) |
| $h$ | km | Height of atmosphere |
| $H$ | Pa m³/mol | Henry constant (substance specific) |
| $k_i$ | 1/h | Degradation constants for each compartment ($i = 1, \cdots, 6$) |
| $k_i^*$ | 1/h | Additional transfer rates for air, water and susp. sediment ($i = 1,2,5$) |
| $kt_i$ | 1/h | Transfer coefficients in 1/h used for the simulations of interphase transfer |
| $K_{oc}$ | L/kg | Organic carbon to water partition coefficient (substance specific) |
| $p_i$ | % | Fraction of water ($i = 2$), susp. sediment ($i = 5$) and biota ($i = 6$) |
| $R$ | J/(mol*K) | Gas constant 8.314 J/(mol*K) |
| $\rho_i$ | kg/L | Density of soil ($i = 3$), sediment ($i = 4$), susp. sediment ($i = 5$) and biota ($i = 6$) |
| $\tau_i$ | d | residence time |

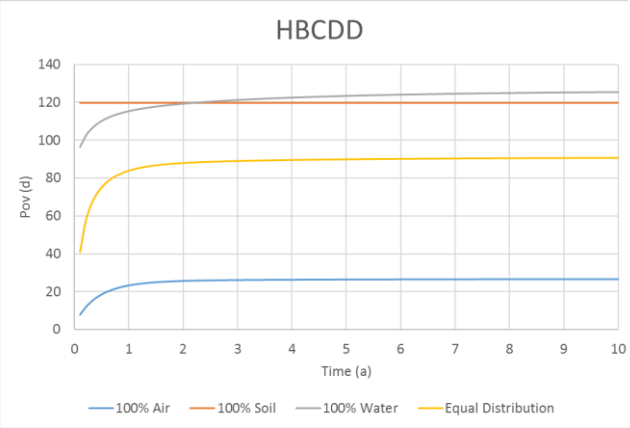
| | | |
|---|---|---|
| $t$ | | time |
| $V_i$ | m³ | Volume of each compartment ($i = 1, \cdots, 6$) |
| $Z_i$ | mol/(m³ Pa) | fugacity capacity for each compartment ($i = 1, \cdots, 6$) |

## 5.5 `Dynamic` overall persistence

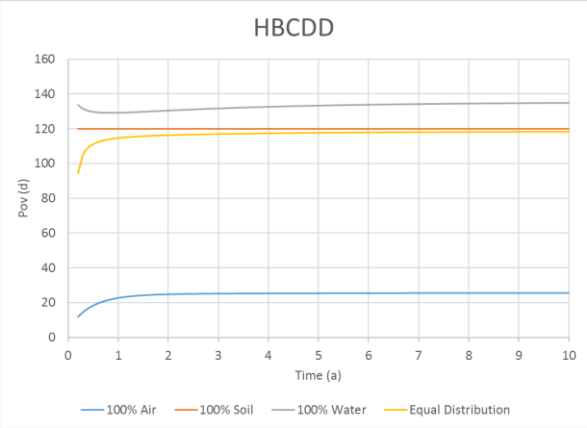
Regional – closed system – no STP




Regional – closed system – STP




Regional – open system – STP

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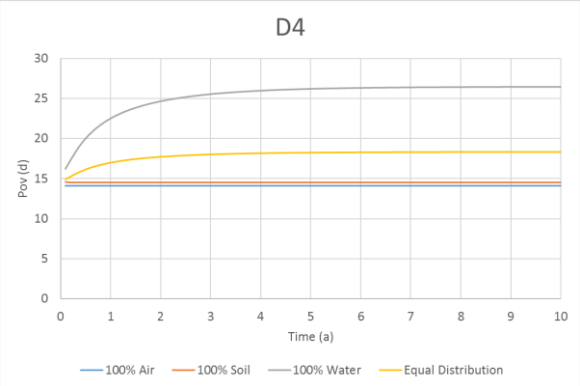
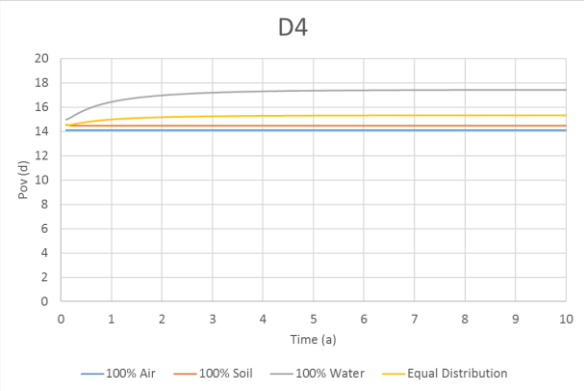



Regional – closed system – STP

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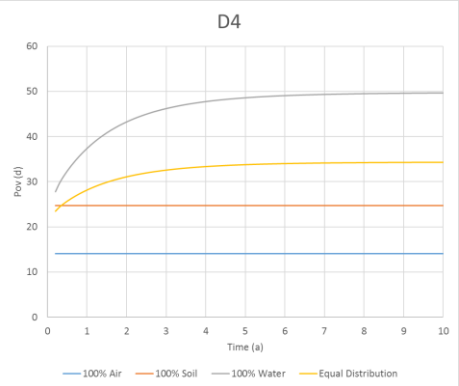

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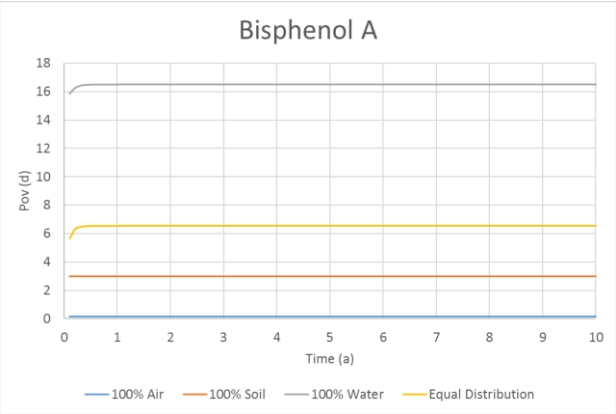
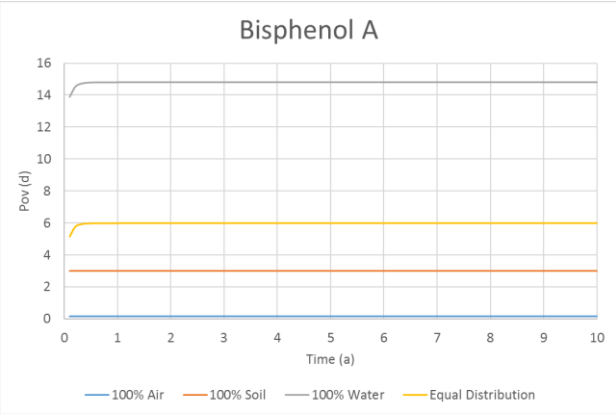
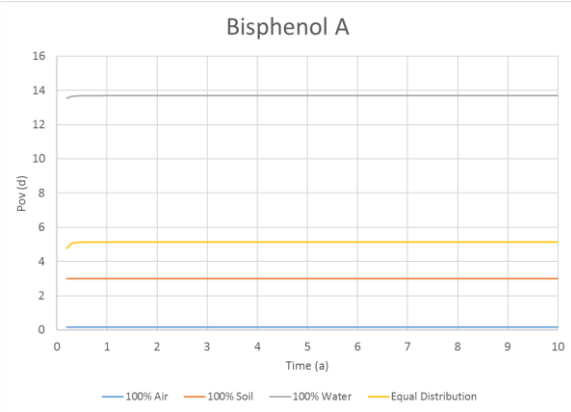


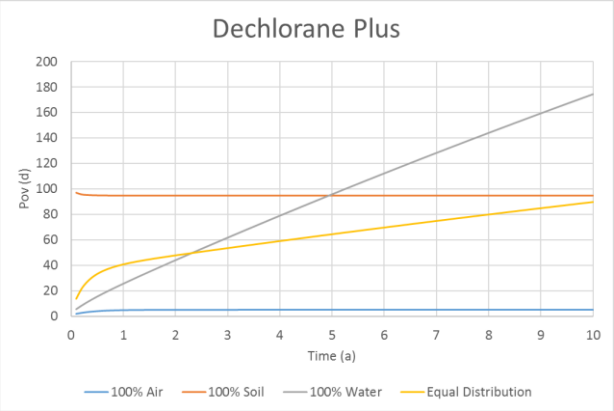

Regional – closed system – STP



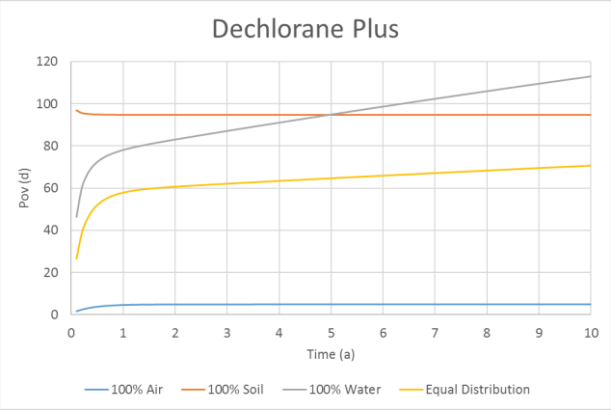

Regional – open system – STP



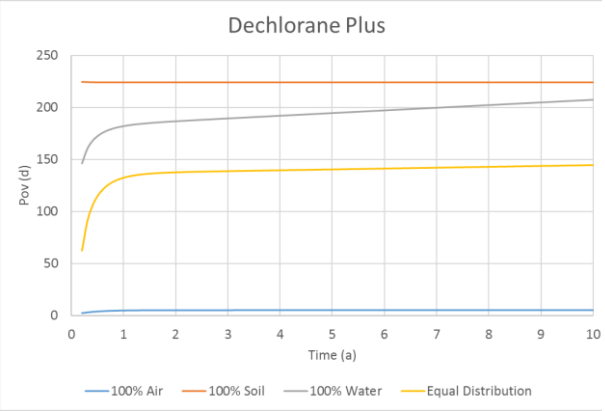

Regional – closed system – no STP



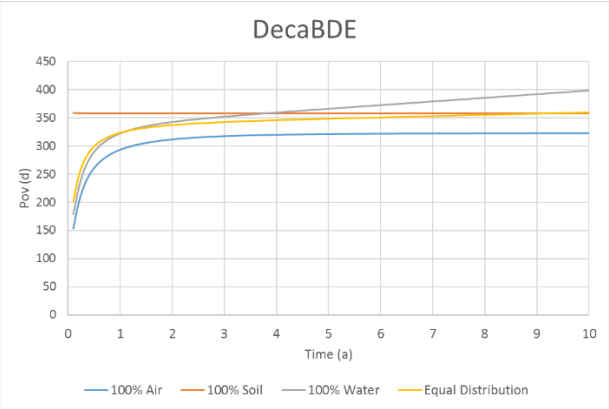

Regional – closed system – STP



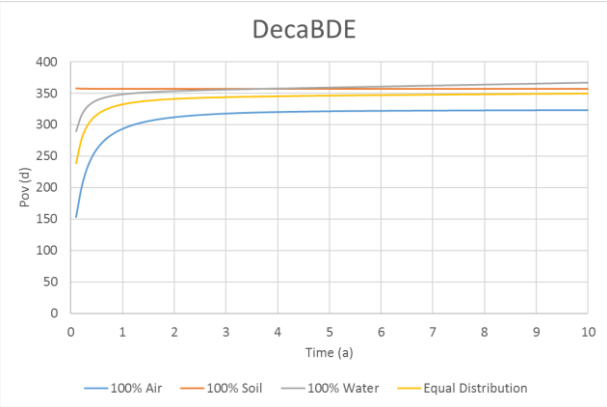

Regional – open system – STP



Regional – closed system – no STP




Regional – closed system – STP




Regional – open system – STP