

Validation of a Regional Distribution Model in Environmental Risk Assessment of Substances

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Summary

The regional distribution model SimpleBox proposed in the TGD (Technical Guidance Document) and implemented in the EUSES software (European Union System for the Evaluation of Substances) was validated. The aim of this investigation was to determine the applicability and weaknesses of the model and to make proposals for improvement. The validation was performed using the scheme set up by SCHWARTZ (2000) of which the main aspects are the division into internal and external validation, i.e. into generic and task-specific properties of the model. These two validation parts contain the scrutiny of theory, sensitivity analyses, comparison of predicted environmental concentrations with measured ones by means of scenario analyses, uncertainty analyses and comparison with alternative models. With its default values, the regional distribution model represents a generic region, and it is connected with a model which estimates indirect emissions from sewage treatment plants. These two points were also considered in this research: Different European scenarios should evaluate the effect of more extreme landscape properties on the modelled results. Furthermore, replacing the implemented sewage treatment model by a simpler one should assess whether a less complex model is able to deliver qualitatively comparable results. The examination was carried out using a set of sample substances, the characteristics of which cover a wide range of different physico-chemical properties, use patterns and emissions. These substances were employed in order to enable us to make common statements on the model's applicability. It came to light that the validation scheme used is applicable for the regional distribution model. Altogether, the model complies with its designated purpose to calculate regional background concentrations. The scrutiny of theory did not show serious errors or defects. Regarding sensitivity, it could be shown that the model contains only few parameters with a negligible influence on the results. The comparison with measured results showed a good agreement in many cases, but often it was impossible to assess the model's accuracy due to missing monitoring data. The highest deviations occur if the preliminary estimations of emissions, degradation rates and partition coefficients deliver unrealistic values. Altering the regional default parameters has a lower influence on the modelled results than replacing unrealistic substance properties by better ones, even though the differences between a northern and a southern scenario can amount to up to two orders of magnitude. Altogether, the parameter uncertainty is relatively low, but using default values can lead to high uncertainties. Statements on the model's applicability for different substance classes could not be made. The reason for this is that it is of great importance for the outcome of the distribution model used where emissions take place and the substance is primarily degraded. Generally, the model employed is a reasonable compromise between complexity and simplification. Simpler models are applicable, too, but in many cases the results can deviate considerably from the measured values. For the sewage treatment model, it could be shown that its influence on the predicted concentration is very low and a much simpler model fulfils its purpose in a similar way. It is proposed to improve the model in several ways, e.g. by including the pH/pK-correction for dissociating substances or by alternative estimations functions for partition coefficients. But the main focus for future improvements should be on the amelioration of release estimations and substance characteristics as degradation rates and partition coefficients.

Abbreviations

DL	Detection Limit
DW	Dry Weight
EC	European Commission
ECETOC	The European Centre for Ecotoxicology and Toxicology of Chemicals
EPA	Environmental Protection Agency
EU	European Union
EUSES	European Union System for the Evaluation of Substances
GIS	Geographical Information System
GREAT-ER	Geography-referenced Regional Exposure Assessment Tool for European Rivers
IC	Industry Category
(I-)TEF/Q	(International) Toxicity Equivalent Factor/Quotient
MC	Main Category
n	Number of Measured Values
NRW	North Rhine-Westphalia
OC	Organic Carbon
OoM	Order of Magnitude
PC	Physico-Chemical
PEC	Predicted Environmental Concentration
PNEC	Predicted No Effect Concentration
RCR	Risk Characterisation Ratio
STP	Sewage Treatment Plant
TGD	Technical Guidance Document
UBA	Umweltbundesamt
UC	Use Category
WWT	Wet weight

1 Introduction

Almost all human lives and all locations on earth are affected by the presence of chemical substances. However, besides its benefits, a substance usually also has a negative effect on the environment and human health. If a substance escapes into the environment, it must not exceed the concentration that leads to adverse effects. A concentration at a target is called exposure (TRAPP AND MATTHIES 1998). Hence, the environmental hazard can be the product of (environmental) exposure and (eco-)toxicological response. If the probability for the occurrence of damage is included, the term risk is used (risk: damage multiplied by the probability of occurrence). It is a common procedure to use the quotient of the *Predicted Environmental Concentration (PEC)* and the *Predicted No-Effect Concentration (PNEC)* as a measure for the risk of a substance. Basic principles on the risk assessment of substances are given by LEEUWEN AND VAN HERMENS (1995). Obviously, there are two different aspects defining risk: the toxicological properties of a substance and the predicted environmental concentrations. This work focuses on the latter aspect.

Numerous works have already dealt with the methods to estimate environmental concentrations of substances. In 1979, D. Mackay presented his concept of an ideal sample world, the *Unit World*, and simultaneously derived models simulating the behaviour of organic substances released into the environment (some exemplary publications are MACKAY 1979, MACKAY AND PATERSON 1981, MACKAY ET AL. 1985, MACKAY ET AL. 1992). The European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) discussed different modelling approaches for the estimation of environmental concentrations (ECETOC 1992) and concluded that multimedia models are of particular interest and that “environmental fate and exposure models can be powerful tools for evaluating the potential hazard of chemicals released in the environment”. In the European Union, both new substances and previously notified ones (so-called “existing” chemicals) are subject to a risk assessment. The basic principles for this procedure are laid down in the Commission Directive 93/67/EEC and the Commission Regulation (EC) No. 1488/94. But these do not contain the technical details concerning hazard assessment, dose (concentration) – response (effect) assessment, exposure estimation and risk characterisation for human health and the environment. These details are laid down in the *Technical Guidance Document (TGD)* (EC 1996A). The TGD is not legally binding. Other methods may be used if they are more appropriate, scientifically justified and compatible with the general principles contained in Directive 93/67/EEC or Regulation 1488/94. The procedures, models and parameters proposed in the TGD were implemented in a computer software system: the *European Union System for the Evaluation of Substances (EUSES)* (EC 1996B). Since the models applied in EUSES were never scrutinised with regard to their applicability and validity, the German Environmental Federal Agency (*Umweltbundesamt – UBA*) supported a project from 1997 to 2000 for the validation of exposure models and parameters. The Institute of Environmental Systems Research (*Institut für Umweltsystemforschung – USF*) of the University of Osnabrück realised this project on the basis of EUSES and the TGD. The results of this project are two doctoral theses that deal with two different aspects of the project. SCHWARTZ (2000) elaborated general strategies for the validation of exposure models, the main focus of which was on human exposure models. The present work used the validation scheme set up by Schwartz and applied it to a regional distri-

bution model proposed in the TGD and contained in EUSES. The regional distribution model is the multimedia model SimpleBox used for the exposure assessment. It estimates the concentrations to which environmental compartments (aquatic environment, terrestrial environment and air) are or may be exposed.

The objective of this work is to validate the regional distribution model SimpleBox, to show limitations in its applicability, and to make suggestions for the further improvement of the model. It is divided as follows: The validation scheme and the basic terms and procedures applied in this work are briefly presented in Chapter 2. The investigations of SCHWARTZ (2000) should be consulted for further detail. Elementary information regarding the model system EUSES and the investigated regional distribution model, the underlying concepts and theories are described in Chapter 3. It is elaborated which general aspects can be treated with this type of model and where the fundamental limitations lie. Since the validation of the model has to use concrete data, in particular the data of substances, the substances used are presented and described in Chapter 4. Since every model comprises numerous assumptions that stipulate the limitations in the model's applicability, in Chapter 5 the theory scrutinised. After having presented and elucidated the methodology, models and data, the following chapters comprise sensitivity analyses that evaluate the influence of single model parameters on the outcome (Chapter 6), a comparison with measured data in a scenario analysis (Chapter 7), a specific problem regarding the scenario analysis and the use of generic data by assessing the use of scenarios based on different European regions (Chapter 8) and the determination of uncertainties by means of probabilistic analyses (Chapter 9). Finally, the model is compared with different modelling approaches to evaluate whether the existing model could (or should) be replaced by a simpler or a more complex one (Chapter 10). In addition, an alternative sewage treatment plant (STP) model is presented in Chapter 11 to evaluate whether less complex models could also be appropriate for a given task. In the final summarising conclusion (Chapter 12), the results are assessed in common and proposals for the improvement of the model and further research suggestions are made. The extensive appendix contains tables containing most of the data used and numerous results that are too detailed and expansive to present in the work itself. It can therefore be treated as a reference for further investigations and for the reproduction of the results of the calculations produced by EUSES.

One of the most important aspects in the structure of this work is the independence of each chapter. If the reader of this work is mainly interested in one particular point of view, she/he is able to understand a certain chapter in its own right, receiving the respective conclusions and summary directly in that context. Of course, references to other chapters can be found in the relevant places so that access to more detailed explanations is always available.

2 Elements of model validation

According to SCHWARTZ (2000), a validation protocol was set up for the evaluation of the regional distribution model of EUSES. Both the model and the whole model system EUSES is described later in Section 3. Here, the general validation scheme is briefly presented. Detailed information can be found in SCHWARTZ (2000).

The use of mathematical models is an important element in the risk assessment of substances. But the use of a model must always deal with the core question of whether the model may at all be used for the specified task. A concept to answer this question is usually called validation. Since there is no consensus about which elements should be included in the validation of a model, SCHWARTZ (2000) developed a validation scheme that takes numerous existing concepts into consideration and that could be viewed as an applicable solution for pragmatic model validation.

Validation is usually understood as a comparison of modelled results with realistic values. But this is not sufficient since the comparison of, for example, predicted environmental concentrations with measured values can only be performed with existing chemicals and sufficient measured data. What if monitoring data are not available? And, naturally, for new chemicals no measured data exist at all. A validation therefore has to contain more than only this element. SCHWARTZ (2000) concluded that a holistic model evaluation has to deal with the question of quality assurance. Such a quality assurance of a model must include the model under investigation as well as the software that contains the model. Thus, the evaluation can basically be divided into two parts: validation and software evaluation. The latter is performed for EUSES in SCHWARTZ (2000); the former will be presented for the regional distribution model SimpleBox in this thesis. Thus, in the following, the validation scheme of Schwartz will be described and then applied to SimpleBox.

A model validation must generally deal with two aspects: the generic and the task-specific properties of a model. With this aim in view, he divided validation into an internal and an external part. These aspects are now described briefly. More detailed information can be found in SCHWARTZ (2000).

2.1 Internal validation

In an internal validation the inner structure of a model and the underlying theories have to be evaluated. Limitations and the model's general applicability must be elaborated. No formal methods exist to validate a conceptual model, i.e. the underlying theory. Visualisation of the complexity of a model and the representation of the single parameters and their dependencies improve our understanding of the model's behaviour and increases its transparency. It is also essential to gain an in-depth insight into the relevant environment processes and the substances in question. Since risk assessment models often extrapolate, a purely data-oriented approach is obsolete. Thus, implicit assumptions and the relevance of the implemented processes must be assessed in order to justify these extrapolations. In the following, this whole process is called scrutiny of theory.

To summarise, an internal validation consists of the following steps:

- Visualisation of the model's structure;
- Data analysis;

- Assessment of the model's concept and scientific background;
- Scrutiny of theory with verification of the implemented equations.

These steps are performed for the regional distribution model SimpleBox and are presented in this work.

2.2 External validation

An external validation deals with the model's behaviour in view of the designated task. Here, the model's outcome is of central importance. Environmental exposure models are used to predict the fate of a substance in the environment. Thus, it must extrapolate the behaviour for new substances from the knowledge available about existing chemicals. But for new substances no measured data exist to compare with the model's output. Nevertheless, it is possible to draw conclusions from the results for existing chemicals, i.e. by running the model for existing chemicals and comparing the results with measured data. These conclusions are only justified if the critical parameters which lead to a deviating (or similar) behaviour of the model are known. One way to obtain this information is to distinguish between important (key) and unimportant (redundant) parameters. SCHWARTZ (2000) suggests using the quotient of key and redundant parameters as a form of measurement. A method to separate the key parameters from the redundant ones is the sensitivity analysis which should be performed before a comparison with measured data is carried out. Theoretically, in a mathematical model the sensitivity of a parameter is the partial derivative to the output parameter. If the derivative is independent of the parameter values used, the sensitivity can be understood as a generic property of the model, and hence the sensitivity analysis could be seen as part of the internal model validation. But since the partial derivative is not easily determined in more complex models, an approximation can be used by altering each input parameter within a specified range and then comparing this alternation with the variation in the outcome. The sensitivity analysis must also be carried out using one or more defined data sets so that it can also be assigned to the external validation. Thus, sensitivity can be assigned to both parts of the model validation. Due to the application of concrete parameter values, the sensitivity analysis in this work forms part of the external validation. As a third step in an external validation, an evaluation of the uncertainties in the model's outcome should be performed. In an uncertainty analysis the variabilities and uncertainties in the input parameters are quantified and an evaluation is made of which uncertainties in the output arise from uncertainties in the input. Another important step in the external validation is the comparison of the present model with alternative models since there may be other model concepts which fit better to the designated task or fulfil the same task in a less complex way.

The external model validation therefore consists of the following parts:

- Sensitivity analysis;
- Comparison with measured concentrations (scenario analysis);
- Uncertainty analysis;
- Comparison with alternative models.

In the following, the central aspects of sensitivity, scenario and uncertainty analyses, and comparison with alternative models will be explained in further detail.

2.2.1 Sensitivity analysis

In a sensitivity analysis the impact of changes in an input parameter on the model's outcome is calculated. A sensitivity analysis can be performed before or after an uncertainty analysis. If it is implemented beforehand, it can be used to reduce costs and expenditure since a detailed investigation is only necessary for key parameters. If it is performed afterwards, it can be utilised for the verification of the preliminary work and can reveal the need for further investigation. In this work the sensitivity analysis is seen as a measure to determine the parameters that have the greatest influence on the results. According to SCHWARTZ (2000), different approaches exist to carry out sensitivity analyses. Either each parameter is examined individually (differential sensitivity analysis) or several parameters are regarded simultaneously (e.g. by Spearman rank correlations, as implemented in CrystalBall™, DECISIONEERING 1999). In this work the preferred method is the differential sensitivity analysis. This is because its results are independent of the number of parameters considered, since it always delivers the same results and it is easily reproducible without further software. This method defines a sensitivity function $S(X_i)$ to the parameter X_i by means of the partial derivative, normalised with the quotient X_i / Y .

$$S(X_i) = \frac{\partial Y}{\partial X_i} \cdot \frac{X_i}{Y}$$

As previously mentioned, calculating the partial derivative is often complicate. Thus it can be approximated with a finite difference (i.e. the denominator of the derivative is replaced by $X_i \pm n \%$).

2.2.2 Scenario analysis

One method to deal with uncertainties in the given model is to execute deterministic assessments (point estimations) for different scenarios. In the following, this method is called scenario analysis. Each scenario is based on a set of possible input data and estimations and can therefore be helpful in considering different uncertainties. Additionally, a scenario analysis can be suitable as an initial step for the following probabilistic analysis. The TGD embodies a standard scenario which serves as a conservative point estimation appropriate in the screening phase of risk assessment. It is important to establish various different scenarios that represent more realistic situations. The differences between the scenarios characterise the model's behaviour by changes in the input parameters and can be quantified in orders of magnitude (OoM). This approach is useful in various situations. It serves as a measure to screen uncertainties and to compare the input data of different levels of quality and sources. But one of the most important tasks of a scenario analysis is the comparison with measured data, i.e. assessment of the model's accuracy. Deviations from the realistic field data can reveal weaknesses in the model's applicability. However, it is often problematical to judge the quality of the model's outcome since measured data may be sparse or of low quality. Therefore, a scenario analysis must always be combined with an assessment of the data quality. Furthermore, it is not always obvious which comparative data are applicable or whether the modelled results are comparable with monitoring data at all. In order to carry out a meaningful scenario analysis, these points must be evaluated beforehand.

2.2.3 *Uncertainty analysis*

Due to their considerable importance, the main aspects of an uncertainty analysis are now presented.

When using a model, one must always consider that the outcome is not necessarily as deterministic as it may suggest. Even though for each input parameter a fixed and unique value is required, they are usually afflicted with different kinds of uncertainties. E.g., environmental parameters as compartment depths or wind speed are heterogeneous, PC data are often difficult to measure and even the model's structure can contain errors and wrong assumptions. Consequently, there cannot be a "true" model result. These uncertainties are always inherent in the model and must be taken into consideration if a model's outcome is to be interpreted. However, methodologies exist to quantify such uncertainties. In the following, methodologies and the types of uncertainty are presented briefly. For further information, refer to SCHWARTZ (2000).

Types of uncertainty

One can distinguish between two types of uncertainty: true uncertainty and variability. The term "true" must not be seen in the sense of finding the real and only uncertainty, the "truth", but in a way that such an uncertainty is only caused by missing knowledge or inadequate measuring methods. In contrast to true uncertainty, variability results from temporal and spatial heterogeneities rather from missing knowledge. A distinction between these two types of uncertainty is essential since true uncertainty can (at least theoretically) be reduced, e.g. by improving the measurements, whilst variability is an elementary part of the environment represented in the simplification of a model that cannot be reduced. Thus, true uncertainty can also be termed reducible uncertainty. In fact, many parameters are not just either truly uncertain or variable but often contain an element of both aspects. One example could be the average depth of water in the system. It is variable in time and space and is also difficult to quantify. This complicates the uncertainty analysis. Nevertheless, the mathematical treatment is similar for both kinds: consideration of probability distributions. If true uncertainty dominates the model's uncertainty more expenditure in the determination of the model's parameters could reduce this uncertainty. If variability is the main source of uncertainty the analysis represents the variability in the result. If both types are negligible the outcome is deterministic. If both types are relevant it is not practicable to give a distribution function that represents variability alone.

Another type of uncertainty in the model's outcome results from conceptual errors in the model itself due to missing scientific knowledge articulated by wrong assumptions, neglecting relevant processes or oversimplifications. This kind of uncertainty cannot be quantified and must be determined by other methods.

Probabilistic analyses

A concept to deal with parameter uncertainties is to provide each input parameter with a probability distribution function that represents true uncertainty or variability (or both, respectively). Corresponding to the given uncertainties in the input parameters, the uncertainty in the output can also be represented by a probability distribution. Varying methods exist to perform probabilistic assess-

ments, of which the Monte-Carlo analysis is the most common and wide-spread. In a Monte-Carlo simulation the outcome of the model is calculated by randomly choosing the parameters corresponding to their given probability distribution function. If this procedure is performed often enough (each step is usually called an MC-shot), it is highly probable that the outcome represents the true distribution of the result. Selection of the random number can be executed by two different methods: *Simple random sampling* and *Latin hypercube sampling*. For more complex models the *Latin hypercube sampling* is recommended, which is why it is used in this study. In a Monte-Carlo analysis the relevance of each input parameter to the model's outcome can easily be calculated by rank correlations. The input and output parameters of the single MC-shots are first stored in lists. Then the lists are sorted and the numeric rank is assigned to each value. Finally, the correlation between each pair of lists is calculated, resulting in the strength of the linear relationship between the two parameters. This relationship is a global one, i.e. it refers to the common uncertainty of each parameter in relation to any other varied one. In CrystalBall™ (DECISIONEERING 1999), the value of the rank correlation is called *sensitivity*, which is different to the term sensitivity used in this work. The correlation coefficients can also be normalised so that they represent the contribution of a parameter's uncertainty to the variance. In CrystalBall™, normalisation is carried out by dividing the square of the correlation coefficient by the square sum of all correlation coefficients.

Distribution functions

According to SCHWARTZ (2000) and following the approach of JAGER ET AL. (1997), three different probability distributions functions can be chosen for the input parameters: log-normal, triangular and uniform distribution. Since detailed data are usually missing, these types can generally characterise the uncertainty and variability of most parameters. In particular, the log-normal distribution is a typical distribution for non-negative data of physical processes. If data are missing, the triangular distribution can be seen as a conservative estimation of a log-normal distribution. Conservatism results from this function's tendency to give a higher probability to the extreme values. This distribution does not represent a realistic distribution, rather it expresses that the triangular shape is an acceptable alternative to the given data set. The uniform distribution represents a conservative estimation if only the minimal and maximal limit of a parameter are known. This distribution should be used as seldom as possible because physical processes do not show such a behaviour.

These functions were used for the selection of the probability distributions of SimpleBox' input parameters¹. A preliminary sensitivity analysis can distinguish between key and redundant parameters so that the main focus for a detailed selection of distribution functions can be set on the important input parameters. If there are sufficient data, the distribution function can be derived directly from the given data. Usually the data set is not representative or simply too small. Consequently, no obvious distribution function follows from the given data. In such a situation, expert judgement rather than statistical methods is required to select a distribution function. In most cases, log-normal distributions are chosen as standard for the parameters. This is implemented not only in

¹ Even though the focus of this work is on the regional distribution model SimpleBox (which is just a part of EUSES) more than only the direct input parameters must be chosen for an uncertainty analysis. In this work, also the input parameters of the sewage treatment model SimpleTreat were selected. For details is referred to Chapter 8.

CalTOX™ (DTSC 1993) but also in this work. Due to a lack of data for many parameters, the CalTOX™ distributions (log-normal distributions characterised by median and variation coefficients) were selected for the input parameters of SimpleBox. Distributions chosen in this work are presented and explained in the appendix (Sections A.1 and A.3). Another important aspect in dealing with uncertainties is the assumption of correlations between the input parameters. JAGER ET AL. (1997) assumed that correlations exist between PC data (water solubility and K_{OW} ; vapour pressure and K_{OW}). This assumption is plausible but the presented correlation coefficients are, however, not scientifically verified and seem to be arbitrary. The effects of possible correlations is discussed later in Section 8.

2.2.4 Comparison with alternative models

Comparison of the model under investigation with alternative models is an important element in the validation process. The comparison has to reveal whether other model concepts can fulfil the designated task better or worse. Therefore, first the general modelling concepts that could come into question must be evaluated. These can be, for example, simpler or more complex approaches. It could also be models following the same approach but with a different structure. If the basic comparable approaches are known, the present model must be compared with the alternatives. The comparison must deal with the internal structures and requirements of the different models, as well as with outcomes. Such a comparison is also possible even if no monitoring data exist if the models are applied to identical problems and the models' outcomes are compared with each other. The result of a comparison with alternatives can be a statement that the given model is too complex or that it can be improved by adding processes.

2.3 Discussion and conclusions

The division of the validation process according to SCHWARTZ (2000) into the two main parts internal and external validation is a fundamental solution to assess a model's quality entirely. It also helps to prevent misunderstandings in terminology. This is not a really new approach but a common sense of numerous existing concepts which can be applied for models in the environmental risk assessment of substances. Its target is the model's quality of which only one part is the comparison of the model's outcome with measured values.

Since for a validation it is essential to understand the model's structure and to define the basis of the evaluation, a presentation of the model's structure, its equations and the purpose is a fundamental part of the validation scheme. Basing on this starting point the generic properties of the model are investigated by the scrutiny of theory and sensitivity analyses. This is the only practicable way to evaluate errors in the model structure and implementation and to distinguish between key parameters and redundant ones. Furthermore, it helps to understand the processes represented in the model and to predict or at least to explain the model's behaviour. It also a contribution to increase the transparency, relevance and robustness of the model. Even though it does not judge directly the quality of the model's outcome, extremely high alternations in the output with only slight changes in the input indicate a low reliability of the model. If the sensitivity analysis cannot be performed analytically its results depend on the chosen data set and are not valid for different sce-

narios. However, the chosen method bases on a linearised function and is not necessarily suitable for non-linear models.

After this step the modelled results can be compared with measured values in scenario analyses. But this step can only be realised if the data basis is defined and the quality of data is evaluated beforehand. This comparison's results serve to assess the model's accuracy and to reveal uncertainties due to different input data sets. A problematical aspect within this point is the assessment of the differences between the outcome and the measured values. Depending on the model's purpose over- and underestimations have to be judged differently. Also the quality of the measured values is an important aspect in assessing the calculated values. In practice, it will often not be possible to judge the results due to insufficient monitoring data.

Another necessary point is then the performance of probabilistic uncertainty analyses. Together with the results of the sensitivity analysis and the scenario analyses it can help to assess the importance of input parameters and to find out which data should be evaluated in detail to improve the model's quality and which parameter values are less important. Additionally, the uncertainty of the model's outcome can be quantified. However, the results of an uncertainty analysis depend on the selected distribution functions for which in the EU no unified scheme exists, yet. Individual approaches are hence always required. In this work log-normal-distributions are primarily chosen because they represent natural phenomena in the most appropriate way. The alternative selection of triangular or uniform distributions if the data base is unclear is a conservative approach. Altogether, the selection of distributions is uncertain itself. To deal with these "uncertainties in the uncertainties" SCHWARTZ (2000) proposes sensitivity studies where the assumed distributions are varied and their effects on the results are assessed. But this type of uncertainty is not researched in the scientific literature, yet.

The comparison with alternative models is important to reveal whether the model's complexity is appropriate or not. Perhaps much simpler models are also able to fulfil the same purpose. On the other hand, more complex may be able to calculate more accurate or detailed results.

Altogether, the presented validation scheme of Schwartz is a suitable approach to validate the regional distribution model. Sensitivity and uncertainty analyses are important contributions to the model validation because they give a deeper insight into the model, evaluate weaknesses and so help to interpret the results. Especially for models used with a generic data set and for new substances inherent sensitivities and uncertainties are interesting because no measured values exist for the comparison of calculated and measured values.

2.4 Summary

A validation scheme which can be used for environmental distribution models is presented. This scheme was developed by SCHWARTZ (2000) and can be divided into the two aspects internal and external validation. In the internal validation the model's structure and the underlying theories and assumptions are evaluated. It treats the generic properties of the model. Here, the model's purpose is worked out, fundamental statements on the model's quality can be made and errors are revealed. The external model validation deals with the task-specific properties of the model. Sensitivity analyses detect the influence of alternations in the input on the calculated values. In scenario

analyses modelled results are compared with measured ones to assess the accuracy of the model and to evaluate the influence of different parameter sets on the results. Probabilistic analyses help to quantify the uncertainties in the outcome due to variable and uncertain input parameters. A comparison with alternative models is proposed to assess whether simpler models are sufficient or more complex models fulfil the designated task better.

3 The regional distribution model

Since the main objective of this work is to evaluate the validity of the regional distribution model SimpleBox, it is first necessary to explain the model system EUSES that contains the model SimpleBox. Furthermore, a less complex description of the underlying model concept and the mathematical background has to be elucidated. These aspects are dealt with in this section.

3.1 Description of the EUSES system

As already explained in the introduction, EUSES was developed for the first and second tiers of risk assessment for chemicals. On the one hand, EUSES calculates regional and local concentrations in the environment (*Predicted Environmental Concentration = PEC*) and intake doses. On the other hand, chronic toxicities (*Predicted No-Effect Concentration = PNEC*) are estimated. The quotient $PEC/PNEC$ characterises the risk of the substance (*Risk Characterisation Ratio = RCR*). EUSES consists of several modules and models that cover the various steps of risk assessment for a substance (Figure 1).

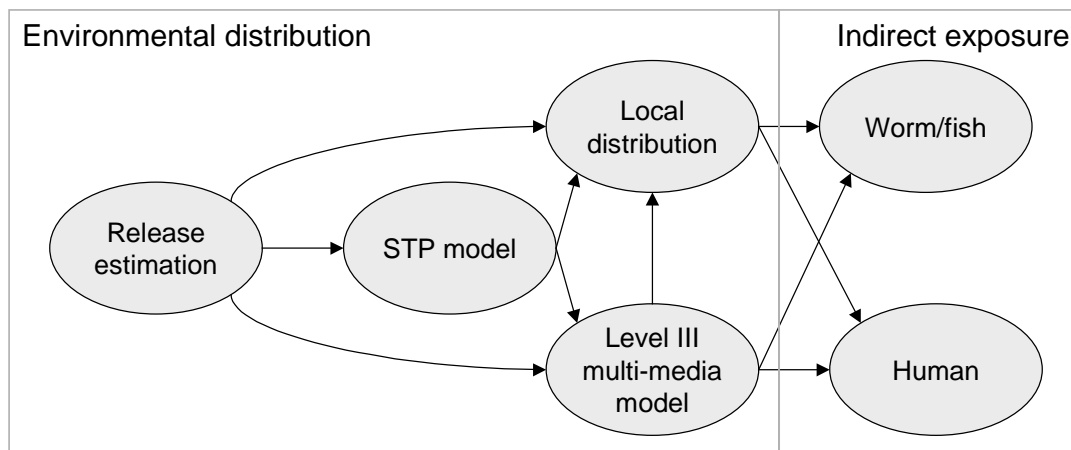


Figure 1 Models and modules in the exposition part of the TGD.

3.1.1 Data input

EUSES contains a separate module for the input of the main data to identify the substance and for its relevant physico-chemical parameters. The primary data entered are used for the estimation of secondary data, such as partition coefficients and degradation rates. This will be explained later in further detail.

3.1.2 Release estimation

Two different spatial scales are assumed: a local scale in the vicinity of a point source and a regional or continental scale, respectively, containing both point sources and diffuse sources. Since the amount of the substance released into the environment is of central importance for environmental concentrations, EUSES includes a release estimation module. Besides some physico-chemical data, it requires data about the main and industrial category, as well as production, import and export volumes. Releases are estimated by means of emission tables (A- and B-Tables). Estimations are carried out for each important life-cycle step and each use of the specific substance.

Emissions take place into the atmosphere, industrial/urban soil, surface water and waste water. While the particular emissions are added to one overall emission on the regional scale, partitioning is retained on the local scale. Here, also the duration of each emission (episode) in which the total emission of the respective life-cycle step occurs is estimated.

3.1.3 *SimpleTreat*

Another model contained in EUSES is the sewage treatment plant model *SimpleTreat*, which estimates the fate of substances in a sewage treatment plant (STP). According to the fraction of inhabitants connected to a sewer system, part of the estimated waste-water emissions are directed to the STP. Using partition coefficients (see Section 3.2.2.2) and the degradation rate for STPs, the model calculates which fractions are emitted to the atmosphere and surface water and which parts remains in the sewage sludge. In doing so, differences occur between the local and the regional/continental scale:

- Locally, for the duration of the episode estimated beforehand (and for each life-cycle step) an indirect emission into the air takes place. For this period the substance's concentration in the STP-effluent and in the sewage sludge is determined, and a PEC for micro-organisms in the STP is calculated.
- On the regional and continental scale, fractions of the substance are directed to the effluent of the STP (surface water), into the air and onto agricultural soil. Continuous emission is assumed. Life-cycle steps are not distinguished. These emissions are the so-called indirect emissions to air, surface water and agricultural soil.

3.1.4 *SimpleBox*

In order to calculate environmental distributions of a substance, the *SimpleBox* model is included in EUSES. It estimates regional and continental background concentrations in air, water, sediment and three soils. This model will be described in detail later in Section 3.2.2.

3.1.5 *Local environmental distribution*

Furthermore, a separate module exists for the calculation of local environmental concentrations. These are calculated for each relevant use and for each life-cycle step, according to the previously estimated local emissions. The model comprises different submodels that calculate concentrations in air, surface water, sediment, soils and ground water.

3.1.6 *Exposure module*

In the exposure module, exposure levels for humans, birds and predatory mammals are estimated. With this aim in view, there are two food chain models that calculate the secondary poisoning of birds and mammals and human exposure. In addition, two models that calculate consumer and workplace exposure are also implemented.

The main focus of this work is on the regional distribution model which is described in more detail in the following section.

3.2 Regional distribution and environmental concentrations

In the risk assessment of substances, the prediction of regional background concentrations is of utmost importance. Average concentrations on a larger spatial scale are estimated without local distinctions. Local concentrations can be calculated with the use of possible refinement steps and special models. Multimedia models can be used to estimate background concentrations on larger spatial scales. Each environmental compartment, e.g. water, air or soil, is assumed to be a well-mixed, homogenous box that is connected to other boxes (environmental media). Differences within a single box are disregarded. For multimedia models, the term level models has been developed, which we shall explain briefly in the following section. A good reference for more comprehensive descriptions is TRAPP AND MATTHIES (1998).

3.2.1 Level models

Level models can be categorised into four parts which differ from each other in terms of equilibrium and their consideration of reactions.

Level 1: In a Level 1 model, it is assumed that the whole mass of the investigated substance is located in the system, distributed according to its partition coefficients. There is no input or output, and no degradation. Moreover, there is no resistance between compartments. Consequently, the concentrations in the separate compartments can easily be calculated using these formulae:

$$C_1 = m / (V_1 + C_1K_{21}V_2 + \dots + C_nK_{n1}V_n)$$

$$C_i = K_{i1}C_1; i = 2, \dots, n$$

m is the mass in the system, V_i is the volume of compartment i , C_i is the concentration in compartment i and K_{ij} is the partition coefficient between compartment i and j (see Section 3.2.2). In thermodynamic equilibrium $K_{ij} = C_i/C_j$.

Level 2: As with the Level 1 model, thermodynamic equilibrium is assumed here, too. Thus, there is no resistance between compartments. The difference to the Level 1 model is the presumption of a continuous input into the system. Steady state is assumed, where the source and sinks are in equilibrium. The sinks represent the outflow out of the system and degradation in the compartments. In steady-state, therefore, $dm/dt = 0$, and the sum of the inputs corresponds to the sum of all elimination processes.

$$\Sigma I_i = \Sigma (V_i C_i \lambda_i)$$

In a state of equilibrium the following applies

$$C_1 = I / (\lambda_1 V_1 + \lambda_2 K_{21} V_2 + \dots + \lambda_n K_{n1} V_n)$$

and

$$C_i = C_1 K_{i1}; i = 2, \dots, n$$

λ_i is the total degradation rate in compartment i . First-order degradation is assumed.

Level 3: In contrast to the Level 2 model, a Level 3 model does not assume equilibrium partitioning. I.e., there are resistances between compartments. But steady state with $dm/dt = 0$ is still assumed. Advective and diffusive flows are possible between compartments. Furthermore, advective flows

into the system and out of the system also take place. With N_{ij} as the sum of flows between compartments i and j , the following mass balance results for compartment i :

$$V_i dC_i/dt = I_i + \sum_j N_{ji} C_j - V_i \lambda_i C_i$$

A linear $n \times n$ -equation system must be solved in order to calculate the concentrations. This can be done, for example, using Gaussian elimination or with the inverse of the matrix. Since in a Level 3 model no thermodynamic equilibrium is assumed, the inputs into the various compartments are of importance.

Level 4: The Level 4 model complies with the Level 3 model, but now steady state is not assumed (i.e. $dm/dt \neq 0$) and flows can be time-dependent. Additionally, initial conditions must be known. An analytical solution can be calculated for a constant or pulse input. Otherwise numerical routines, e.g. Runge-Kutta or Euler, can be applied.

3.2.2 *SimpleBox*

The regional distribution model of EUSES, entitled SimpleBox, is a Level 3 model. It consists of two nested spatial scales: the continental and the regional scale. Each scale contains the six compartments air, surface water, sediment, agricultural soil, industrial/urban soil and natural soil. Continuous emissions take place into air, water, agricultural soil and industrial/urban soil. First-order degradation is assumed in each compartment. A schematic illustration of the flows can be seen in Figure 2. The following description corresponds to the EUSES documentation (EC 1996B).

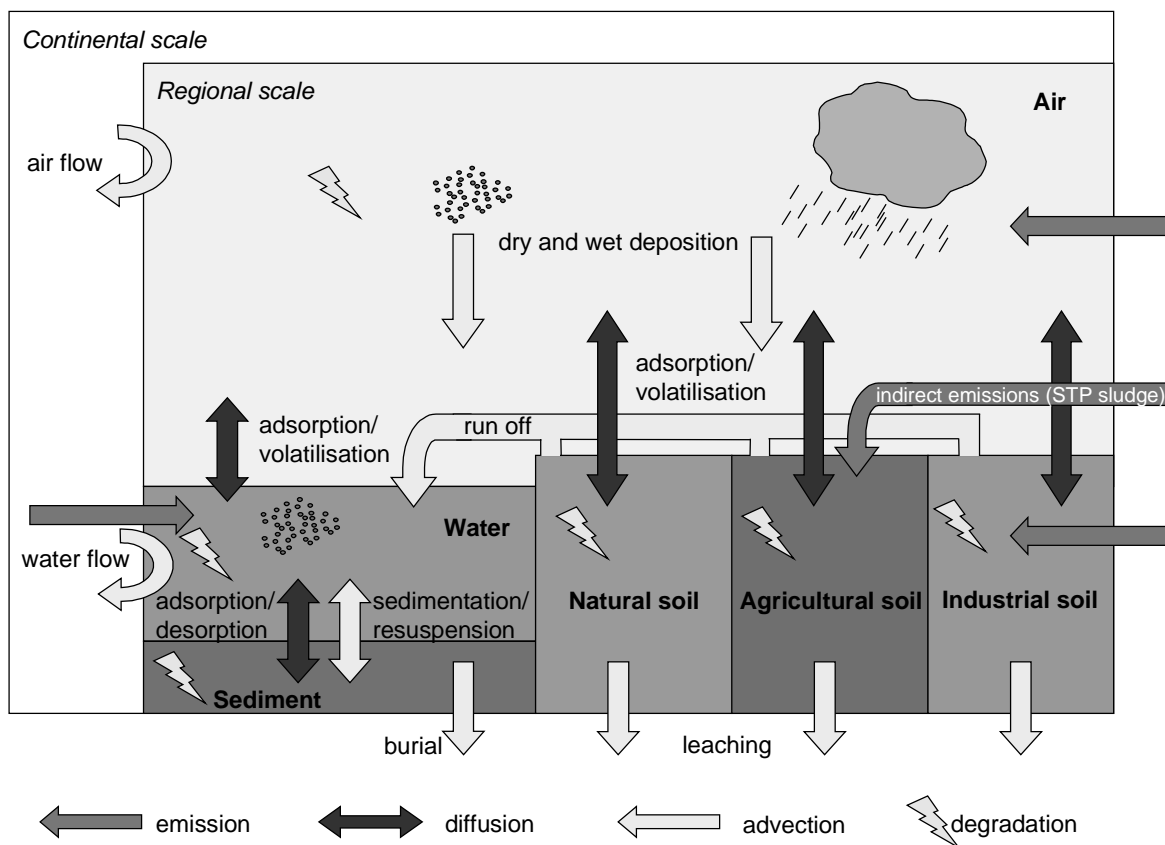


Figure 2 Structure of SimpleBox; adopted from EC (1996B).

3.2.2.1 Compartments

Atmosphere

In SimpleBox, the atmosphere consists of air, rainwater and particles. Thermodynamic equilibrium is presumed for these three components. Rainwater and particles serve as carriers of the substance for advective processes, such as deposition and washout. There are both direct and indirect emissions into the atmosphere. Diffuse exchange takes place with water and the soils. The diffusive exchange can be described using the two-film theory (TRAPP AND MATTHIES 1998). For transport through the air-water interface the total resistance is calculated by the sum of the resistances on the gas and the water side. In the case of transport via the air-soil interface, the resistances at the soil side are in parallel. Advective flow with the phase takes place out of the continental scale and between the continental and the regional scale.

Surface water

The water compartment represents the surface water in the system and contains both water and suspended matter. Both phases are assumed to be in thermodynamic equilibrium. The surface water is connected with the air and sediment by diffusive and advective exchange. The diffusive exchange is characterised by serial (to the atmosphere) and parallel (to the sediment) resistances, as already described for the atmosphere. Further processes are sedimentation and resuspension between water and sediment. The surface water receives input by direct and indirect emissions and via run-off from soil. There is also an advective exchange between the two spatial scales.

Sediment

No direct or indirect emissions take place into the sediment. The only input originates from advective and diffusive exchange with water. The sediment consists of a solid phase and a pore-water phase which are in thermodynamic equilibrium. Only the thin top layer of sediment is represented in the model. If sedimentation is higher than resuspension (positive net sedimentation) the layer is continuously filled with newly deposited material. The old sediment is buried and leaves the system.

Soils

SimpleBox contains three soils at each spatial scale: agricultural soil, industrial/urban soil and natural soil. Similar to sediment, the soils consist of three phases that are in thermodynamic equilibrium: solids, water pores and air pores. As already described above, the soils are connected to the atmosphere by advective and diffusive exchange. Outflow to water occurs by erosion from all three soils. Leaching is also assumed. The three soil types can be distinguished by the characteristics depth, organic carbon content, fractions of water and air pores and emissions. Agricultural soil receives indirect emissions via sewage sludge, industrial/urban soil receives direct emissions, and no emissions take place on natural soil.

The most important parameters of each compartment are listed in Table 1.

Table 1 Parameters characterising the compartments.

Air	Water	Sediment	Soil
<ul style="list-style-type: none"> • mixing height • area • residence time of air in the system • aerosol surface area; is used in the "Junge equation" • precipitation rate • aerosol-collection efficiency of rainwater • deposition velocity of aerosol • temperature 	<ul style="list-style-type: none"> • water depth • area • residence time of water in the system • concentration of suspended solids in water • deposition velocity of suspended particles 	<ul style="list-style-type: none"> • mixing depth • area • net sedimentation rate 	<ul style="list-style-type: none"> • mixing depth • area • fraction of rainwater infiltrating into the soil • fraction of rainwater running off to surface water • soil erosion rate

3.2.2.2 Partition coefficients

Partition coefficients are of major importance to the estimation of environmental substance distributions. As already described in the context of the level models, distribution in accordance with partition coefficients requires thermodynamic equilibrium. In such a case, the quotient of the concentrations of a substance in two considered compartments adopts a substance-specific value. This value applies to the partition coefficient. Thus, $K_{ij} = C_i/C_j$. Many partition coefficients can be determined by measurement, whilst others must be estimated by physico-chemical parameters or other partition coefficients using regression equations. EUSES requires the input of the octanol-water partition coefficient (K_{OW}) which characterises the lipophilicity of a substance. Furthermore, data on water solubility (SOL), vapour pressure (VP), melting point (TEMP_{melt}) and molecular weight (MOL) must be entered. By default, these values are used for the estimation of the requisite partition coefficients.

Gas-particle distribution

The particle-bound fraction ($F_{\text{ass}_{\text{aer}}}$) of a substance is estimated in EUSES according to the JUNGE equation (1977). Besides vapour pressure and melting point, the equation requires the surface area of aerosol particles (SURF_{aer}) and the Junge constant ($\text{CON}_{\text{junge}}$). Since the equation also requires the vapour pressure of the sub cooled liquid (VP_{L}), two cases are distinguished:

If $\text{TEMP}_{\text{melt}} \leq \text{TEMP}$ (the substance is liquid), $\text{VP}_{\text{L}} = \text{VP}$. Otherwise (the substance is solid) VP_{L} is estimated according to MACKAY (1991):

$$\text{VP}_{\text{L}} = \text{VP} / e^{6.79 \cdot (1 - \text{TEMP}_{\text{melt}}/\text{TEMP})}$$

The fraction associated to aerosol particles is then calculated using the following equation:

$$F_{\text{ass}_{\text{aer}}} = (\text{CON}_{\text{junge}} \cdot \text{SURF}_{\text{aer}}) / (\text{VP}_{\text{L}} + \text{CON}_{\text{junge}} \cdot \text{SURF}_{\text{aer}})$$

Air-water distribution

Partitioning a substance between the water phase and the gas phase is calculated using the Henry's law coefficient (HENRY). If it is not entered by the user it can be estimated using the following equation:

$$\text{HENRY} = \text{VP} \cdot \text{MOL} / \text{SOL}$$

The unit of the Henry's law coefficient is $\text{Pa} \cdot \text{m}^3/\text{mol}$. The dimensionless Henry's law coefficient, the gas-water partition coefficient (K_{AW}), can be calculated using the Henry's law coefficient, the gas-constant (R : $8.314 \text{ Pa} \cdot \text{m}^3/(\text{mol} \cdot \text{K})$) and the temperature:

$$K_{\text{AW}} = \text{HENRY} / (R \cdot \text{TEMP})$$

Solids-water distribution

Besides volatilisation, adsorption to the surface of solids is of great significance to the dispersal of the substance in the environment. Normally, it is assumed that adsorption takes place at the organic carbon of the medium. Due to their different composition, sorption is different for the single environmental compartments. Thus, normalisation to the organic carbon content is used to reduce the variances of sorption measured in the different media. Thus, the partition coefficient organic carbon-water (K_{OC}) is used. If the K_{OC} is not available it can be estimated by the K_{OW} . EUSES uses the following estimation by SABLJIC ET AL. (1995) that was derived for organic, non-ionic substances (EC 1996B):

$$K_{\text{OC}} = 1.26 \cdot K_{\text{OW}}^{0.81} / 1000 [\text{m}^3/\text{kg}]$$

The regression was calculated for hydrophobic substances with $\log K_{\text{OW}}$ from 1 to 7.5. The partition coefficient solids-water (K_{p}) in the separate compartments (soil, sediment, suspended matter) can be estimated using the K_{OC} . K_{p} always refers to the solid phase of the compartment and is the concentration of the substance adsorbed to solids. To gain a dimensionless partition coefficient between the compartment and water, we require the densities of solids ($\text{RHO}_{\text{solid}}$) as well as the fraction for solids ($F_{\text{solid}_{\text{comp}}}$), water ($F_{\text{water}_{\text{comp}}}$) and air ($F_{\text{air}_{\text{comp}}}$), and the organic carbon content ($F_{\text{oc}_{\text{comp}}}$) in the respective compartment and the partition coefficient air-water (K_{AW}). Thus, the following calculation arises for the partition coefficients solids-water in soil, sediment and suspended matter: $K_{\text{p}_{\text{comp}}} = F_{\text{oc}_{\text{comp}}} \cdot K_{\text{OC}}$.

The partition coefficients are calculated as follows:

$$K_{\text{soil-water}} = F_{\text{air}_{\text{soil}}} \cdot K_{\text{AW}} + F_{\text{water}_{\text{soil}}} + F_{\text{solid}_{\text{soil}}} \cdot K_{\text{p}_{\text{soil}}} \cdot \text{RHO}_{\text{solid}}$$

$$K_{\text{sed-water}} = F_{\text{water}_{\text{sed}}} + F_{\text{solid}_{\text{sed}}} \cdot K_{\text{p}_{\text{sed}}} \cdot \text{RHO}_{\text{solid}}$$

$$K_{\text{susp-water}} = F_{\text{water}_{\text{susp}}} + F_{\text{solid}_{\text{susp}}} \cdot K_{\text{p}_{\text{susp}}} \cdot \text{RHO}_{\text{solid}}$$

3.2.2.3 Degradation rates

In the environment, substances are subject to different biotic and abiotic transformation processes. Since degradation data are not available for all environmental media they must be extrapolated in many cases from standardised laboratory tests. In EUSES, rates for abiotic degradation (hydrolysis, photolysis) and biotic degradation (in soil, sediment, water and sewage sludge) are estimated. If no data for hydrolysis and photolysis are available, a value of 0/d is assumed. Biodegradation rates in the various media are estimated by means of the indication of biodegradability in the screening test (*readily biodegradable*; *readily biodegradable, but failing 10-d window*; *inherently biodegradable, fulfilling specific criteria*; *inherently biodegradable, not fulfilling specific criteria*; *not biodegradable*). Detailed data can be found in the appendix (Section A.2, Table 30). The total degradation rates result from the sum of the rates for abiotic and biotic degradation.

3.2.2.4 The generic region

SimpleBox is based on a generic region, the characteristics of which reflect a densely populated European average region. Consequently, the model's intention is not to estimate "real" environmental concentrations but to deliver conservative values for an overview. Nevertheless, it is possible to fit the model's parameters to a realistic environment (see also Chapter 7). The investigated region has an area of 40 000 km² and a population of 20 million inhabitants. By default, the values for the regional production and use of a chemical amount to 10% of the European mass.

The default standard values comprise all parameters of the region model, apart from the required input parameters for the substance (PC data, tonnages, categories for production and use, biodegradability in the screening test):

- number of inhabitants,
- regional area and area fractions for water and the three soils,
- mixing heights and depths,
- compartments' properties, such as densities and contents of OC, water, air and solids,
- environmental temperature and wind speed,
- transfer resistances and data for diffusive exchange, such as deposition and sedimentation rate,
- fraction connected to sewer systems and per-capita sewage flow.

A list of all parameters relevant to this investigation containing a brief description can be found in the appendix (Sections A.1 and A.3). The data are represented according to the structure described in the following section.

3.2.2.5 Data structure

The input parameters of the regional model can be divided into two groups: substance parameters and regional parameters. The substance parameters contain the three groups degradation rates, emissions and PC data. Although degradation rates and emissions are usually estimated by EUSES, a facility exists to enter them directly. By regional parameters we mean the remaining input parameters of SimpleBox. These can also be divided into two groups: volumetric parameters, process parameters and other model parameters. The volumetric parameters summarise all parameters that influence the compartments' volumes. These parameters include areas and area fractions, as well as heights and depths of the mixing zones. The process parameters include such parameters that directly describe the advective and diffusive processes. Thus, all velocities (air, precipitation, deposition, erosion, transfer coefficients), but also the fraction of precipitation running off the soil (which directly results in an advective flow from the soil to surface water) and the fraction of water flow from the continental to the regional scale, as well as the collection efficiency of aerosol particles. The remaining parameters describe the compartments' properties (densities, contents of OC, temperatures, etc.) and are called other model parameters. The two STP parameters BOD (mass of O₂-binding material) and Q_{STP} (per-capita sewage flow) also belong to this category because they can be regionally different and hence interpreted as regional parameters.

3.3 Parameters in EUSES

3.3.1 Visualisation of the parameter structure

In order to facilitate comprehension of EUSES and to gain an overview of the connections between the single parameters, a graphical representation is useful. Such a representation can be realised by depicting each parameter in the model by a box with the appropriate identifier. The relationship between the parameters can be expressed by connecting lines: If parameter A is used to calculate parameter B, a line can be drawn from box A to box B. This can be carried for each model parameter.

Different shapes and background colours can assist in the comprehension of the part a parameter plays in the whole system, i.e. which submodel it belongs to. This work was performed for the whole model system EUSES by means of the EUSES documentation (EC 1996B) and the Excel[®]-version of SimpleBox². Only the STP model SimpleTreat could not be represented in detail since only a black-box description is given in the EUSES documentation. Figure 3 shows the resulting connectivity graph.

² Because of missing documentation the Excel[®]-version of SimpleBox was the only way to elucidate the internal structure of this model.

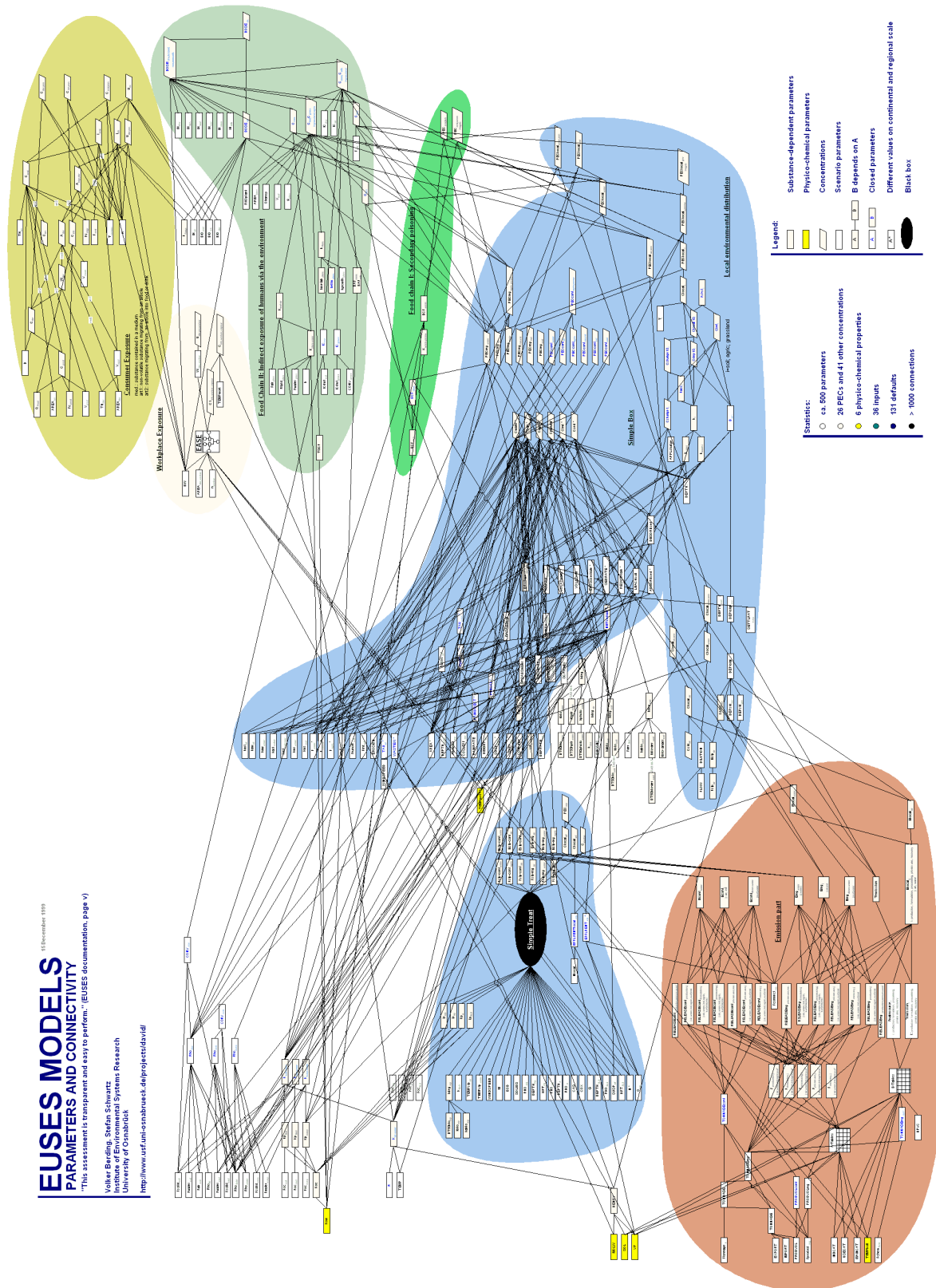


Figure 3 Parameters and connectivity in EUSES.

3.3.2 Quantification of the complexity (variety, connectivity, dimension)

Up to now, the term complexity has only been used in a descriptive and more qualitative sense. However, it is also possible to quantify the model's complexity. The most important parameters quantifying the model's complexity are the total number of elements (*variety*) and the number of

connections (*connectivity*). Additionally, models of which the parameters can have a discrete number of states the overall number of possible states can also be a measure. But since EUSES primarily consists of continuous parameters this number cannot be used as a parameter characterising complexity (in fact, complexity would then quantify infinity, which is not a constructive or useful result). However, variety and connectivity can easily be ascertained: All in all, the model system consists of more than 500 parameters and over 1 000 connections.

One further characteristic parameter to describe the model's complexity is the dimension of the variables. In this context, this term is understood as the depth in the graph, i.e. the number of intermediate steps that is needed to determine a parameter's value. Therefore, input parameters have the dimension 0, parameters calculated directly from them have the dimension 1, etc.

The highest dimension of a regional PEC is 14. Other parameters, for example, daily doses, can have higher dimensions because environmental concentrations are used as input for subsequent modules. A more detailed description of EUSES' parameter structure and its complexity can be found in BERDING ET AL. (1999A).

3.4 Purpose of models and software

The system to be investigated consists of mathematical models and the appropriate software EUSES. After the results of the previous sections, the goal is to estimate the environmental concentrations in accordance with the TGD. This shall be valid for a multitude of new and existing substances. The result is a point estimation of an environmental concentration that should not underestimate the real concentration, but which can possibly overestimate it distinctly (EC 1996A, PART I: 31-33, EC 1996B, VI-3). These conditions are called *reasonable worst cases*. Even though the system is based on a generic environment and is consequently not developed for individual spatial structures, a facility exists to adapt the default values. In doing so, an insight into individual local and regional realities is facilitated, possibly leading to more realistic estimations. With this function, the system is suitable for the first and second (refined) stage of risk assessment in the framework of the scheme proposed by the OECD (1989).

3.5 Probabilistic extension of the model

The investigation of uncertainties is a common requirement for exposure estimation and is an integral part of the quality assurance of models (see also SCHWARTZ 2000). Unfortunately, EUSES does not offer the facility to perform uncertainty analyses. Therefore, an Excel[®]-spreadsheet version of the main parts of EUSES was developed. It contains, among other things, the regional distribution model SimpleBox. Numerous calculations were carried out to demonstrate that the developed spreadsheet version delivers the same results. Moreover, sensitivity analyses for both the original EUSES and the Excel[®]-version were executed. It emerged that the results were similar enabling the equivalence of the two versions to be confirmed. Based on this version and by means of the risk analysis software CrystalBall[™] 2000 (DECISIONEERING 1999), uncertainty analyses considering most sensitive parameters were possible. For each assessment 5 000 Monte-Carlo shots were undertaken (Latin hypercube sampling). According to SCHWARTZ (2000), the median is gained with a certainty of 95% by an error of $\pm 1.4\%$. The results of the uncertainty analysis are given in Chapter 9.

3.6 Discussion and conclusions

The regional distribution model is implemented to calculate regional background concentrations, i.e. it is not able to predict the concentration of a substance geographically referenced. Therefore, the purpose of the model is not to estimate maximal environmental concentrations, but average concentrations on a larger spatial scale. If a regional model predicts elevated concentrations it is shown that for a longer period and on a large environmental section a substance can occur in high quantities. On a local scale, concentrations can be even higher. This raises the question as to why a regional model is needed if a local model delivers higher concentrations that already show the potential risk of a substance. If a local model estimates concentrations with a low risk, a regional model will not calculate higher ones (especially if, as is the case with EUSES, the local PEC is calculated by the sum of the regional PEC and the concentration is calculated directly by the local model). Or, vice versa, if a regional calculation shows that concentrations are below a certain limit, this is not necessarily the case on the local scale. Consequently (one could argue), the regional model is not needed since the real worst case can only be calculated by a local model. But this is not the whole truth. A regional model is needed, together with a local one, to give a complete overview of a substance's fate in the environment. Local models depend mainly on the estimated local emissions and assumed dilution factors. But regional models are developed to estimate fate in a multimedial environment. Thus, users of the model system should not simply compare the calculated concentrations with toxicity. A holistic consideration of all results must be undertaken to assess the risk of a substance over a short period of time (locally) and over a longer period (regionally). The purpose of a regional calculation is therefore not to estimate a substance's highest concentration in order to estimate maximal risk, but to give long-term concentrations and accordingly to represent the risk posed by a substance in all environmental compartments over a longer period. After the purpose of a regional model has been recognised as useful, it must be discussed whether the Level 3 approach used is adequate to fulfil this task. This shall be investigated in detail in the following sections. The assessment is based on the previously described validation scheme, i.e. on the scrutiny of theory, sensitivity and uncertainty analyses, comparison of calculated with measured data, and comparison with alternative models. Such an assessment is required to lend confidence to the model used and to determine the advantages and disadvantages of this approach. Namely, the quantitative and qualitative specification of uncertainties is needed to produce greater acceptance of the model.

3.7 Summary

The terminology used and the model system EUSES with its regional distribution model SimpleBox is briefly presented together with the objective of the model. It is also described how the regional model is embedded in the total system. SimpleBox is a Level 3 model (steady state and transfer resistances) that aims to estimate regional background concentrations in air, water, sediment and soils. It represents numerous processes and is relatively complex. Since the documentation does not describe the SimpleBox version contained in EUSES in detail, the model was re-implemented to elucidate its internal structure. Re-implementation is also the only way to perform Monte-Carlo analyses for this model.

4 Substances

For the external validation of an environmental distribution model an input data set is needed to gain a concrete output of the model. The investigated model's task is to predict the fate of a distinct substance in the environment, i.e. to calculate predicted environmental concentrations (PECs). For this, substance data are obviously required. As previously described, the regional distribution model SimpleBox requires physico-chemical data as well as information about releases and degradation properties of a substance. To cover different types of substances it is useful to select a set of sample substances with different properties that are representative for as many substance classes as possible. The quality of the model's outcome depends considerably on the quality of the input data. Thus, a main focus of model validation must be on the determination of appropriate substance data. In this chapter the selected substances are presented and their characteristic properties are described. The detailed values are listed in the appendix (Sections A.2 and A.3).

4.1 Selected substances

The selected substances are all existing chemicals that are characterised by their (more or less) ubiquitous occurrence, wide-spread emissions and relatively good availability of data. The properties considered in the selection of the different substances are lipophilicity/hydrophilicity, water solubility, volatility, extent of use and degradability. Here the relevant information on the substances' characteristics and properties as well as on the general availability data are given. Remarks on the concrete availability of PC data are made in the respective chapters (scenario analyses and comparison with measured data in Chapter 7 and uncertainty analyses in Chapter 9).

4.1.1 Polychlorinated Dibenzo-*p*-dioxins (PCDD)

PCDD are non-polar, barely water-soluble, lipophilic and highly persistent. Altogether 75 congeners exist. They have never been produced, but can result as spin-off in the production of organic chloro compounds (e.g. Pentachlorophenol) or in combustion processes (HORSTMANN AND MCLACHLAN 1994, JONES AND STEWARD 1997, NRW 1996). Due to the high toxicity of the PCDD-congeners which are chlorosubstituted in positions 2, 3, 7 and 8, these substances are well examined. The most toxic PCDD is 2,3,7,8-Tetrachloro-dibenzo-*p*-dioxin (TCDD). It serves as a reference substance for toxicity equivalents (TE) which have been introduced to assess the toxicity of the PCDD-mixtures. In this scheme each PCDD-congener receives a factor to characterise its toxicity in relation to 2,3,7,8-TCDD. Multiplying the concentration of each congener with the toxicity equivalence factor (TEF) and finally adding them results in a total toxicity of a PCDD-mixture. Different assessments for the toxicity of PCDD exist, the most common of which are the International toxicity equivalence factors (I-TEF) that are described in, e.g. BALLSCHMITER AND BACHER (1996). Since PCDDs usually occur in the form of mixtures, of which the concentrations are mostly nominated in I-TEs, it is not always obvious how high concentrations are for each congener. However, there are congener patterns which characterise specific sources (NRW 1996) so that it is at least approximately possible to reconstruct the individual concentrations from the I-TEs and emission source. The PCDD-congeners chosen for this work are the following (abbreviations in brackets): 2,3,7,8-

Cl₄CDD (TCDD), 1,2,3,7,8-Cl₅CDD (PeCDD), 1,2,3,4,7,8-Cl₆CDD (HxCDD-1), 1,2,3,6,7,8-Cl₆CDD (HxCDD-2), 1,2,3,7,8,9-Cl₆CDD (HxCDD-3), 1,2,3,4,6,7,8-Cl₇CDD (HpCDD), and Cl₈CDD (OCDD). Because of the similarity of the three Hexachloro-dioxins, in several cases only the first is used for modelling purposes. It is then simply labelled with the abbreviation HxCDD. These seven congeners are those with the highest environmental concentrations and the best data availability.

4.1.2 *Di-(2-ethylhexyl)phthalate (DEHP)*

Phthalic acid esters (also called phthalates) occur almost ubiquitously. The reason for this is that they are produced and used in great amounts in many areas, they have a tendency to bio- and geo-accumulate and a certain persistence. DEHP as a member of this class is a substance with high lipophilicity which is produced in great amounts and mainly used as a softener in plastics. It is also used as a solvent, in lubricating oils, in the production of pulp and paper, in cosmetics, as a carrier for pesticides and in the production of paints and varnish (LWA 1993).

Approximately 50 % of the amount of production of phthalates is due to DEHP. Thus, DEHP was selected as a reference substance of this group of substances. Environmental releases are estimated at 1 500 t/a in Germany (UBA 1996). Availability of data is relatively good.

4.1.3 *1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-[g]-2-benzopyrane (HHCB)*

HHCB (trading name: e.g. Galaxolide[®]) is a polycyclic musk fragrance used in perfumes, cosmetics, detergents and cleaning agents. It is mainly emitted into water by sewage treatment plants. Recently, this substance became controversial because of its high bio-accumulation potential and its ubiquitous occurrence in the aquatic environment (MRASEK 1998). Up to 2 400 t/a of HHCB is produced in Europe, and the chemical is used in many areas (PLASSCHE AND BALK 1997). Nevertheless, it has only poorly been investigated, thus rendering an entire ecological assessment is impossible. In the present work, this substance is of interest due to its occurrence in the aquatic environment (where several measurements exist) combined with its lipophilicity and emissions that can be specified by a per-capita consumption.

4.1.4 *1,2-Dichloroethane (EDC)*

1,2-Dichloroethane (or Ethylenedichloride) and other compounds of the chlorinated alkanes are primarily used in the chemical industry as solvents and bases for further syntheses, e.g. for Polyvinylchloride (PVC). Their high volatility and water solubility give these substances the ability to spread widely. Due to these properties and their high emission rates, these substances can be found ubiquitously in the environment (BUA 1995). EDC is a typical air pollutant.

4.1.5 *Benzene (BENZ)*

The simplest aromatic hydrocarbon forms the basis of numerous other aromatic compounds. It is used for many purposes in organic synthesis as an extracting, solving and cleaning agent. Furthermore, great quantities of this substance are emitted into the atmosphere during the combustion of fossil sources of energy. Benzene is readily biodegradable and is hence only slightly persistent. Due to its volatility, it is a typical air pollutant. This substance is well investigated (BUA 1998 and BUA 1993).

4.1.6 *Linear alkyl benzene sulfonates (LAS)*

LAS serves as an example of a versatile mixture of anionic surfactants that is produced in high quantities and mainly used as sodium salt in cleaning and washing detergents. It is predominantly emitted into water by sewage treatment plants and is easily degradable under aerobic conditions. Due to its slight volatility, high water solubility and use pattern, it is a typical water pollutant. LAS chiefly consists of different substituted sodium-n-dodecylbenzenesulfonates which are regarded here (IPCS 1996).

4.1.7 *Ethylendiaminetetra acetic acid (EDTA)*

Due to its chelating properties, EDTA is used in a wide range of sectors. It is especially used in washing and cleaning agents and as a bonding substance and preservative. Its versatile applicability, its good water solubility and hard degradability, even in the aerobic treatment process, lead EDTA to be seen as a xenobiotic substance with the highest concentrations in surface waters (ROSSKNECHT 1991). EDTA exposure in the environment is of importance due to its capability of mobilising heavy metals. In natural waters EDTA does not occur as an acid but mainly as an iron-complex or salt (BUA 1996). EDTA was selected as a sample substance because of its similarity to LAS (high water solubility, emission to surface and waste water), although it is only slightly degradable in the environment.

4.2 **Data availability**

Even though the selected substances are well investigated and a relatively large amount of information is obtainable for them, not every required value is always attainable. For external model validation, both monitoring data and essential substance data are required. In the following, problems that arise in the determination of substance data are discussed and gaps in the data are determined.

4.2.1 *Measured concentrations*

The validation of a regional distribution model is problematical since it calculates regional background concentrations, while measured values can represent local hot spots that are frequently much higher than the background concentrations. In the TGD (EC 1996A), the following requirements are established for regional monitoring data: "Data from a prolonged monitoring program, where seasonal fluctuations are already included, are of special interest. If available, the 90-percentile values of the measured data are of highest preference. If only maximum concentrations are reported, they should be considered as a worst-case assumption, whereas using the average concentrations can result in an underestimation of the existing risk, because temporal and/or spatial concentrations do not reflect periods and/or locations of high exposure." The TGD also suggests when measured values can be assigned to regional PECs: "If there is no spatial proximity between the sampling site and point sources of emission (e.g. from rural regions), the data represent a background concentration (PEC_{regional}) (...)."

According to these requirements, it was attempted to obtain measured values for all investigated substances and environmental media. But complete monitoring programs were only available in

very few cases; frequently, only a few measured values existed. For this reason, an assessment of the modelled results is not possible in all cases. To compare the modelled results with the measured data, the minima, median values and maxima of the obtainable data were taken. In Table 2, a list is given of which data were available for each environmental compartment. An adequate data set for all substances could not be found for any compartment. The most comprehensive data exist for dioxins, for which only concentrations in water are missing. The other substances were mainly measured in water, but rarely in each of the remaining compartments.

Table 2 Sources of monitoring data.

Substance	Water	Air	Soil	Sediment
PCDD	Estimated from air concentrations	Chloraromatenprogramm 1990 (NRW 1991)	Chloraromatenprogramm 1990 (NRW 1993)	8 measuring points on the river Rhine and river Elbe 1987 (UBA 1995)
Benzene	Single measured values from the Rhine 1990-1994 (HOWARD 1990)	Rural areas FRG 1988 (BUA 1988)	Detection limit (min.) and contaminated soil (max.) (HOWARD 1990, BUA 1988)	USA, Japan (RIPPEN 1995)
DEHP	Measured values for the Rhine between Honnef and Bingen, 4 measuring points with 83 measured values 1991-1992 (NRW 1993)	Regions with clean air 1985 (HOWARD 1990), no NRW or coherent data	German soils 1995 (DECHEMA 1995)	Rhine (NRW 1993)
EDC	Single measured values from the river Rhine 1987-1992 (BUA 1995)	Only single values (RIPPEN 1995)	Detection limit (BUA 1995)	No data
EDTA	Single measured values from the river Rhine and its tributaries 1980-1994 (BUA 1996)	No data (not volatile)	Estimated values after application of fertilisers (BUA 1996)	Japan 1979, only min. and max. (ECDIN) (EC 1999)
HHCB	30 measured values from the river Ruhr 1994/1995 (ESCHKE ET AL. 1994, ESCHKE ET AL. 1995)	5 measurements in Norway (KALLENBORN ET AL. 1999)	No data	Single measured values from the river Ruhr 1994/1995 (ESCHKE ET AL. 1994, ESCHKE ET AL. 1995)
LAS	Measured values between 1989 and 1992 for the river Rhine (BKH 1993)	No data (not volatile)	Agricultural soils after sludge application (WHO 1996, FIGGE AND SCHÖBERL 1989)	River Lippe (SCHÖBERL AND SPILKER 1996)

4.2.2 Input parameters

As described in Section 3.2.2, several substance parameters are needed to perform model calculations with EUSES: production and emissions data, as well as substance-specific parameters.

4.2.2.1 Production and emissions

EUSES contains emission tables that serve to estimate releases by means of the substance's tonnage, use and main category (UC and MC), and a number of PC parameters. This information has to be detected for each of the chosen substances. The release estimations represent a significant uncertainty for the calculation of environmental concentrations. On the one hand, it is in some cases not easy to clearly assign one UC and IC to the substance. On the other hand, the release estimations in the emission tables are not always based on realistic data, but are estimated themselves. Hence, for consistent validation it is useful to know the real releases for the year of measurement. In fact, these are obtainable for almost every selected substance. The selected UC and

IC and the releases are listed in the substance data tables in the appendix (Table 31 and Table 32 to Table 42). Since data on production and use are, of course, not available for PCDD and releases cannot be estimated, emissions have to be entered directly at the appropriate place in EUSES. The required emissions could not be gained for several substances and media for North Rhine-Westphalia, but only for Germany. In such a case they were estimated from the available emissions.

4.2.2.2 Substance-specific parameters

Physico-chemical properties and partition coefficients have to be detected for each of the substances used. The input parameters required are the molecular weight, melting and boiling point, vapour pressure, water solubility and the partition coefficient octanol/water (K_{OW}). The Henry's law coefficient and partition coefficient organic carbon/water (K_{OC}) can often be found in the literature, but are also calculated in EUSES. The investigated and calculated parameter values are presented in the appendix (Section A.2, Table 27 to Table 28). Additionally, it is possible to input substance-specific degradation rates for air, water, soil and sediment. Table 29 in appendix A.2 shows the values used. It must be taken into consideration that the degradation rates chosen for PCDD are highly uncertain since they are quite difficult to measure.

4.3 Summary

Different substances were selected for the external validation of the regional distribution model. The aim was to cover different substance classes considering lipophilicity, water solubility, vapour pressure, production and use. The chosen substances are seven congeners of the polychlorinated Dibenzo-*p*-dioxins (PCDD), DEHP, HHCb, EDTA, LAS, EDC and benzene. For use with EUSES and for validation, several substance parameters are needed (PC data, degradation data, information on production and use, emissions). Measured values are required in order to compare the modelled concentrations with realistic ones. Data availability is insufficient to perform a meaningful external validation for every substance. But all in all, the selected substances are a tolerable compromise between acceptable data availability and variety of substance properties.

5 Scrutiny of theory

The assumptions made during the process of modelling lead to limitations in the model's applicability. One example for such an implicit assumption is the steady state. Steady state renders the model time-independent and represents a situation in which the input into the system corresponds to the output. But this condition does not imply thermodynamic equilibrium. Every model contains a number of such assumptions. The objective of this section is to evaluate the underlying theories of the model. In so doing, statements on the verification of the model are made and the underlying assumptions are collected and assessed. With these results, statements about the theoretical applicability of the model can be made.

One part of the scrutiny of theory is verification, i.e. to evaluate whether the implementation of the model and its equations is performed correctly or not. Another important element is to evaluate the applicability of the model type used, i.e. in this case a Level 3 model. Furthermore, it is necessary to evaluate to which substance classes the model can be applied.

5.1 Verification

In the TGD (EC 1996A), use of a model for the estimation of regional background concentrations in all environmental compartments is claimed. They do not, however, describe exactly which model should be used. However, application of a box model with several compartments is proposed. It should contain the compartments air, water, sediment and soil. Advective and diffusive processes should be included, as well as emissions and degradation. Consequently, a Level 3 model should be used. The model SimpleBox contained in EUSES fulfils these requirements. However, model verification cannot be performed without further ado since even the EUSES documentation does not contain a detailed description of SimpleBox. Only equations for the following calculations are presented:

- regional and continental areas and number of inhabitants,
- residence time of air and water,
- net sedimentation rate,
- regional and continental sewage flow,
- dissolved concentration in surface water by the total concentration and
- pore water concentration in agricultural soil.

The SimpleBox version included in EUSES is therefore not documented. In order to perform a model verification nonetheless, SimpleBox was reimplemented using the later developed version 2.0 of the model, for which complete documentation is available (BRANDES ET AL. 1996). The more complex version 2.0, which contains additional compartments and spatial scales, was transformed to a version similar to the EUSES version of SimpleBox, using the description in the EUSES documentation.

5.1.1 Structure of the regional model

The new implementation showed that the present SimpleBox version differs in one point from the regional model proposed in the TGD: In the TGD, water flow from the continental to the regional

scale and vice versa is assumed. This flow is also mentioned in the EUSES documentation. But only the flow from the continental to the regional scale is implemented as expected. Instead of the flow back to the continental scale, a flow leaving the system is realised. The consequences for the regional concentrations are negligible. But for substances with high water solubility the continental concentrations can differ slightly.

5.1.2 Equations

Scrutiny of the equations revealed one error (EUSES documentation, p. III-42): The calculation of the residence time of air in the system is performed using the area and the wind speed, assuming a circular base. Residence time is calculated by the quotient of the area's (A) diameter (d) and the wind speed (w), hence d/w . But since the residence time at the circle's border equals zero, the *average* residence time of air in the system is lower than the presumed one. Assuming a square base, the residence time would be the same everywhere, namely \sqrt{A}/w . Examination of the appropriate equations also showed an error in the calculation of the residence time based on a circular base: Given area A, diameter d is $2\sqrt{A/\pi} = \sqrt{A \cdot 4/\pi}$. But in EUSES, residence time is calculated using the formula $\sqrt{A \cdot \pi/4}$. The correctly calculated residence time (assuming a circular base) is higher than the one used by a factor of 1.27. Besides this, residence time calculated with the formula used is even lower than a residence time that would result in the assumption of a square base ($A \cdot \pi/4 < A$). Thus, the incorrect implementation of a theoretical overestimation results in an underestimation.

5.2 Applicability of the Level 3 model

The regional distribution model SimpleBox applied in EUSES is a Level 3 model. I.e., steady state is assumed but not thermodynamic equilibrium. Furthermore, there is a constant input into the several compartments, as well as sinks in the form of advective and diffusive flow and (pseudo-) first-order degradation. In comparison to a Level 2 model (in which steady state, thermodynamic equilibrium, sources and sinks are assumed) the data requirement of a Level 3 model is much higher. But its advantage is the facility to define the emission compartment. The estimation of transfer resistances is problematical, especially between soil and air. Because of the division into homogeneous compartments, the assumption of complete mixing and steady state, both Level 3 and Level 2 models are suitable to estimate environmental concentrations in larger spatial scales, i.e. regional background concentrations. Assuming steady state is always problematic because it is difficult to decide whether or not it has already been reached.

Compared to the local and global scale, use of a regional scale is more sophisticated. On a local scale, physical processes, such as advection, dispersion, mixing and dilution, usually predominate. In most cases, typical local models refer only to one environmental medium. Global models serve to calculate the substance's behaviour on a large spatial scale. The most important processes on this scale are equilibrium distribution, degradation and diffusive exchange. Both local and global models neglect numerous processes and hence have a clear number of equations and parameters.

Regional models lie between these two scales and consequently have to take all relevant environmental processes and factors into consideration. These, however, are usually difficult to quantify. According to their structure, regional distribution models are suitable for substances that are emitted diffusely or by a large number of point sources. The calculations are based on a region with defined borders and characteristics, such as, e.g. land use or climatic conditions. But the properties of this region do not necessarily have to represent a concrete region. Depending on the model's purpose, for example, a generic region could be the basis of the calculation, as is the case with EUSES. In such a case, calculated concentrations do not have to correspond to measured values. But in principle, this is only a question of choosing the model's parameter values. It does not affect the fundamental facility to use a concrete region. However, use of realistic values on a regional scale does not lead to a spatial reference within the compartment. The compartments are well mixed and do not contain an inner structure. For both air and water, this simplification is not too problematic since mixing is achieved relatively quickly, since the phases themselves move. But for soil, complete mixing can hardly be assumed. Furthermore, soil itself is a very heterogeneous compartment which contradicts the assumption of homogeneity. Thus, the values calculated for soil in particular are subject to high uncertainties.

5.3 Validity for substance classes

Applicability of a model is not only influenced by the immanent model properties but also depends on the properties of the investigated substance. SimpleBox requires data for water solubility, vapour pressure, molecular weight and K_{OW} , as well as biodegradability. Moreover, emissions must be quantifiable. This is usually done using estimations that employ tonnages and information on production and use of the substance. Consequently, estimation is only possible for substances for which these data are available. Thus, EUSES is, e.g. by default not applicable for dioxins since they were never intentionally produced. But thanks to the function allowing emissions to be entered directly, the regional model can also be used for this substance class.

Another restriction is the regression range of the used estimation of K_{OC} from K_{OW} with the regression equation of SABLJIC ET AL. (1995). It is only valid for (hydrophobic) substances with a $\log K_{OW}$ of between 1 and 7.5 (EC 1996B). Thus, regarding the substances under investigation, the regression cannot be applied for EDTA ($\log K_{OW}$: -3.34) and the higher chlorinated PCDD ($\log K_{OW}$ for HxCDD: 7.8). The equation should also not be used with LAS because this substance is hydrophilic. If the regression is nevertheless used, restrictions must be considered assessing the results, especially for concentrations in soil and sediment.

SimpleBox does not consider dissociation for the estimation of environmental concentrations. Since ions are hydrophilic, the values for K_d and K_{OW} are influenced by the pH-value of the medium if the substance dissociates. Consequently, the partition coefficients of dissociating substances can only be used for the neutral fraction. The model is also not applicable for metals because the regressions used for the distribution coefficients are based on organic compounds. Likewise, it is not possible to apply this model for mixtures of substances because it is impossible to determine unique substance properties. All results on the assessment of applicability of the regional distribution model are listed in Table 3.

Table 3 Assessment of assumptions in calculating regional background concentrations.

Assumption	Assessment
1. All compartments are homogeneous and completely mixed.	For atmosphere and water, homogeneity and complete mixing may be assumed although the soil is very heterogeneous. This can lead to uncertainties. E.g., elimination processes can be very different for the single soil layers. It is also difficult to quantify the compartments' properties because they represent a spatial and temporal average value which is usually difficult to determine and has to be estimated.
2. A steady state is assumed.	Steady-state may only be assumed on larger spatial scales. The question of whether and when this occurs is difficult to answer and depends significantly on the substance under investigation.
3. There are transfer resistances between the compartments.	Thermodynamic equilibrium can only be assumed on very small spatial scales. Thus, the assumption of transfer resistances as well as diffusive and advective exchanges between the compartments is sensible. However, quantification of these processes is often difficult and afflicted with high uncertainties.
4. Input into the system is continuous.	The presumption of emissions of diffusive sources or numerous point-sources justifies the assumption of a continuous input into the system. But this does not apply to the soil compartment. In EUSES, a constant input of sewage sludge to agricultural soils is assumed, which can not be found in reality. This must be taken into consideration in the comparison with measured values.
5. Degradation processes are (pseudo-) first-order.	All degradation processes considered in SimpleBox expect a linear first-order degradation. This, together with the assumption of spatial and temporal constant degradation rates, represents a simplification.
6. There is no dissociation.	Ions are principally hydrophilic. Therefore, the K_d - and K_{OW} -values of dissociating substances may only be applied for the fraction of neutral molecules.
7. The investigated substance is hydrophobic and its log K_{OW} is between 1 and 7.5.	This is the valid range of the regression equation used for the estimation of the K_{OC} -value. If a substance that does not fulfil these criteria is regarded, either a different regression (if available) or a measured value must be employed. If the regression is nevertheless used, this must be considered in the assessment of the calculated environmental concentrations.
8. The investigated substance is organic.	The model was developed for organic substances and the represented processes are only valid for such substances.

5.4 Conclusions

The structure of the Level 3 model SimpleBox incorporated in EUSES applies exactly to the set requirements: calculation of regional background concentrations. When employing this model, the assumptions and restrictions of the approach should always be considered. I.e., the oversimplifications that are inevitable in modelling with a multimedia compartment model must be borne in mind if the results are to be assessed. Uncertainties arising from the difficult quantification of transfer resistances or properties of compartments and from the assumption of homogeneity of all compartments, especially of soil, must also be considered. In most cases, the errors contained in SimpleBox (faulty equations, neglect of one flow) have only a slight effect on the model's outcome. In some cases, deviations of the calculated PECs compared to those of a correct model can amount to up to approximately 30 %.

The regional distribution model cannot be applied to substances for which no emission data are available, e.g. PCB. Applicability to the selected substances is principally given because they are

organic substances that are emitted on a wide scale for which the required input data are obtainable. If we are strict with the regression ranges of the equations used for the estimation of K_{OC} from K_{OW} , these estimations must not be applied to LAS, EDTA, HxCDD, HpCDD and OCDD ($\log K_{OW}$ is lower than 1 or higher than 7.5), nor to BENZ and EDC (not hydrophobic). Since dissociation is neglected, such substances should also not be applied to SimpleBox. The reason for this neglect is not comprehensible because an appropriate pH/pKa-correction could easily be integrated into the model, especially since it is even proposed and described in the TGD (Part II, Chapter III, p. 501). However, the Level 3 concept and specifically the SimpleBox model are in principle suitable for the calculation of regional background concentrations.

5.5 Summary

In this chapter the theoretical applicability of the model is discussed. For this reason, the implicit assumptions of the model are listed and assessed. The main restrictions result from the consideration of homogenous environmental properties. It emerged that these assumptions limit the applicability of the model and lead to the calculation of unrealistic concentrations. Additionally, the ranges of regressions used in the model and the neglect of dissociation limit the model's applicability and could lead to deviations from measured concentrations and to uncertainties in the outcome. However, the Level 3 approach, and hence the SimpleBox model, are basically appropriate for the calculation of regional background concentrations.

6 Sensitivity analyses

6.1 Introduction

The assessment of local sensitivity was performed with the Excel[®]-version of EUSES. All input parameters (including the degradation rates and emissions, without the estimated partition coefficients) varied $\pm 10\%$ from the value used by means of the Tornado-Charts[®] of Crystal Ball[™]. Within this range functional plots of the regarded output parameters were generated (Figure 4) to identify non-linearities and non-monotonies. Evaluation of the plots showed that all functions are monotone and nearly linear in the 10%-range around the base case. Thus, the results can be applied for the assessment of local sensitivities.

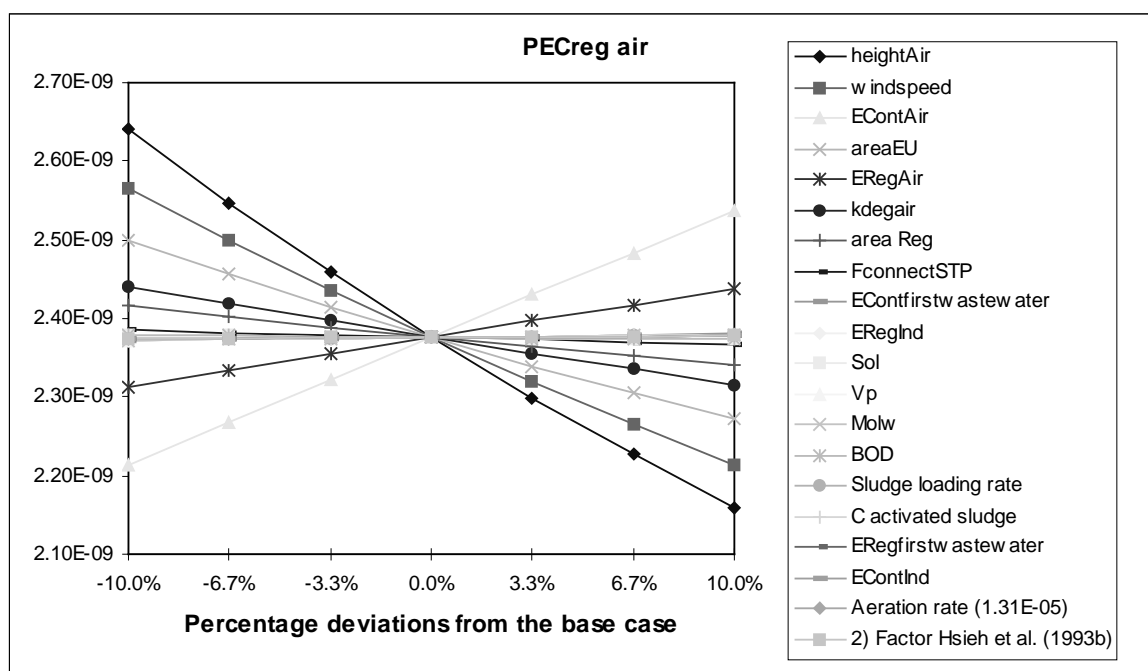


Figure 4 Example of a sensitivity graph (PECreg air of benzene).

To assess the sensitivities three classes were established (rounded absolute values):

- no or negligible sensitivity: < 0.1
- average sensitivity: ≥ 0.1 and < 0.5
- high sensitivity: ≥ 0.5

For a better generalisation of the results, the substances are divided into four classes that consider the parameters volatility, lipophilicity and degradability (Table 4).

Table 4 Substance classes.

Class	Characteristics	Substances
I	hardly volatile, very lipophilic, hardly degradable	PDCC (highly chlorinated: OCDD, HpCDD, HxCDD)
II	semi-volatile, lipophilic, hardly degradable	PCDD (slightly chlorinated: PeCDD, TCDD), HHCb, DEHP
III	volatile, slightly lipophilic, hardly degradable	BENZ, EDC
IV a	not volatile, hydrophilic, degradable	LAS
IV b	not volatile, hydrophilic, not degradable	EDTA

The sensitivity analysis is founded on the regional distribution model SimpleBox (an exact description of this model can be found in Section 3.2.2). PECs for the six regional compartments were chosen as forecast cells, i.e. PECs for air, water, sediment, agricultural soil, pore water in agricultural soil, industrial/urban soil and natural soil.

As already described in Section 3.2.2, sediment does not receive emissions directly, but only via the surface water. The calculated sensitivities are therefore usually equal for both compartments, except for parameters that directly describe sediment properties or behaviour of the substance in sediment.

In the following, sensitivities are described according to the type of input parameter. We distinguish between STP parameters, substance parameters and regional parameters. The parameter set used is described in Appendix A.5. The objective of this investigation is to make statements about the influence of each model parameter, as well as to show general coherences between the model's behaviour and the substance's properties.

Before the results are elucidated, the use of the term "sensitive" must be defined. Usually, if this term is used, the input parameter is called "sensitive" (or "not sensitive", etc.). For example, it is commonly stated that "The input parameter A is a very sensitive one" if A has a significant influence on an output parameter. But a strict sense this use of this term is incorrect since, in reality, it is the output parameter that is *sensitive* to changes in an input parameter. Consequently, an input parameter is not sensitive, but it significantly influences the output parameters. In the following, this rather uncommon use of the term "sensitivity" is intended.

6.2 Sensitivities of STP parameters

The sewage treatment plant model SimpleTreat quantifies indirect emissions into air, water and agricultural soil. These are usually much lower than direct emissions. As a result, most of the PECs are not sensitive to the STP parameters. Only emissions to agricultural soil depend completely on the STP model. However, PECs for agricultural soil are also only slightly sensitive to the STP parameters. Only concentrations of LAS in soil and sediment are sensitive to some sludge - parameters. The remaining substances only have an average or low sensitivity. The high sensitivity of LAS can be explained by the following reasons: It is primarily emitted to waste water, it is readily biodegradable and the residue is partly bound to the sewage sludge. Altering STP parameters changes the substance's behaviour in the STP and, hence, explicitly the emissions. Despite having similar characteristics, EDTA is only very slightly sensitive to STP parameters. The cause of this is its high water solubility and very low lipophilicity, combined with very low biodegradability. EDTA remains in the water phase and passes the STP without being influenced. Generally, substance concentrations are only sensitive to STP parameters if they are emitted to waste water and have a certain biodegradation potential. Sensitivity increases with increasing biodegradability. Due to the minor importance of the model for the calculated PECs combined with its very high complexity, a simpler approach could be considered. Such an alternative STP model has already been developed and is presented and discussed in Chapter 11.

6.3 Sensitivities of substance parameters

Substance parameters can be divided into three groups: degradation rates, physico-chemical data (PC data) and emissions.

6.3.1 Degradation rates

Degradation rates have a high impact on the respective PEC and also influence other PECs indirectly by, for instance, changing deposition or volatilisation amounts. A PEC's sensitivity to a degradation rate depends considerably on the absolute value of the rate itself: The higher the degradation rate, the higher the sensitivity of the respective PEC because the influence of degradation is higher compared to other processes. On the other hand, very high emissions of a substance into several compartments lead to a reduced sensitivity of the respective degradation rate since the relation of degraded mass to emitted mass (per time unit) decreases with increasing emissions. Sensitivity also increases if the mass fraction of the substance in the respective compartment increases. Thus, the influence of a degradation rate on a PEC also depends on the PC data of the substance, especially lipophilicity. Inversely, very low degradation rates in a compartment lead to raised sensitivity to the PC data. The reason for this is that the diffusive exchange or partition coefficients, respectively, dominate the concentrations while higher degradation rates increase the influence of the elimination processes.

Degradation rate in air

Alterations in the degradation rates in air influence PECs in air as well as those in the soil. The PECs of HHCB show the highest sensitivities. DEHP is also sensitive, but to a lower extent. The remaining substances are only slightly sensitive to this degradation rate. An explanation for the high sensitivity of HHCB is that this substance is only marginally emitted to air, but its fastest degradation rate is in this compartment. The most important input to the air is volatilisation from soil, which is HHCB's main emission compartment.

Degradation rate in water

PECs in water and sediment are equally sensitive to the degradation rate in water as the sediment concentration results directly from water concentrations. PECs in other compartments are not sensitive. High sensitivities only exist for LAS in water and sediment because, on the one hand, its concentrations are the highest in water and, on the other hand, the degradation rate in water is very high.

Degradation rate in sediment

The degradation rate in sediment only influences concentrations in sediment and water. The PEC of LAS in sediment has the highest sensitivity, followed by DEHP. The high sensitivity of LAS can, analogous to water, be explained by the high degradation rate in sediment and the high concentration in water. Likewise, the sensitivity of DEHP is primarily so high because of its high degradation rate in sediment and, additionally, due to its high lipophilicity, which increases the concentrations in sediment. The degradation rate of benzene is assumed to be as high as that for DEHP, but be-

cause of its lower lipophilicity it is by far less sensitive. Inversely, the degradation rate of dioxins is assumed to be relatively low (the same value for all dioxins), but because of their high lipophilicity they are still sensitive. Hence, sensitivity rises with increasing lipophilicity. For HHCB, EDC and EDTA sensitivities are weak, too, because of their low degradation rates.

Degradation rate in soil

High sensitivity to degradation rates in soil only exist for lipophilic substances (PCDD, DEHP) in soil because they have a high mass fraction in soil. Otherwise, only the PEC of LAS in air is also sensitive. The reason for this is the dependency of the concentration of LAS in air on the concentration in soil. The only input to air arises from volatilisation from this compartment (EUSES requires a vapour pressure larger than zero). Thus, alterations in the concentrations in soil directly influence the concentration in air, even though the changes for soil are only minor. This effect can also be expected for EDTA, but because of its very low degradation rate the sensitivity is also very low. Altogether, sensitivity to this degradation rate also depends considerably on the absolute value of the rate itself. Simultaneously, a certain lipophilicity must be given so that the substance occurs in relevant concentrations in soil.

6.3.2 Physico-chemical data (PC data)

Each studied substance must be characterised by its physico-chemical data. These include the K_{OW} , molecular weight, melting point and vapour pressure. These serve as a basis for various estimations and are of central importance in the calculation of concentrations.

K_{OW}

The octanol-water partition coefficient K_{OW} describes the lipophilicity of a substance and, hence, mainly affects concentrations in water and soil. Very lipophilic substances, with the exception of HHCB, are only slightly sensitive to K_{OW} in soil and sediment, but highly sensitive to PECs in water (dissolved fraction) and pore water. For HHCB, the reverse applies: PECs in soils and sediments are most sensitive, unlike those in water and pore water. This can be explained by the very low degradation rates of HHCB in soil and sediment (3 to 4 OoM lower than those assumed for PCDD) which lead to a higher distribution of the substance with regard to alterations in the K_{OW} . The absolute value of the sensitivities of PCDD concentrations in pore water and in the dissolved fraction of water rises with increasing lipophilicity. Thus, OCDD has the highest and EDTA the lowest sensitivity. Even more sensitive to changes in the K_{OW} than HHCB are the PECs of BENZ, EDC and LAS in agricultural soil. This is caused, on the one hand, by the increased partitioning towards soil and, on the other hand, by increasing emissions due to higher fractions in sewage sludge.

Molecular weight, vapour pressure and water solubility

Molecular weight, vapour pressure and water solubility are used to calculate the Henry's law constant, i.e. the partition coefficient air-water ($H = VP \cdot MOLW / SOL$). Sensitivities to these parameters have, with some exceptions, identical absolute values. However, sensitivities to water the solubility always have the opposite sign since it is in the denominator of the formula. All PECs of HHCB

show an average to high sensitivity to these three substance parameters. Volatile substances (BENZ, EDC) are sensitive to their PECs in soil. The reason for this are their very low concentrations in soil. Thus, alterations in the distribution of the substance lead to relatively low but absolutely high changes in the concentrations since emissions and lipophilicities are low. The same applies to EDTA in agricultural soil, as well as to EDTA and LAS in air because their concentrations in these compartments are very low. But the PECs of LAS in agricultural soil and of LAS and EDTA in industrial soil are almost insensitive to changes in these three parameters because emissions to these compartments overlap such marginal changes. Accordingly, LAS and EDTA are very sensitive to PECs in natural soil since no emissions take place to this compartment. The altogether high sensitivity of HHCb is due to its low degradation rates. Sensitivity is only lower in air, where degradation is the highest.

While sensitivities to molecular weight and water solubility are always the same as their absolute values, they may differ from the vapour pressure. This is because vapour pressure is also needed to calculate the fraction bound to aerosol particles (Junge-equation, Section 3.2.2.2). Substances with a "variable" fraction bound to aerosol particles, i.e. substances that are neither completely bound to particles (very low vapour pressure) nor entirely gaseous (very high vapour pressure), are hence more sensitive to changes in the vapour pressure. This applies to all PECs of TCDD, PeCDD and DEHP.

Melting point

The melting point affects the vapour pressure in the Junge-equation (and hence the fraction bound to aerosol particles) if it is higher than the environmental temperature, i.e. if the substance is solid. This only applies to PCDD and EDTA. Sensitivities of all concentrations increase with the vapour pressure value. As a result, TCDD definitely shows the highest sensitivities. Concentrations in soil are the most sensitive. These are the highest sensitivities of all input parameters.

6.3.3 Emissions

On the whole, emissions have a linear influence on the PECs if the ratio between the individual emissions is not altered. This means that if each emission is altered in the same way, the PECs also change with this factor. Since the underlying model is a Level 3 model, the emission compartment is of great importance for the predicted concentrations. In EUSES, emissions take place into air, water, wastewater and industrial soil (direct emissions) on both a continental and a region scale. The wastewater emissions are divided into a fraction that enters a sewage treatment plant and another fraction that is not treated and is consequently directly emitted to surface water. The treated wastewater causes indirect emissions to air, water and agricultural soil. These so-called indirect emissions are calculated using the STP model SimpleTreat (Section 3.1.3). Since in this analysis the direct emissions are changed separately, there is no linear influence of each single emission to the calculated concentrations.

Nevertheless, even in a Level 3 model the concentrations in several compartments are more considerably affected by the emissions to this compartment than by emissions to other compartments.

This means that, for example, in most cases emissions to water have a higher influence on PECs in water than on PECs in other compartments.

The sensitivity analyses show that continental emissions are not very important because only regional PECs are taken into account. The only exception is BENZ: For this substance the continental emissions to air are so high (40 times higher than the regional emissions instead of 10 times by default) that alterations of this parameter also lead to variations in the regional PECs because changes in the advective input have a high impact on the relatively low regional emissions. PECs sensitive to regional emissions to air are usually less sensitive to emissions to wastewater and vice versa.

Emissions to air

Emissions to air have an impact on nearly every PEC because the air compartment is in contact with any other compartment, except for sediment. But since the sediment concentrations depend greatly on the water concentrations, this compartment is (indirectly) influenced by emissions to air, too. Substances that are assumed to be not emitted to air are, of course, not sensitive. These are EDTA, LAS and HHCB. Concentrations of BENZ and EDC are also only slightly sensitive emissions to air because the advective input from the continental scale in the model is three times higher than the regional emissions. The sensitivities of concentrations in water and soil to emissions into the air depend on the direct and indirect emissions into the appropriate compartment. If input from air is the only source, sensitivity is high; otherwise it is lower.

Emissions to water and industrial/urban soil

Emissions to water and industrial/urban soil are zero or nearly zero for most of the substances, so that sensitivities are accordingly low. Only BENZ is directly emitted to surface water, which leads to a high sensitivity of the concentrations in water and sediment. Emissions to industrial/urban soil only exist for BENZ, EDC, LAS and EDTA. These emissions have a direct influence (sensitivity is 1) on the concentrations in industrial/urban soil because the other inputs (by deposition from air) are relatively low and the degradation rates in soil are slow, too. These emissions also have an effect on the concentrations of LAS and EDTA in air and in natural soil because volatilisation (even if it is quite small) is the only input path for these two substances and again deposition is the only input path for natural soil.

Emissions to waste water

Emissions to waste water cause indirect emissions to air, water and agricultural soil. Depending on the substance properties, the fate of a chemical in an STP and hence the indirect emissions are different. A PEC's sensitivity is directly affected by the amount of the indirect emissions and its respective relevance in comparison to the direct emissions. Consequently, only PECs in air from EDC, EDTA, LAS and HHCB are sensitive to wastewater emissions. However, only HHCB is highly sensitive while EDC, EDTA and LAS are slightly sensitive. HHCB's high sensitivity can be explained by the missing direct emissions to air and its relatively high volatility, which leads to a comparatively high indirect emission to air. Thus, also sensitivities of the concentrations in indus-

trial/urban and natural soils are high. Here, the sensitivity again depends on the absolute amount of the emissions: The higher the emissions, the higher the sensitivity. Although, as already mentioned, EDTA is only weakly bound to sewage sludge and is only slightly degraded, changes in the wastewater emissions lead to changes in the charge of agricultural soil because the absolute emissions, even if they are low, change in accordance with the changes in the input.

6.4 Sensitivities of regional parameters

Here, regional parameters are those parameters that are input parameters of SimpleBox, but not substance parameters. The following parameter groups can be distinguished: volumetric parameters, process parameters and other parameters. The exact description of each parameter is given in Chapter 4 and in the appendix (Sections A.1 and A.3)

6.4.1 Volumetric parameters

Volumetric parameters define the volumes of the compartments. These are the regional and continental area, the area fractions for water and soils, as well as depths and heights. The regional area forms the basis for the volume of every compartment and, hence, can have an influence on concentrations. Additionally, in a Level 3 model the exchange area between the compartments is of concern since deposition, volatilisation, adsorption between air and water and air and soils, as well as sedimentation, resuspension, adsorption and deposition between water and sediment are affected. A PEC's sensitivity to the area depends on the substance properties and emissions. An enlargement of the area causes an enlargement of the volume and, hence, to the diminution of the concentrations. At the same time, the exchange area is increased, which can cause an increase of the exchange processes so that both effects can compensate one another. Altogether, however, it is difficult to generalise every sensitivity concerning the compartment volumes because numerous different, particularly opposite, processes are affected at the same time. Whether the volume of a compartment influences the concentrations or not depends, for example, considerably on the input compartments, degradation rates, partition coefficients and other substance parameters (water solubility and vapour pressure). EDC concentrations are, for example, independent of the volumes and are only influenced by the exchange area. For LAS, it is exactly inverse. The other substances depend in different ways on volumes and areas. As can be expected, the volume of a compartment particularly influences the concentration in this compartment and to a lesser extent those in other compartments.

Generally, the volumetric parameters strongly influence the substances' concentrations. Each of the regional parameters is important, while the continental parameters do not make a remarkable difference, since only regional concentrations are regarded. The only substances of which concentrations are affected by the continental area are BENZ in air and EDTA in water and sediment. For BENZ, this can again be explained by the high continental concentrations. If the exchange processes, and accordingly the output from the system, are increased by a higher continental area, the region loses input, and the concentrations decrease. EDTA's sensitivity can be attributed to the high fraction dissolved in water. Enlarging the continental area causes an increased water flow from the regional scale and thus, the output from the system increases.

6.4.2 Process parameters

Process parameters affect advective and diffusive flows between the compartments. Resistances, collection efficiency for aerosol particles, rain rate, deposition rate, wind speed, fractions for runoff and flow out, erosion and settle velocity for suspended matter belong to this group.

Resistances

Resistances are only important for volatile substances (BENZ, EDC) or substances with a negligible release to air (HHCB, EDTA, LAS). The latter are very sensitive to resistances because the only input to air and natural soil is by volatilisation and deposition. Resistances between the compartments can affect these very low concentrations quite considerably, while this is not important for other substances that have a much higher input.

Collection efficiency of aerosol particles

The collection efficiency of aerosol particles is required to calculate the washout rate from air. It is a proportionality constant that is multiplied by the fraction associated to aerosol particles. Thus, it only influences substances of which this fraction is not negligible, i.e. PCDD and DEHP. Increasing this parameter slightly decreases the air concentration and increases more distinctly the concentrations in water and soil. TCDD and PeCDD show the highest sensitivities. Higher chlorinated PCDD and DEHP with an increasing fraction associated to aerosol particles are less sensitive, even though a higher sensitivity could be expected because of the higher factor which the collection efficiency is multiplied by. The reason for the decreasing sensitivity can be found in the simultaneously decreasing emissions to air compared with the emissions to water and soils. Compared to the latter emissions, the increasing deposition is less important.

Rain rate

Due to their very low concentrations in air and their very low K_{AW} , the concentrations of EDTA and LAS in air are highly sensitive to the rain rate. The higher the rate, the more is washed out. Soil concentrations of lipophilic substances (DEHP, PCDD) are also sensitive to this parameter, for the same reason as these parameters are sensitive to the collection efficiency. Both collection efficiency and rain rate have an influence on the deposition and, hence, on the concentrations in soil and air. Because of the missing emissions, sensitivities are higher for industrial/urban and natural soils than for agricultural soil. Since PCDD are mainly emitted to air, input to soil increases with a higher precipitation and thus, the soil concentrations increase. For EDTA and LAS the opposite applies. These have a very high water solubility and are not emitted to air. A higher rain rate leads to a higher runoff from soil and consequently to decreased concentrations in soil. The water concentrations also decrease since the runoff is part of the advective flow out of the system. As EDTA is not emitted to soil and has a high water solubility, it is more sensitive than LAS.

Deposition rate of aerosol particles

The deposition rate of aerosol particles only has a slight influence on the concentrations because it is very low compared to washout and gas adsorption via the water-air interface.

Wind speed

The wind speed has an important impact on the concentrations in air because the residence time in air depends on this parameter. Therefore, only substances with very low concentrations in air (LAS, EDTA) are not sensitive. Due to changes in the air concentrations the wind speed also affects the concentrations of lipophilic substances in soil and water.

Fractions of rain water running off soil and water flow from continental to regional scale

The fraction for rain water runoff from soil to surface water is an important parameter for concentrations of EDTA in water and soil since this substance has the lowest K_{OW} of all regarded substances and is almost completely dissolved to water without being bound to suspended matter. This is also the reason for the high sensitivity of this substance to the fraction of water flow from the continental to the regional scale. The other substances are only negligibly influenced by these parameters.

Erosion

Erosion is an important factor for the net sedimentation rate. Accordingly, an increase of this parameter leads to lowered concentrations in water and sediment. This applies to lipophilic substances with a significant fraction bound to suspended matter (PCDD, DEHP). The higher the lipophilicity, the higher the sensitivity. The effect on concentrations is insignificant.

Settle velocity of suspended matter

The settle velocity of suspended matter only slightly influences the concentrations. It is merely one of a number of parameters that determine the flow between water and sediment.

All in all, the process parameters have a moderate effect on the investigated PECs. Resistances are less important than the regional parameters, such as the wind speed and rain rate.

6.4.3 *Other model parameters*

The last category of model parameters comprises those parameters that can not be assigned to the first two groups. Within this group we find parameters that describe compartment properties, such as contents of organic carbon, water, air and solids, densities, suspended matter contents and parameters defining the aerosol properties. But more regional properties, such as the fraction of inhabitants connected to sewer systems, per capita wastewater flow and the number of inhabitants are also contained in this group.

Number of inhabitants, OH-concentration in air, fractions of air in soil, density of air

The numbers of inhabitants on both scales do not have an impact on the regional concentrations, nor do the OH-concentration in air (degradation rates were entered by the user), fraction of air in soil and the density of air.

Fraction of inhabitants connected to sewer systems and rain water infiltrating soil

The most important parameter is the fraction of inhabitants connected to sewer systems. Any substance emitted to the wastewater and which is degraded very well and/or is very lipophilic is sensitive to this parameter. Such a substance is either degraded and consequently removed from the system or it is transferred via the STP from water to sewage sludge. Changing the fraction connected to sewer systems leads to distinct changes in the emissions to water and soil and hence to high changes in the concentrations in water, sediment and agricultural soil. Since most of the substances are usually not emitted directly to surface water, the indirect emissions are mostly much higher than the direct ones. For this reason, concentrations are less sensitive to changes in the direct emissions than to alternations in the fraction connected to sewer systems. EDTA is the only substance that is not sensitive to this parameter because it is only dissolved in the water phase and not degraded in the STP. Thus, nearly 100% of the substance is always emitted to surface water. Because of this property, EDTA is the only substance that is sensitive to the fraction of rain water infiltrating the soil.

Fractions of solids in soil, density of soil and organic carbon content in soil

The soil concentrations of most substances are sensitive to the fraction of solids in soil and the density of solids because the PEC in soils does not refer to volume but to the soil mass. If only the volume is taken into consideration, both of these parameters are not relevant to soil. But for the concentrations in water, the fraction of solids in soil is important because it is used for the calculation of the partition coefficient water-soil and it has a distinct influence on the very low concentrations of lipophilic substances in water. Similarly, the organic carbon content in soil has an influence on the pore water concentrations of lipophilic substances.

Content of suspended matter in water

Another influential parameter for lipophilic substances is the content of suspended matter in water. The more lipophilic a substance is, the higher the sensitivities of water concentrations are.

Environmental temperature

Only TCDD and PeCDD are moderately sensitive to the environmental temperature because their fractions bound to aerosol particles are, in contrast to the other substances, not either 0 or 1 but within a flexible range. The temperature is one of the input parameters contained the Junge-equation and hence has a significant influence.

6.5 Discussion and conclusions

It is almost impossible to determine coherences between substance classes and sensitivities. Correlations between physico-chemical properties and sensitivities emerge at best indirectly due to the mass distribution and concentrations of a substance. Much more important are the combination of emissions and degradation rates. In the Level 3 model SimpleBox, the emission compartment and where the substance is degraded by which rate are of central importance. From this and the PC data we obtain the mass distribution of a substance. Consequently, the affiliation of a substance to a specified class is circumstantial if common statements on sensitivities are required. Summarising, the following correlations between model parameters and sensitivities can be established:

1. The higher the absolute value of an input parameter, the higher the sensitivity to this parameter.
2. The higher the emission to a compartment, the lower the sensitivity to the respective degradation rate.
3. The lower the degradation rate in a compartment, the higher the sensitivity to PC data.
4. The higher the mass fraction in a compartment, the higher the sensitivity to the respective degradation rate.
5. The lower the mass fraction in a compartment, the higher the sensitivity to the relevant PC data.
6. The lower the concentrations in a compartment, the higher the sensitivities.
7. The lower the direct emissions to a compartment, the more important the respective indirect emissions are and hence, the higher the sensitivity to parameters that determine the substance's fate in the STP.
8. The lower the total emissions in a compartment, the more important the respective exchange processes are and hence, the higher the sensitivity to parameters that influence these processes (i.e. possibly also to emissions to other compartments).
9. The higher the volatility, the lower the sensitivity to changes in the volume.
10. The higher the volatility, the higher the sensitivity to the exchange area.
11. Substance properties (mass distribution) determine which advection parameters are influential (hydrophilic → water flow; lipophilic → sedimentation, erosion; volatile → air transport).

If all substances are regarded, altogether 61 of 79 (77%) model parameters have a sensitivity of over 0.1. This means that a large part of the parameters are relevant for the model. However, regional concentrations are not sensitive to the following parameters:

- Continental emissions to surface water and to industrial soil: These only influence the regional concentrations indirectly, and because of their relatively low absolute value they are merely of secondary relevance.
- Concentration of biota in water: This parameter only plays a part in the calculation of the fraction dissolved in water and even there it is unimportant to lipophilic substances because of its low quantity.
- Fraction of air pores in soil: This influences the $K_{\text{soil-water}}$ and density of soil; since the fraction of air pores in soil and the density of air is very low, its influence is negligible.

- Numbers of inhabitants in the system: On the regional and continental scales they only influence the wastewater production. They are of secondary importance for the calculation of the mass flows because of their very low absolute value.
- OH-concentration in air: By default, this parameter is used in the calculation of the atmospheric degradation rate; this parameter is not used since the degradation rates are varied directly.
- Density of air: This only influences the density of soil but has a negligible impact because of its low amount.
- Soil-side transfer coefficient soil-water: Of all transfer coefficients that are relevant to soil, this one's absolute value is the lowest and hence has a negligible impact in the sum of all resistances.
- Water-side transfer coefficient water-sediment: Of all transfer coefficients that are relevant to sediment, this one's absolute value is the lowest and hence has a negligible impact in the sum of all resistances.
- Depth of continental water: This only plays a role in the volume of continental water and consequently has a negligible influence on the regional concentration.

Of all these, the continental parameters are unimportant because only regional concentrations are regarded. They are not even important for the whole regional distribution model. A similar situation applies for the OH-concentration in the atmosphere. This parameter has no impact on the results because the degradation rates are varied directly. The remaining parameters are actually unimportant and could be neglected, especially because of their low absolute values.

Altogether, only seven out of 79 SimpleBox' input parameters (concentration of biota in water, fraction of air pores in soil, numbers of inhabitants in the system, density of soil and the mentioned transfer coefficients) do not influence the calculated environmental concentrations. This shows that most of the parameters are meaningful in the regional distribution model and that the model's concept does not need to be revised.

Due to the high sensitivities of mixing heights and depths, emissions and degradation rates these must be determined very carefully. However, emissions and degradation rates are estimated in EUSES, which makes very high demands on the respective sections of the model. This is quite problematical for the mixing heights and depths since these numbers are difficult to determine. The relevance of these parameters is presented in the uncertainty analyses (Chapter 9).

The STP parameters are less important for most of the substance concentrations and only play a role if the emissions primarily take place into waste water and simultaneously biodegradation of the substance occurs. This shows that for the calculation of regional background concentrations a simpler model would be sufficient to estimate indirect emissions. Such a model is presented later (Chapter 11).

6.6 Summary

By means of the differential-quotient approach sensitivity analyses were carried out to determine the parameters which are important for the estimation of regional background concentrations. It turned out that an assignment of substance class, i.e. PC data of the substance, and sensitivities is

not possible for the regional distribution model. Since the investigated model is Level 3-model it is of essential importance where the substance is emitted and where it is degraded. Accordingly, these parameters have an important influence on the resulting sensitivities. Furthermore, the analysis revealed that nearly all input parameters (>90%) of the regional model have a relevant influence on the results. Seven parameters have no relevant influence on the calculated concentrations and are therefore insignificant for the regional distribution model. The STP model plays only a minor part in calculating regional background concentrations so that the calculation of indirect emissions could be performed in an easier way.

7 Scenario analyses and comparison with measured data

In order to compare measured with calculated values it is necessary to use spatially and temporally coherent data for the chosen substances. This is also proposed by the TGD: “A standardised regional environment should be used for the first approach in the calculation of PEC_{regional} . When more specific information is available on the location of production/emission sites, this information can be applied to refine the regional assessment. The second approach may sometimes result in a better estimation of the concentrations for a specific country.” Hence a comparative region is selected which forms the basis of surveying monitoring data. The chosen region is North Rhine-Westphalia for the year 1990. The aim of the study is to show for which of the selected substances and for which environmental media the regional distribution model delivers realistic values. General statements about the model’s applicability and validity are derived from this.

As already explained by BERDING ET AL. (2000), for the external validation it is necessary to specify all input and output parameters of the investigated model.

- The output parameters of SimpleBox are the continental and regional PECs for air, water, sediment, the three soils and the pore water of agricultural soil.
- The input parameters are, on the one hand, substance parameters, such as physico-chemical properties (PC data), the use and production category, as well as amounts for production and import. On the other hand, these are the regional environmental parameters.

Most of these parameters are simultaneously input parameters of other sub-models of EUSES.

7.1 Scenarios

The substance parameters play a central part in the calculation of environmental concentrations. They serve to estimate emissions (by means of emission tables – see Section 3.1.2) and partition coefficients (by regression equations – see Section 3.2.2.2). Regional and environmental parameters characterise the underlying region (by default this is the given generic standard region). These include, e.g. the area, area fractions for the different land uses, number of inhabitants, fraction connected to sewer systems, wind speed, precipitation rate, etc. Most of these parameters must be changed if a real region is to be considered. In the same way, the substance-specific estimations can be replaced by more realistic values, i.e. by differently estimated or measured ones. Accordingly, it is possible to set up different scenarios that are each based on varying data sets. This comparison of modelled results with measured ones is based on three different scenarios: the scenario *Default*, the scenario *NRW standard* and the scenario *NRW realistic*. In the *Default* scenario only the minimum of required inputs is made. I.e., only the required substance information is entered. The *NRW standard* scenario still uses substance-dependent estimations, but the values for the regional and environmental parameters are in accordance with North Rhinish-Westphalian properties (see Table 5). The most realistic scenario is *NRW realistic*. Here, in addition to the regional parameters, all available substance information is used. Estimated emissions are replaced by realistic ones (either by changing the emission factors or by directly entering the release rates), measured values for the partition coefficients (Henry’s law constant, K_{OC}) are used instead of esti-

mations, and realistic degradation rates are employed. (Table 6 briefly shows the characteristics of the scenarios.) A more detailed analyses for HHCB can be found in SCHWARTZ ET AL. (2000). As previously mentioned, the PCDD are a special case since they have never been produced on purpose. Therefore, it is not possible to estimate emissions by given production data. Model calculations are hence only possible if the release rates are entered directly. Emission data to air for PCDD are available for North Rhine-Westphalia (NRW 1996), but only in the form of emissions in total I-TEQ (BALLSCHMITER AND BACHER 1996). Consequently, congener-specific releases had to be estimated by means of congener patterns. PCDD-emissions also take place into the waste water since clothes are often contaminated with Pentachlorophenol (PCP), which may again be polluted with PCDD. According to HORSTMANN AND MCLACHLAN (1994) and JONES AND STEWARD (1997), a per-capita emission can for this reason be estimated. Another difference between PCDD and the other substances is the high heterogeneity of the measured partition coefficients (MACKAY ET AL. 1991-1997). Thus, no measured partition coefficients were inserted; instead only estimated partition coefficients were used. The PCDD-scenarios hence differ from the others in that, on the one hand, measured emissions are always used and, on the other hand, measured partition coefficients are never employed. All substance data used for the scenario analyses can be found in the appendix (Section A.3).

Table 5 Regional and environmental parameters used in the scenarios.

Parameter	Standard Scenario	NRW Scenarios
Constant of Junge equation [Pa m]	0.01	0.172 (FALCONER & BIDLEMAN 1994)
Environmental temperature [°C]	12	11 (NRW 1995A)
Surface area of particles [m ² /m ³]	0.01	1.5E-4 (FALCONER & BIDLEMAN 1994)
Number of inhabitants feeding one STP	10 000	17 225.7 (STATISTISCHES BUNDESAMT 1998)
Sewage flow [l/(eq-d)]	200	200.47 (STATISTISCHE ÄMTER DES BUNDES UND DER LÄNDER 1998)
BOD [g/d]	54	60 (German value for calculation of inhabitant equivalent)
Area of regional system [km ²]	40 000	34 400 (NRW 1998)
Number of inhabitants of region	20 000 000	17 816 100 (STATISTISCHE ÄMTER DES BUNDES UND DER LÄNDER 1998)
Area fraction of water of the regional system	0.03	0.018 (NRW 1998)
Area fraction of natural soil	0.6	0.26 (NRW 1998)
Area fraction of industrial/urban soil	0.1	0.202 (NRW 1998)
Area fraction of agricultural soil	0.27	0.52 (NRW 1998)
Fraction of water flow from the continental to the regional scale	0.034	0.029 (estimated)
Wind speed in the system at a height of 10 m [m/s]	3	3.1 (NRW 1995)
Average annual precipitation [mm/yr]	700	679 (NRW 1995A)
Fraction connected to sewer systems	0.7	0.92 (STATISTISCHE ÄMTER DES BUNDES UND DER LÄNDER 1998)
Sewage treatment: Mode of aeration	surface	bubble

Table 6 Overview of the scenarios used; (R) pre-set regional data are replaced by realistic data, (P) estimated substance-specific parameters and emissions are replaced by measured or investigated values, respectively.

Scenario	R	P	Characterisation
Default			Only the minimum of substance-specific data was inserted. The values given by EUSES were not changed.
NRW standard	✓		The parameters of the EUSES standard region were replaced by values representing the region North Rhine-Westphalia.
NRW realistic	✓	✓	The same as NRW standard, but the estimated emissions, partition coefficients and degradation rates were substituted by measured ones.

7.2 Results and discussion of the scenario calculations

In the following, the model results are presented as a comparison of calculated with measured regional concentrations for air, water, sediment and agricultural soil. The scenario results and measured values are shown in Figure 5 to Figure 8. A summarising assessment is listed in Table 7. The following criteria have been developed to evaluate the results:

“Good” are modelled results between the median and maximum of the measured concentrations or less than half an order of magnitude above the measured maximum.

The modelled results are “fair” if they are less than half an order of magnitude below the measured minimum and less than one order of magnitude above the maximum. These results are already further beyond the measured values. Since an underestimation is beyond the scope of a conservative estimation, the underestimation must not be higher than half an order of magnitude, while the overestimation may be up to one order of magnitude.

Higher over- or underestimations are classified as “poor”.

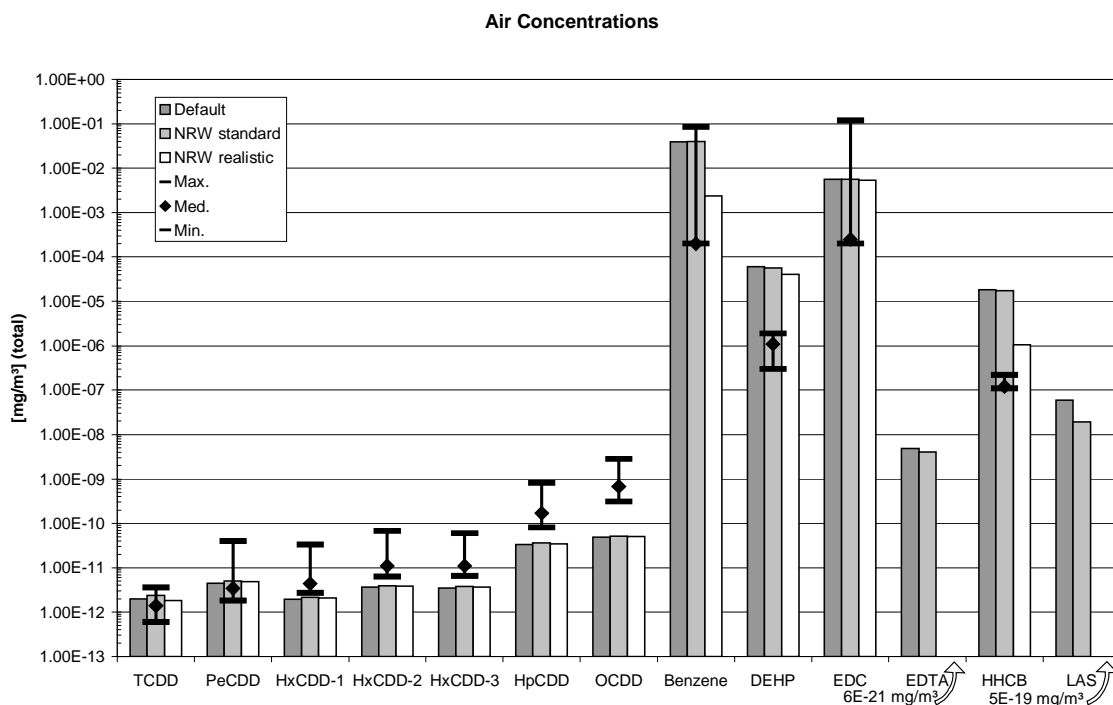


Figure 5 Comparison of calculated air concentrations with measured values.

7.2.1 Air

No measured values of EDTA and LAS exist for the compartment air since these substances are not volatile. Nevertheless, EUSES delivers PECs for these substances because a vapour pressure larger than 0 has to be entered, even though it is not measurable for these substances. The minimum that can be set without a warning for this parameter in EUSES is $1\text{E-}6$ Pa. With the *NRW realistic* scenario, EUSES calculates infinitely small PECs (EDTA $6\text{E-}21$ mg/m^3 , LAS $5\text{E-}19$ mg/m^3), which is assumed to be the most realistic estimation. Here, the calculated emissions to air are additionally set to 0 kg/d, and the Henry coefficient is set to the minimum ($4\text{E-}10$ Pa m^3/mol), too. At this point, the recommended parameter ranges must be questioned. It is possible to use

lower values than the advised minima that are closer to 0, which of course produces lower air concentrations. As a consequence, the *Default scenario* would already lead to qualitatively different results if the advised minima were lower or ignored by the user. It is not evident why the vapour pressure's minimum has to be 1E-6 Pa and the Henry's minimum 4E-10 Pa m³/mol, since mathematically correct results are possible with lower values. The reason to exclude 0 as the minimal value is to prevent division by zero, but the set ranges should be discussed.

There are no measured air concentrations for HHCB either. This can be attributed to the low total number of measurements of this substance to date. In any case, the likeliest occurrence is in water and thus the main focus so far has been concentrated on that compartment. For this substance the difference between the two standard scenarios is negligible. But replacing the estimated degradation rate for air by a measured one decreases the predicted concentration by more than one order of magnitude.

The modelled results for typical air pollutants (benzene, EDC) are good, since they are between the measured medians and maximums. A distinct enhancement of the modelled results for benzene, i.e. an approach to the median, can be noticed in the *NRW realistic* scenario with set emissions and degradation rates. The reason for this is the high overestimation of benzene emissions into air using the emission tables.

The regional model predicts PCDD concentrations less accurately with increasing lipophilicity. While TCDD and PeCDD are estimated nearly to the measured median, the results are fair for HxCDDs and HpCDD (slight underestimations). Results for OCDD are poor because of the clear underestimation by nearly one order of magnitude. The reason for these different estimations could be the difficulty in approximating emissions (from I-TEQs and the appropriate congener patterns). It is noticeable that the use of degradation rates for air only marginally decreases the predicted concentrations. This can result from the very low mass fraction of PCDD in the air and the fact that advective processes are much more important loss paths than degradation.

It is wrong to conclude from this that very lipophile substances are always underestimated. Even though the K_{OW} of DEHP is between PeCDD and HxCDD, the predicted concentration is even more than one order of magnitude higher than the measured maximum. An explanation for this high deviation could be that monitoring data were only obtainable from clean air (rural areas). The use of investigated partition coefficients, degradation rates and emissions leads to a slight improvement, even though the estimated emissions are lower than in reality. The improvement could be caused by the relatively high degradation rate for air that is assumed in the realistic scenario. Nevertheless, the underestimation of emissions to air is remarkable because the emission tables usually calculate releases very conservatively. However, the modelled results do not differ from one another by more than half an order of magnitude.

Only few measured values are available for HHCB. Hence, an assessment of the modelled results is not possible. However, it is remarkable that the two standard scenarios (*Default* and *NRW standard*) overestimate the concentrations considerably (2 OoM), while the realistic scenario is only approximately one OoM higher than the measured data.

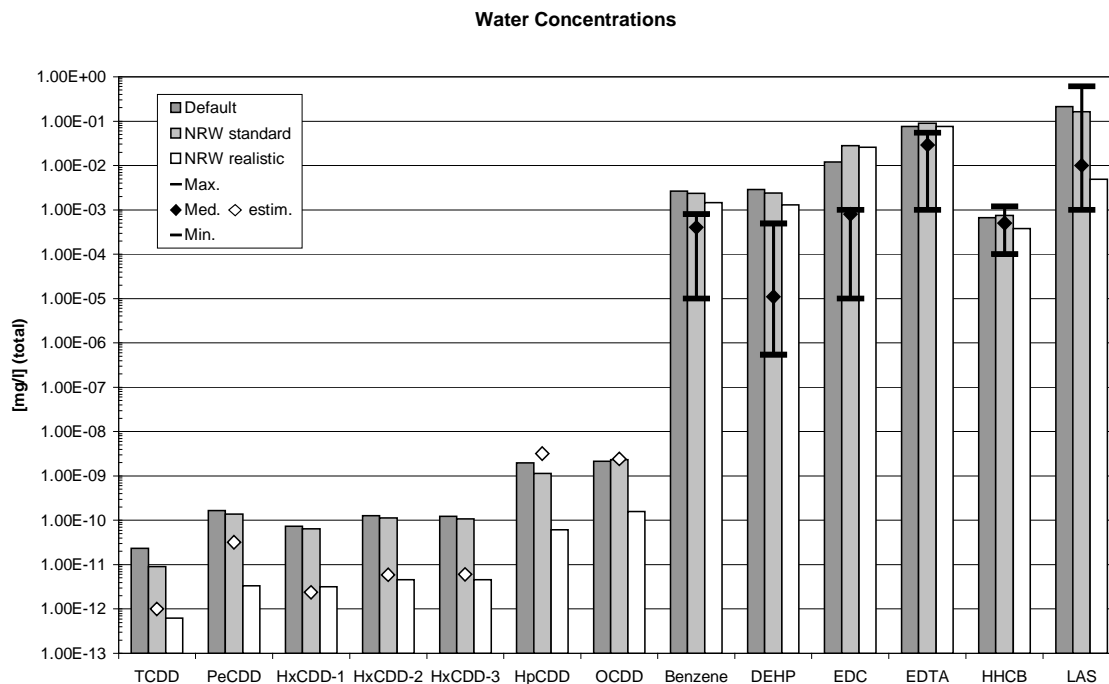


Figure 6 Comparison of calculated water concentrations with measured values; comparative concentrations for PCDD are estimated from air concentrations.

7.2.2 Water

Regional concentrations were available for the water compartment for all substances apart from dioxins.

For dioxins comparative values are derived from air concentrations using the partition coefficients. This is why they cannot be utilised to evaluate the validity of SimpleBox, but can only serve as an orientation. The assumption of degradation in the *NRW realistic* scenario leads to a much more considerable decrease of the predicted concentrations than the use of realistic regional instead of default values.

Estimations for benzene are only slightly too high and thus are classified as good. The modelled results improve, i.e. they are nearer to the median, when realistic values are inserted. But altogether they differ only negligibly (< 0.5 orders of magnitude).

The measured DEHP concentrations are exceeded in the standard scenarios by slightly more than half an order of magnitude. These overestimations decrease in the realistic NRW-scenario to under half an order of magnitude. Hence the estimations are conservative, but nevertheless good when realistic values are used.

The model clearly overestimates the measured EDC concentrations. Bad monitoring data (only single values) or wrong emissions could be the reason for this error. Only emissions could be estimated because real data were not available. This is why the modelled results are not easy to assess for this substance, and are rather poor.

The scenario outcomes for EDTA barely differ. A slight increase of water concentration can be noticed when real regional parameters are used. This results from a lower area fraction for water and a regional area reduction with otherwise unchanged emission data. Inserting realistic degrada-

tion rates decreases the concentrations again to the results of the *Default* scenario. Altogether, EDTA is estimated rather conservatively, but well. The same applies for LAS. The measured concentrations are estimated well from the scenarios. The results of the standard scenarios are between the measured median and maximum. With more realistic degradation rates and emissions the modelled results slightly underestimate the measured median. The reason for the good estimations of EDTA and LAS could be their “unequivocal” environmental behaviour: They are scarcely volatile and are exclusively emitted into water. The degradation rates of both substances are well known, and the supposed emissions seem to be near to the real numbers.

A similar situation applies for HHCB. The modelled values of this substance are between the measured median and maximum or (NRW realistic) only slightly below the median, even though the difference between the measured minimum and maximum is only one order of magnitude.

Altogether, it can be stated that the regional PECs for water are estimated quite well. The modelled results are only worse when no real emissions are available and monitoring data are sparse. The estimations are best for substances that are typically found in water (EDTA, LAS, HHCB). Underestimations only take place with dioxins, but it has to be taken into consideration that the only comparative values are estimations, which are thus unsuitable.

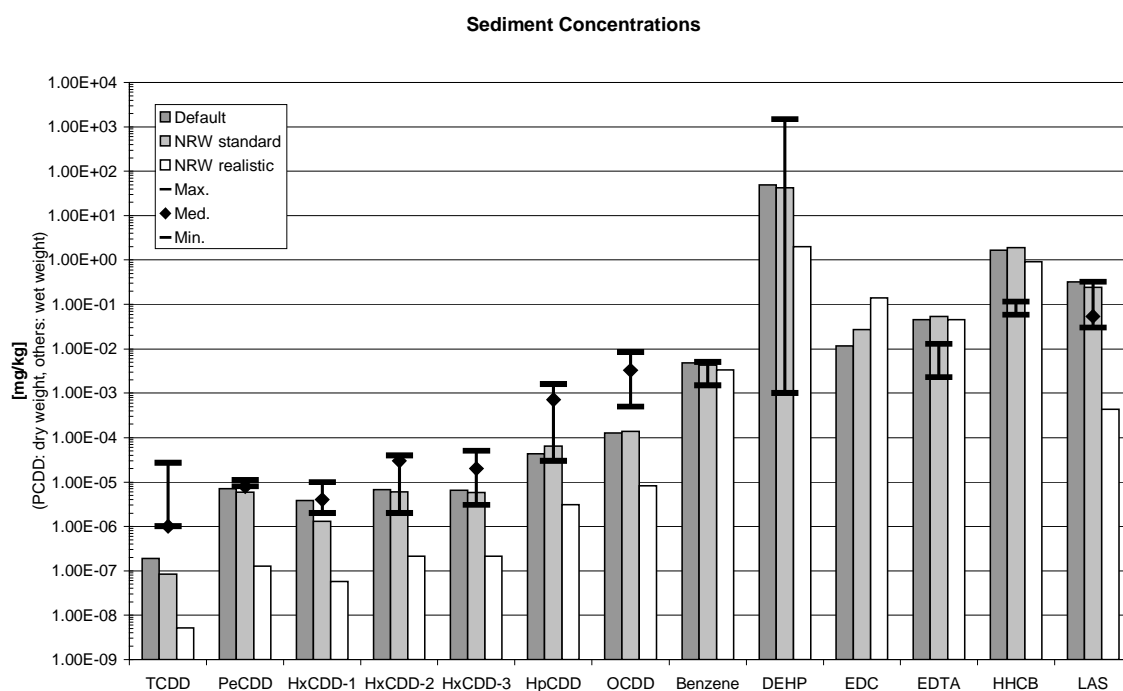


Figure 7 Comparison of calculated sediment concentrations with measured values.

7.2.3 Sediment

There are no direct emissions into sediment. Hence, the concentration depends on emissions into water (direct, indirect, deposition) and the sedimentation rate, combined with the fraction of substance associated to suspended matter. Analogous to soil, there were only a few measured values for sediment.

Although the monitoring data for PCDD are sparse (eight measuring points at the Rhine and Elbe), it is possible to carry out a rough comparison. Overall, the concentrations of PCDD in sediment are underestimated. The difficult estimation of PCDD emissions to water could be a reason for this. But estimations are only poor for TCDD and OCDD. The other considered dioxins are estimated fairly in the standard scenarios. With the presumed degradation rates, the predicted concentrations decrease considerably. As previously discussed in the context of soil, degradation rates for sediment may be too high. Difficulties arise in three fields, which may explain this phenomenon:

- The measurement of PCDD-degradation rates is problematical.
- It is not certain whether they are degraded in sediment at all.
- The consideration of the sediment as one compartment.

Even if there are measured values for benzene, they can only serve as an orientation because the data were taken in Japan and the USA. Nevertheless, the modelled results of the three scenarios lie between these two, only slightly differing, values. This is a good result.

Sufficient measured values exist for DEHP. But because of the very high variation of these data (factor 1 000 000 between minimum and maximum), a classification of the modelled results is not feasible. One can only state that the modelled results are within the measured values. The use of realistic values for emissions, degradation and partition coefficients leads to a distinct reduction (one order of magnitude) of the predicted concentrations in sediment.

There are no monitoring data for EDC, so a comparison of the model and reality is impossible. But it is worth noting that the modelled results increase from the scenario *Default* to *NRW realistic*, although the standard scenario should deliver the most conservative prediction.

EDTA has not been measured sufficiently either. The two values from Japan and USA can only serve as an orientation. They are overestimated by about one to 1.5 OoM. The scenarios do not differ very much.

The monitoring data for HHCb are also poor since there are only single values which are overestimated by about one order of magnitude.

LAS concentrations are estimated well with the standard scenarios. The use of realistic values, i.e. lower emissions and higher degradation rates for water and sediment, leads to an underestimation of more than two orders of magnitude. Consequently, the results have to be classified as poor.

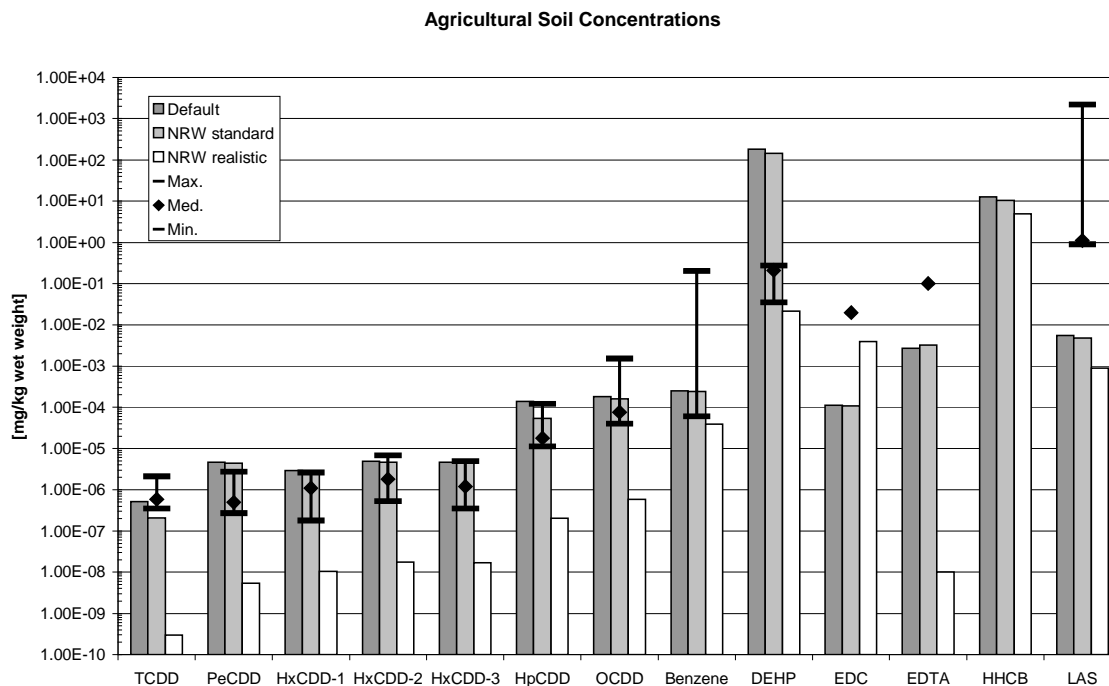


Figure 8 Comparison of calculated agricultural soil concentrations with measured values.

7.2.4 Soil

Assessing the modelled results for the compartment soil is difficult since monitoring data are poor (exception: PCDD) and emissions have to be estimated. Any monitoring data used are related to agricultural soil. Hence the PEC for agricultural soil is taken for the comparison. When evaluating these results, it must be taken into consideration that EUSES assumes a continuous sewage sludge application rate on agricultural soil. The STP model calculates fractions for indirect emissions, substances remaining in the sludge and degradation. It uses PC data, biodegradability, STP properties and environmental parameters. The calculated fractions are multiplied by the emissions to waste water. Thus, the emission rate to agricultural soil is the emission rate to waste water multiplied by the fraction directed to sludge. Hence, measured concentrations from agricultural soil with sludge application were chosen if available.

Sufficient measured values were only obtainable for PCDD. These substances are estimated well in the standard scenarios, even though the emissions are based on approximated releases to waste water. The calculated values do not diverge by more than one order of magnitude from the measured medians and lie, with the exception of TCDD, between the median and maximum or slightly above the maximum. The use of regional data decreases the calculations slightly. The difference is only larger for TCDD because changing the parameters for particle content and properties has a more serious effect on the fraction associated with aerosol particles. This leads to a lower deposition rate and consequently to lower emissions to soil. The use of degradation rates leads to a high underestimation of the measured soil concentrations. This shows that the rates used (MACKAY ET AL. 1991-1997) may still be too high, even if the half-lives are between 17 000 h (TCDD) and 55 000 h (OCDD). One generally has to bear in mind that degradation rates for PCDD

can hardly be measured, especially for soil, and any value used is worth discussing. Additionally, it must be considered that in the regional model each soil is treated as a homogenous compartment, i.e. degradation is assumed to take place in the whole soil at the given rate, although PCDDs are best degraded at the thin top layer while the rest in the deeper soil is degraded much more slowly, and no biodegradation is known.

The calculated soil concentrations for benzene are near the detection limit (about half an order of magnitude above in the standard scenarios and marginally below in the realistic scenario) but nearly two orders of magnitude lower than the only measured value. Since benzene can not usually be found in soil, except for local hot spots, these results well represent the real circumstances. The clear difference between the standard scenarios and the realistic scenario comes from the starkly altered emissions.

The data available for DEHP enable the modelled results to be assessed. The two standard scenarios overestimate the concentrations considerably (about 2.5 orders of magnitude). The use of realistic emissions and degradation rates leads to a marginal underestimation of the measured minimum, i.e. a clear improvement of the predicted concentration. As the measured values have a narrow range the underestimation is only slight. Due to this the result for the realistic scenario is fair, and the standard scenarios must be considered poor.

No statements are possible for EDC because the only comparative value is the detection limit. But the clearly increasing modelled result in the scenario "NRW realistic" is noticeable. Since K_{OC} is raised by a factor of 10, the degradation rate in the sewage treatment plant decreases evidently and hence the emissions to agricultural soil increase.

The only value obtainable for EDTA is an estimation after sludge application. Hence, no comparison is possible for this substance either. In any case, the considerable difference between the standard scenarios and the realistic scenario is significant. This results from the very low air concentration, which leads to a lower deposition rate and hence to decreasing soil concentrations. Even though EDTA is not biodegraded in sewage treatment plants, input via sludge does not play a significant role. Because of its very low lipophilicity ($\log K_{OW} -3,34$), EDTA is chiefly dissolved in water, but is not bound to sludge.

No classification is possible for HHCB either, since no measured values are available. The several scenarios barely differ from each other.

The monitoring situation for LAS is poor. There are only single values for agricultural soil after sludge application. These are maximal values which are, as expected, underestimated. Indeed, the explicitness of the underestimation is noticeable (minimum/median about 2.5 orders of magnitude, maximum about 5 orders of magnitude). The realistic scenario does not produce significantly reduced soil concentrations because, for LAS, deposition is a less important process in comparison with indirect emissions via STP sludge. LAS is readily biodegradable, but there is also a significant fraction of the non-degraded substance that is bound to sludge.

Altogether, the monitoring data are only sufficient for PCDD and DEHP. For the other substances the measured concentrations are rather maximum values than regional background concentrations. Furthermore, one has to bear in mind that the estimation of the agricultural soil concentration is based on the results of the STP model SimpleTreat (which is expressly left unregarded here) which

calculates indirect emissions. Hence the statements on the validity of SimpleBox only have little impact on this compartment.

Agricultural soil concentrations tend to be underestimated. The overestimation of emissions in the standard scenarios compensate the general underestimations; thus these results are closer to the measured values than those of the realistic scenario.

Table 7 Summarising assessment.

Substance	Compartment			
	Water	Air	Soil	Sediment
TCDD	#	+	+	-
PeCDD	#	+	+	o
HxCDD-1	#	o	+	o
HxCDD-2	#	o	+	o
HxCDD-3	#	o	+	o
HpCDD	#	o	+	o
OCDD	#	-	+	-
DEHP	+	-	o	#
HHCb	+	#	#	#
EDC	#	+	#	#
Benzene	+	+	#	#
EDTA	+	#	#	#
LAS	+	#	#	-

+: good (modelled results between median and maximum or <0.5 orders of magnitude (OoM) above maximum)

o: fair (modelled results <0.5 OoM below minimum and ≤1 OoM above maximum)

-: poor (modelled results ≥0.5 OoM below minimum or >1 OoM above maximum)

#: not assessable (no sufficient monitoring data)

7.2.5 Improvements by alternative regression equations for the K_{OC}

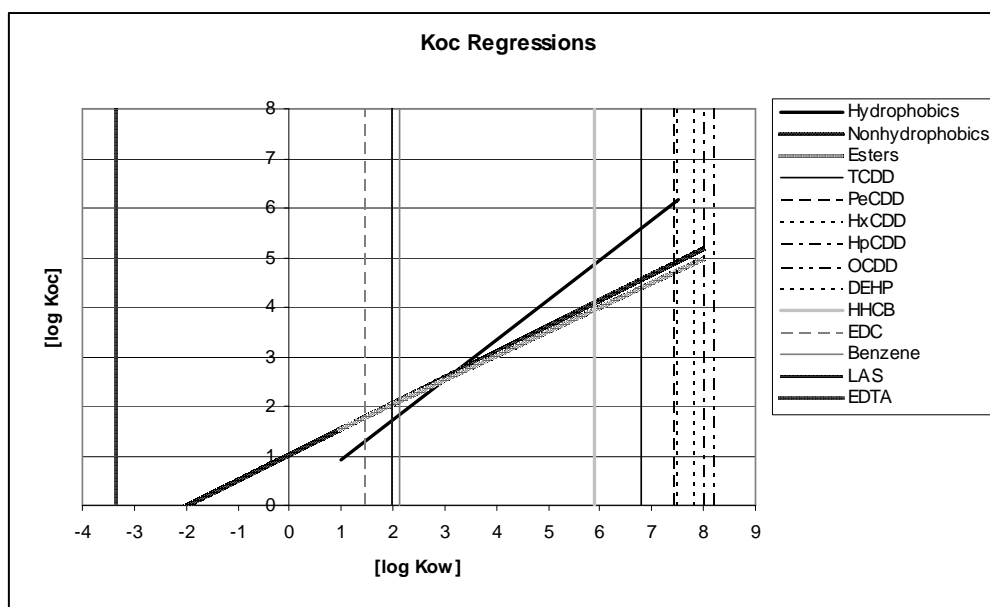
The scrutiny of theory showed that the regression equation for the estimation of K_{OC} from the K_{OW} used in EUSES is only valid for hydrophobic substances with a $\log K_{OW}$ between 1 and 7.5. The TGD (Part III, p. 541) suggests numerous regressions, among others specific ones for non-hydrophobics and esters (phthalates). Thus, for DEHP (phthalate), EDC, BENZ, EDTA and LAS (all non-hydrophobics), other regressions could improve the results. Since K_{OC} is applied in the calculation of $K_{\text{sediment-water}}$ and $K_{\text{soil-water}}$, different results can usually be expected for water, sediment and soil. To examine potential improvements for these substances, additional calculations were carried out. The standard regression by SABLJIC ET AL. (1995) ($\log K_{OC} = 0.81 \cdot \log K_{OW} + 0.1$) was replaced for DEHP by the regression $\log K_{OC} = 0.49 \cdot \log K_{OW} + 1.05$ (regression range for $\log K_{OW}$: 1 to 8) and for EDC, BENZ, EDTA and LAS by $\log K_{OC} = 0.52 \cdot \log K_{OW} + 1.02$ (regression for $\log K_{OW}$: -2 to 8). The K_{OC} values for these substances are listed in Table 8. EDTA's $\log K_{OW}$ (-3.34) is still outside the regression range, but since the equation is applied to non-hydrophobics and the range starts at a value of -2, these estimations could nevertheless fit better to EDTA. Figure 9 shows the three relevant regression equations within their regression ranges together with the $\log K_{OW}$ -values and measured K_{OC} -values of the regarded substances.

Table 8 K_{OC} values with different regression equations.

Substance	$\log K_{OC}$ (standard regression)	$\log K_{OC}$ (alternative regression)	$\log K_{OC}$ (measured)
DEHP	6.16	4.72	4.94 ^a
EDC	1.28	1.78	2.30 ^b
BENZ	1.82	2.12	1.96 ^b
EDTA	-2.61	-0.72	n.a.
LAS	1.69	2.04	n.a.

^a DECHEMA (1995)^b RIPPEN (1995)

n.a.: not available

Figure 9 Different K_{OC} -Regressions together with $\log K_{OW}$ -values of substances.

As can be seen in Table 8 and in Figure 9 the standard regression for hydrophobics equation overestimates the K_{OC} of DEHP. The alternative regression equation estimates a K_{OC} which is much nearer to the measured value. For the non-hydrophobic substances the alternative regression delivers higher K_{OC} -values than the standard equation. EDTA shows the most distinct difference. Its K_{OC} is estimated at about 1.9 OoM higher if the alternative regression is used.

Only for EDC and BENZ measured values are obtainable. The K_{OC} of EDC is underestimated from both equations but the underestimation is lower with alternative equation. For BENZ the measured value is between the two results: While the standard equation underestimates the measured K_{OC} the alternative one overestimates it.

Because of the very low sensitivity of DEHP concentrations to K_{OW} , no significant changes in the results can be expected by altering K_{OC} . In fact, there are usually no differences in the results if the altered regression equation is used. Also for EDC, BENZ and LAS, only minor changes are caused by the altered estimations. Concentrations in water decrease slightly, those in sediment and soil become marginally higher, even though the K_{OW} in the sensitivity analyses showed a significant influence on the concentrations in soil for these substances. But since the K_{OW} also affects the fate of the substance in the STP (and hence the emissions), K_{OC} only influences the partition coefficients to soil and sediment. This explains the negligible effects of changes in the K_{OC} on the con-

centrations of these non-hydrophobic substances in soil and sediment. Only the concentrations of EDTA change distinctly. Because of the high alteration of the K_{OC} due to the alternative regression equation and the high mass fractions of EDTA in water, concentrations in sediment and soil become much higher. In sediment, the concentration increases by 0.8 OoM, whereas in soil the increase in concentration amounts to 2.3 OoM. This could indicate for soil an improvement in the results since the (one) measured value is generally underestimated. For sediment the (also not representative) data are overestimated so that the better regression could deteriorate the result due to higher overestimation. However, a clear assessment of the results is not possible because the monitoring data are too sparse and measured values for EDTA's K_{OC} are not obtainable.

7.3 Discussion and conclusions

The evaluation has shown that the use of regionally specific values instead of the defaults of the generic standard region only leads to small deviations of the predicted environmental concentrations. There could be two reasons for this that have to be further evaluated: On the one hand, the sensitivity of the regional parameters could be very low so that changes only slightly affect the results. On the other hand, the slight differences between the first two scenarios could result from the similarity of the standard region and the chosen comparative region.

More serious changes are effected by inserting measured and investigated values for degradation rates, partition coefficients and emissions. If these parameters are known without having to be estimated, the results of the *NRW realistic* scenario approach the median of the measurements. The predicted concentrations decrease in the *NRW realistic* scenario with only a few exceptions (these are: DEHP air, EDC soil, EDC sediment). Since underestimations are possible, this can even lead to a weakening of the model results. However, underestimations can usually be attributed to inapplicable measured data or insufficient degradation and emission rates. Consequently, EUSES can still be viewed as a conservatively functioning model system.

Because of the particularly poor availability of monitoring data, it is not easy to judge the applicability of the regional fate model for the different substances and environmental media. In principle, it can be stated that the modelled results depend strongly on the quality of the input data used, which is not surprising. An evaluation of SimpleBox irrespective of the whole EUSES system is almost impossible since preliminary calculations are indispensable. This particularly concerns the results of the STP model. It is the only facility to quantify the emissions to agricultural soil, since investigated data are not obtainable for this parameter. With a good monitoring data set and good – or well estimated – input data the regional model delivers realistic results. Changing the regression equation of the K_{OC} to alternative ones for esters and non-hydrophobic substances leads to more or less strong deviations in the K_{OC} but to only slight effects on the concentrations. The differences are only high for EDTA. But because there are no sufficient monitoring data for sediment and soil, the changes cannot be assessed.

The worst results are achieved with very lipophilic substances (higher chlorinated PCDD, DEHP). However, it must be considered that the estimation of congener-specific PCDD emissions from I-TEQ-values is problematic and involves considerable uncertainties. It is remarkable that the results are very near to the measured values for substances whose physico-chemical properties are such

that they can typically be found in one medium (e.g. BENZ and EDC in air, EDTA, HHCB, LAS in water, and PCDD in soil when no degradation is supposed). In other media, the model results may deviate more clearly from the measured values. One point to discuss is the assumption that soil and sediment are simple homogenous compartments without different layers. The use of degradation rates for the bulk compartment can, as seen for PCDD, lead to underestimations that could be avoided with a more detailed model structure. BENNETT ET AL. (1998) suggested using a soil penetration depth specific for each substance, instead of a fixed soil depth. Presuming or calculating an average degradation rate that includes the different degradations in the several soil layers could also be a solution to this problem. This confirms the presumption that many uncertainties are usually based on poor data and that the model is generally applicable to calculate regional background concentrations.

7.4 Summary

The scenario analysis showed that the use of specific regional data instead of the generic region's default values only leads to negligible deviations in the predicted concentrations even though the sensitivity analysis revealed a relatively high concern of the regional parameters. The reason for this are the comparable low differences between the selected reference region North Rhine-Westphalia and the standard region. More distinct changes are achieved by inserting measured or investigated values for degradation rates, partition coefficients and emissions. If these parameters are known and do not have to be estimated the calculated concentrations get nearer to the median of the measured values. In the according scenario (*NRW realistic*) the PECs are lower than in the standard scenarios apart from some exceptions (DEHP in air, EDC in soil and EDC in sediment). Since also under-estimations are possible this can also lead to deteriorations in the modelled results. However, in the most cases under-estimations can be explained by weaknesses in the monitoring data and by missing degradation and emission data. Thus, EUSES can still be seen as a conservatively working model system. Due to the in some cases bad availability of monitoring-data the applicability of the model can for some substances and some environmental media hardly be assessed. Basically, the modelled results depend strongly on the quality of the input data which is not a surprising finding. An assessment of SimpleBox free from the whole EUSES-system is nearly impossible since preliminary estimations are essential. This is particularly applied to the sewage treatment model SimpleTreat which represents the only facility to estimate emissions to agricultural soil since measured data are not obtainable for this parameter. If there are sufficient and appropriate measured values as well as good input data (or good estimations, respectively) the regional model calculates realistic results. The worst estimations result for very lipophilic substances (higher chlorinated PCDD and DEHP), But it has to be considered that the assumed congener-specific emissions for PCDD are calculated from I-TEQ-values which is highly uncertain. Substances which can be found typically in a several environmental compartment due to their PC data (e.g. BENZ and EDC in air, HHCB, LAS and EDTA in water and PCDD in soil if no degradation is assumed) are predicted well for this compartment. In the other media the results can partly deviate distinctly from the measured values.

8 European scenarios for SimpleBox

8.1 Introduction

From the scenario analysis it emerged that the realistic data rather than the default values can distinctly improve the model's outcome if the results are compared with measured values of an existing region. Furthermore, it was shown that the standard region contained in EUSES represents a European average region that resembles the realistic region chosen for the comparison with measured results. Consequently, the differences in the model's output are low if only the regional parameters are altered. Thus, the question arises as to whether the calculated PECs change more significantly if other regions are used instead of North Rhine-Westphalia. JAGER ET AL. (2000) carried out calculations using data representing Finnish and Spanish conditions for two substances, and determined alterations within a factor of 10, with Spain being the worst case for water and Finland for soil. For air the differences were negligible. The regional data for these two countries were not investigated exhaustively and could therefore not be used for this work. However, the present approach is based not only the work of JAGER ET AL. (2000), but also on the idea that regions located in the north and south of Europe could depict more extreme environmental characteristics. In this section, this approach is presented. Characteristic regions have to be selected and parameterised. Due to a lack of data, however, regional data (including emissions and monitoring data) are not obtainable for every substance. However, the results of the calculations can help to determine the "intra-European" variations and to characterise the degree of conservatism represented by the standard region. At the beginning, this region's parameter values are scrutinised.

8.2 The standard region

The parameters of the standard region and their values were already shown in the scenario analysis (Section 7, Table 5). But the sources for this average region have not yet been evaluated. Although the TGD (Part II, Chapter 3, p. 315) claims that "it is extremely difficult to select typical or representative values for a standard European region" and it is stated that "therefore, the rationale behind the values (...) is limited" the given sources must lead in a comprehensible way to at least some of the chosen values. But comparing the generic data proposed in the TGD (Part II, Chapter 3, Table 10) to data in the stated source (ECETOC 1994) reveals inexplicable differences. In the TGD, it is stated that "the area fractions for water and for natural, agricultural and industrial/urban soils, are average values obtained from ECETOC (1994b) [here: ECETOC 1994] supplemented with data from Sweden and Finland". However, ECETOC (1994) only contains data for water, agricultural soil, pasture, forest and other soils. The values for natural and industrial/urban soils are hidden in the categories forest and other soils. Also it is not apparent where the data for Sweden and Finland exactly come from since no source is presented. Consequently, the data shown in the TGD cannot be verified with ECETOC (1994) and seem not to be seriously explicable, but rather guessed. Also the value for the fraction of rainwater running off soil (TGD: 25 %) does not correspond to the average of the given data in ECETOC (1994). The weighted average is about 45 %. It is true that the data for Sweden, Finland, Norway and Austria are missing, but even if the values for

these countries were theoretically 0 %, the average value of 25 % would still be too low. Furthermore, the TGD proposes a value of 25 % for the fraction of rainwater infiltrating the soil, which is not commented upon at all. It must be criticised that the values listed in the TGD only seem to be derived from serious sources. They may be reasonable but it would be better to emphasise the arbitrary character of the chosen standard values. Nevertheless, it is possible to derive one essential (and perhaps trivial) conclusion out of this: the parameterisation of a regional model is much more difficult than it seems to be at first sight. Many data can only be estimated and must be chosen by expert judgement. This applies also for the European scenarios presented in the following section.

8.3 European scenarios

Europe can roughly be divided into three characteristic regions: the northern, central and southern parts.

The northern part of Europe (Scandinavia and Finland) is characterised by

- a low population density,
- high area fractions for water (up to 10 %) and natural soil (up to 80 % with a high fraction of forests),
- low fractions of agricultural and industrial soil,
- low average temperatures,
- moderate to higher precipitation
- and a high fraction connected to sewer systems.

The Central European part (Benelux countries, United Kingdom, Ireland, Germany and France) is characterised by the EUSES standard region.

The southern part of Europe is characterised by

- a low population density, but higher than in the north of Europe,
- a high area fraction for agricultural soil,
- low area fractions for water and natural soil,
- high average temperatures,
- low precipitation (but higher rain rates at the coast)
- and a low fraction connected to sewer systems.

To elucidate the effect of using different European regions instead of the EUSES standard region, it is helpful to perform a scenario analysis that considers such regions. As described in Section 3, the spatial scale of the regional distribution model is located between the global and the local scales. The size of the default region is 40 000 km². Consequently, the dimension of a region should generally be around this value since a greater area would probably cover too heterogeneous landscape properties. Therefore, it is not advisable to apply the model to an area of a whole country. On the other hand, it is almost impossible to find a complete data set for such a small region. Even though the European NUTS 1 and 2 regions basically represent appropriate areas, the available data are usually insufficient. Nevertheless, it is possible to establish characteristic scenarios. Here, the following method is chosen: Based on an area of 40 000 km², typical values for the respective

parameters can be selected using the available data of different European countries. These values do not have to be realistic for one of the countries or a concrete region but should characterise the respective part of Europe. In this case, the comparison of modelled results is not interesting for measured values but only for other scenarios since the purpose of the scenario is to find out which changes in the outcome result from changes in the regional properties. By means of the results of the sensitivity analysis, the influence of the use of different regions on the calculated concentrations can be estimated. Substance properties (including emissions) are not changed to keep the results comparable.

Table 9 shows the range of parameter values for the northern and southern parts of Europe together with the values of the generic region and selected representative values for a *North* and a *South* scenario. The values for land use and land cover fractions are taken from INTEMANN ET AL. (1999), HIZ (1969) and VAN DE VELDE ET AL. (1994). Values for Denmark, Sweden, Norway and Finland were analysed for the northern countries, while values for Portugal, Spain, Italy and Greece were analysed for the southern countries. ECETOC (1994), MICROSOFT (1995-1997), INTEMANN ET AL. (1999) and HIZ (1969) form the basis of climatic data for the countries in question. Values for the regional data for the fraction of inhabitants connected to sewer systems, rain water running off soil and per-capita waste water production were taken from ECETOC (1994) and the TGD. Sensitivity to the respective parameter and the resulting expectable influence of changes to the result are also described in the table.

In the following, single parameters are described briefly with the data ranges, the chosen values for the scenarios, their sensitivity and their expected influence on the result.

Density and number of inhabitants

Since the area is expected to be the same for all regions, the density of inhabitants is chosen as the characterising value. Deviations to the average region are very high because both Northern and Southern Europe are not very densely populated. However, because the number of inhabitants always has a negligible influence on the regional concentrations, it will nearly always be the same whichever value is chosen for this parameter.

Area fraction water

The standard value of the generic region for the regional area fraction of water is much lower than the northern value. Since there are many lakes in Norway, Sweden and Finland, the area fraction of water is approximately 10 %. Therefore, this value is chosen for the scenario *North*. In the south of Europe the opposite applies. Only few inland waters exist so that the fraction is only 1 % or even lower. For the *South* scenario a value of 1 % is assumed. The influence of this parameter on concentrations in water and sediment is high, especially for HHCB, EDC, BENZ, LAS and EDTA. Thus, higher changes in the results can be expected using different regional data.

Area fraction agricultural soil

In the north of Europe a lower area fraction is used for agriculture, while this fraction is much higher in the south of Europe. Because of its influence on concentrations in agricultural soil changes in the regional data, it will have a remarkable effect on the concentrations in agricultural soil.

Area fraction industrial/urban soil

Because the fractions for industrial and urban soil are not given in most of the sources (even in ECETOC 1994 it cannot be found), the values more or less had to be guessed. Because of the large area and low number of inhabitants in the north of Europe, the value for these countries is expected to be lower than in the generic region. For the southern countries the values will be higher and close to the average value. Because of its influence on regional concentrations of EDC, BENZ, LAS and EDTA in industrial/urban soil, the changes will be remarkable in this parameter. But since the differences between the countries are relatively low, alterations will not be very significant.

Area fraction natural soil

The fraction of natural soil is much higher in the north of Europe than in the average scenario. In the south of Europe it is lower due to the high area fraction used for agriculture. But because of the low sensitivities of environmental concentrations to this parameter, the changes using specific regional data will be low.

Depth of water

The depth of water is very difficult to determine. In fact, there is no source for regional values of this parameter. It can only be estimated that the average depth in the north of Europe is higher because of the numerous inland lakes, while it is probably lower in the south of Europe. Therefore, a northern value of 4 m and a southern value of 2 m was taken, even though it cannot be ascertained using literature sources. The influence of this parameter is usually low, and may only be high for concentrations of LAS in water and sediment. Altogether, alterations will be low using regional data for this parameter.

Temperature

It is obvious that average temperatures are lower in the north of Europe and higher in the south of Europe. The selected values for the two scenarios seem to be characteristic for the regions. However, sensitivities to the environmental temperature are low so that it makes no significant difference whether average or representative value are selected.

Precipitation

Average precipitation varies over the whole of Europe. In both northern Europe and the southern part it ranges from 400 to over 1 500 mm/a at coastal regions. However, a lower rain rate can be assumed for the south, especially if a country like Spain with a relatively low coastal area is regarded. A slightly higher value is chosen for the northern scenario. But because of its slight influ-

ence on the calculated concentration, selection of this parameter is not very important and deviations do not have significant consequences.

Fraction of rain water running off soil

The generic value of 25% cannot be verified with the given source (ECETOC 1994) because there the rain access is specified as between about 25 % to 75 % with a mean at about 50 %. This is also the value for the northern countries. For the southern countries the lowest access (25 %) is stated for Portugal so that 60 % is assumed to be typical for the southern scenario. Again, the influence of this parameter on the outcome is relatively low. Therefore, changes in this parameter in the regional scenarios will not lead to high alterations in the predicted concentrations.

Fraction connected to sewer systems

This parameter reveals high differences throughout Europe. In the north the value is much higher than the average value, while in the south it is remarkably lower. Because of its high influence on the modelled results, changes in this parameter will have an important impact on the outcome.

Waste water production

For the generic scenario a value for wastewater production is chosen that cannot be proved with the given data (TGD). 200 l/eq/day are characteristic for Germany, but in most of the other European countries this value is higher. Significant differences between northern and southern Europe cannot be stated. Consequently, a higher value is selected for both scenarios, even though sensitivities to this parameter are relatively low and important changes due to alterations in the sewage flow cannot be expected.

Altogether, realistic regional values will only have an important influence on the calculated concentrations for three regional parameters: area fraction of water, area fraction of agricultural soil and fraction connected to sewer systems. In some cases, other parameters also considerably influence predicted concentrations. Changes of up to 2.5 OoM can be expected, but will rarely occur. On average, changes will be within 1 OoM and usually lower (10 – 50 %). Concentrations in water and sediment will be lower in the *North* scenario since the fraction connected to sewer systems is higher there and the area fraction for surface water is higher. But for this reason concentrations in agricultural soil will be higher in the north than in the south because of higher emissions to the agricultural soil and a lower area fraction for this compartment.

A scenario analysis will show if these suppositions can be verified. The scenario calculations are based on the *NRW realistic* scenario and the *Default* scenario, i.e. entered emissions and partition coefficients and the regional and environmental data of the generic region or NRW. The different scenarios only deviate in their regional and environmental properties; substance data, such as emissions and degradation rates, remain unchanged. In fact, it is of secondary importance which substance data are chosen for the scenarios if they are the same for all scenarios because only the influence of changes in the regional properties are of interest. The NRW scenario used does not correspond exactly to the *NRW realistic* scenario presented in the previous chapter because, for

practical reasons, estimations for K_{OC} and the Henry's law coefficient are retained³. To keep the results directly comparable to those of the European scenarios, the area was also set to 40 000 km² and other parameters, such as wind speed, BOD, etc. were also left unchanged. The *Default* scenario used only represents the generic model with its regional parameters, while the substance properties are the same as in the regional scenarios. However, this is the only sensible way in which to carry out comparable calculations. Thus, for these scenario calculations the following four scenarios can be established: *NRW* with the Rhine-Westphalian regional data and the substance data as presented in the scenario analysis, *South* and *North* with the regional data given in Table 9, the substance data of the *NRW* scenario and, apart from that, generic data and the *Default* scenario with generic regional and environmental data but substance data as used in the *NRW* scenario. Table 9 shows the data of the generic region (*Default*), the data ranges for northern and southern Europe and values for the two scenarios *North* and *South*. Additionally, sensitivity to the respective parameter (see Chapter 6) and the expected influence on the outcome are characterised.

Table 9 Characteristics of different European regions.

Parameters	Default	Northern	Southern	Scenario North	Scenario South	Sensitivity	Influence
Density of inhabitants [inh./km ²]	500	13 to 20	80 to 200	15	100	0	no
Number of inhabitants	20 000 000			600 000	4 000 000	0	no
Area fraction water	3 %	10 %	<1%	10 %	1 %	up to -1 (high)	up to factor -3 (high)
Area fraction agricultural soil	27 %	5 – 15 %	60 %	10 %	60 %	up to -1 (high)	up to factor -3 (average)
Area fraction industrial/urban soil	10 %	3 – 5 %	5 – 8 %	5 %	9 %	up to -1 (average)	low
Area fraction natural soil	60 %	70 – 80 %	25 – 35 %	75 %	30 %	up to -0.2 (low)	low
Depth of water [m]	3			4 [#]	2 [#]	up to -1 (low, high for LAS)	low (high for LAS)
Temperature [°C]	12	2 – 5	13 – 19	4	17	up to 0.4 (low)	low
Precipitation [mm/a]	700	400 – 1 780 (coast)	400 – 1 500 (coast)	800	500	up to 0.5 (average)	low
Fraction of rain water running off soil	25 % (data: 50–65 %)	50 – 60 %	45 – 75 %	50 %	60 %	low (high for EDTA)	low (up to factor -3 for EDTA)
Fraction connected to sewer systems	70 %	75 – 98 %	10 – 60 %	95 %	25 %	up to -5 (very high)	up to factor 15 (high)
Waste water production [l/eq/d]	200 (data: 200 – 300)	250 – 280 (DK: 170)	200 – 280	250	250	sometimes up to 0.5 (low)	low

[#] estimated

8.4 Results of the regional scenarios

According to the scenario analysis presented in Chapter 7, the regional calculations were performed for concentrations in air, water, sediment and agricultural soil for each of the investigated substances. The results are shown in Figure 10 to Figure 13.

³ This scenario is also used in the following Chapter for the probabilistic analyses. There it is called *NRW base*. The reason for this is that changes in the scenario data and in the data transfer are easier to handle with the Excel®-spreadsheet version of EUSES.

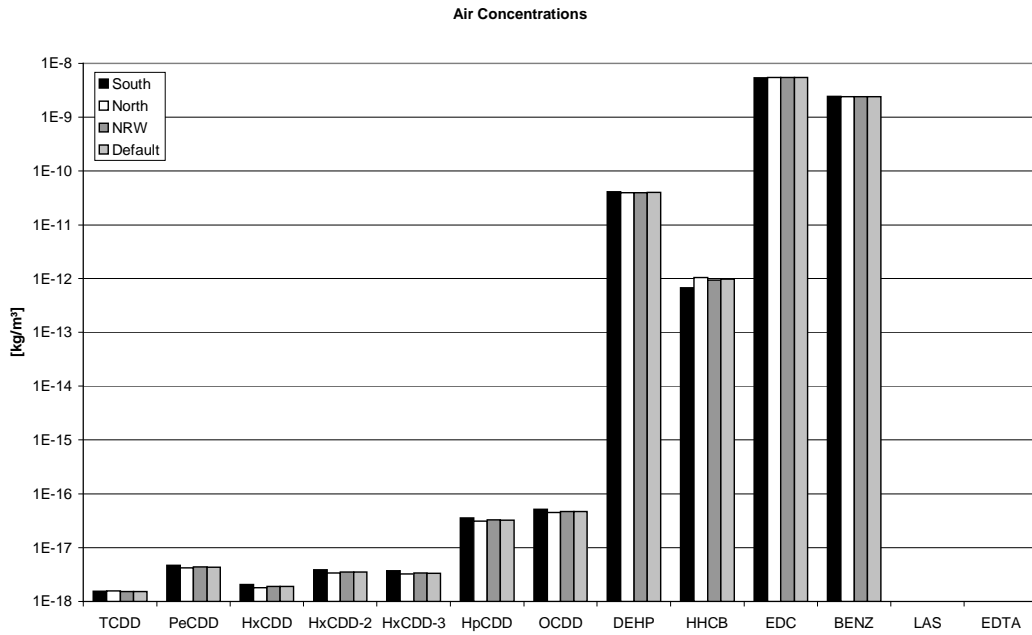


Figure 10 Comparison of concentrations in air using different regional scenarios.

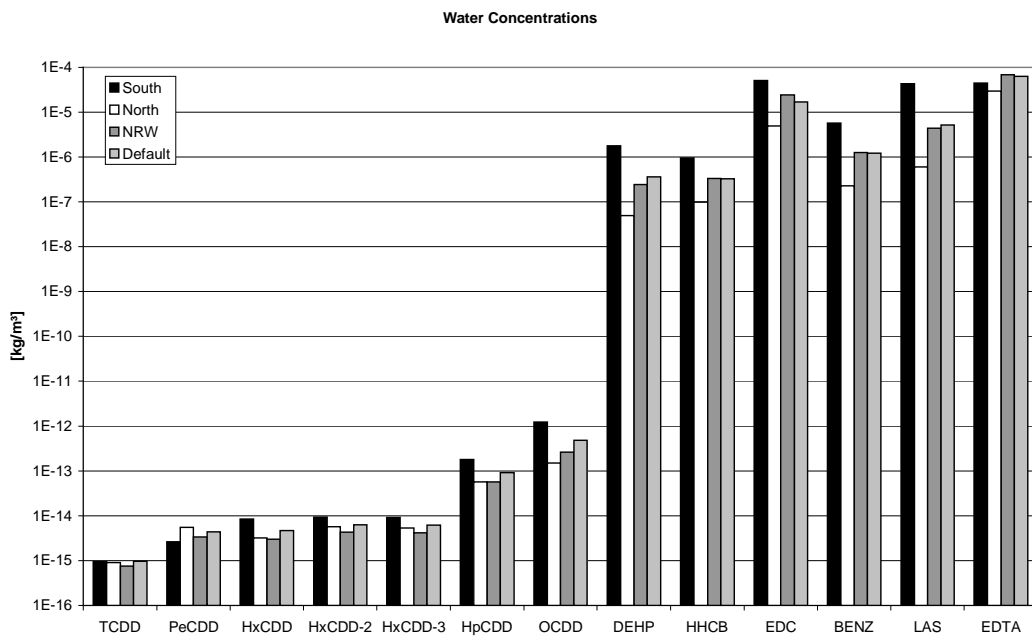


Figure 11 Comparison of concentrations in water using different regional scenarios.

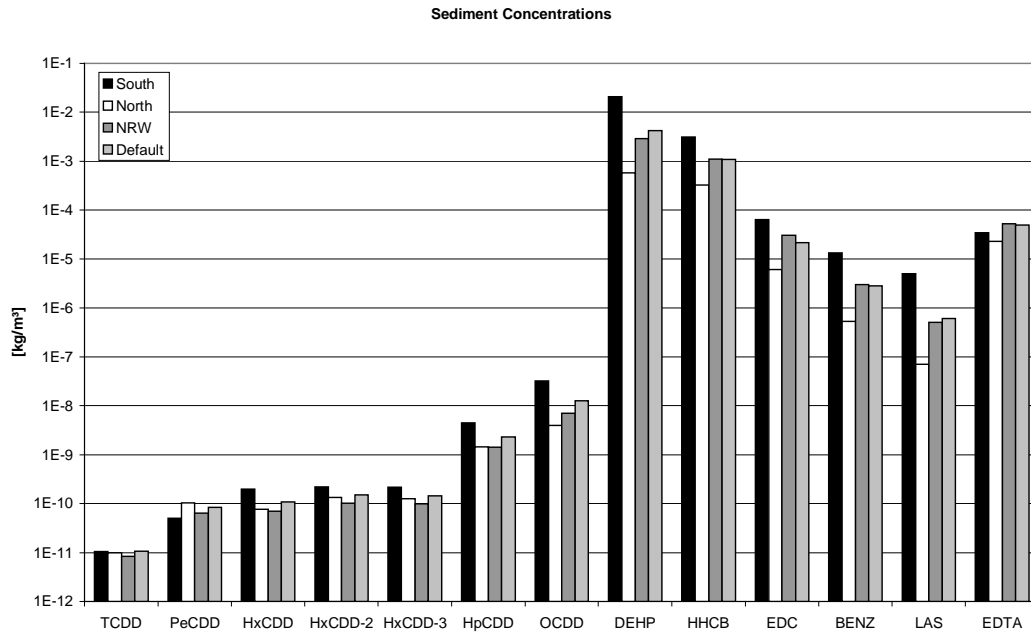


Figure 12 Comparison of concentrations in sediment using different regional scenarios.

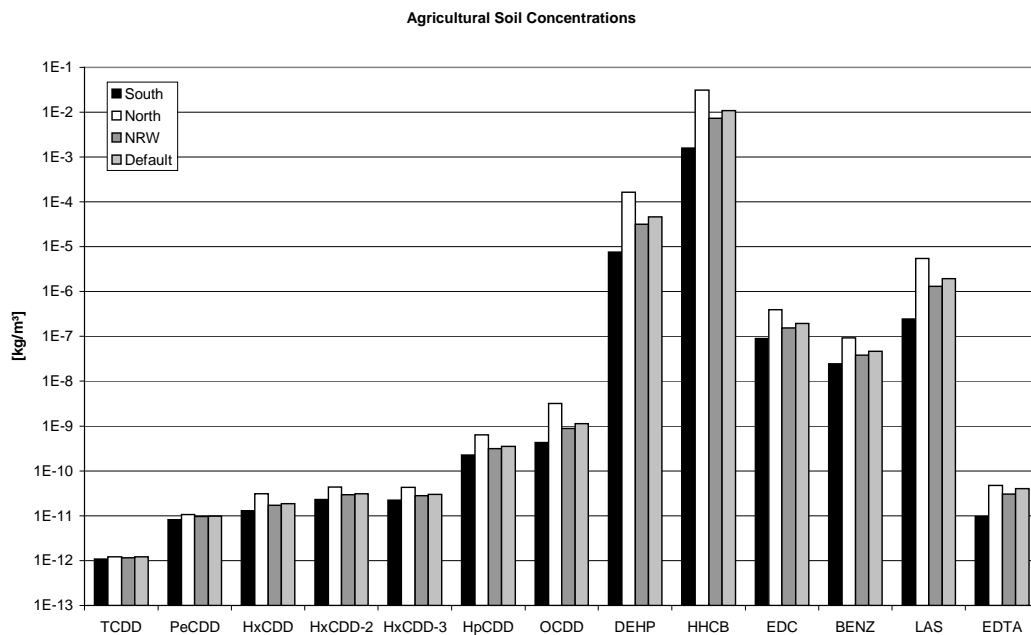


Figure 13 Comparison of concentrations in soil using different regional scenarios.

As expected, concentrations in air are nearly the same for all four scenarios. In most cases, differences between the *NRW* and *Default* scenarios are lower than between *North* and *South*. This shows that the region of North Rhine-Westphalia is rather similar to the generic region, while the differences between the northern and southern part of Europe are much greater. All in all, concentrations in water and sediment are higher in the *South* than in the *North* scenario. For agricultural soil it is exactly the opposite. The reason for this can be found in the fraction connected to sewage systems and for agricultural soil and water. In the south of Europe, the fraction connected to sewer systems is lower. Consequently, direct emissions to surface water are higher and indirect emis-

sions to agricultural soil are lower. Furthermore, the area fraction for water is lower and that for agricultural soil is higher. As a consequence, the effect is again enforced. Exceptions of this behaviour are only demonstrated by PeCDD. The concentrations of this substance are estimated lower in the *South* scenario for both water and agricultural soil. In this case, the low sensitivity of concentrations to the fraction connected to sewer systems is the explanation for this effect. Due to this fact, the influence of changes in the area fractions can affect concentrations in water more significantly. Since sensitivity of the water concentrations to the area fraction of water is positive for this substance (see Table 48 in appendix A.5), the water concentration is higher in scenario *North* than in scenario *South*. For the other substances, the effect is the opposite and the effects of changes in other parameters are higher.

The range of the highest and lowest concentration of a substance is always within two OoM. In most cases, the scenarios *North* and *South* represent the extreme value, i.e. maximum and minimum of all scenarios. The concentrations estimated by the *Default* scenario always lie between the scenarios *North* and *South*.

8.5 Discussion and conclusions

The regional scenarios lead to clearly different results in the concentrations in water, sediment and soil, although not every possible difference was considered (e.g. fraction OC in soil, wind speed, suspended matter concentration in water or particle content in air). In particular, the different values for the fraction connected to sewer systems and for the area fractions result in considerable changes of up to two orders of magnitude. Since the outcome of the *Default* scenario always lies between the *North* and *South* scenarios, it can be regarded as an average scenario, even though the chosen values are not always average but guessed values. Assessing the conservatism of the *Default* scenario is therefore difficult. Concentrations in water and sediment are overestimated if southern regional data are used so that the *Default* scenario may underestimate the worst case. But using southern regional data underestimates concentrations in agricultural soil due to lower indirect emissions caused by a lower fraction connected to sewer systems. Consequently, use of the *Default* scenario can be justified. JAGER ET al. (2000) claimed that the use of alternative scenarios "increases the realism of the assessment" but "it will complicate decision-making as the relevance of each scenario has to be discussed." But choosing realistic parameter values for a regional model is always virtually impossible due to missing or unsuitable data. This applies to the selection of average values for Europe (as in the TGD for the standard region) as well as for a northern or a southern region. Nevertheless, it is feasible to select reasonable values that can not be ascertained by sources, but that seem to be realistic. If the data values are comprehended as suggested in the TGD, namely as average values, the European scenarios may, however, be used. It must always be heeded that such average values are not likely for a comparison to measured values, but are sufficient for the screening phase of the risk assessment of substances. Setting up different regional scenarios can help to estimate the range of possible concentrations, and overcomes the weaknesses of one given generic data set suggesting truth and conservatism. Thus, these two scenarios should not replace the standard scenario, but should be added to it to cover more or less the whole range of European heterogeneities. One scenario alone can not fulfil the

task of performing a (reasonable) worst-case estimation of regional background concentrations. However, the uncertainties due to regional heterogeneities (maximal range of ≈ 2 OoM) are altogether lower than those caused by uncertain substance parameters (maximal range >5 OoM). Both together can lead to very high ranges in possible environmental concentrations.

8.6 Summary

The generic region incorporated into EUSES is used for the estimation of conservative regional environmental concentrations. To consider different, more extreme regional properties in Europe two additional scenarios were contrived: a scenario representing a typical region in the north of Europe (high fraction connected to sewer systems, lower environmental temperature, high fractions for surface water and natural soil and a low fraction for agricultural soil) and another scenario representing a typical region in the south of Europe (low fraction connected to sewer systems, higher environmental temperature, low fractions for surface water and natural soil, and a high fraction for agricultural soil). The two scenarios are based on average data of countries in Northern and Southern Europe, but are not realistic for any countries located in these regions. Scenario calculations were undertaken using these two scenarios in addition to the generic region and a North Rhine-Westphalian region. The substance properties, including emissions, were left unchanged for all scenarios.

All in all, it can be stated that

- determining parameter values for average regional properties is quite difficult,
- the generic region represented in EUSES contains values that are not ascertained by literature sources, but rather seem to be guessed,
- the standard region does not necessarily represent the worst case since concentrations in the north and south of Europe may be higher,
- uncertainties due to regional heterogeneities within Europe are high, but are lower than those caused by uncertain substance data.

It is therefore recommended to use these two additional scenarios for an improved estimation of possible concentration ranges in Europe.

9 Probabilistic uncertainty analyses

In this section, the effects of uncertainties in the input parameters to the results of the regional distribution model are analysed. The uncertainty analysis of the regional distribution model SimpleBox was performed for those output parameters that formed the basis of the scenario analyses. These are the regional concentrations for air, water, sediment and agricultural soil.

As already explained in Section 2.2.3, for an uncertainty analysis it is, necessary to provide the input parameters with probability distributions. The uncertainty analysis is based on the Excel[®] version of EUSES. With CrystalBall[™] it was possible to provide the parameters with distributions and to perform Monte-Carlo analyses. The analyses were carried out using a fixed parameter set which represents a combination of different point scenarios (see Chapter 7). This scenario is called *NRW basic* and is based on the *NRW realistic* scenario. It uses the regional parameters of North Rhine-Westphalia and as many measured and investigated substance data as is available. However, in the sense of a profound uncertainty analysis, estimations rather than entered values still have to be used for some parameters. This concerns the Henry's law constant and K_{OC} . These coefficients are estimated from PC data for which probability distributions are used.

Separation into variability and true uncertainty cannot be carried out unequivocally for all parameters. Both parameter groups (substance parameters and regional parameters) contain uncertain parameters as well as variable ones. The group of substance parameters include, e.g. uncertain PC data (difficult measurements), whilst the degradation rates are both uncertain and variable (according to environmental properties). The regional parameters include, e.g. environmental temperature, precipitation rate or wind speed spatially and temporarily variable, whilst the compartments' depths are both variable and, due to the difficult condition of data, uncertain. There are no solely true uncertainties within the regional parameters because they always have temporal and spatial variabilities and at the same time are often difficult to determine.

9.1 Results of the uncertainty analyses

The results of the uncertainty analyses can be evaluated relating two different aspects:

- Assessment of the contribution of single parameter uncertainties to the total uncertainty.
- Comparison of uncertainties with the underlying point estimation and the measured values.

Compared to the sensitivity analyses, in the uncertainty analyses fewer parameters were varied because for some insensitive parameters no distributions were researched. Also, some parameters were not assumed to be uncertain so they were not included, although they are sensitive. This is described in more detailed in the appendix (Section A.1).

The relative influence of the single parameter uncertainties on the total uncertainty is important for interpretation of the results and comparison with the sensitivities. In CrystalBall[™], this contribution to the uncertainty is calculated by a rank correlation, and is also called sensitivity. This terminology is confusing because in this work sensitivity is understood as the "local" influence of a single parameter on the result, while in a rank correlation the relative influence of a parameter is regarded. Therefore, the term sensitivity is not used in this context but in the expression of contribution to the total uncertainty. The results of the rank correlations are explained in the following section.

9.1.1 Results of the rank correlations

The rank correlations represent the contribution of a single parameter to the total uncertainty. The results of simultaneously varying all model parameters are listed in Table 10 to Table 13. The results are closely connected to the results of the sensitivity analyses since here the influence of a single parameter on the result is also regarded. At this place, however, it is considered together with uncertainties of the other parameters.

Table 10 Results of the rank correlations between concentrations in air and the single input parameters. Only correlation coefficients with an absolute value higher than ≥ 0.1 are listed. For each substance the parameter with the highest influence is typed in bold face.

*: not varied (set to zero)

Type	Parameter	TCDD	PeCDD	HxCDD	HpCDD	OCDD	DEHP	HHCB	EDC	BENZ	LAS	EDTA	
Degradation rates	kdegair	0.1					0.2	0.5	0.1	0.1		*	
	kdegwater										0.2		
	<i>Negligible impact: kdegsoil</i>												
Emissions	EContAir	0.3	0.2	0.3	0.3	0.3	0.1	*	0.3	0.6	*	*	
	EContfirstwastewater							0.1	0.1			0.1	
	ERegAir	0.5	0.7	0.5	0.6	0.5	0.7	*	0.4	0.2	*	*	
	ERegfirstwastewater							0.5	0.1		0.3	0.2	
	<i>Negligible impact: EContfirstwater, EContlnd, ERegfirstwater, EReglnd</i>												
PC data	K _{ow}								-0.1				
	Sol						-0.2				-0.6	-0.6	
	Vp	0.1	0.2	0.1	0.3		0.1				0.3	0.6	
	<i>Negligible impact: none</i>												
Process parameters	DepRateAer		-0.1		-0.1								
	FrunoffSoil											-0.3	
	Rainrate		-0.1		-0.1		-0.1	-0.1			-0.1	-0.2	
	windspeed	-0.3	-0.2	-0.3	-0.3	-0.3	-0.1		-0.3	-0.2	0.1	0.1	
	<i>Negligible impact: CollEffAer, Erosion, kasl air, kasl soilair, kasl soilwater, kwsSed, kwsWater, SETTLEvelocity</i>												
Volumetric parameters	depthAgric								-0.1				
	depthWater Reg										-0.4		
	fAgric Reg										-0.1	-0.1	
	fNatural Reg										-0.1	-0.1	
	fWater Reg							0.2				0.2	
	heightAir	-0.7	-0.5	-0.7	-0.6	-0.7	-0.5	-0.6	-0.8	-0.7			
	<i>Negligible impact: area Reg, depthlnd, depthNat, depthSed, flnd Reg</i>												
Other model-parameters	SurfAer		-0.1	-0.1	-0.1						0.4	0.1	
	<i>Negligible impact: FWaterSed, BOD, FconnectSTP, FlnfSoil, FocSed, FocSoil, FocSusp, FSolidSoil, FWaterSoil, Qstp, RhoSolid, SuspEff, SuspWater Reg, Temperature</i>												

Table 11 Results of the rank correlations between concentrations in water and the single input parameters. Only correlation coefficients with an absolute value higher than ≥ 0.1 are listed. For each substance the parameter with the highest influence is typed in bold face.

*: not varied (set to zero)

Type	Parameter	TCDD	PeCDD	HxCDD	HpCDD	OCDD	DEHP	HHCB	EDC	BENZ	LAS	EDTA
Degradation rates	kdegscd			0.1	0.1	0.1	0.2					
	kdegsoil				0.1			0.1		0.1		
	kdegwater				0.1		0.1					
	<i>Negligible impact: kdegair</i>											
Emissions	EContAir	0.2			0.1			*			*	*
	ERegAir	0.2		0.1	0.1		0.1*			*		*
	ERegfirstwastewater	0.1		0.4	0.3	0.5	0.5	0.8	0.8	0.3	0.4	0.6
	ERegfirstwater	*		*	*	*	*			0.4		
	ERegInd	*	*	*	*	*	*	*		0.3		
<i>Negligible impact: EContfirstwastewater, EContfirstwater, EContInd</i>												
PC data	Kow	0.1					-0.1			-0.1		
	Sol	0.3			0.1		0.1	0.1				
	Vp	-0.7		-0.2	-0.2		0.1					
	<i>Negligible impact</i>											
Process parameters	DepRateAer		0.1									
	Erosion	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1					
	FrunoffSoil	-0.1		-0.1	-0.1	-0.1	-0.1	-0.1		0.1	-0.1	-0.7
	Rainrate											-0.3
	windspeed	-0.1	-0.1		-0.1				-0.1			
<i>Negligible impact: CollIEffAer, kasl air, kasl soilair, kasl soilwater, kwsSed, kwsWater, SETTLEvelocity</i>												
Volumetric parameters	depthAgric							-0.1				
	depthInd									-0.2		
	depthNat		-0.1									
	depthSed	-0.1	-0.1	-0.2	-0.2	-0.2	-0.3					
	depthWater Reg	-0.1	-0.1	-0.1			-0.1			-0.1	-0.7	
	fAgricReg		-0.1		-0.1	-0.1						
	fWater Reg	0.1	0.2	-0.1		-0.1	-0.2	-0.4	-0.5	-0.7	-0.3	
	heightAir	-0.3	-0.3	-0.1	-0.2							
<i>Negligible impact: area Reg, flnd Reg, fNatural Reg</i>												
Other model parameters	FconnectSTP	-0.1		-0.2	-0.2	-0.3	-0.3			-0.2	-0.2	
	FInfSoil							-0.1		-0.1		
	FocSoil									-0.1		
	FSolidSoil	-0.1	-0.2	-0.2	-0.2	-0.2	-0.1	-0.1		-0.1		
	FWaterSed	0.1	0.1	0.1	0.1	0.1	0.2					
	SuspEff			0.2	0.2	0.2	0.3	0.1				
	SuspWater Reg	0.3	0.7	0.7	0.7	0.7	0.4	0.3				
	<i>Negligible impact: BOD, FocSoil, FocSusp, FWaterSoil, Qstp, RhoSolid, SurfAer, Temperature</i>											

Table 12 Results of the rank correlations between concentrations in sediment and the single input parameters. Only correlation coefficients with an absolute value higher than ≥ 0.1 are listed. For each substance the parameter with the highest influence is typed in bold face.

*: not varied (set to zero)

Type	Parameter	TCDD	PeCDD	HxCDD	HpCDD	OCDD	DEHP	HHCB	EDC	BENZ	LAS	EDTA
Degradation rates	kdegsead	0.1	0.2	0.2	0.2	0.2	0.3			0.1	0.3	
	kdegsoil		0.1									
	kdegwater		0.1		0.1		0.1				0.2	
	<i>Negligible impact: kdegair</i>											
Emissions	EContAir	0.2	0.2		0.1				*		*	*
	EContfirstwastewater					0.1						0.1
	ERegAir	0.2	0.4	0.1	0.2		0.1	*			*	*
	ERegfirstwastewater	0.1		0.5	0.4	0.6	0.5	0.6	0.6	0.2	0.3	0.4
	ERegfirstwater	*		*	*	*	*	*		0.3		
	ERegInd	*		*	*	*	*	*	*	0.2		
<i>Negligible impact: EContfirstwater, EContInd</i>												
PC data	Kow	0.5							0.2	0.3	0.3	0.2
	Sol	0.3			0.1	0.03						0.5
	Vp	-0.6	-0.1	-0.3	-0.2							
<i>Negligible impact: none</i>												
Process parameters	DepRateAer		0.1		0.1							
	Erosion		-0.1	-0.1	-0.1	-0.1	-0.1					
	FrunoffSoil		-0.1	-0.1	-0.1	-0.2	-0.1		-0.1	0.1	-0.1	-0.4
	kwsSed									0.1		0.1
	Rainrate			-0.1	-0.1	-0.1						-0.2
	SETTLEvelocity									0.1	0.2	
	windspeed	-0.1	-0.1		-0.1				-0.1			
<i>Negligible impact: CollEffAer, kasl air, kasl soilair, kasl soilwater, kwsWater</i>												
Volumetric parameters	depthAgric					-0.1		-0.1				
	depthNat		-0.1									
	depthSed	-0.1	-0.3	-0.2	-0.3	-0.2	-0.5			-0.2	-0.5	
	depthWater Reg	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1			-0.1	-0.5	
	fAgricReg		-0.1	-0.1	-0.1	-0.1						
	fWater Reg	0.1	0.2	-0.1	-0.1	-0.1	-0.2	-0.3	-0.4	-0.4	-0.2	
heightAir	-0.3	-0.4	-0.1	-0.2								
<i>Negligible impact: area Reg, depthInd, flnd Reg, fNatural Reg,</i>												
Other model parameters	FconnectSTP	-0.1		-0.3	-0.2	-0.3	-0.3			-0.1	-0.1	
	FInfSoil							-0.1		-0.1		
	FocSoil									-0.1		
	FocSusp	0.1						0.3	0.3	0.3	0.1	0.2
	FSolidSoil	-0.1	-0.3	-0.3	-0.3	-0.3	-0.1	-0.1		-0.1		
	FWaterSed	-0.2	-0.4	-0.4	-0.4	-0.4	-0.2	-0.5	-0.5	-0.4	0.1	-0.4
	SuspEff			0.2	0.2	0.3	0.3	0.1				
SuspWater Reg		-0.1		-0.1		-0.1			0.2	0.4		
<i>Negligible impact: BOD, FocSed, FWaterSoil, Qstp, RhoSolid, SurfAer, Temperature</i>												

Table 13 Results of the rank correlations between concentrations in soil and the single input parameters. Only correlation coefficients with an absolute value higher than ≥ 0.1 are listed. For each substance the parameter with the highest influence is typed in bold face.

*: not varied (set to zero)

Type	Parameter	TCDD	PeCDD	HxCDD	HpCDD	OCDD	DEHP	HHCB	EDC	BENZ	LAS	EDTA
Degradation rates	kdegsoil	0.3	0.4	0.4	0.4	0.4	0.4	0.1	0.2	0.4	0.4	
	<i>Negligible impact: kdegair, kdegsead, kdegwater</i>											
Emissions	EContAir	0.1	0.1									
	ERegAir	0.1	0.3	0.1	0.2		0.1	*			*	*
	ERegfirstwastewater	0.1		0.3	0.2	0.4	0.3	0.7	0.5	0.4	0.4	0.4
	<i>Negligible impact: EContfirstwastewater, EContfirstwater, EContlnd, ERegfirstwater, EReglnd</i>											
PC data	Kow							0.2	0.4	0.3	0.4	0.2
	Sol						0.1					-0.3
	Vp	-0.5	-0.2	-0.2	-0.3							0.3
<i>Negligible impact: none</i>												
Process parameters	DepRateAer		0.1									
	FrunoffSoil							-0.2	-0.2	-0.1	-0.1	-0.5
	Rainrate	0.1	0.1					-0.1	-0.1			-0.3
	windspeed	-0.1	-0.1		-0.1				-0.1			0.1
	<i>Negligible impact: CollEffAer, Erosion, kasl air, kasl soilair, kasl soilwater, kwsSed, kwsWater, SETTLEvelocity</i>											
Volumetric parameters	depthAgric	-0.6	-0.7	-0.7	-0.7	-0.7	-0.7	-0.2	-0.4	-0.6	-0.6	
	fAgric Reg	-0.1		-0.1	-0.1	-0.2	-0.1	-0.3	-0.2	-0.2	-0.2	-0.1
	fWater Reg											0.2
	heightAir	-0.2	-0.2	-0.1	-0.2		-0.1		-0.1			
<i>Negligible impact: areaReg, depthlnd, depthNat, depthSed, depthWater Reg, flnd Reg, fNatural Reg</i>												
Other model parameters	FInfSoil							-0.2	-0.1	-0.1		-0.2
	FocSoil							0.4	0.3	0.1	0.1	
	FSolidSoil	-0.3	-0.3	-0.3	-0.3	-0.3	-0.3	-0.1	-0.2	-0.3	-0.3	-0.4
	Qstp								-0.1	-0.1	-0.1	-0.1
	SurfAer	0.2	0.2	0.1	0.1							
	<i>Negligible impact: FWaterSed, BOD, FconnectSTP, FocSed, FocSusp, FWaterSoil, RhoSolid, SuspEff, SuspWater Reg, Temperature</i>											

For 12 of the altered 53 parameters, the absolute value of the contribution to the uncertainty is less than 0.1. These are the parameters that already showed a very low influence in the sensitivity analyses, those with very low uncertainties and parameters that lose their influence due to the variation of all parameters simultaneously. This will be explained in the following section.

The influence of uncertainties in the degradation rates on the uncertainties of concentrations in the individual media basically corresponds to the results of the sensitivity analyses. Here, degradation in a determined compartment generally has the highest influence on the concentration in the appropriate compartment. For the concentration of HHCB in air, the influence of the degradation rate in air is extremely high since HHCB is not emitted to air but has the highest degradation rate in this compartment. Differences to the sensitivities result from the fact that sensitivities only consider the local influence of a single parameter on the regarded output parameter, whilst uncertainty analyses consider the relative contribution of a parameter in relation to all simultaneously varied parameters. Thus, different parameters can compensate or increase their influence. An example will explain this in further detail: The (very low) concentration of LAS in air is sensitive to the degradation, emission and volumetric parameters of soil. But in the uncertainty analysis they have a very low or even no contribution to the total uncertainty. Instead, now the relative parameters in water are relevant. This indicates such an effect since the relative changes for degradation rates and emissions are the same for both sensitivity and uncertainty analyses. The reason for this change of influence from soil to water can in this case be found in the parallel variation of the transfer coefficients between soil and air. In the uncertainty analyses, probabilistic distributions are assumed for these parame-

ters, of which the median is several OoM lower than the default value. Consequently, the resistance for diffusion out of the soil is much higher. Accordingly, the influence of the soil parameters on the concentrations in air decreases. Another example is the parameter FWaterSoil (fraction of water pores in soil) which in the sensitivity analysis shows a strong influence on the concentrations of EDTA in soil, but makes no relevant contribution to the uncertainty. This is caused by the simultaneous variation of the parameters FSolidSoil (fraction of solids in soil), which counteracts FWaterSoil and also has a higher uncertainty⁴. This leads to a decline of the influence of FWaterSoil.

The emissions' contributions to uncertainty correspond to their sensitivities. But also here, exceptions occur that again can be explained by uncertainties of the transfer coefficients. The total of Emissions into one compartment contribute significantly to the total uncertainty of the corresponding concentration.

From the PC data taken into consideration in the uncertainty analysis (K_{OW} , water solubility, vapour pressure), only those with a relevant contribution to the total uncertainty turned out to be influential in the sensitivity analysis. Deviations take place if the uncertainties of a parameter are very high or low, i.e. relatively low sensitivities coincide with very high uncertainties and vice versa. The highest contribution to the total uncertainty is the uncertainty of the vapour pressure of TCDD. This can be explained by its high sensitivity and at the same time high uncertainty of this parameter. Altogether, uncertainties in the PC data only make a significant contribution to the total uncertainty in some cases.

The process parameters also only make a minor contribution to the uncertainty. The few sensitive parameters (rain rate and wind speed) for North Rhine-Westphalia show relatively low uncertainties and variabilities, respectively.

This is similar to volumetric parameters. Here, only the atmospheric mixing height is at the same time sensitive and uncertain. This leads to high uncertainties of the concentrations in air of all substances showing high sensitivities. For the concentrations in air, this parameter is that with the highest influence on the total uncertainty. The compartment depths also make a substantial contribution to the total uncertainty of the corresponding concentrations if they were influential in the sensitivity analyses. Hence, the results of the uncertainty analyses again correspond to those of the sensitivity analyses.

On the whole, the influence of the other model parameters is low. Very sensitive parameters, such as, e.g. fractions of solids in soil or water in sediment, only make a minor contribution to the total uncertainty. As already seen with the degradation rates, the explanation can again be found in the low medians of the probability distributions assumed for the transfer coefficients. A parameter that makes a remarkable contribution to the total uncertainty is the concentration of suspended matter in surface water. In the sensitivity analysis, this parameter had a high influence on the concentrations of lipophilic substances in the surface water, and because of its high variability ($CV = 0.78$), it behaves in a similar fashion in the uncertainty analysis.

⁴ Here turns out an inconsistency in the choice of the distributions. FSolidSoil is varied in the range of 0 to 1, FWaterSoil is simultaneously varied in the range of 0.2 to 0.3. The sum of both fractions can consequently be unequal to 1.

In general, the results of the uncertainty analyses are only different to those of the sensitivity analyses in a few cases. This applies, on the one hand, to parameters that are sensitive but not or only slightly uncertain, e.g. many volumetric or process parameters. On the other hand, this applies to parameters that have a relatively high influence locally but of which the contribution to the total uncertainty is reduced due to the parallel variation of the transfer coefficients soil-air. This shows that in an uncertainty analysis the entire consideration of all varied parameters is of prime importance.

The results are graphically represented in Figure 14 to Figure 17. The figures show the relative contribution of the single parameter groups to the total uncertainty if all model parameters are varied. They allow some general and summarising statements to the contributions of parameter groups on the total uncertainty.

It is noticeable that, all in all, the process parameters make a very minor contribution to the uncertainties. The most distinct exception is EDTA. Due to its very low lipophilicity and its very high water solubility, it is strongly influenced by the parameter *Frunoffsoil* (fraction of rainwater running off soil to surface water).

The volumetric parameters have a high influence on the total uncertainty. But the concentrations of the lipophilic substances in water represent an exception. For these, the influence of the other model parameters is the highest.

Apart from this, the other model parameters are of minor relevance for the uncertainties, but can not altogether be neglected.

With regard to substance parameters, in the most cases the degradation rates make a relatively low contribution to the total uncertainty, even though they vary within one order of magnitude. They are only relevant for HHCB in air and the soil concentrations of most of the substances.

In contrast, the uncertainties of emissions are quite important. Exceptions are again the concentrations in soil of most substances, as well as TCDD in water and sediment, and the concentrations of LAS and EDTA.

The contribution of uncertainties in the PC data is varied. Most remarkable is the low influence on concentrations in water (with the exception of TCDD). Uncertainties in this compartment arise especially from uncertainties in emissions.

The exact appearance of the resulting probability distributions is explained in the following section.

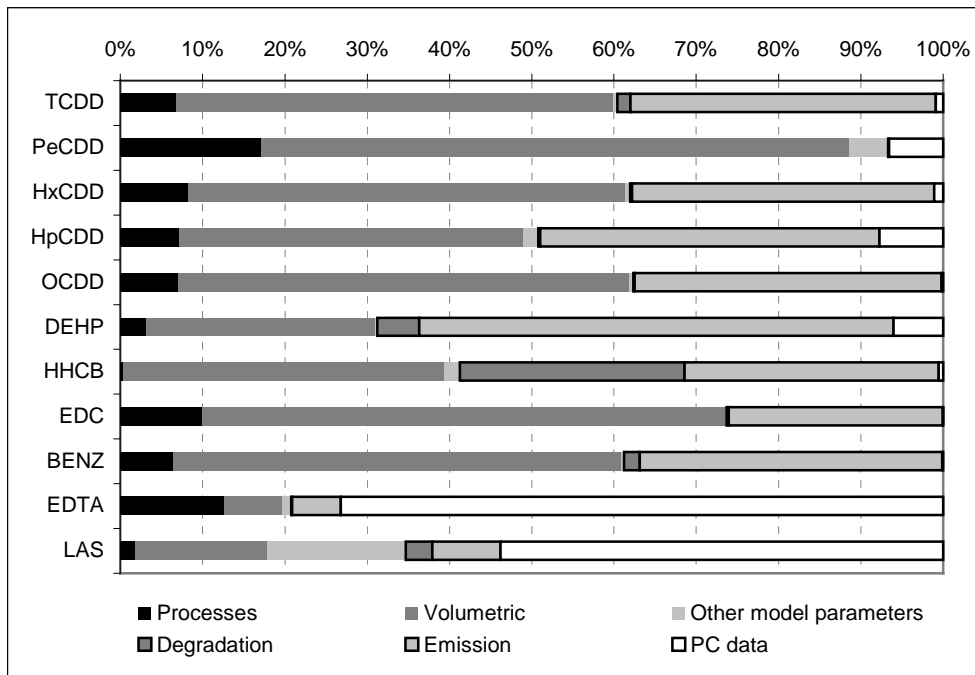


Figure 14 Contribution of regional parameters (processes, volumetric parameters and others) and substance parameters (degradation rates, emissions, PC data) to the variance of concentrations in air.

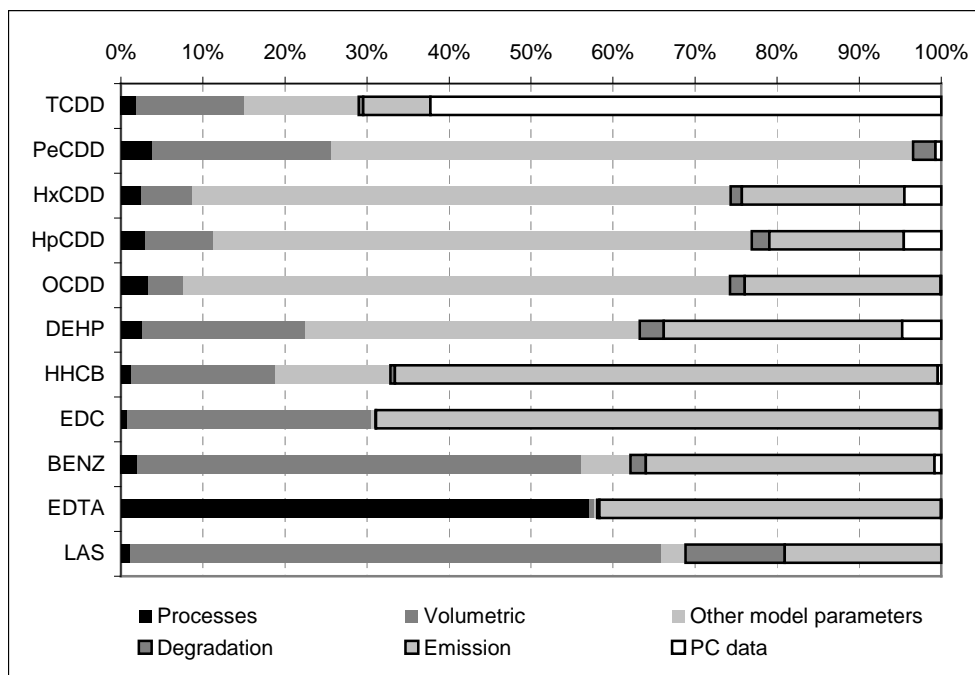


Figure 15 Contribution of regional parameters (processes, volumetric parameters and others) and substance parameters (degradation rates, emissions, PC data) to the variance of concentrations in water.

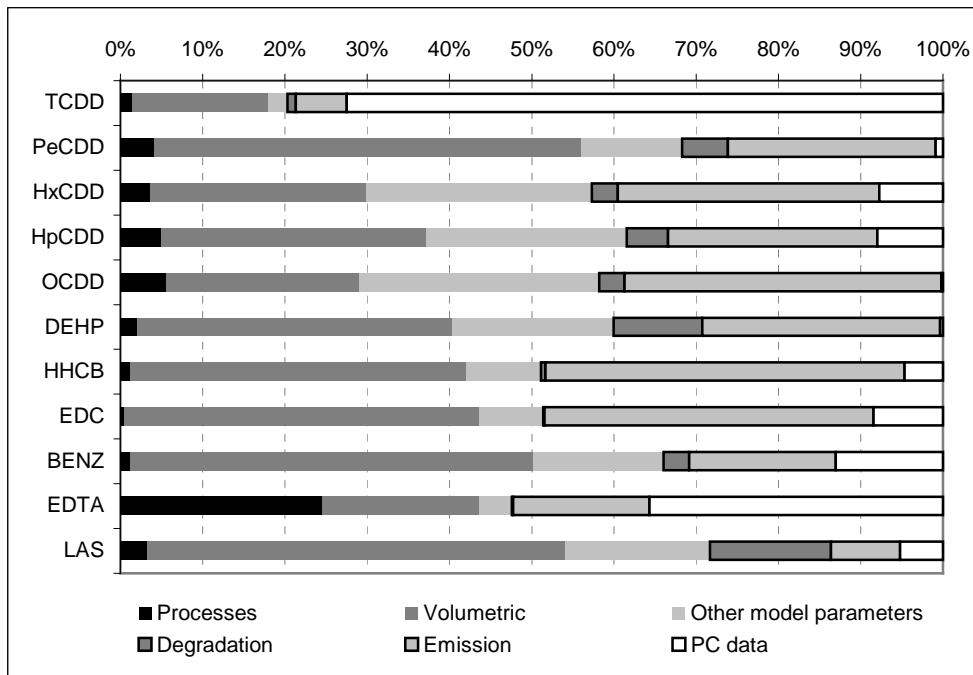


Figure 16 Contribution of regional parameters (processes, volumetric parameters and others) and substance parameters (degradation rates, emissions, PC data) to the variance of concentrations in sediment.

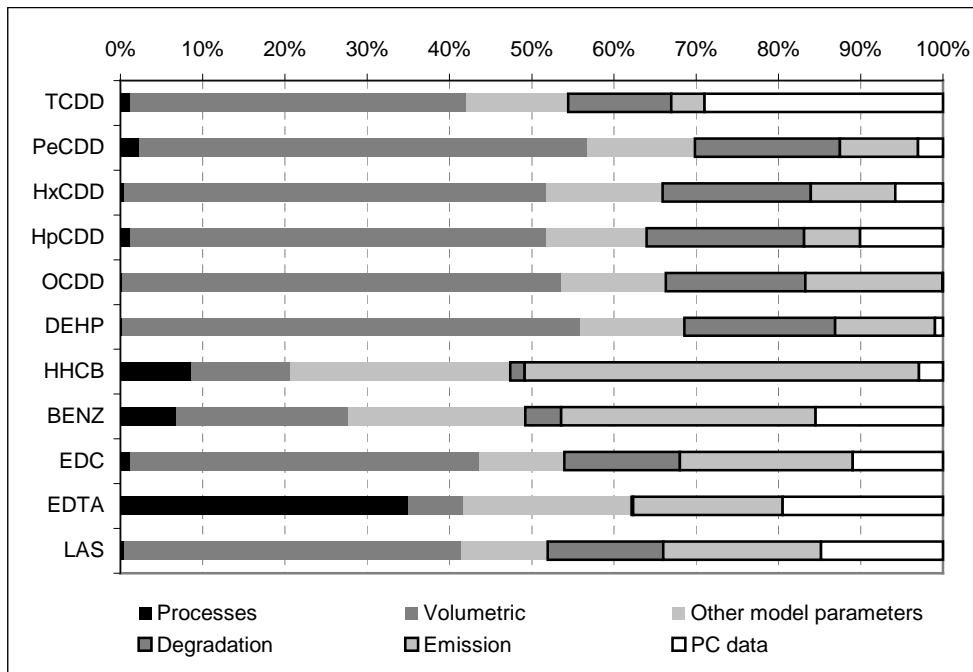


Figure 17 Contribution of regional parameters (processes, volumetric parameters and others) and substance parameters (degradation rates, emissions, PC data) to the variance of concentrations in soil.

9.1.2 Cumulative distribution functions of environmental concentrations

The results of the uncertainty analyses presented in the previous sections were related to the simultaneous variation of all parameters. But to assess the influence of single parameter groups on the resulting cumulative distribution functions of the environmental concentrations it makes sense

to divide the input parameters into two groups: substance parameters and regional parameters. The group of substance parameters contains PC data, degradation rates and emissions. The remaining parameters of SimpleBox, i.e. volumetric parameters, process parameters and other model parameters, are designated regional parameters. In accordance with this division, three simulation runs were carried out for every substance, each with varying regional and/or substance parameters (see Table 14).

Table 14 Representation of the three simulation runs for each substance.

Run	Varied parameters
(I)	All parameters of the whole model
(II)	Only regional parameters (without substance parameters)
(III)	Only substance parameters (without regional parameters)

The plots of the distribution functions are represented in appendix A.6 (Figure 29 to Figure 72). The tables of the probabilistic distributions (appendix A.3, Table 32 to Table 42) show that the mean and median values, respectively, of the used probability distributions do not always correspond with the input values of the point estimation. This can lead to a deviation of the mean values of the resulting distributions from the results of the point estimations. Also the mean of the uncertainty scenarios is by this reason not equal. To verify this aspect, some alternative uncertainty analyses and the resulting distributions are presented in the discussion of the results (Section 9.3).

The result of the point estimation is not always within the range of the measured values. The reasons for these deviations are explained in further detail in the scenario analysis (Chapter 7). Another much more important aspect of the uncertainty analysis is the range of the concentrations' distributions if different uncertainties and variabilities are assumed.

With regard to all distribution functions, it is remarkable that uncertainty is, as expected, the highest (i.e. the distribution's range is the widest) if all model parameters are varied. Additionally, if only the substance parameters are varied, uncertainty is lower than if only the regional parameters are altered. The amounts of uncertainties for each parameter group is presented in more detail in Section 9.1.3. Here, the course of the distribution functions themselves shall be emphasised.

To begin with, we must briefly go into the representation of the distributions. For all resulting cumulative distribution functions a log-normal-distribution was chosen, even though this cannot necessarily be expected if only the substance parameters are varied since the number of altered parameters is quite low⁵. For the resulting distributions the goodness of fit to the log-normal distribution was tested. A value of the Kolmogorov-Smirnov test lower than 0.03 (DECISIONEERING 1999) represents a good fit. As expected, this value is often exceeded. But since the amounts of excess are basically very low, the representation of a log-normal distribution is an acceptable and meaningful approximation of the resulting distribution. A correlation between the extent of uncertainty and deviation from the log-normal distribution was not noticed.

⁵ According to the central limit theorem, the sum of a *sufficiently high* number of independent random variables is approximately normal distributed.

Comparing the outcomes of the resulting distribution functions with those of the corresponding point estimation, it is remarkable that for concentrations in air the 50-percentiles of all substances (except for EDTA and LAS) are close to the value of the point estimation if only the regional parameters are varied. Deviations of other distributions from the point estimations are higher. The reason for this is that parameters with a high influence on the concentrations in air are less uncertain and the mean of the parameter with the highest influence on the results (heightAir) corresponds to the value used in the point estimation. This is also an explanation for the distinct deviation of the means of concentrations of LAS and EDTA: For these two substances, the atmospheric mixing height makes no contribution to the total uncertainty. But therefore, the means of the distribution functions are closer to the value of the point estimation if the substance parameters or all parameters are varied. The reason for this is that, due to a lack of data, for these parameters triangular distributions were chosen, of which the most frequent value (mode) is the value of the point estimation.

For the remaining output parameters, the 50-percentiles of the distributions are usually higher than the point estimations, which emphasises the conservative character of the chosen distribution functions. But there are exceptions. For example, if regional parameters are varied, the means of both distribution functions of EDTA in sediment are much lower (nearly four OoM) than the value of the point estimation. The reason for the deviation can again be found in the transfer coefficients. The difference between the default value and the median of the chosen distribution of the transfer coefficient water-sediment at the water side is extremely high. In the sensitivity analysis this parameter showed only a slight influence on the output. But since EDTA is the only substance that is in principle totally dissolved in water and hence is not moved to the sediment by sedimentation (as is the case, e.g. for LAS, which has a certain lipophilicity), the transfer coefficient water-sediment gains central importance for the concentrations of EDTA in sediment. Consequently, such a serious alteration of resistance must have a remarkable influence on the resulting concentrations in sediment. This shows that the chosen distribution function for this parameter must be scrutinised.

Summarising, it can be stated that the run of the distribution functions themselves is relatively unimportant. The means can, according to the assumed distributions, deviate more or less distinctly from the values of the point estimations and are therefore more or less within the range of the measured values. Thus, findings concerning this question are generally poor. Much more important is the amount of total uncertainties and where the uncertainties originate from. This is presented in the next section.

9.1.3 *Ranges of the distributions*

The logarithm of the quotient of 90-percentile and 10-percentile of the resulting probability distributions was chosen as a measure for a comparative assessment of the uncertainties. In the following, this number is called the range of distribution. The ranges are represented graphically in Figure 18 to Figure 21. The average values of the ranges of all substances in the various compartments are listed in Table 15.

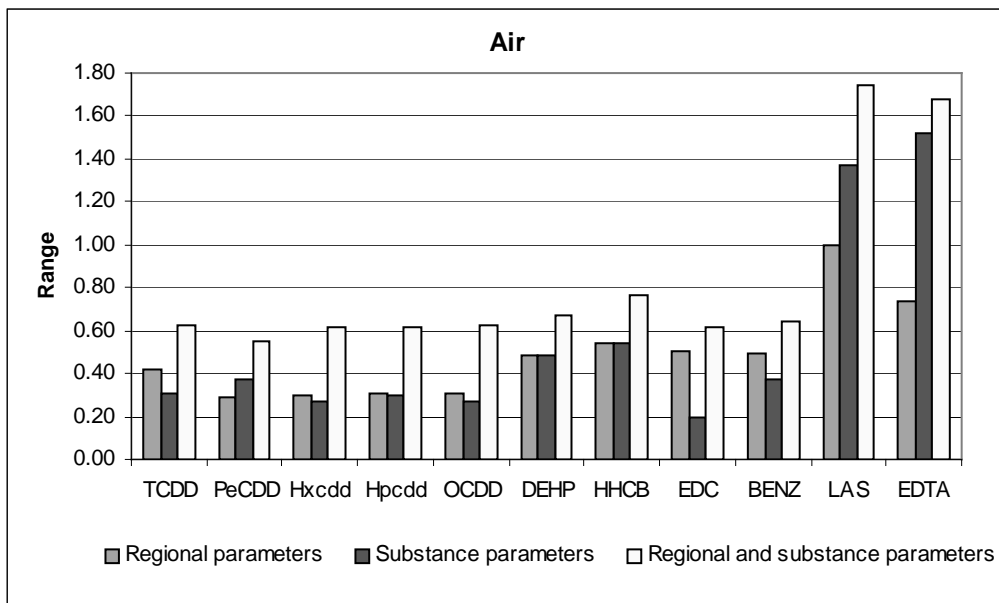


Figure 18 Ranges between 90- and 10-percentiles for PECs in air.

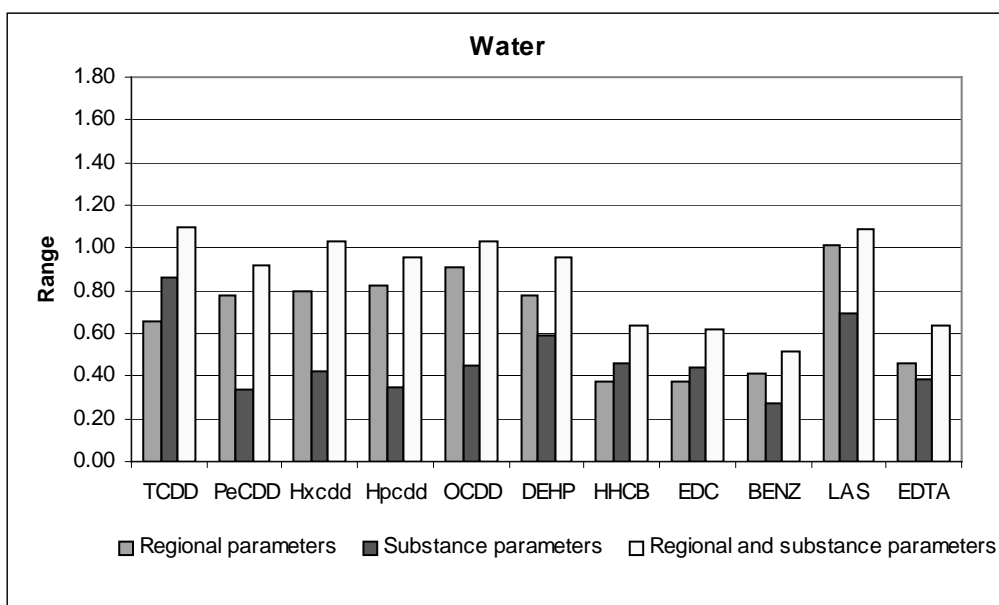


Figure 19 Ranges between 90- and 10-percentiles for PECs in water.

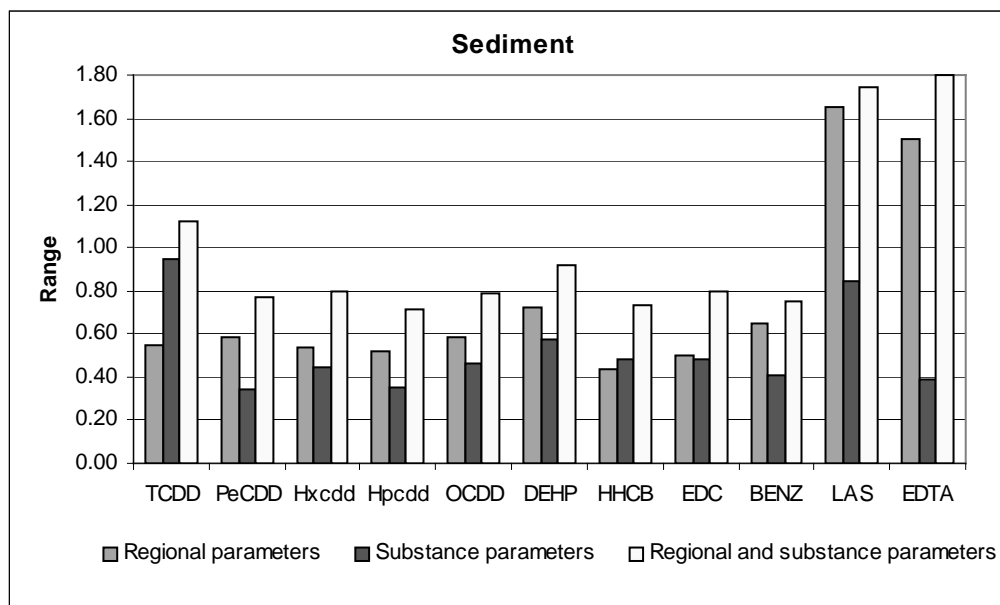


Figure 20 Ranges between 90- and 10-percentiles for PECs in sediment.

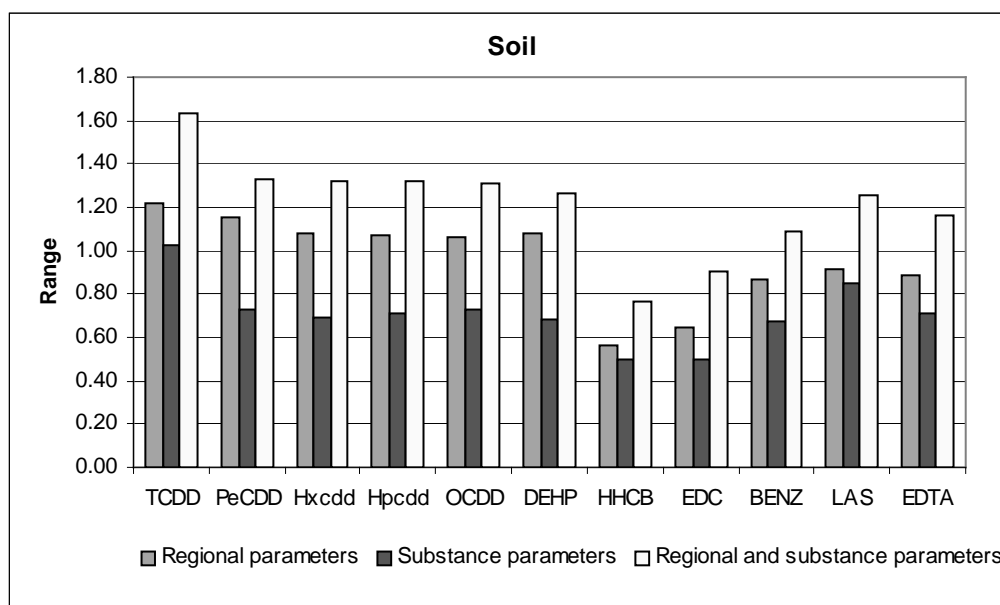


Figure 21 Ranges between 90- and 10-percentiles for PECs in soil.

Table 15 Average ranges of the resulting distributions in OoM.

Compartment	Variation of regional parameters	Variation of substance parameters	Variation of regional and substance parameters
Air	0.49	0.55	0.83
Water	0.67	0.48	0.86
Sediment	0.75	0.52	0.99
Soil	0.96	0.71	1.22

The distributions' ranges are an elementary result of the uncertainty analyses. They represent the amount of the total uncertainty as well as the different influences of the single parameter groups. Uncertainties in the concentrations of lower chlorinated PCDD and for EDC and BENZ in air are primarily produced by the regional parameters. For the higher chlorinated PCDD (HxCDD, HpCDD, OCDD), DEHP and HHCb, uncertainties of both parameter groups are almost the same, whilst

uncertainties in the concentrations of LAS and EDTA in air are mainly affected by the uncertainties in the substance parameters. The explanation for this can be found in the sensitivities of the input parameters:

Air

Uncertainties in the concentrations of PCDD in air caused by uncertainties in the regional parameters decrease, in accordance with the sensitivities, with increasing chlorination. I.e., the higher chlorinated the PCDD, the lower the sensitivities of the regional parameters and, hence, the lower the uncertainties caused by regional parameters. Consequently, for TCDD and PeCDD the regional parameters make a high contribution to the total uncertainty and for HxCDD, HpCDD and OCDD the influence becomes lower. Altogether, uncertainty in the atmospheric mixing height has the highest impact on the total uncertainty. Since DEHP and HHCb are sensitive to the degradation rates, high uncertainties arise due to the substance parameters. For these substances the uncertainties caused by the regional parameters are higher than those of the PCDD, too, because sensitivities are also higher. The sensitivities of the regional parameters of EDC and BENZ are almost as high as those of DEHP and HHCb, which leads to similar uncertainties. The low sensitivities of EDC's and BENZ's substance parameters result in low uncertainties. LAS and EDTA are highly sensitive to their substance parameters so that uncertainties in these parameters have a high influence on the results. Because of the high sensitivities to the regional parameters the uncertainties of these substances' concentrations are much higher than those of the other substances. Accordingly, these substances show the highest uncertainties in the concentrations in air.

Water

Uncertainties in the water concentrations of PCDD and DEHP are mainly caused by uncertainties in the regional parameters, especially by the concentration of suspended matter in surface water. From the group of substance parameters, only emissions to water have a high impact on these substances' concentrations. The only exception is TCDD. For this substance, high uncertainties arise due to uncertainties in the substance parameters. The reason for this effect is its high sensitivity to vapour pressure. Regional parameters also effect the highest uncertainties for LAS. But here, uncertainties in the regional depth of water has the highest influence on the total uncertainty. This corresponds to the results of the sensitivity analysis, where the parameters showed the highest influence on the regional concentrations in surface water. Compared to the concentrations in air, the concentrations of PCDD in water are more uncertain since a higher number of model parameters is sensitive. This does not apply to HHCb, EDC, BENZ and EDTA. Due to their lower sensitivities, their uncertainties are also lower.

Sediment

Except for EDTA and LAS, concentrations in sediment basically show uncertainties akin to concentrations in water since sensitivities are also similar. For LAS, the high uncertainties effected by the regional parameters result from the high sensitivities of the mixing depth of water and sediment.

EDTA's uncertainties arise from the high uncertainty of the fraction of rainwater running off soil combined with a high sensitivity to this parameter.

Soil

Concentrations in soil show the highest uncertainties (see mean values in Table 15) with the uncertainties in the regional parameters having the highest influence on the total uncertainties. The high total uncertainties of PCDD and DEHP can be attributed to the high sensitivities to degradation rates in soil and to the mixing depth of agricultural soil. Thus, uncertainties in these parameters make an important impact to the concentrations in soil.

All in all, uncertainties in the regional distribution model are relatively low. The highest occurring range between the 90-percentile and 10-percentile is 1.8 OoM. In most cases, the range is even within one OoM. Hence, uncertainties in the modelled results are mostly lower than those of measured values.

9.2 Comparison to other uncertainty analyses

The uncertainty analyses carried out in this work are not the only ones performed for EUSES and SimpleBox. ETIENNE ET AL. (1997) and JAGER ET AL. (2000) already made uncertainty analyses dealing with different aspects of SimpleBox. ETIENNE ET AL. (1997) dealt with operational uncertainties in the air-water concentration ratio of volatile compounds. Parts of their work have found their way into these investigations. Especially several probability distributions were adopted from their analyses due to a lack of own data. The main difference between the work of ETIENNE ET AL. (1997) and the present work is that they only varied the input parameters of SimpleBox, neglecting the STP model SimpleTreat. They also omitted variabilities and uncertainties in the emissions and only varied emissions to soil. But, on the other hand, they avoided uncertainties due to calculating K_{oc} and Henry's law constant from given PC data by directly varying these parameters. All in all, the investigations are not comparable since ETIENNE ET AL. (1997) chose the quotient of the concentrations in air and in water (the so-called SBCR: SimpleBox Concentration Ratio) as the output parameter and ignored concentrations in soil and sediment. They also used a different set of substances (only volatile ones) which does not overlap with the substances chosen for this work. Nevertheless, the height of the air in their investigation also shows a high contribution to uncertainties if the input of a substance via air is assumed. Other important parameters are wind speed and the half-life in air. In the present work these parameters also had a significant effect on the concentrations of EDC and BENZ in air.

Another investigation that deals with uncertainties in EUSES was performed by JAGER ET AL. (2000). Their analysis was not restricted to SimpleBox but included the whole model system, i.e. also the food chain module and the effect module. They carried out probabilistic risk assessments for a new and an existing chemical in order to find out whether probabilistic analyses are suitable to ameliorate the findings from the model's outcome. They used the same methods as ours to perform the uncertainty analyses: The basis of the analyses was EUSES 1.0 in the form of an Excel[®]

spreadsheet. The tool used to carry out Monte-Carlo simulations was CrystalBall™. They also used the Latin-Hypercube sampling method and assumed 2 000 runs to be sufficient. Additionally, they also restricted their choice of probability distributions to log-normal, triangular and uniform distributions. Since the only output parameters relevant to this investigation were PECs in water and in soil, and none of the substances considered in this work were employed in the work of JAGER ET AL. (2000), the results can not directly be compared. However, the work of JAGER ET AL. (2000) can serve as a confirmation of the method used in this work.

Obviously, the results presented in this work cannot be compared to the other investigations. Together with the work of SCHWARTZ (2000), they are an important contribution to recognising uncertainties in the risk assessment of substances with EUSES.

Finally, the aspect mentioned at the beginning which concerns the choice of the distributions' means and the differences to the point estimations has to be discussed. For three substances (TCDD, LAS, BENZ) additional uncertainty analyses were performed. The distribution functions were chosen in the way that their means correspond to the values used for the point estimations and the variation coefficients remain unchanged for each distribution. The resulting cumulative distributions are presented in appendix A.6 (Figure 73 to Figure 84). As expected the distribution functions get nearer to each other and meet in many cases nearly in one point. More important is the question whether the distributions' ranges are wider or narrower. These examples show that the deviations between the ranges are negligible. Therefore, the statements concerning the influence of parameter groups to the total uncertainty are still correct.

9.3 Discussion and conclusions

The most important results do not arise from the representation of the resulting distribution functions. Much more information and better findings result from the representation of the contributions to the total uncertainties and the ranges of the uncertainties. The representations enable us to quantify and judge the importance of uncertain and variable input parameters to the model's outcomes. The position of the distribution, i.e. the distance to the point estimations and the measured concentration, is of lesser relevance since statements on deviations and the reasons for it can better be made regarding the scenario analyses.

Another important aspect in the assessment of the results of the uncertainty analysis is the lacking consideration of correlations between the input parameters. Correlations can be expected for numerous input parameters, e.g. between K_{OW} and water solubility or degradation rates or between wind speed and atmospheric mixing height. But since there were no sufficient consistent data available, correlations could not be considered. But it can be expected that assuming correlations leads to an overall reduction of the uncertainties so that this approach complies with a conservative estimation.

Additionally, it is obvious that uncertainty analyses can only be plausibly interpreted if preliminary sensitivity analyses were performed. The sensitivities form the basis of the selection of distribution functions for the input parameters, as well as for the assessment of contributions to the total uncertainty. In view of the strong correlation between a parameter's sensitivity and the contribution to uncertainty it can be questioned whether uncertainty analyses are really required. Is it not it ex-

travagant to perform uncertainty analyses? The answer is that the expenditure can be justified, since the strong correlation is one of the results of the concrete investigation. According to the model and the chosen parameters and distributions, the result may be different if the common impact of uncertainties leads to effects that contradict the results of the sensitivity analyses. Such cases also occurred in this work. Thus, the statement on the degree of correlation between the results of the sensitivity and uncertainty analyses is an important result and makes clear that both analyses are highly relevant for the assessment of the model.

Another significant result of the uncertainty analyses is the impossibility of assigning substance parameters to the contributions to uncertainties. A Level 3 model's behaviour is influenced by the PC data of the investigated substance, but many more parameters play a part than only these. As already be seen in the sensitivity analyses, out of the group of substance parameters emissions and degradation rates in particular have an important impact on concentrations in the environment. This means that these parameters' values have to be chosen carefully if the modelled results have to be realistic. Therefore, the parts of EUSES that estimate emissions and degradation rates are of particular importance for the estimated concentrations. Thus, the quality of the modelled results depends strongly on the quality of these estimations.

The volumetric parameters – and here specially the mixing heights and depths of the compartments – have an important impact on the estimated concentrations. But these parameters are especially difficult to determine and hence have a high uncertainty. Due to the elevated sensitivity of these parameters, they make a crucial contribution to the total uncertainty. This is a fundamental problem of compartment models that can scarcely be solved. It is true that standard values became established for depth and height (e.g. water depth 3 metres, atmospheric mixing height 1 000 metres) but it is not clear how well they correlate to realistic values.

9.4 Summary

To determine the influence of uncertainties and variabilities in the input parameters on the calculated environmental concentrations, uncertainty analyses were performed for the regional distribution model SimpleBox. To this end, the input parameters of SimpleBox were divided into two groups: substance parameters and regional parameters. Three scenarios were set up: variation of only the substance parameters, variation of only the regional parameters and variation of all input parameters at the same time. These three scenarios were calculated for each of the considered substances. The basis for the required Monte-Carlo analyses was the Excel[®] version of SimpleBox and the program CrystalBall[™]. For the representation of the resulting probability distribution function, a log-normal-distribution was assumed. To verify if this assumption can be justified for all distribution functions, a Kolmogorov-Smirnov test was performed. It emerged that the assumption is appropriate for all distributions, even though deviations can occur if only the substance parameters are varied. The most useful parameters for the assessment of the uncertainties were the ranges of distributions and the contributions of single parameters to the total uncertainty. The run of the distribution function itself was less relevant. Deviations from the point estimations can be explained by the fact that the median values of the considered distribution functions differ from the values used for the point estimation. As could be expected, the total uncertainties are highest if all model pa-

rameters are varied. In most cases, the contribution of the regional parameters to the total uncertainties is higher than that of the substance parameters. Exceptions only arise if substance parameters have an exceptionally high sensitivity. While SCHWARTZ (2000) could determine a correlation between the substance class (PC data) and the resulting uncertainties in the total daily intake for the human exposure module, this can not be shown for the regional distribution model. There is also no relationship between the amount of uncertainty and deviations of the resulting distribution from the log-normal distribution as SCHWARTZ (2000) remarked in his investigation. Concentrations in air have the lowest average uncertainty due to variation of all parameters, followed by concentrations in water and sediment. Concentrations in soil distinctly have the highest uncertainties. The order is the same if the average uncertainties are regarded due to variation of the regional parameters alone. If only substance parameters are altered, the uncertainties are nearly the same for concentrations in air, water and sediment. Again, the soil concentrations are the most uncertain. For water, sediment and soil the uncertainties due to variations of the substance parameters are lower than due to variations in the regional parameters; for air they are higher. The highest occurring range is 1.8 OoM, which means that the total uncertainty of the regional model is relatively low and usually lower than uncertainties in the measured values.

10 Comparison with alternative models

As already explained in Section 2, comparisons with alternative models must also be included in a complete model validation. In so doing, it is possible to ascertain whether more complex models or perhaps simpler ones fit better to the requirements, i.e. if they can fulfil the model's task in a more efficient way. For the calculation of regional background concentrations, this means that one must prove if the Level 3 model SimpleBox is really the most eligible system. There are two alternative model concepts that fulfil the same task:

On the one hand, it is possible to use the simpler Level 2 approach instead of the Level 3 approach (Section 3.2.1). It also assumes continuous input into the system and a first-order degradation. But since neither transfer resistances, nor advective flows, nor diffusive processes between the compartments are assumed, but a distribution according to the thermodynamic equilibrium, this model approach needs a distinctly lower number of input parameters. Thus, it is much easier to implement, considerably more transparent and, due to its lower number of parameters, contains fewer parameter uncertainties. But the quality of the model's outcome may be worse because of the neglect of many important processes. Therefore, in the next section we investigate to what extent the Level 2 approach can be an alternative to the Level 3 approach.

On the other hand, a more complex method is conceivable that takes into account the spatial relation of regional concentrations. In this context, a geography-referenced model is imaginable that uses concrete geographical information and that is capable of representing environmental concentrations in maps. Due to its higher complexity, this concept is more detailed but many more data are required. The question of whether this additional effort is justifiable will also be investigated in this section on the basis of sample calculations with the model GREAT-ER and of the results of BERDING ET AL. (1999B).

10.1 Comparison with the Level 2 approach

On the basis of the Level 3 model SimpleBox, an equivalent Level 2 model was implemented. It also contains two nested spatial scales and the properties of its compartment correspond to those of SimpleBox. Deviating from this model, the three soils were subsumed to one compartment because division is not necessary if thermodynamic equilibrium is assumed. For the implementation of the Level 2 concept, emissions, compartments' volumes, degradation rates, partition coefficients and the amount of advective flows between the spatial scales are required. Accordingly, the following formulae arise for the calculation of regional concentrations:

$$C_{RegWater} = (E_{RegAir} + E_{RegStpAir} + E_{Regdirectwater} + E_{RegstpEffl} + E_{RegstpSludge} + E_{RegInd}) / (k_{degwater} \cdot V_{WaterReg} + FLOW_{waterReg} + K_{airwater} \cdot (k_{degair} \cdot V_{AirReg} + FLOW_{airReg}) + K_{sedwater} \cdot k_{degssed} \cdot V_{SedReg} + K_{soilwater} \cdot k_{degsoil} \cdot V_{SoilReg})$$

$$C_{RegAir} = C_{RegWater} \cdot K_{airwater}$$

$$C_{RegSed} = C_{RegWater} \cdot K_{sedwater}$$

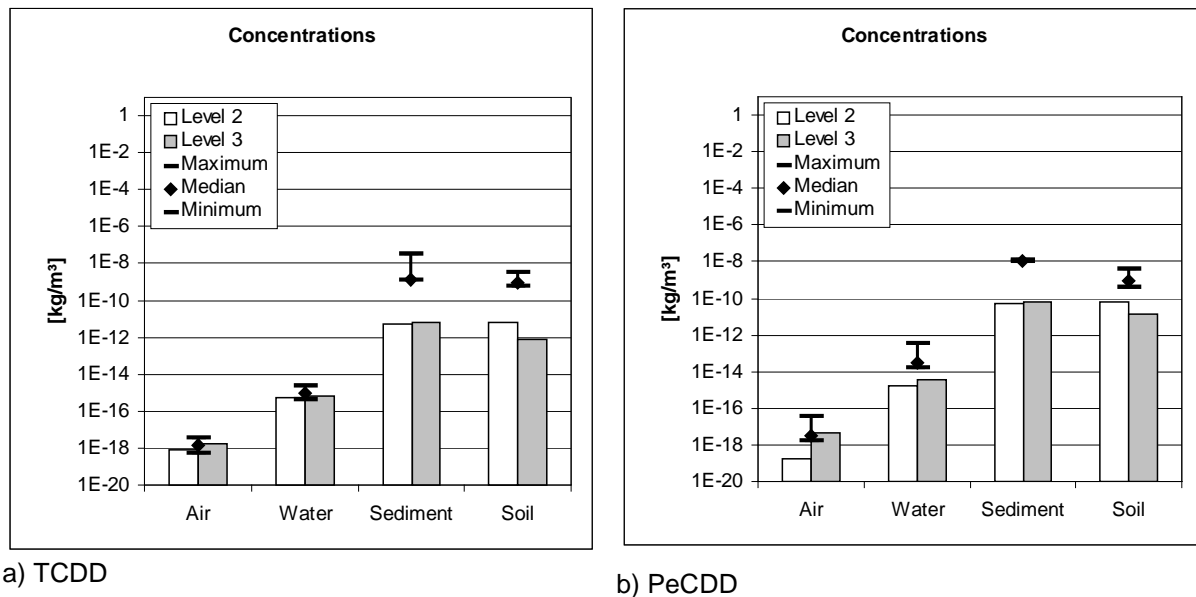
$$C_{RegSoil} = C_{RegWater} \cdot K_{soilwater}$$

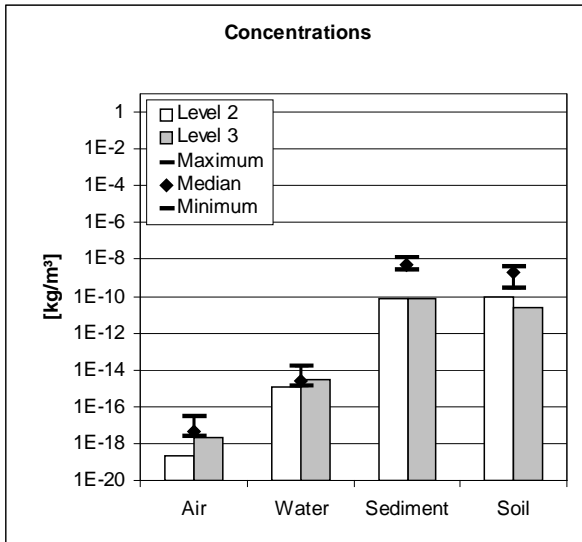
In this context, the EReg... represent the resulting direct and indirect emissions to air, water, agricultural and industrial/urban soil. kdeg... are the total degradation rates in the separate compartments, V... are the volumes of the compartments and FLOW... are the advective flows leaving the regional scale. The volumes are calculated using the data for areas, heights and depths of the compartments. The advective flows result from the values used in SimpleBox for the residence time of air in the system and for water from precipitation rate, water running off soil and sewage flow. Continental concentrations are calculated analogous to the corresponding continental values. To assess whether the Level 2 model can be an alternative, it must be evaluated whether the calculated environmental concentrations compared to measured values are better than, equal to or worse than the results of the Level 3 model.

10.1.1 Results of Level 2 calculations

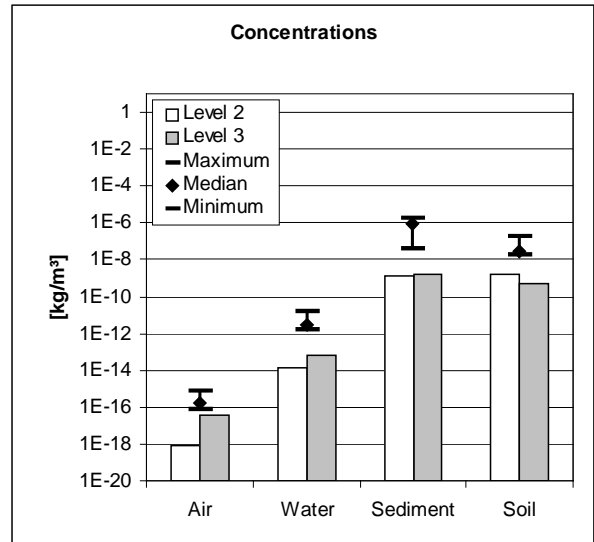
For Level 2 calculations the same substances are used as for Level 3 calculations. The basis of these calculations is the *NRW realistic* scenario of the scenario calculations. The underlying region is hence North Rhine-Westphalia, and for emissions, degradation rates and partition coefficients, measured values are preferred to estimated values. The results of these calculations are represented in Figure 22 together with the calculations of the Level 3 model and the measured values.

Figure 22a - k Comparison of Level 2 with Level 3 results together with measured values.

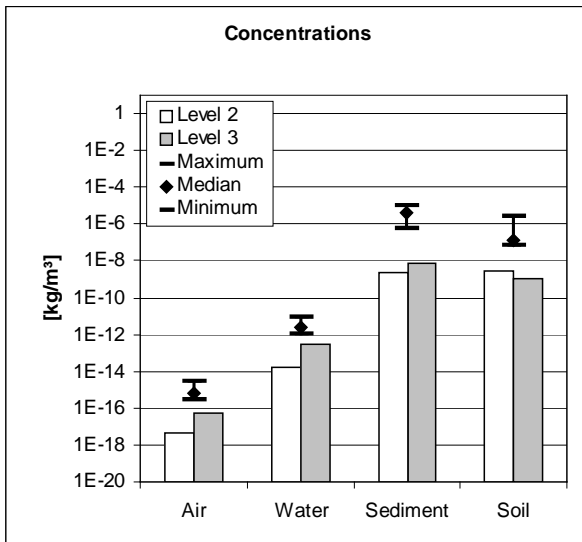




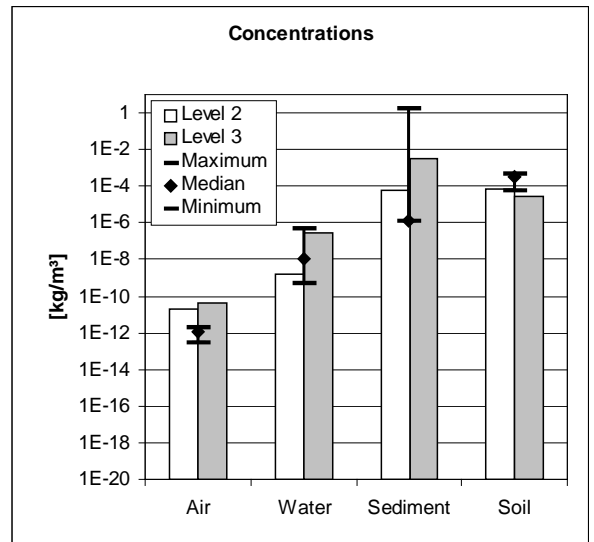
c) HxCDD



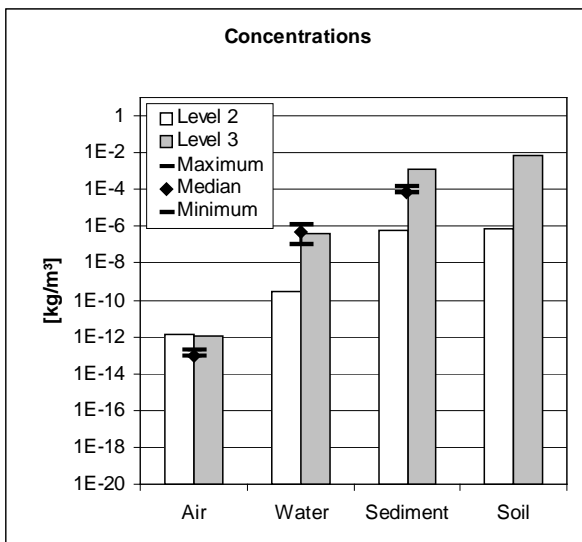
d) HpCDD



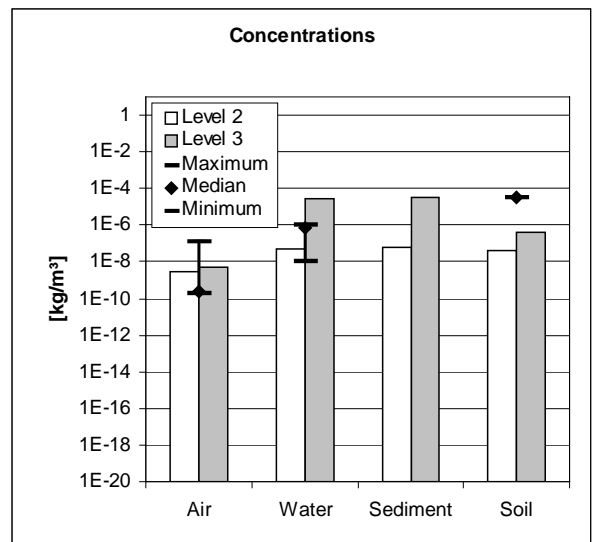
e) OCDD



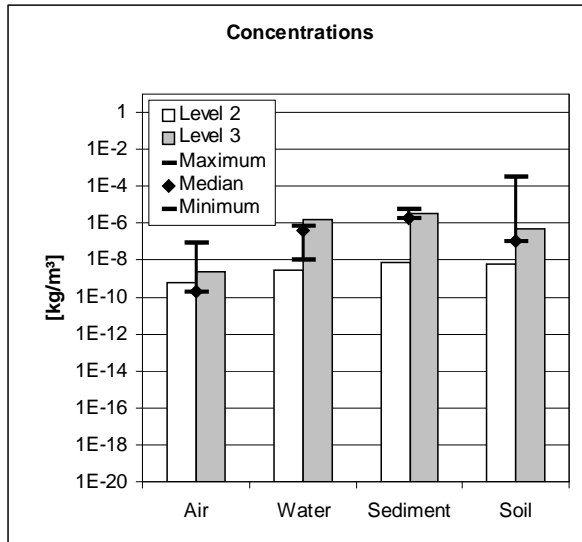
f) DEHP



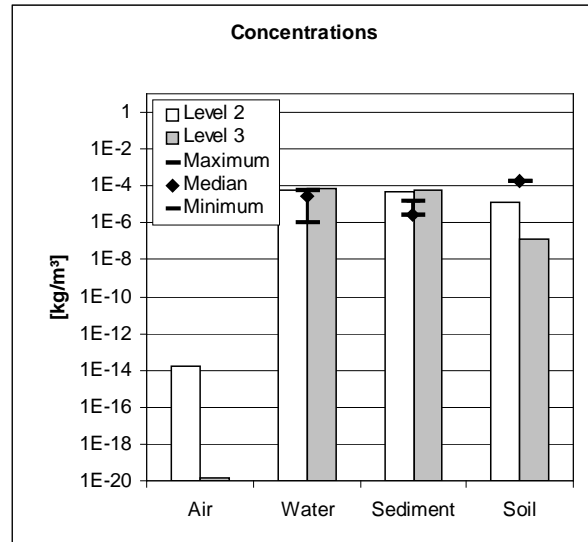
g) HHCb



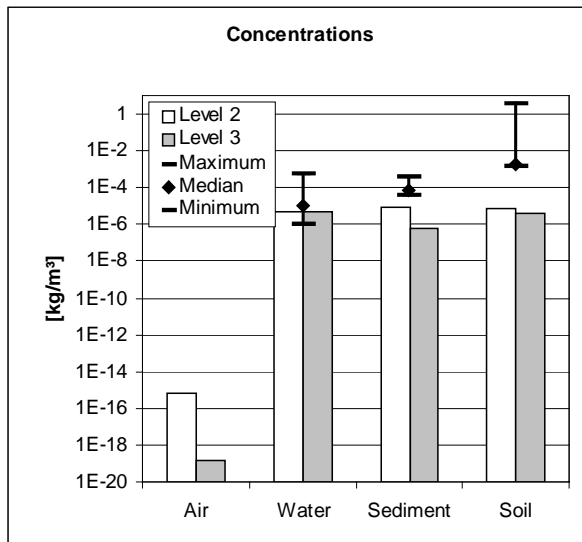
h) EDC



i) Benzene



j) EDTA



k) LAS

It is shown that the results of the Level 2 model for air, water and sediment are usually lower than the Level 3 results. In the most cases, this means a deterioration of the results because many measured concentrations are presently underestimated. The only exceptions are the concentrations of HHCB, LAS and EDTA in air. The concentrations of the latter two substances are much lower in the Level 3 model than in the Level 2 model. For HHCB the deviations are only marginal. The concentrations of PCDD, DEHP, LAS and EDTA in soil are estimated higher with the Level 2 model than with the Level 3 model. Compared with the level measured values, this means a decrease of the underestimation and hence an amelioration of the results. Especially for EDTA, this amelioration is very clear. While the (one) measured value is underestimated by 3 OoM with the Level 3 model, this distance decreases to one OoM with the Level 2 model. Table 16 shows a summary of whether the results of the Level 2 model are better (++), equal (o) or worse (-, --) than the Level 3 results. The assessment scheme established in the scenario analysis was used to assess the results. According to the extent of amelioration or deterioration, at each case two steps are chosen: Strong deterioration (--) can be stated if a good result turns to a poor one, a slight de-

terioration (-) is given if a good result turns into an average one or an average result turns into a poor one. This applies in a similar way to a strong or slight improvement. In many cases, assessment is impossible due to a lack of or inadequate monitoring data (#).

Table 16 Summarising assessment of the improvements or deteriorations using a Level 2 model instead of a Level 3 model.

Substance	Air	Water	Sediment	Soil
TCDD	o	#	o	o
PeCDD	--	#	o	o
HxCDD	-	#	o	o
HpCDD	-	#	o	o
OCDD	o	#	o	o
DEHP	o	-	#	o
HHCb	o	--	-	o
EDC	o	#	#	#
BENZ	o	-	#	#
LAS	# (-)	o	+	#
EDTA	# (-)	o	#	#

++: high amelioration, +: slight amelioration, o: no difference,

-: slight deterioration, --: high deterioration, #: not assessable

One can see that the results are better in one case (LAS in sediment) if a Level 2 model is applied instead of a Level 3 model. Deteriorations occur for dioxins in air, for concentrations of DEHP, HHCb and BENZ in water and for HHCb in sediment. In the remaining cases, both models lead to equal results.

10.1.2 Discussion of the results

Differences between the results of the Level 2 and the Level 3 models can occur if the main compartment for emissions and the compartment with the highest degradation rate are different. In such a case, resistances between the compartments reduce the quantity of substance that reaches the compartment with high degradation. This is why concentrations in the Level 2 model are lower in many cases. A good example for high differences between Level 2 and Level 3 calculations is HHCb. For this substance the Level 2 model delivers concentrations in water, sediment and soil of about 3 to 4 orders of magnitude lower. But also higher concentrations can occur if a Level 2 model is used. This is the case if a substance mainly emitted to its "preferred" compartment (e.g. a hydrophilic substance to water) and if it is additionally hardly degraded. In such a case, in a Level 3 model, the main mass will be found in this compartment while concentrations in the other compartments will be lower because resistances to pass the phases' boundaries will reduce the transfer. These resistances do not exist in a Level 2 model. The distribution is simply calculated by the partition coefficients. This can lead to higher concentrations and mass fractions in the remaining compartments. EDTA is a good example of such a behaviour. It is mainly emitted to water and remains in this compartment because of the transfer resistances. Distribution according to partition coefficients leads in the Level 2 model to higher concentrations in air and in soil. Analogous to this, the difference between the two models is low if the degradation rates and emissions are similarly high or if the compartment with the highest degradation rate is simultaneously the one that receives the highest emissions. An example of low differences between both models is TCDD. For this substance, concentrations in air, water and sediment are nearly equal for both models. Only concentrations calculated for soil are higher using the Level 2 model.

10.1.3 Conclusion – an assessment scheme for the applicability of Level 2 models

As a concluding addition to the previously discussed results, it is helpful to put forward an assessment scheme as to whether a Level 2 model is sufficient or not. Such an assessment scheme should be relatively simple and depend on only elementary and given substance information. Since differences mainly occur if the emission compartment and the compartment with the highest degradation are different, these information must be considered in the assessment. Secondly, mass distribution due to the partition coefficients plays an important part. If an emission takes place into a compartment in which only a very low mass fraction can be expected (in thermodynamic equilibrium), a Level 2 model will deliver lower concentrations than a Level 3 model because no resistances are assumed. Thus, this case must also be included in the assessment scheme.

A very simple approach could therefore be to answer the following questions:

1. Is the main emission compartment different to the main degradation compartment?
2. Are there emissions into a compartment for where a very low mass fraction (in thermodynamic equilibrium) can be expected?

If these two questions are answered negatively, the Level 2 model is probably adequate. But problems may arise with this very simple approach. For example, more than 99% of TCDD is emitted into the air, but its main mass fraction is located in soil. According to this simple scheme, the Level 2 model should not be applied for TCDD. But a comparison of the results shows that the differences between the two models are very slight, and the Level 2 approach seems to be sufficient. In fact, this scheme only allows application of the Level 2 model for EDTA and LAS. But, obviously, the model also works well for TCDD, PeCDD, HxCDD and HpCDD. The reason for this difference can be found in the fact that the substances are lipophilic and emissions take place into air. Due to a relatively fast and easy transport from air to the other compartments (due to advective processes and lower resistances), the PCDDs do not stay in a high fraction in air but are transferred to soil. Such cases must be considered in a useful assessment scheme. Additionally, the scheme should not deliver binary results as “applicable” and “not applicable” but should provide a value of applicability. Such a sophisticated approach is now presented:

For a simple implementation and normalised representation, emissions and degradation rates for compartments are expressed by their relative amount in comparison to the sum of all rates. Hence, the percentage fraction for each rate must be calculated. A measure for the importance of this factor must also include the difference between the highest and the second highest degradation since it makes a difference if, e.g., the substance is only degraded in one compartment (e.g. HHCB: $\approx 100\%$ air) or if there are several degradation compartments (e.g. TCDD: $\approx 76\%$ air and $\approx 23\%$ water)⁶. Let Ce_i be the compartment with the i -highest emission (E_i) and let Cd_i be the compartment with the i -highest degradation rate (D_i). If Ce_1 is not equal to Cd_1 , a measure for applicability could be $a_1 := D_1 - D_2$, i.e. the (percentage) difference between the highest and the second highest degradation rate. The higher the value, the worse the applicability. Because not only the main emission compartment is of importance, the compartment with the second highest emission rate should be

⁶ One should remember that these numbers are related to the degradation rates.

included into the assessment. I.e., if C_{e2} is not equal to C_{d2} , the measure is $a_2:=D_2-D_3$. $A:=a_1+a_2$ is then the resulting value for this part of the assessment.

The other part is the consideration of emissions into a compartment with a negligible mass fraction (under thermodynamic equilibrium). In such a case the degradation rate in this compartment is relevant for the concentration. The lower the degradation rate, the higher the impact of the emissions. Thus, if an emission takes place into compartment j where the mass fraction is approximately zero, and if d_j is the degradation rate in this compartment, the measure is $1-d_j$. If E_j is emission into compartment j and f_j is the mass fraction in this compartment, the subsequent scheme can be derived: If f_j is approximately zero and E_j is not equal to zero, then $b_j:=1-d_j$ otherwise $b_j:=0$. $B:=\sum b_j$ is then the measure for this part of the assessment.

The total value for applicability is hence $A+B$. A borderline value could be unity. Using this assessment scheme gives the results listed in Table 17. Obviously, the scheme's results now correspond to the previously derived findings: The Level 2 model should not be applied for OCDD, DEHP, HHCb, EDC and BENZ.

Table 17 Results of the assessment schemes for the Level 2 model.

Substance	Simple scheme (Level 2 applicable?)	Sophisticated scheme (assessment value > 1: not applicable)	
TCDD	no	0.47	= yes
PeCDD	no	0.98	= yes
HxCDD	no	0.49	= yes
HpCDD	no	0.49	= yes
OCDD	no	1.1	= no
DEHP	no	1.05	= no
HHCb	no	2	= no
EDC	no	1.56	= no
BENZ	no	1.74	= no
LAS	yes	0.23	= yes
EDTA	yes	0	= yes

It is important to bear in mind that these results depend strongly on the assumed emission compartments and the system's properties. Different scenarios (e.g. emissions of PCDD not into air but mainly onto soil, emissions of BENZ not to air but to water or different fractions and depths/heights for the compartments) would naturally lead to differing results. The applicability of the Level 2 model for the listed substances can therefore not be generalised to a statement like "for substance X the Level 2 approach is always/never sufficient". If, e.g., emissions of BENZ to water are set to 0, the differences between both models become very low and, hence, the Level 2 model would be sufficient. This is also expressed by the assessment scheme which then delivers a value of 0 instead of 1.74. For TCDD the contrary is valid: If emissions to air are set to 0, the Level 2 model underestimates concentrations in water and sediment, and an assessment value of 1.52 instead of 0.47 is calculated.

Even though this scheme seems to be rather complicated, it is easy to implement by an Excel® spreadsheet. Its advantage is the consideration of only fundamental and necessary substance properties. However, a Level 1 model has to deliver the mass distribution. But if a Level 2 model is already available, the mass fraction in the compartments can be taken from this model. Thus, this scheme is suitable if a Level 2 model is already employed. However, it must be decided on a case-by-case basis whether this model is sufficient or whether a Level 3 model should be used.

10.2 Comparison with the Geography-Referenced Model GREAT-ER

The Geography-referenced Regional Exposure Assessment Tool for European Rivers (GREAT-ER) is a support tool for environmental risk assessment and river basin management which focuses on a more refined stage of risk assessment (tier 2) (ECETOC 1999). It uses a Geographic Information System (GIS) to produce a visualisation of predicted chemical concentrations along a river (MATTHIES ET AL. 1997). Additionally, it is possible to produce profiles of Predicted Environmental Concentrations (PECs) throughout the studied catchment. Such profiles illustrate chemical fate from a river's headwaters down to its mouth, and can be used to compare model predictions with monitoring data. Furthermore, geo-referenced model results can be aggregated to obtain a spatially averaged PEC, which is representative of the river basin under investigation (BOEIJE ET AL. 2000). In accordance to this, a comparison with the results of a Level 3 model is suitable. Admittedly, this comparison can only be applied to concentrations in surface water. Since an investigation with the GREAT-ER system requires much more data than for the use of the regional distribution model, the comparison had to be limited to one substance. A substance was required that is mainly emitted to waste water and for which a per-capita consumption can be specified. For this reason, the musk fragrance HHCB was chosen. The idea of this study is to start with the EUSES standard region and to fit it to several scenarios in a specific region and finally to use GREAT-ER for geographical-referenced modelling. For the spatial refinement a stepwise approach is pursued: Firstly, a scenario analysis is performed with EUSES to discover how spatial refinement can ameliorate the predicted concentrations. In a subsequent step, the data of the Ruhr catchment are entered into GREAT-ER, and concentrations along the river are calculated. The aggregated results are compared with monitoring data and the results of the EUSES scenario calculations. The EUSES scenarios of the first two steps correspond to the scenarios *Standard* and *NRW realistic*, as suggested in the scenario analyses (Chapter 7). A third scenario was added containing the river Ruhr catchment and which represents a further step of refinement (Figure 23). In a fourth scenario, supplementary ready biodegradation was assumed. The GREAT-ER calculations were performed for the Ruhr catchment. Ready biodegradation was also assumed for this scenario.

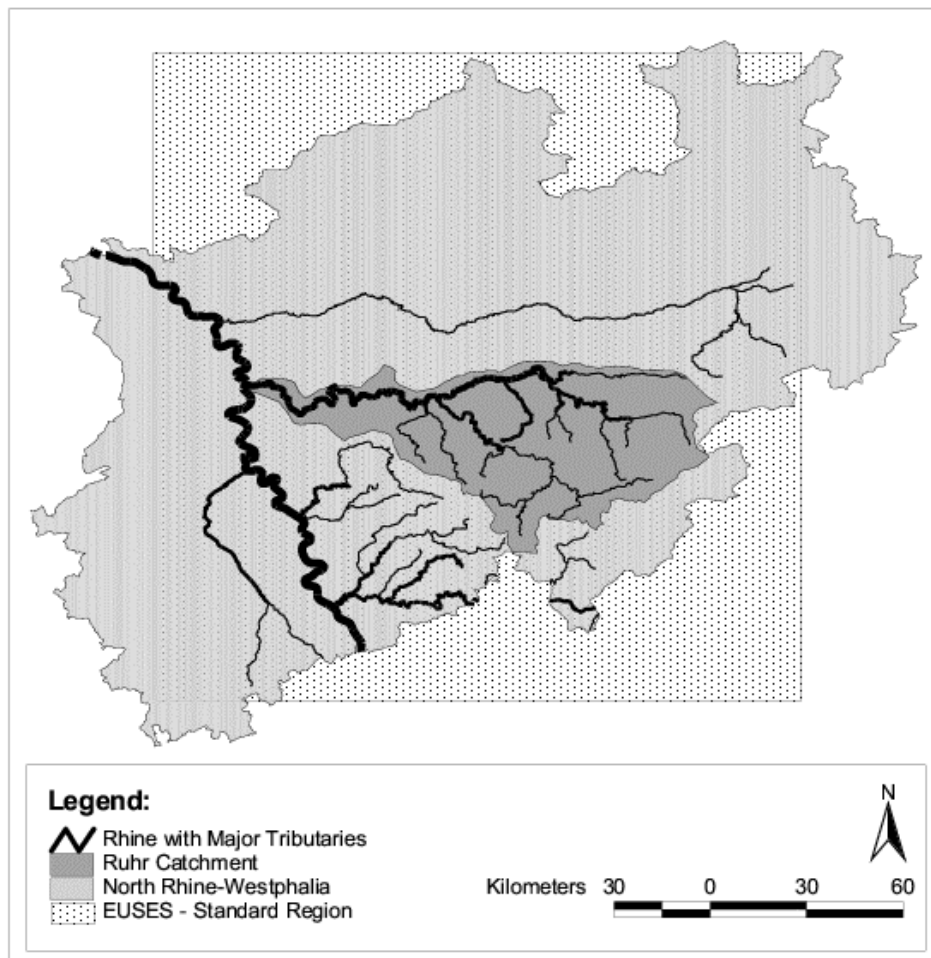


Figure 23 Regions considered for the spatial refinement.

10.2.1 The GREAT-ER model

In the following, the GREAT-ER model is described briefly. The simulation system GREAT-ER can be divided into two sections: 1. the water flow with its two modules emission, sewer and sewage treatment plant and 2. the river. These are connected to each other in a model chain. To deal with reality, the river modules can be connected to a network. Moreover, GREAT-ER offers the facility to perform probabilistic assessments by specifying probabilistic distribution functions for each input parameter, which are then used in a Monte-Carlo analysis. For a model calculation with GREAT-ER, the regarded river catchment must be available or entered as digital maps. Geographical information are needed, as well as hydrological data. Furthermore, the STP sites must be known in addition to the number of inhabitants connected. GREAT-ER offers several modes of complexity, of which the simplest is chosen in this investigation. I.e., the sewer was switched off and for each STP and each river segment the elimination rate was presumed. Information regarding the treatment plants was provided by the Ruhrverband (Institution for River Ruhr Water Management, RUHRVERBAND 1999) and the river catchment data were made available by the UBA (Gewässer-GIS Deutschland/Umweltbundesamt). The monitoring data of HHCB served as comparative data, as already used in the scenario analysis.

10.2.2 Results and Discussion of the GREAT-ER calculation

The median of the measured values is chosen for a comparison of modelled results with monitoring data. The comparative GREAT-ER-value is the $PEC_{\text{catchment}}$, which is the weighted spatial and temporal mean of all (polluted) stretches in a catchment, representing an average concentration of the Ruhr catchment.

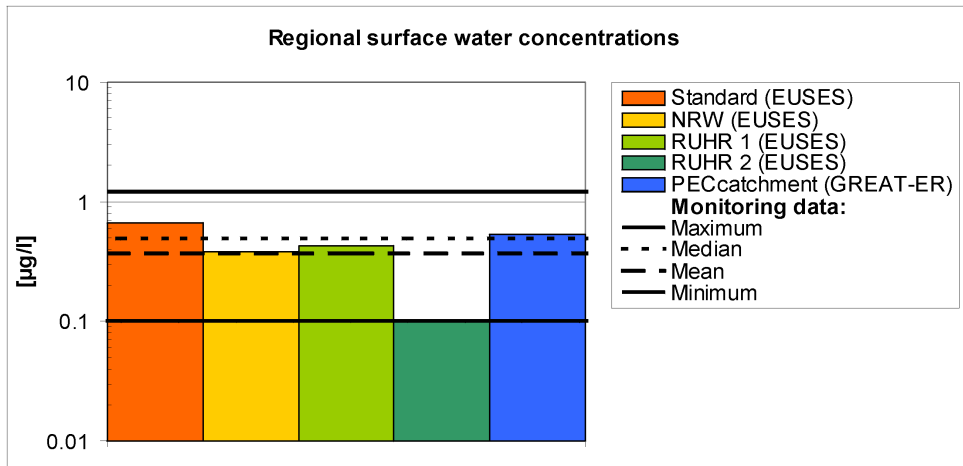


Figure 24 Comparison of calculated HHCB concentrations in surface water with measured values.

Figure 24 shows the results of model calculations. On the regional scale, the results of the first three EUSES scenarios are very close to the measured concentrations and hit the median almost directly. Thus, estimations are good. It is remarkable that the results of these three scenarios only differ slightly from each other. This confirms the results of the scenario analyses which state that alternations in the regional parameters only lead to slight changes in the regional concentrations. But the assumption of a ready degradability of HHCB in surface water leads to a distinct underestimation of the median in the scenario *Ruhr 2*, whilst the average PEC of the GREAT-ER calculation corresponds almost exactly to the median of the measured values, even though the same high degradation rate has been assumed. Altogether, all values – measured as well as calculated values – are within one order of magnitude, which is a narrow range.

The reasons for the underestimation of the measured values in the scenario *Ruhr 2* are diverse: On the one hand, the degradation rate could be too high, which is confirmed by the results of the scenario *Ruhr 1*, but in contradiction to the GREAT-ER result. On the other hand, the measured values used may not be representative. The comparative data were all taken in winter (February 1994, average temperature 2°C, NRW 1994) and could be higher than average because of reduced degradation processes. In addition, it must be mentioned that the data were taken in the lower courses of the river where concentrations are expected to be higher than average for the catchment. This would mean that the concentration calculated by GREAT-ER is too high. But in view of the low range of the measured values, all calculated results range from average to good. Because of the numerous and difficult to determine reasons for the underestimation of the *Ruhr 2* scenario, it cannot be ascertained in conclusion whether the GREAT-ER results are really better than the EUSES

calculations. However, an important advantage of GREAT-ER is its capability to produce colour-coded maps to visualise the spatial distribution of substance concentrations (Figure 25).

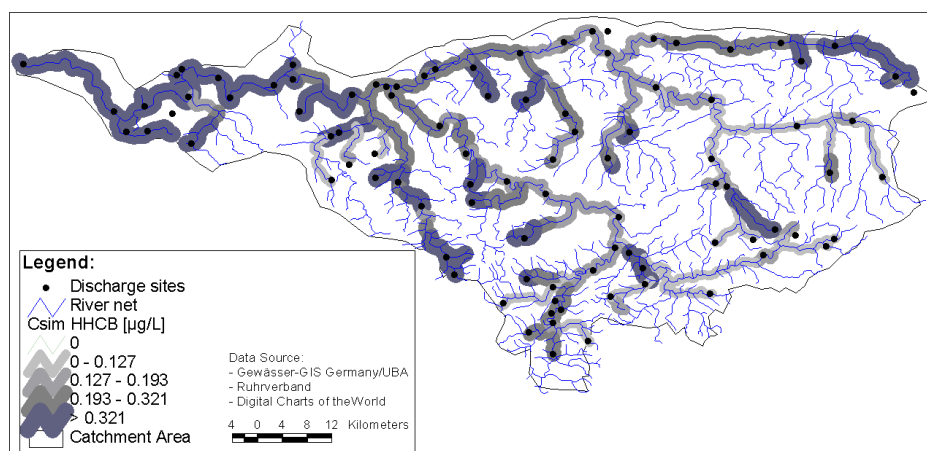


Figure 25 Map of HHCb concentrations in the river Ruhr catchment. C_{sim} is the average concentration in the appropriate river segment.

10.3 Discussion and conclusions

In many cases, the Level 2 model delivers results similar to those of the Level 3 model. But high deviations can occur if the compartments for the main emission and degradation differ. This means that a Level 2 model can be used if such a case can be excluded. All in all, applicability of a Level 2 model is subject to stronger restrictions than that of a Level 3 model. For the estimation of environmental concentrations of a band of substances as large as possible, the Level 3 model is preferable to the Level 2 model. By neglecting many processes, the Level 2 model is much easier to implement and use, but the quality of calculated concentrations may be insufficient for a realistic estimation of environmental concentrations. Furthermore, in many cases, the concentrations calculated by the Level 2 model are lower than those of the Level 3 model, which is in contradiction to a conservative estimation of environmental concentrations.

The comparison of the Level 3 model with the geography-referenced simulation system GREAT-ER shows that both the Level 3 model and GREAT-ER are able to calculate realistic HHCb-concentrations in surface water. Using a higher degradation rate, EUSES calculates concentrations lower than the median of the measured values, whilst GREAT-ER hits the median almost exactly. However, deviations of the EUSES calculations are quite low and all estimations are within the measured values. The differences between the separate scenarios are lower than the range of measured concentrations. Furthermore, the GREAT-ER result and the result of the appropriate EUSES scenario do not differ more than a factor of 5 from each other. In view of this fact, one must assess whether the gain of information is sufficiently high to justify the very high demand of data required for a GREAT-ER simulation. Another aspect in assessing the GREAT-ER results is that the monitoring data were taken in the lower course of the river while GREAT-ER calculates the $PEC_{catchment}$ (per definition) for the whole catchment. This may indicate an overestimation since the

substance will be higher concentrated in the lower course than in the headwaters of the river and the average concentration of the whole river is lower than the average of the measured data. However, the uncertainties in the results are quite high due to the unknown degradation behaviour of the substance and the missing knowledge about the real emissions. Consequently, the GREAT-ER calculations are difficult to assess with the given data. Further research is needed to evaluate these points.

Altogether, it can be stated that the Level 3 model is a good compromise between simplification and level of detail if the purpose is to calculate regional background concentrations. The reduction to a Level 2 model is a too strong simplification, whereas the high data requirement for the use of a geography-referenced model cannot be justified if only regional background concentrations have to be calculated. Moreover, the geography-referenced model regarded can only calculate concentrations in rivers and neglects concentrations in air, sediment and soil.

10.4 Summary

The regional Level 3 distribution model was compared to two alternative model approaches: the Level 2 concept and a geography-referenced river model (GREAT-ER). To evaluate whether a Level 2 model is sufficient or not a simple assessment scheme was developed. It turned out that the Level 2 approach represents in many cases a too high simplification. For many substances degradation and emissions take place in different compartments which is not considered in a Level 2 model. Hence, this model is only appropriate for few substances. The much more complex geography-referenced approach is able to calculate comparable average concentrations. But due to the higher data requirements this method is too expensive for only calculating background concentrations. However, if the data are given this kind of model enables the calculation of spatially detailed concentrations and the representation in maps. For the prediction of regional background concentrations the Level 3 approach is a good compromise between complexity and simplification.

11 An alternative STP model: VerySimpleTreat

11.1 Introduction

EUSES contains the model SimpleTreat (STRUIJS ET AL. 1991), which calculates a substance's fate in a sewage treatment plant (STP). Since the SimpleTreat version included in EUSES is not documented, documentation from the later version 3.0 (STRUIJS 1996) was used for this work. On the regional scale, the STP model only has to calculate fractions for degradation and indirect emissions to water, air and sludge or agricultural soil, respectively. Therefore a much simpler model can be considered. The aim is to develop a model that needs as few parameters as possible and that can easily be integrated into the EUSES system. Even though it does not directly concern the validation of the regional distribution model, such a model is presented in the following. This slight deviation from the actual work can show, using the example SimpleTreat, that complex models do not necessarily lead to better results. Firstly, the idea and the new model's structure is elaborated.

11.2 Model structure

SimpleTreat is a Level 3 model consisting of 6 or 9 compartments, depending on the assumption of a primary sedimentation. It assumes advective and diffusive flows between compartments and thus considers numerous processes that take place in an STP. But the sensitivity analysis (Chapter 6) showed that the influence of the model's parameters on the predicted concentrations are in most cases very low. Consequently, for an elementary estimation of a chemical's fate in a sewage treatment plant a basic approach with only a few processes can perhaps be sufficient and much more transparent. Generally, it can be assumed that a sewage treatment plant consists of the three elementary parts water, sewage sludge and the air column above the plant. A substance is entered via wastewater into the STP. The substance can be biodegraded in the water basin of the plant. It enters into the atmosphere via volatilisation and into sewage sludge via sedimentation. Advective outputs from the system take place via movements of the air (wind) and the water phase (water flow). Additionally, the sludge is continuously removed so that this process can be seen as an advective output via sludge. Thus, there are only three kinds of processes: emissions, advective flows and degradation. Diffusive processes or different sections within the plant with additional exchange processes are neglected. Figure 26 gives a graphical representation of this structure.

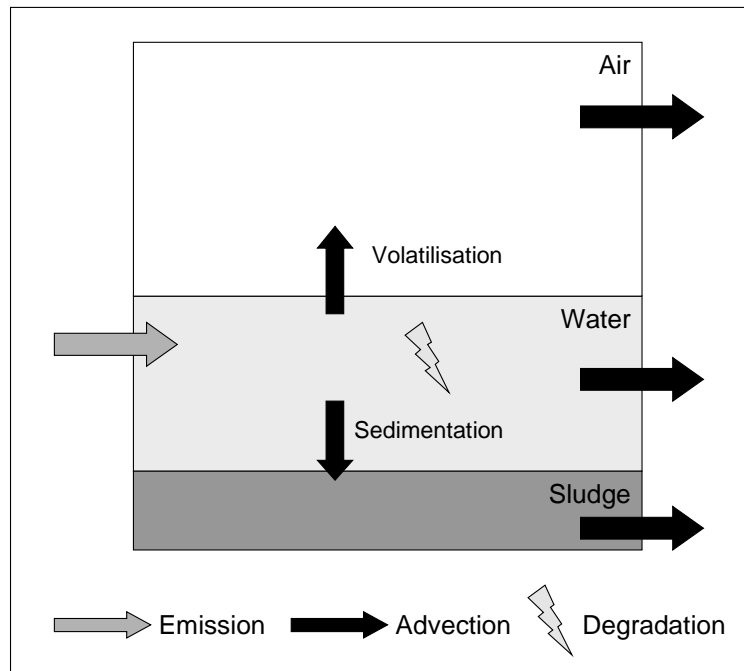


Figure 26 Structure of the STP model VerySimpleTreat.

A very simple STP model can be built founded on this approach. A Level 3 model is appropriate for this task since advective flows between the compartments, degradation in only one compartment and emission to only water have to be regarded. The processes can be quantified easily, as already performed in the models SimpleTreat and SimpleBox. Because this model is much simpler than the STP model SimpleTreat, it is called VerySimpleTreat. Table 18 shows the parameters used in VerySimpleTreat. The use of these parameters, the chosen values and the equations are described in the following.

Table 18 Parameters of VerySimpleTreat.

Parameter	Unit	Value	Description
Regional and environmental parameters			
N	eq	EUSES	Number of inhabitants
Api	m ² /eq	0.04 (ST)	STP area per inhabitant
AreaSTP	m ²	calc.	Area of STP
Q	m ³ /d	EUSES	Per-capita sewage flow
S	kg/eq/d	0.09 (ST)	Daily per-capita production of solids
Rhosolid	kg/m ³	2500 (EUSES)	Density of solids
windspeed	m/d	EUSES	Wind speed
Focsludge	-	0.3 (ST)	Fraction OC sewage
suspwaterSTP	kg/m ³	0.02 (EUSES)	Susp. matter concentration in water
settlratesludge	m/d	70 (VST)	Settling rate of solids in STP
volatSTP	m/d	calc.	Volatilisation rate in STP
volfactor	-	3 (VST)	Factor considering better volatilisation in STP
fconnect	-	EUSES	Fraction of inhabitants connected to sewer systems
GASABSwater	m/d	EUSES	Gas absorption at the air-water interface
Substance data			
Input	kg/d	EUSES	Input of substance to STP
kdegstp	1/d	EUSES	Bio-degradation rate of substance
FdisslvdSTP	-	calc.	Fraction dissolved in STP water
Fassaer	-	EUSES	Fraction bound to aerosol particles
Volumetric parameters			
depthwaterSTP	m	1.5	Depth of the water basin
depthsludgeSTP	m	0.1	Depth of the sewage sludge
heightairSTP	m	10	Height of the air column
VwaterSTP	m ³	calc.	Volume of water
VsludgeSTP	m ³	calc.	Volume of sludge
VairSTP	m ³	calc.	Volume of air
Advective flows			
flowwaterSTP	m ³ /d	calc.	Advective water flow through STP
flowairSTP	m ³ /d	calc.	Advective air flow
flowsludgeSTP	m ³ /d	calc.	Advective sewage flow
Output			
fair	-	output	Fraction of substance indirectly emitted to air
fwater	-	output	Fraction of substance indirectly emitted to surface water
fsludge	-	output	Fraction of substance indirectly emitted to sewage sludge
fdegr	-	output	Fraction of substance that is degraded
Cwater	kg/m ³	output	Concentration in STP effluent
Csludge	kg/m ³	output	Concentration in sewage sludge
Cair	kg/m ³	output	Concentration in air

EUSES: Parameter values are set or calculated in EUSES.

ST: Parameter is set in SimpleTreat.

VST: Parameter is set for specific use in VerySimpleTreat.

calc.: Parameter is calculated by others (see following description).

output: Model's output.

Volumetric parameters

In EUSES, it is assumed that there is one large STP on the regional scale. This assumption is also made for the VerySimpleTreat model. The area of the plant is therefore calculated by the number of inhabitants connected to sewer systems and a constant representing the STP area for each inhabitant. Here, the value of this constant is the same as in SimpleTreat: ≈ 0.04 m²/inh.

$$\text{AreaSTP} = \text{Api} \cdot \text{N} \cdot \text{fconnect}$$

The height of the air column is 10 m, the depth of the water basin is 1.5 m and the depth of the sludge is 0.1 m. These are reasonable values for a sewage treatment plant.

Emissions

Emissions to waste water are calculated by the release estimation module. This value is used as an input for the new model. However, it is shown in the following that this parameter is not sensitive if the concentrations in the compartments are not regarded, but only the fractions degraded and directed to air, water and sludge. Consequently, it is nevertheless the amount emitted to the STP.

Advective parameters

The advective flow of water is given by the product of per-capita wastewater flow and the number of inhabitants connected to sewer systems. These parameters are input parameters of EUSES and do not have to be further determined.

$$\text{flowwaterSTP} = Q \cdot N \cdot \text{fconnect}$$

The air flow is calculated by the length of one side of the quadratic plant, the height of the air column and the wind speed.

$$\text{flowairSTP} = \sqrt{\text{Area}} \cdot \text{heightairSTP} \cdot \text{windspeed}$$

The STP sludge is continuously removed (and recharged) analogous to the per-capita sewage flow. To obtain a volumetric rate, the value must be divided by the density of solids.

$$\text{flowsludgeSTP} = S \cdot N \cdot \text{fconnect} / \text{RHOsolid}$$

Due to sedimentation, there is an advective flow between water and sludge. It is calculated by the settling rate and the fraction associated to suspended matter.

$$\text{flowwater_sediment} = \text{settlerratesludge} \cdot (1 - \text{FRdisslvdSTP}) \cdot \text{AreaSTP}$$

Volatilisation out of the STP is calculated as in the regional distribution model.

$$\text{volatSTP} = \text{GASABSwater} / (1 - \text{Fassaer}) \cdot K_{\text{airwater}} \cdot \text{FRdisslvdSTP} \cdot \text{volfactor}$$

The parameter GASABSwater (gas absorption at the air-water interface) represents the transfer with resistances via the air-water interface and is taken from the regional distribution model as well as from Fassaer (the fraction of substance bound to aerosols).

The fraction of substance dissolved in the STP water is calculated in the same way as in the regional distribution model.

$$\text{FdisslvdSTP} = 1 / (1 + (\text{Focsludge} \cdot K_{\text{OC}} \cdot \text{SuspWaterSTP}))$$

However, there is one difference between the regional volatilisation and that in sewage treatment plants. In an STP, a higher volatilisation can be assumed due to aeration. Therefore, a (reasonable but guessed) factor of 3 is considered by which the volatilisation is multiplied.

With these parameters and C_{air} , C_{water} and C_{sludge} being the concentrations in air, water and sludge of the STP, it is easy to set up the mass balance equations for the Level 3 model:

$$\begin{aligned}V_{\text{air}} \cdot dC_{\text{air}}/dt &= -\text{flowair} \cdot C_{\text{air}} + \text{volatSTP} \cdot \text{AreaSTP} \cdot C_{\text{water}} \\V_{\text{water}} \cdot dC_{\text{water}}/dt &= -(\text{flowwater} + \text{kdegstp} \cdot V_{\text{waterSTP}} - \text{VOLATstp} \cdot \text{AreaSTP} + \text{settlerate_sludge} \cdot (1-\text{FRdisslvdSTP}) \cdot \text{AreaSTP}) \cdot C_{\text{water}} + \text{Input} \\V_{\text{sludge}} \cdot dC_{\text{sludge}}/dt &= \text{settlerate_sludge} \cdot (1-\text{FRdisslvdSTP}) \cdot \text{AreaSTP} \cdot C_{\text{water}} - \text{flowsludgeSTP} \cdot C_{\text{sludge}}\end{aligned}$$

In a Level 3 model, $dm/dt = 0$. Thus, an equation system as follows results:

$$\begin{aligned}-\text{flowair} \cdot C_{\text{air}} + \text{volatSTP} \cdot \text{AreaSTP} \cdot C_{\text{water}} &= 0 \\-(\text{flowwater} + \text{kdegstp} \cdot V_{\text{waterSTP}} - \text{VOLATstp} \cdot \text{AreaSTP} + \text{settlerate_sludge} \cdot (1-\text{FRdisslvdSTP}) \cdot \text{AreaSTP}) \cdot C_{\text{water}} &= -\text{Input} \\\text{settlerate_sludge} \cdot (1-\text{FRdisslvdSTP}) \cdot \text{AreaSTP} \cdot C_{\text{water}} - \text{flowsludgeSTP} \cdot C_{\text{sludge}} &= 0\end{aligned}$$

With

$$\begin{aligned}a_{11} &= \text{flowairSTP} \\a_{12} &= \text{volatSTP} \cdot \text{AreaSTP} \\a_{22} &= \text{flowwaterSTP} + \text{kdegstp} \cdot V_{\text{waterSTP}} - \text{VOLATstp} \cdot \text{AreaSTP} + \text{settlerate_sludge} \cdot (1-\text{FRdisslvdSTP}) \cdot \text{AreaSTP} \\a_{32} &= \text{settlerate_sludge} \cdot (1-\text{FRdisslvdSTP}) \cdot \text{AreaSTP} \\a_{33} &= \text{flowsludgeSTP}\end{aligned}$$

The equation system can be written shorter in this way:

$$\begin{aligned}-a_{11} \cdot C_{\text{air}} &+ a_{12} \cdot C_{\text{water}} &= 0 \\&- a_{22} \cdot C_{\text{water}} &= -\text{Input} \\a_{32} \cdot C_{\text{water}} &- a_{33} \cdot C_{\text{sludge}} &= 0\end{aligned}$$

This equation system can easily be solved:

$$C_{\text{air}} = \frac{a_{12} \cdot \text{Input}}{a_{11} \cdot a_{22}}$$

$$C_{\text{water}} = \frac{\text{Input}}{a_{22}}$$

$$C_{\text{sludge}} = \frac{a_{32} \cdot \text{Input}}{a_{22} \cdot a_{33}}$$

The calculation of the fractions of substance that is degraded and indirectly emitted to air, water and sludge is performed in the same way as in SimpleTreat by dividing the single mass flows by the total mass flow through the system, hence (in a Level 3 model like this one) the emissions. The fractions are thus calculated as follows:

$$f_{\text{air}} = \text{flowairSTP} \cdot C_{\text{air}} \cdot \text{Input}^{-1}$$

$$f_{\text{water}} = \text{flowwaterSTP} \cdot C_{\text{water}} \cdot \text{Input}^{-1}$$

$$f_{\text{sludge}} = \text{flowsludgeSTP} \cdot C_{\text{sludge}} \cdot \text{Input}^{-1}$$

$$f_{\text{degraded}} = \text{kdegstp} \cdot V_{\text{waterSTP}} \cdot C_{\text{water}} \cdot \text{Input}^{-1}$$

Together with the equations for the concentrations, it follows:

$$f_{air} = \frac{a_{12} \cdot \text{flowairSTP}}{a_{11} \cdot a_{22}} = \frac{a_{12}}{a_{22}}$$

$$= \frac{\text{volatSTP} \cdot \text{AreaSTP}}{\text{flowwaterSTP} + k_{degstp} \cdot V_{\text{waterSTP}} - (\text{VOLATstp} + \text{settlerate_sludge} \cdot (1 - \text{FRdisslvdSTP})) \cdot \text{AreaSTP}}$$

$$f_{\text{water}} = \frac{\text{flowwaterSTP}}{a_{22}}$$

$$= \frac{\text{flowwaterSTP}}{\text{flowwaterSTP} + k_{degstp} \cdot V_{\text{waterSTP}} - (\text{VOLATstp} + \text{settlerate_sludge} \cdot (1 - \text{FRdisslvdSTP})) \cdot \text{AreaSTP}}$$

$$f_{\text{sludge}} = \frac{a_{32} \cdot \text{flowsludgeSTP}}{a_{22} \cdot a_{33}} = \frac{a_{32}}{a_{22}}$$

$$= \frac{\text{settlerate_sludge} \cdot (1 - \text{FRdisslvdSTP}) \cdot \text{AreaSTP}}{\text{flowwaterSTP} + k_{degstp} \cdot V_{\text{waterSTP}} - (\text{VOLATstp} + \text{settlerate_sludge} \cdot (1 - \text{FRdisslvdSTP})) \cdot \text{AreaSTP}}$$

$$f_{\text{degraded}} = \frac{k_{degstp} \cdot V_{\text{waterSTP}}}{a_{22}}$$

$$= \frac{k_{degSTP} \cdot V_{\text{waterSTP}}}{\text{flowwaterSTP} + k_{degstp} \cdot V_{\text{waterSTP}} - (\text{VOLATstp} + \text{settlerate_sludge} \cdot (1 - \text{FRdisslvdSTP})) \cdot \text{AreaSTP}}$$

Finally, only the quotients of the flows concerning the regarded path divided by the overall flow remains. It is obvious that the emissions are not sensitive since this parameter is no longer needed. Consequently, the value of this parameter has no influence on the results. Also, the parameters flowairSTP (a_{11}) and flowsludgeSTP (a_{33}) and all volumetric parameters for air and sludge are not needed for simply calculating the fractions. But, if the concentrations are desired for additional information, they can still be calculated in a simple way. The final STP model to calculate the fractions is very simple since for each fraction only one equation is necessary. In Table 19, all input parameters needed for `VerySimpleTreat` are listed, including the PC parameter, transfer coefficients and environmental parameters. Altogether, only 20 parameters are needed, while `SimpleTreat` needs about 40 parameters and contains many more equations and intermediate steps to estimate the fate of the substance in the plant.

Table 19 Input parameters needed to calculate the fractions.

Parameter	Unit	Value / Formula	Description
N	eq.	EUSES	Number of inhabitants
fconnect	-	EUSES	Fraction connected to sewer systems
Api	m ² /eq.	0.04 (ST)	Per-capita STP area
depthwaterSTP	m	1.5 (VSTP)	Depth of STP water
Q	m ³ /eq./d	EUSES	Per-capita daily waste water flow
kdegstp	1/d	EUSES	Bio-degradation rate of substance
settlratesludge	m/d	70 (VST)	Sedimentation rate of suspended solids in STP
volfactor	-	3 (VST)	Volatilisation factor
kawair	m/d	EUSES	Air-film partial mass-transfer coefficient (air-soil interface)
kawwater	m/d	EUSES	Water-film partial mass-transfer coefficient (air-soil interface)
VP	Pa	EUSES	Vapour pressure
SOL	kg/m ³	EUSES	Water solubility
MOLW	kg/mol	EUSES	Molecular weight
TEMPmelt	K	EUSES	Melting point
K _{ow}	-	EUSES	Octanol-water partition coefficient
CONjunge	Pa·m	EUSES	Junge constant
SURFaer	m ² /m ³	EUSES	Surface area of particles
TEMP	K	EUSES	Environmental temperature
Focsludge	-	0.3 (ST)	Fraction OC of sewage sludge
suspwaterSTP	kg/m ³	0.02 (ST)	Suspended matter concentration STP

EUSES: Parameter values are set or calculated in EUSES.

ST: Parameter is set in SimpleTreat.

VST: Parameter is set for specific use in VerySimpleTreat.

11.3 Results – comparison with SimpleTreat

The main task of the STP model SimpleTreat is to estimate the fate of a substance in the STP and to calculate fractions for degradation, direction to air, water and sludge. These fractions are therefore the output parameters that have to be regarded and that are compared with the results of the model VerySimpleTreat. The model VerySimpleTreat is assessed according to the results of SimpleTreat. To this end, the spreadsheet version of EUSES was employed, and the STP model VerySimpleTreat was added in the form of a spreadsheet. Some additions to the given spreadsheet of EUSES made it possible to switch between both models. For a comparison of the two models' outcomes, the substances used in the previous chapters are taken. This examination uses the *NRW base* scenario that is explained in the uncertainty analysis (Chapter 9).

The results of both models are shown in Table 20 and Figure 27. Additionally, the local concentrations in water and sludge and the daily indirect emissions to air are calculated on the basis of a local standard emission of 1 kg/d to the STP. These data are calculated to judge whether VerySimpleTreat could also be used to estimate local concentrations. The results of both models are presented in Table 21

Table 20 Fractions calculated by VerySimpleTreat and SimpleTreat.

Substance	VerySimpleTreat				SimpleTreat			
	Air [%]	Water [%]	Sludge [%]	Degraded [%]	Air [%]	Water [%]	Sludge [%]	Degraded [%]
TCDD	0.24	9.15	90.61	0.00	0.09	8.69	91.22	0.00
PeCDD	0.01	7.51	92.48	0.00	0.00	7.71	92.29	0.00
HxCDD	0.02	7.08	92.92	0.00	0.00	7.45	92.55	0.00
HpCDD	0.00	6.95	93.05	0.00	0.00	7.38	92.62	0.00
OCDD	0.00	6.87	93.13	0.00	0.00	7.33	92.67	0.00
DEHP	0.27	7.00	87.69	5.03	0.11	7.54	92.02	0.33
HHCb	2.80	18.12	79.08	0.00	1.15	14.30	84.55	0.00
EDC	37.77	62.13	0.10	0.00	37.85	61.93	0.22	0.00
BENZ	7.76	11.26	0.06	80.91	22.34	7.66	0.60	69.40
LAS	0.00	12.21	0.05	87.74	0.00	11.52	0.46	88.03
EDTA	0.00	100.00	0.00	0.00	0.00	100.00	0.00	0.00

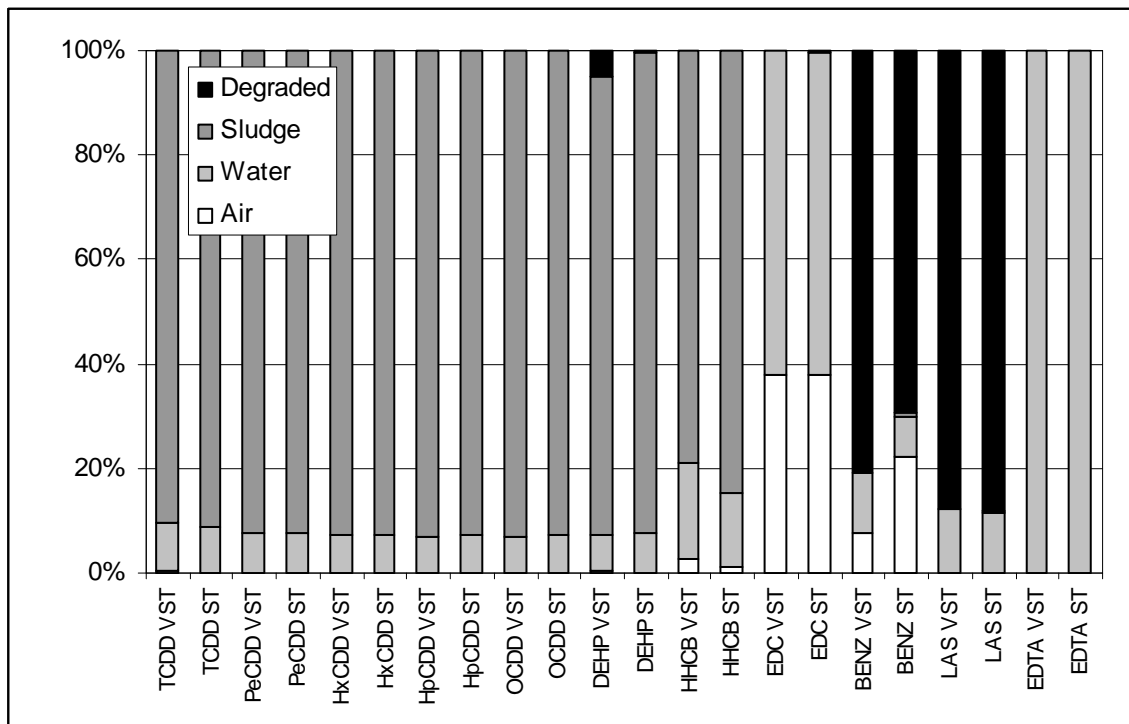


Figure 27 Fractions calculated by VerySimpleTreat (VST) and SimpleTreat (ST).

Table 21 Local concentrations and emissions calculated by VerySimpleTreat and SimpleTreat based on a local standard emission of 1 kg/d.

Substance	VerySimpleTreat			SimpleTreat		
	Air [kg/d]	Water [kg/m ³]	Sludge [kg/kg]	Air [kg/d]	Water [kg/m ³]	Sludge [kg/kg]
TCDD	2.40E-03	2.79E-08	6.14E-07	9.15E-04	2.43E-08	6.26E-07
PeCDD	6.98E-05	2.29E-08	6.27E-07	2.61E-05	2.16E-08	6.34E-07
HxCDD	5.72E-05	2.15E-08	6.30E-07	2.13E-05	2.09E-08	6.35E-07
HpCDD	1.17E-05	2.12E-08	6.31E-07	4.36E-06	2.07E-08	6.36E-07
OCDD	4.07E-05	2.09E-08	6.31E-07	1.51E-05	2.05E-08	6.36E-07
DEHP	2.71E-03	2.13E-08	5.94E-07	1.11E-03	2.11E-08	6.32E-07
HHCb	2.80E-02	5.51E-08	5.36E-07	1.15E-02	4.00E-08	5.80E-07
EDC	3.78E-01	1.89E-07	6.77E-10	3.78E-01	1.73E-07	1.54E-09
BENZ	7.76E-02	3.43E-08	4.20E-10	2.23E-01	2.14E-08	4.12E-09
LAS	1.18E-09	3.72E-08	3.38E-10	1.22E-09	3.22E-08	3.14E-09
EDTA	1.78E-08	3.04E-07	1.41E-13	1.11E-08	2.80E-07	2.22E-13

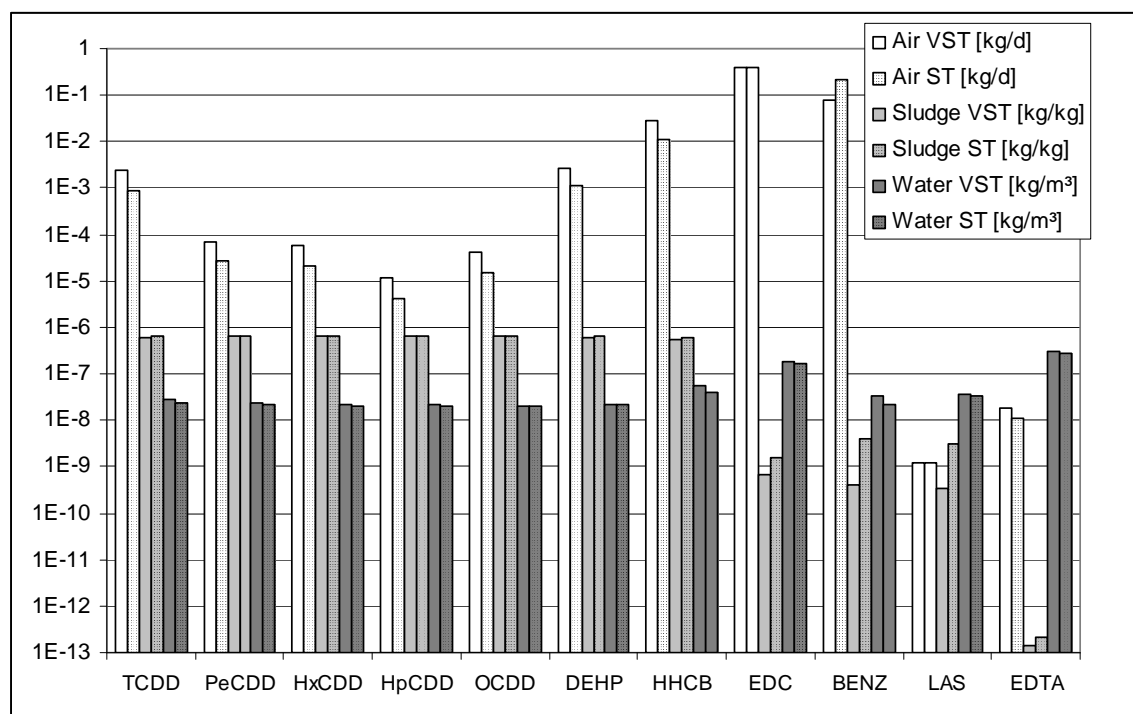


Figure 28 Local concentrations and emissions calculated by VerySimpleTreat and SimpleTreat based on a local standard emission of 1 kg/d.

Both Table 20 and Figure 27 and Table 21 and Figure 28 show that the differences between the two models' results are only small. The qualitative behaviour of both models is comparable. Both models calculate almost similar results for PCDD, i.e. no degradation, under 10 % of the substance stays in the water and the main part is directed to the sewage sludge. For DEHP, VerySimpleTreat calculates a degradation of about 5 %, which could also be plausible since a slight bio-degradation is assumed for this substance. For HHCb, EDC, LAS and EDTA, the results of both models are almost similar, too. The differences for LAS in the percentage fractions directed to sludge are relatively high (1 OoM difference) but absolutely low (0.5 % to 0.05 %). This difference can also be seen in the local concentrations in sewage sludge, which is approximately 1 OoM higher in SimpleTreat than in VerySimpleTreat. For benzene, remarkable deviations between the two models occur: SimpleTreat calculates a higher fraction in air and a lower one for degradation than VerySimpleTreat. However, the results are still similar.

11.4 Discussion and conclusion

The differences between the two models are very slight. In view of the very low complexity and the simple structure of VerySimpleTreat compared to SimpleTreat, the results of the new model can be judged as very good. Only three equations make it possible to obtain results that are similar to those of the much larger and complex model SimpleTreat. Since on the regional scale the STP model is only used to estimate indirect emissions, its role in the prediction of regional environmental concentrations is a minor one. SimpleTreat is also used to estimate local concentrations. But even a comparison of these values shows that the simpler model can lead to comparable results with a much lower expenditure. It is true that VerySimpleTreat incorporates much fewer internal processes and the behaviour of different STP types cannot be represented. Nevertheless, it

can also be easily improved, e.g. by a pH-dependency of the partition coefficients, as performed in SimpleTreat 3.0, but not in the EUSES version of this model. The advantage of VerySimpleTreat is its high transparency and clear structure. Almost every parameter has a high influence on the results. At the same time, this is a disadvantage since the choice of the model's parameter values can be discussed. Changing, e.g. depth of water or the area of the STP can lead in several cases to distinct alterations in the calculated fractions. However, the overall influence of the model to the calculated environmental concentrations is so low that the simple model fulfils the task sufficiently well. Altogether, this model can replace the complex and less transparent STP model SimpleTreat without a significant deterioration of the results.

11.5 Summary

The STP model SimpleTreat contained in EUSES was replaced by a simpler one. This model entitled VerySimpleTreat is a Level 3 model consisting of the three compartments water, sewage sludge and air. Because of its simple structure it requires only few input parameters and is much more transparent than SimpleTreat. Using a set of sample substances, the results of SimpleTreat and VerySimpleTreat were compared with each other. It emerged that the outcomes of both models are similar and deviate only in one case significantly without being qualitatively different results. Therefore, it is suggested to use the simpler model instead of the complex one.

12 Summarising conclusion

Even though the opposite is often said, it must be considered that Level 3 models, as e.g. Simple-Box, are not simple. In spite of strong simplifications many processes are still represented, and their interactions and parameters are not easy to understand. Thus, the model's behaviour is difficult to predict exactly in advance. Only elaborated investigations can help to obtain a better understanding of the model and its weaknesses and capabilities. The aim of this work was therefore to perform a validation of the regional distribution model SimpleBox. The single aspects and relevant steps were presented and discussed. However, a whole validation is not complete after completing step by step the several working packages. It then has to aggregate all results and to assess them to come to an overall conclusion for which purposes the model may be employed and for which it is not suitable. This will be done in this chapter. Furthermore, proposals for the future enhancement of the model are made. It is also discussed where data gaps exist and on which kind of data the main focus should be set to improve the model's results. Some recent developments in this context are also presented.

This work showed that the comparison of modelled results with measured ones is not the only criterion to assess a model's quality. Although it is a very significant aspect, the scrutiny of theory, sensitivity, scenario uncertainty analyses as well as the comparison with measured values are also fundamental aspects in model validation. Especially if the model was made to be applied for new substances that were not emitted to the environment and for which no measured concentrations yet exist, these analyses are of great importance to judge the model's quality and to obtain information about its limits, requirements and implicit assumptions. Employing existing substances and performing simulations for these can help us to understand the model's behaviour and lead by analogies (substances with similar properties will lead to similar results) to common statements. Nevertheless, it was shown that the physico-chemical parameters alone are not sufficient to determine a substance's fate in the environment. Other parameters, such as emissions and degradation rates, are of great significance for concentrations calculated by the regional distribution model. Therefore, the quantification of the model's uncertainties by probabilistic analyses is unavoidable. Only combining both makes it possible to evaluate the complex system as a whole, to assess the applicability of the model and to derive proposals and recommendations for improvements.

12.1 Implicit assumptions and simplifications

The scenario analysis showed that in most cases estimations of the regional distribution model are close to the measured data. Deviations especially occur if the data for emission and degradation are insufficient. PCDD can serve as a good example for this case. For this substance class only relatively inexact data for congener-specific emissions exist, and the degradation rates in soil and sediment are very difficult to determine. This example shows two problems in estimating regional background concentrations: 1. Many substantial data are difficult to measure and hardly obtainable even though they have a high influence on the modelled results. 2. The assumption of homogeneous compartments leads to high uncertainties, especially for the heterogeneous compartments soil and sediment. If a severe scientific standard is presumed, measured and calculated concentra-

tions are not comparable for these two compartments, and hence, the model is not assessable in these cases. Here, two points are of importance.

- The heterogeneity of soil and sediment leads to high uncertainties in the measured concentrations: The temporal and spatial variations are in many cases so high that the assumption of homogenous mixing is practically out of the question. Degradation processes depend on many parameters, such as the type and depth of the soil, environmental temperature and solar radiation. Only long-term monitoring programmes on a wide spatial scale could deliver a suitable mean value.
- Moreover, due to the previously mentioned aspects, utilisation of a compartment model is a very strong simplification since, e.g., one fixed degradation rate has to be entered for the whole soil. This assumption is also a simplification for atmosphere and water but it is less unrealistic due to the large mixing zones and movement of the medium itself.

A further weakness of a Level 3 model is the assumption of steady state and hence of continuous emissions. Since this applies also to emissions of sewage sludge to agricultural soil, this can lead to the paradox case that reducing the fraction connected to sewage systems causes a lower total mass of substance in the system: If the substance is degraded well in water (e.g. by photolysis) but only slightly in the STP and it is simultaneously bound in a high fraction to sewage sludge, the total fraction degraded decreases with an increased fraction connected to sewer systems. On the other hand, the assumption that sewage sludge is re-emitted to the environment and is not interpreted as an elimination path represents a conservative estimation which makes concessions to the demand of calculating reasonable worst-case concentrations.

All in all, in this modelling approach it must be questioned whether calculating regional background concentrations for soil and sediment really is sensible.

12.2 Input data

It is obvious that the quality of a model's outcome depends strongly on the quality of the input data. Even the best model will not be able to deliver accurate results if the parameter values used are afflicted with high uncertainties or are simply wrong. Therefore, improving data quality is one possible way to ameliorate the modelled results. For the regional distribution model there are two relevant parameter classes that can lead to uncertainties in the predicted environmental concentrations: the substance data and the regional data. Summarising the results of scenario and uncertainty analyses (Chapter 7, 8 and 9), the following points can be stressed:

1. The differences between the scenarios *Default* and *NRW standard* (using realistic data for regional properties but still estimated data for substance properties) are low.
2. The differences between the *Default* scenario and the *NRW realistic* scenario (using realistic data for the regional properties and for emissions, degradation rates and partition coefficients) are very high, up to seven OoM (factor 10 million).
3. The deviations of calculated concentration for the generic region to a northern and a southern region are lower than the differences between *NRW standard* and *NRW realistic*.
4. The overall uncertainties calculated on the basis of the *NRW* scenario are lower (maximal up to two OoM = factor 100) than the differences between *Default* and *NRW realistic*.

These facts clearly show that even strong alterations in the regional parameters (see Northern vs. Southern Europe) have a lower impact on the predicted concentrations than the uncertainties in the substance data. Especially the estimation of environmental releases using emission tables causes high uncertainties, as well as the estimation of degradation rates. The results of the sensitivity, scenario and uncertainty analyses show clearly that emissions and degradation rates are both sensitive and uncertain. Since the behaviour of a Level 3 model depends considerably on the compartment that receives the emissions and where it is mainly degraded, these are the primary factors of uncertainty in estimating environmental concentrations. Consequently, improvements in the modelled concentrations can rather be achieved by advanced substance data than by alternative regional data. Therefore, the main focus for future enhancements in the risk assessment of substances should be on the improvement of the release estimation and in the accuracy of the substance data (physico-chemical properties and degradation rates). High expenditure in finding more appropriate regional data is not needed since the potential for improvement is reduced.

12.3 Monitoring data

Up to now, there has been no uniform assessment scheme for the judgement of data quality. Also, it is usually not known under which conditions monitoring data were taken. I.e., usually neither exact information on the time and site of the measurement is given, nor are other parameters available, such as, e.g. environmental temperature, depth of the soil or the pH-value, even though their influence on the environmental concentrations is high. As a result of this, assessing the applicability of monitoring data is impossible in many cases. For the use of measured concentrations in a model validation, several improvements and recommendations can be considered. Monitoring programmes should be performed in such a way that a comparison of the data with modelled results is possible. From this, the following requirements can be derived:

1. An assessment scheme for monitoring data must be developed. It has to include the quality of the measuring method and the survey of secondary data. This directly leads to the next requirement.
2. Each survey of measurements should include relevant (and yet to be determined) secondary parameters, and the method of measurement should be documented and judged.
3. Measurements at one site should always be taken simultaneously in all relevant environmental compartments to obtain consistent data sets.
4. The uncertainties in the measurement should, if possible, also be quantified. This leads to the last requirement.
5. Monitoring data should receive a judgement of their quality and assessment of their applicability in accordance with the proposed scheme. For users, this "mark of quality" is sufficient to judge the relevance of the monitoring data for comparison with modelled results and for the consideration of possible uncertainties.

The assessment of the modelled results then has to include uncertainties in the monitoring data as well as those of the model itself. Statements on the model's quality could then be as follows: "The

results are probably bad." Or: "The results are perhaps average." Or: "The results tend to be rather good." Terms like "perhaps" or "probably" indicate that the assessment is in many cases quite rough. Thus, this could be a point of departure for the use of Fuzzy-sets. Establishing such an assessment scheme based on the Fuzzy-methodology is a problem that is yet to be solved. However, there are already approaches which include Fuzzy-sets in the level models (SALSKI ET AL. 1996, GUYONNET ET AL. 1999). But further research is still needed.

12.4 Recent developments

The problem of estimating a substance's fate in the environment is commonly known. Several weaknesses in the present risk assessment scheme are recognised and lead to continuous developments. Some of the recent developments which comprise the release estimation and further approaches in the risk assessment of substances using substance-immanent properties are presented in the following.

12.4.1 Release estimation

As described, a main difficulty in predicting environmental concentrations is the release estimation. The emission tables included in EUSES are afflicted with high uncertainties and require improvement. On the one hand, it is often difficult to choose the correct industry category (IC) and use category (UC) of a substance. Selecting different categories can change the estimated release factor distinctly. Benzene is a good example of this. It can be assigned to the mineral oil and fuel industry (IC 9). In this case, an emission factor to air of 0.01 is estimated. But if this substance is seen as a basic chemical in the chemical industry (IC 2), the emission factor to air is 0.5. This means a difference of a factor of 50. Therefore, clear and precise use patterns are required, as already claimed by VAN DER POEL (1999). There are several examples for improving the emission tables by more detailed emission scenarios that are based on the investigation of realistic emissions. WAGNER ET AL. (1999) reported intensified research in this field. While the release estimation of EUSES is based on emission factors, improvements in the methodology are based on so-called emission scenarios. In the Emission-Scenario-Documents (ESDs), algorithms to calculate emissions are provided. "ESDs constitute the basis of a realistic worst-case estimate in a particular industrial or professional branch. Such scenarios are elaborated in several European countries in close co-operation between the respective industrial or professional association and the environmental authorities for European legislation. Recently, the OECD Exposure Assessment Working Group was given the task of harmonising these emission scenario documents within the OECD and within the Pollution Release and Transfer Registry (PRTR) philosophy. (...) emission scenarios for industrial chemicals as well as for human and veterinary medicinal and biocidal products (...) will be introduced into EU legislation as technical guidance to estimate exposure." (WAGNER ET AL. 1999) Another example for the further development of the release estimation is a study on the examination of wastewater discharges in the production of lacquer and varnishes and cooling lubricants (SCHÖNEICH ET AL. 1997). In this study, statistical data on discharges and dilution of wastewater in Germany were investigated for these branches of industry. Such detailed information make it possible to estimate releases in a more sophisticated way. In this context, it can be discussed whether these data should really only be used for emission tables, i.e. in an aggregated

state. If the information exist, it would even be possible to employ a geography-referenced model system and to receive spatially dissolved concentrations with the facility to recognise hot spots and local maxima.

12.4.2 Risk assessment by substance-immanent properties

The risk assessment of substances using the PEC/PNEC approach contains several disadvantages: A large number of toxicological tests is needed to receive an applicable Predicted No-Effect Concentration, and the PEC (and hence the risk characterisation) depends directly on emissions to the environment. With substances for which these data are not known, not assessable or not obtainable, a risk assessment is impossible or very uncertain. On the other hand, if the PEC/PNEC-quotient can be calculated and if it is less than one, the risk of a substance is assessed to be low. However, a substance can cause adverse effects that are independent of the amount of emission and toxicological data. Such an effect that can not be quantified with the PEC/PNEC approach is the long-range transport potential. Substances can be transported over very long distances up to the polar regions, where they accumulate in the marine environment. These substances, which are presently under discussion, are called POPs (Persistent Organic Pollutants). POPs are problematic because of their combination of bio-accumulation, persistence, distribution and transport (see, e.g. BEYER ET AL. 2000). Therefore, POPs may be mostly harmless on a local and regional scale, but pose a risk on the global scale, which is not regarded in the present risk assessment scheme. In order to deal with this problem, we propose a closer consideration of the substance-immanent properties in the first place without regarding possible effects and emissions (SCHERINGER AND BERG 1994, BERG AND SCHERINGER 1994, MATHES ET AL. 1999). Such a process, called hazard assessment, could easily be integrated into the existing risk assessment scheme and into EUSES and would support the precautionary principle in the evaluation of substances (AHLERS 1999). Proposals for maximal values for long-range transport potential (LRTP) and persistence already exist (BEYER ET AL. 2000, MACKAY ET AL. 2000) but are still under discussion. Thus, the calculated values for these parameters cannot be used in the same way as the PEC/PNEC-quotient and therefore, these parameters can, up to now, only serve as additional information to assess the risk of a substance.

12.5 Proposals for improvement

To summarise the conclusions made in this chapter, several proposals can be given to improve the modelling of regional background concentrations and the validation procedure. These proposals can be divided into two groups that correspond to the two basic parts of model validation. Improvements in the model structure, i.e. the generic properties of the model, using the results of the internal model validation, and improvements in the parameter values, i.e. the task-specific properties, using the results of the external model validation. Possible improvements of the model are listed in Table 22 together with their expenditure and expected influence.

Table 22 Assessment of possible improvements in the model.

Type of improvement	Expenditure	Influence
Realistic values for PC data, degradation rates and emission.	Often high. Data availability can be bad. The development of alternative emission tables is difficult and expensive.	Very high. Especially improvements in emission data can lead to distinct improvements in the modelled results.
Inclusion of probabilistic assessments.	High. The methodology exists but its implementation concerns the whole model system.	High. Qualitatively different statements are possible.
Consideration of substance-immanent properties for global effects.	Low. Equations exist and could easily be implemented.	High. Additional information is given. However, the interpretation and assessment of the results is still under discussion.
Consideration of dissociation by pH/pK-correction.	Low. Equations exist and could easily be implemented.	Maybe high. Not assessed.
Consideration of penetration depth for degradation rates in soil and sediment.	Probably low. Equations for the penetration depth exist but how to consider this parameter in the model has not yet been evaluated.	Maybe high since the compartments' volumes become flexible. However, the real influence must still be evaluated.
Use of concrete regional data, different European scenarios.	Low because the data need not be very accurate. Easily to implement.	Average. Up to 2 OoM in extreme cases.
Replacement of the STP model by a simpler one.	Low. Model already exists.	Low. The results are rather similar. But the complexity of the model is reduced.
Neglect of redundant parameters.	Low. The parameters are known.	Low. The results are rather similar. But the complexity of the model is reduced.
Correction of known errors in the model.	Low.	Low. The errors are not very serious.
Different regression equations depending on substance properties.	Low. Equations exist and could easily be implemented.	Low. Higher changes can only be expected for a few substances.

12.6 Final remarks

The results of this work comprise two general fields. On the one hand, the applicability of the regional distribution model is assessed and proposals for improvements are made. On the other hand, this work helps to establish a validation scheme and can give proposals about how model validation should be performed and how it can be improved. The results of the first point can be summarised by the following statements:

- The regional distribution model is applicable for the estimation of regional background concentrations in the screening phase of risk assessment.
- Improvements in the results can mainly be achieved by better substance data, especially emissions, partition coefficients and degradation rates.

For the second point the results are not easy to determine. But generally the following statements can be made:

- The validation scheme of SCHWARTZ (2000) is useful, practical and practicable for the validation of environmental exposure models. The division into internal and external validation serves to assess a model's applicability beyond the simple comparison with measured values.

- Sensitivity and probabilistic analyses are fundamental to comprehend a model's behaviour and to determine its appropriateness. Therefore, a model used in environmental risk assessment should offer the possibility to perform probabilistic analyses.
- The availability of data is essential to the quality of a model validation. Thus, monitoring programmes should consider the use of data for modelling and validation purposes.
- Model validation can help to increase confidence in the modelled results and is needed to understand the model. Therefore it is an indispensable step following the modelling processes.

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Appendix

A.1 Model parameters and probabilistic distributions

According to the methodology presented in Section 2.2.3, probabilistic distribution functions were investigated for the input parameters of the regional distribution model. However, it is not always possible to determine a distribution function for each parameter that is justified by sufficient measured data. Generally, three types of distribution functions were applied: log-normal distribution, triangular distribution and uniform distribution (Table 23).

Table 23 Distribution functions used.

Distribution	Parameter (CrystalBall™-compatible)	Abbreviation
Log-normal	Mean, standard deviation	L(M, SD)
Triangular	Minimum, mode, maximum	T(min, mode, max)
Uniform	Minimum, maximum	U(min, max)

The explanation for this method is also given in Section 2.2.3. Whilst selecting the distribution functions, the results of the sensitivity analyses which are presented in Chapter 6 were considered. The distribution functions were chosen as follows:

- *Log-normal distribution:* If sufficient data are available ($n \geq 25$) a log-normal distribution with the mean and standard deviation of the given data basis is chosen.
- *Triangular distribution:* A triangular distribution is suitable if the data basis is too deficient to assume a log-normal distribution. Thereby, the triangular distribution represents a conservative estimation of the parameter distribution. The minimum, median and maximum of the given data are the values for the minimum, mode and maximum of the distribution function. In this context, it is necessary to explain the distributions that were selected for emissions and degradation rates. The data basis for these parameters is so poor that it is impossible to derive distribution functions. But, due to the high influence of these parameters on the predicted concentrations (see Chapter 6) and because they have high uncertainties and variabilities, it is highly recommended to consider them in the uncertainty analyses. Therefore, based on the value selected for the point estimation, a triangular distribution was selected of which the mode is the value of the point estimation. Half of the value was chosen as the minimum, for the maximum the value was multiplied by five. Thus, the range between minimum and maximum is one OoM, and the estimation is conservative. This does not apply to the degradation rates since a higher rate leads to lower concentrations. Consequently, instead of the rates the half-lives of the values were taken and varied accordingly.
- *Uniform distribution:* A uniform distribution was used if only two values were available.

In the following data tables the column *Default* designates the default values for the standard scenario proposed by the TGD. In the column *Realistic* the parameter value for the point estimation of the realistic scenario and the probability distributions are listed. If obtainable, in column *CV* the variation coefficient ($CV = SD / M$) is given.

For the parameters of the regional distribution model (volumetric, process and other model parameters) in many cases no original data were attainable. In such cases, two different sources were employed: Often distributions researched by ETIENNE ET AL. (1997) could be taken. If this source did not offer information, a log-normal distribution was selected, the mean value of which is the value of the point estimation. Then the standard deviation could be calculated from the variation coefficient used in CalTOX (DTSC 1993).

The distributions of the *volumetric parameters* were chosen in accordance with the method described above. It must be noted that the regional area and fractions for soils and water represent North Rhine-Westphalian properties. Thus, uncertainties are relatively low. For the area a uniform distribution with two values from NRW (1998) was taken which differ only marginally from each other. For the distributions of the area fractions, the values of the districts in North Rhine-Westphalia were used.

Only few original data were obtainable for the *process parameters* so that for most of them the distributions were chosen from ETIENNE ET AL. (1997) and DTSC (1993). Only for *FRunoffSoil*, *Rainrate* and *windspeed* could researched values serve as a basis for the distribution functions. Selecting distributions for the transfer resistances is very problematical. ETIENNE ET AL. (1997) uses variation coefficients of up to $1.8E7$ for these parameters, which seems to be unrealistic. Due to the lack of other data, only these values could be taken. To what extent these distributions cause distortions in the results is discussed in Chapter 9 in the course of the uncertainty analyses. For the transfer resistances of the air-water interface a different approach could be undertaken by using a regression of BRANDES ET AL. (1996) which is based on wind speed and molecular weight. It is true that in so doing, the uncertainty of these parameters is no longer regarded directly, but in view of the strong problems in determining distribution functions for these parameters this strategy is justified.

Also the distributions of the remaining parameters were determined in accordance with the method presented above. But here again it must be considered that, as already mentioned for the volumetric parameters, the basis of the distributions is North Rhine-Westphalia which in several cases leads to very low uncertainties and variabilities, respectively. This especially applies to the very sensitive fraction connected to sewer systems. For this parameter the variation coefficient is only 0.05 so that the influence of this parameter is quite low.

Table 24 Volumetric parameters.

Name	Description	Unit	Default	Realistic	CV	Reference
area Reg	Area of the region	m ²	4E10	3.44E10 U(3.406, 3.434)		NRW (1998)
area EU	Area of the EU	m ²	3.56E12	3.56E12 (constant)		
depthAgric	Mixing depth of agricultural soil	m	0.2	0.2 L(0.2, 0.2)	1	CV: DTSC (1993)
depthInd	Mixing depth of industrial soil	m	0.05	0.05 L(0.05, 0.05)	1	CV: DTSC (1993)
depthNat	Mixing depth of natural soil	m	0.05	0.05 L(0.05, 0.05)	1	CV: DTSC (1993)
depthSed	Mixing depth of sediment	m	0.03	0.03 L(0.03, 0.03)	1	CV: DTSC (1993)
depthWater Cont *	Depth of continental water	m	3	3 (constant)		
depthWater Reg	Depth of regional water	m	3	3 L(3, 4.74)	1.58	CV: DTSC (1993)
fAgric Cont	Fraction of agricultural soil on continental scale	m	0.27	0.27 (constant)		
fAgric Reg	Fraction of agricultural soil on region scale	m	0.27	0.52 L(0.52, 0.101) [#]	0.192	NRW (1998) for realistic NRW value, STATISTISCHE ÄMTER DES BUNDES UND DER LÄNDER (1998) for distribution
fInd Cont	Fraction of industrial soil on continental scale	m	0.1	0.1 (constant)		
fInd Reg	Fraction of industrial soil on region scale	m	0.1	0.202 L(0.1917, 0.047) [#]	0.24	see fAgric Reg
fNatural Cont	Fraction of natural soil on continental scale	m	0.6	0.6 (constant)		
fNatural Reg	Fraction of natural soil on region scale	m	0.6	0.26 L(0.2707, 0.102) [#]	0.393	see fAgric Reg
fWater Cont	Fraction of water on continental scale	m	0.03	0.03 (constant)		
fWater Reg	Fraction of water on region scale	m	0.03	0.018 L(0.0176, 0.007) [#]	0.395	see fAgric Reg
heightAir	Atmospheric mixing height	m	1000	1000 L(1000, 461)	0.461	CV: for data researched by ETIENNE ET AL. (1997)

*: not sensitive

[#]: Values base on data of the five districts in NRW.

Table 25 Process parameters.

Name	Description	Unit	Default	Realistic	CV	Reference
CollEffAer	Collection efficiency of aerosol particles	-	2E5	2E5	5E-4	ETIENNE ET AL. (1997)
DepRateAer	Deposition rate of aerosol particles	m/d	86.4	L(2E5, 10) 86.4	1.5	CV: DTSC (1993)
Erosion	Soil erosion rate in the regional system	m/d	8.22E-8	8.22E-8 L(8.22E-8, 1.644E-8)	0.2	CV: DTSC (1993)
FFlowOutReg	Fraction of water flow from continental to regional scale	-	0.034	0.029		AreaReg/ AreaEU-depthwater
FrunoffSoil	Fraction of rain water running off soil	-	0.25	0.4 L(0.4, 0.22)	0.55	ECETOC (1994) for realistic German value, CV: DTSC (1993)
kasl air	Air-film partial mass-transfer coefficient (air-soil interface)	m/d	120	120 L(120, 8.64E6)	7.2E5	author, analogue to ETIENNE ET AL. (1997)
kasl soilair	Soil-air partial mass-transfer coefficient (air-soil interface)	m/d	0.48	0.48 L(0.48, 8.64E6)	1.8E7	ETIENNE ET AL. (1997)
kasl soilwater *	Soilwater-water film partial mass-transfer coefficient (air-soil interface)	m/d	4.8E-5	4.8E-5 L(4.8E-5, 8.64E6)	1.8E11	ETIENNE ET AL. (1997)
kawAir	Air-film partial mass-transfer coefficient (air-soil interface)	m/d	120	$0.01 \cdot (0.004 + 0.00004 \cdot \text{windspeed}) \cdot (0.032 / \text{molweight})^{0.4047}$		BRANDES ET AL. (1996)
kawWater	Water-film partial mass-transfer coefficient (air-soil interface)	m/d	1.2	$0.01 \cdot (0.3 + 0.2 \cdot \text{windspeed}) \cdot (0.018 / \text{molweight})^{0.4355}$		BRANDES ET AL. (1996)
kwsSed	Pore water partial mass-transfer coefficient (sediment-water interface)	m/d	0.0024	0.0024 L(0.0024, 8.634E6)	3.6E9	ETIENNE ET AL. (1997)
kwsWater*	Water-film partial mass-transfer coefficient (sediment-water interface)	m/d	0.24	0.24 L(0.24, 8.64E6)	3.6E7	ETIENNE ET AL. (1997)
Rainrate	Average daily precipitation rate	m/d	1.92E-3 (= 700 mm/a)	1.86E-3 (= 679 mm/a) L(2.32E-3, 4.19E-4)	0.181	NRW (1995A, 1995B, 1995C)
SETTLEvelocity	Settling velocity of suspended solids	m/d	2.5	2.5 L(2.5, 0.75)	0.3	CV: DTSC (1993)
windspeed	Wind speed in the system	m/d	2.59E5 (3 m/s)	2.69E5 (=3.1 m/s) L(2.69E5, 4.82E4)	0.179	NRW (1995A, 1995B, 1995C)

*: not sensitive

Table 26 Other model parameters.

Name	Description	Unit	Default	Realistic	CV	Reference
BIOwater *	Concentration of biota	kg/m ³	0.001			
BOD	Mass of O ₂ binding material per person per day	kg/eq/d	0.054	0.06 U(0.054, 0.06)		German standard value
ConJunge	Constant in Junge equation	Pa·m	0.01	0.172 (constant)		FALCONER AND BIDLEMAN (1996)
FAirSoil *	Volume fraction of air in soil	m ³ /m ³	0.2			
FconnectSTP	Fr. action of inhabitants connected to sewer systems	-	0.7	0.92 L(0.904, 0.045) [#]	0.05	NRW (1998) for realistic NRW value, STATISTISCHE ÄMTER DES BUNDES UND DER LÄNDER (1998) for distribution
FInfSoil	Fraction of rainwater infiltration soil	-	0.25	0.25 L(0.25, 0.1375)	0.55	CV: DTSC (1993)
FocSed	Mass fraction of OC in sediment	kg/kg	0.05	0.05 U(0.04, 0.05)		distribution: EUSES default value and MACKAY ET AL. (1991-1997)
FocSoil	Mass fraction of OC in soil	kg/kg	0.02	0.02 L(0.0577, 0.03627)	0.629	SCHACHTSCHABEL ET AL. (1989)
FocSusp	Mass fraction of OC in suspended matter	kg/kg	0.1	0.1 U(0.1, 0.2)		see FocSed
FSolidSed	Volume fraction of solids in sediment	m ³ /m ³	0.2	0.2 L(0.2, 0.04)	0.2	CV: DTSC (1993) (porosity)
FSolidSoil	Volume fraction of solids in soil	m ³ /m ³	0.6	0.6 T(0, 0.4, 1)		ETIENNE ET AL. (1997)
FWaterSed	Volume fraction of water in sediment	m ³ /m ³	0.8	0.8 L(0.5, 0.8, 0.999)		ETIENNE ET AL. (1997)
FWaterSoil	Volume fraction of water in soil	m ³ /m ³	0.2	0.2 U(0.2, 0.3)		see FocSed
N Reg *	Number of inhabitants on regional scale	eq	2E7	17 816 100 (constant)		NRW (1998)
NEU *	Number of inhabitants in EU	eq	3.7E8	3.7E8 (constant)		
OHconair *	Concentration of OH radicals in air	molec/m ³	5E11			
Qstp	Sewage flow	m ³ /eq/d	0.2	0.20047 L(0.196, 0.0229) [#]	0.12	see FconnectSTP
RHOair *	Density of air	kg/m ³	1.3			
RhoSolid	Density of solids	kg/m ³	2 500	2 500 L(2500, 125)	0.05	CV: DTSC (1993)
RhoWater	Density of water	kg/m ³	1 000	1 000 (constant)		
SurfAer	Surface area of aerosol particles	m ² /m ³	0.01	1.5E-4 L(4.2E-5, 1.5E-4, 1.1E-3)		FALCONER AND BIDLEMAN (1997)
SuspEff	Concentration of solids in STP effluent	kg/m ³	0.03	0.03 L(0.03, 0.0234)	0.78	like river water (IKSR 1996)
SuspWater Reg	Concentration of suspend solids in regional water	kg/m ³	0.015	0.015 L(0.0297, 0.02315)	0.78	values from IKSR (1996)
SuspWater Cont *	Concentration of suspend solids in continental water	kg/m ³	0.025	0.025 (constant)		
Temperature	Environmental temperature	°C	12	11 L(10.3, 1.6)	0.15	NRW (1995A, 1995B, 1995C)

*: not sensitive

#: Values base on data of the five districts in NRW.

A.2 Overview of substance data

Table 27 Substance identification.

Substance	Chemical declaration	Sum formula	CAS
PCDD	Polichlorinated dibenzo-<i>p</i>-dioxins		262 - 12- 5
TCDD	2,3,7,8-Tetrachloro-dibenzo- <i>p</i> -dioxin	C ₁₂ H ₄ O ₂ Cl ₄	1746 - 01 - 6
PeCDD	1,2,3,7,8-Pentachloro-dibenzo- <i>p</i> -dioxin	C ₁₂ H ₃ O ₂ Cl ₅	40321 - 76 - 4
HxCDD-I	1,2,3,4,7,8-Hexachloro-dibenzo- <i>p</i> -dioxin	C ₁₂ H ₂ O ₂ Cl ₆	39227 - 28 - 6
HxCDD-II	1,2,3,6,7,8-Hexachloro-dibenzo- <i>p</i> -dioxin	C ₁₂ H ₂ O ₂ Cl ₆	57653 - 85 - 7
HxCDD-III	1,2,3,7,8,9-Hexachloro-dibenzo- <i>p</i> -dioxin	C ₁₂ H ₂ O ₂ Cl ₆	19408 - 74 - 3
HpCDD	1,2,3,4,6,7,8-Hexachloro-dibenzo- <i>p</i> -dioxin	C ₁₂ HO ₂ Cl ₇	5822 - 46 - 9
OCDD	Octachloro-dibenzo- <i>p</i> -dioxin	C ₁₂ O ₂ Cl ₈	3268 - 87 - 9
DEHP	Di-(2-ethylhexyl)phthalate	C ₂₄ H ₃₈ O ₄	117 - 81 - 7
HHCB	1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-[g]-benzopyrane	C ₁₈ H ₂₆ O	1222 - 05 - 5
EDC	1,2-Dichloroethane or ethylenedichloride	C ₂ H ₄ Cl ₂	107 - 06 - 2
BENZ	Benzene	C ₆ H ₆	71 - 43 - 2
LAS	Linear alkyl benzene sulfonates	C ₁₈ H ₃₀ O ₃ S (salt: C ₁₈ H ₂₉ NaO ₃ S)	85536 - 14 - 7 (salt: 25155 - 30 - 0)
EDTA	Ethylendiamintetra acetic acid	C ₁₀ H ₁₆ N ₂ O ₈ (salt: C ₁₀ H ₁₂ N ₂ O ₈ Na ₄)	60 - 00 - 4 (salt: 64 - 02 - 8)

Table 28 Physico-chemical properties.

Substance	M [g/mol]	log K _{ow} [-]	log K _{oc} [l/kg]	BP [K]	MP [K]	VP [Pa at 25°C]	WS (25°C) [mg/l]	H [Pa·m ³ /mol]
TCDD	322 ^a	6.8 ^a	5.61 [§]	720 ^b	578 ^a	2.0E-07 ^a	1.9E-05 ^a	3.34 ^a
PeCDD	356.4 ^a	7.4 ^a	6.09 [§]	738 ^b	469 ^a	8.8E-08 ^a	1.2E-04 ^a	0.26 ^a
HxCDD	391 ^a	7.8 ^a	6.42 [§]	761 ^b	546 ^a	5.1E-09 ^a	4.4E-06 ^a	0.45 ^a
HpCDD	425.2 ^a	8.0 ^a	6.58 [§]	780 ^b	538 ^a	7.5E-10 ^a	2.4E-06 ^a	0.13 ^a
OCDD	460 ^a	8.2 ^a	6.74 [§]	783 ^b	608 ^a	1.1E-10 ^a	7.4E-08 ^a	0.68 ^a
DEHP	390.56 ^c	7.48 ^c	4.94 ^d	658 ^b	233 ^c	1.9E-03 ^c	2.9E-2 ^c	17.51 ^b
HHCB	258.4 ^e	5.9 ^e	4.86 ^e	605 ^e		7.3E-02 ^e	1.75 ^e	11.3 ^e
EDC	98.96 ^c	1.46 ^c	2.3 ^c	356 ^c	238 ^a	11 300 ^c	8 600 ^c	96.66 [§]
BENZ	78.12 ^c	2.12 ^c	1.96 ^c	353 ^c	279 ^c	12 700 ^c	1 760 ^c	448.30 [§]
LAS	348.48 ^c	1.96 ^c	1.69 [§]		263 ^a	-	1 100 ^c	-
EDTA	292.25 ^f	-3.34 ^f	-2.61 [§]		493 ^f	-	500 (20°C) ^f	-

Sources: ^a SHIU ET AL. (1988), ^b MACKAY ET AL. (1991-1997), ^c RIPPEN (1995), ^d DECHEMA (1995), ^e PLASSCHE AND BALK (1997), ^f EC (1996c), [§] estimated from available data.

M = Molecular weight, BP = boiling point, MP = melting point, VP = vapour pressure, WS = water solubility, H = Henry's law constant.

Table 29 Degradation rates and half-life times.

Substance	BC	Air		Water		Sediment		Soil	
		[h]	[1/h]	[h]	[1/h]	[h]	[1/h]	[h]	[1/h]
TCDD	0	170 ^a	4.1E-3	550 ^a	1.3E-3	55 000 ^a	1.3E-5	17 000 ^a	4.1E-5
PeCDD	0	550 ^a	1.3E-3	550 ^a	1.3E-3	55 000 ^a	1.3E-5	17 000 ^a	4.1E-5
HxCDD	0	550 ^a	1.3E-3	1 700 ^a	4.1E-4	55 000 ^a	1.3E-5	55 000 ^a	1.3E-5
HpCDD	0	550 ^a	1.3E-3	1 700 ^a	4.1E-4	55 000 ^a	1.3E-5	55 000 ^a	1.3E-5
OCDD	0	550 ^a	1.3E-3	5 500 ^a	1.3E-4	55 000 ^a	1.3E-5	55 000 ^a	1.3E-5
DEHP	1 ^b	17.5 ^b	0.04	360 ^b	1.9E-3	7 200 ^c	9.6E-5	1 663 ^b	4.2E-4
HHCb	0 ^c	3.22 ^c	0.22	11 880 ^s	5.8E-5	2.4E8 ^s	2.9E-9	2.4E7 ^s	2.9E-8
EDC	0 ^d	2 772 ^d	2.5E-4	2.4E8 ^s	2.9E-9	2.4E8 ^s	2.9E-9	2 160 ^e	3.2E-4
BENZ	4 ^b	240 ^b	2.9E-3	191 ^b	3.6E-3	7 200 ^s	9.6E-5	1 680 ^s	9.6E-4
LAS	4 ^g	24 ^g	2.9E-2	24 ^h	5.8E-2	480 ^h	1.4E-3	1 680 ^s	9.6E-4
EDTA	0 ⁱ			11 880 ^f	5.8E-5	2.4E8 ^s	2.9E-9	2.4E7 ^s	2.9E-8

Sources: ^a MACKAY ET AL. (1991-1997), ^b EC (1999), ^c PLASSCHE AND BALK (1997), ^d BUA (1995), ^e BUA (1985), ^f BUA (1996), ^g EC (1996c), ^h WHO (1996), ⁱ EUROPEAN AMINI-CARBOXYLATES PRODUCERS COMMITTEE (1990), ^s TGD standard value assumed for the given biodegradability.

BC = Biodegradation class; see Table 30.

Table 30 Biodegradation assigned to biodegradation class according to TGD.

BC	STP [h]	[1/h]	Water [h]	[1/h]	Sediment ^a [h]	[1/h]	Soil ^b [h]	[1/h]
4	0.69	1	360	1.9E-3	>7200	<9.6E-5	>720	<9.6E-4
3	2.3	0.3	1 200	5.8E-4	>21 60	<3.2E-5	>2 160	<3.2E-4
2	6.9	0.1	3 600	1.9E-4	>72 000	<9.6E-6	>7 200	<9.6E-5
1	∞	0	3 600	1.9E-4	>72 000	<9.6E-6	>7 200	<9.6E-5
0	∞	0	∞	0	∞	0	∞	0

BC: Biodegradation class 0 - not biodegradable; 1 - inherently biodegradable, not fulfilling specific criteria; 2 - inherently biodegradable, fulfilling specific criteria; 3 - readily biodegradable, but failing 10-d window; 4 - readily biodegradable (see TGD pp. 280)

^a biodegradation in sediment is assumed to be 10 times slower than in soil

^b depending on K_{ps}oil

Table 31 Production and use data for the default estimation.

Substance	EU production / import [t/a]	IC/UC [#]
PCDD	-	-
DEHP	1E6 / 0 ^a	3/47 ^b
HHCb	0 / 2 400 ^c	5/9 ^c
EDC	8.5E6 / 0 ^d	3/33 ^e
BENZ	6.1E6 / 0 ^d	9/28 ^d
LAS	5E5 / 0 ^f	5/9
EDTA	2.65E4 / 0 ^g	5/9 (8%), 2/2 (26%), 10/42 (29%), 13/11 (4%), 15/55 (17.2%), 12/11 (3%), 8/17 (7%), 1/19 (3%), 5/15 (3%) ^g

[#] The meaning of the category-numbers is explained in EC (1996b).

^a LWA (1993), ^b DECHEMA (1995), ^c PLASSCHE AND BALK (1997), ^d EC (1999), ^e BUA (1995), ^f EC (1996c), ^g BUA (1996)

A.3 Substance parameters and probability distributions

In this section the data tables for the selected substances are listed. For each substance one table is given (Table 32 to Table 42). The column *Realistic* contains the values of the point estimation used for the scenario *NRW realistic* (see Chapter 7) and the distribution functions applied for the uncertainty analyses (Chapter 9). If available, column *CV* contains the variation coefficient ($CV = SD / M$). The remaining substance data as well as the values used for the *Default*-scenario can be found in Table 28 and Table 29.

The selection of the distribution function was undertaken in accordance to the described method. I.e., half-lives and emissions always receive, as described above, a triangular distribution. The value of the realistic point estimation is the mode of the triangular distribution. For a shorter representation the abbreviation $T^*(value)$ is used (i.e. $min=value/2$, $mode=value$, $max=value \cdot 5$). The emissions are calculated by default using the tonnages for production and import as well as the use and industry category (UC, IC). In Table 31, the data used are listed. If a different value is used for the realistic estimation, the relative source is given. For PCDD only regional emission data exist. The continental data were estimated from these values in such a way that the sum of continental and regional emissions are 10 times higher than the regional emissions. This corresponds to the standard relationship of these two emissions in EUSES.

Table 32 TCDD.

Parameter	Description	Unit	Realistic	CV	Reference
K_{ow}	Octanol-water partition coefficient	-	6.31E6 L(3.08E7, 1.26E8)	4.09	SHIU ET AL. (1988) for realistic value, MACKAY ET AL. (1991-1997) for distribution
Sol	Water solubility	mg/l	1.9E-5 L(1.65E-4, 1.25E-4)	0.76	see K_{ow}
VP	Vapour pressure	Pa	2E-7 L(1.24E-5, 3.07E-5)	2.47	see K_{ow}
kdegair	Total degradation rate air	d	$T^*(7.08)$		MACKAY ET AL. (1991-1997)
kdegwater	Total degradation rate water	d	$T^*(22.92)$		see kdegair
kdegscd	Total degradation rate bulk sediment	d	$T^*(2292)$		see kdegair
kdegsoil	Total degradation rate bulk soil	d	$T^*(708.3)$		see kdegair
ERegAir	Total emission to regional air	kg/d	$T^*(7.4E-5)$		NRW (1996)
ERegFirstWater	Total direct emission to regional surface water	kg/d	0		HORSTMANN AND MCLACHLAN (1994), JONES AND STEWARD (1997)
ERegFirstWastewater	Total emission to regional waste water (before division into treated/untreated water)	kg/d	$T^*(2.04E-7)$		see EReg-FirstWater
ERegInd	Total emission to regional industrial soil	kg/d	0		
EContAir	Total emission to continental air	kg/d	$T^*(6.81E-4)$		calculated from regional emission
EContFirstWater	Total direct emission to continental surface water	kg/d	$T^*(4.35E-11)$		calculated from regional emission
EContFirstWastewater	Total emission to continental waste water (before division into treated/untreated water)	kg/d	$T^*(1.84E-6)$		calculated from regional emission
EContInd	Total emission to continental industrial soil	kg/d	0		calculated from regional emission

Table 33 PeCDD.

Parameter	Description	Unit	Realistic [#]	CV	Reference
K _{OW}	Octanol-water partition coefficient	-	2.5E7 L(2.89E9, 3.37E9)	1.19	SHIU ET AL. (1988) for realistic value, MACKAY ET AL. (1991-1997) for distribution
Sol	Water solubility	mg/l	1.2E-4 L(1.18E-3, 2.62E-3)	2.22	see K _{OW}
VP	Vapour pressure	Pa	8.8E-8 L(6.96E-7, 5.26E-7)	0.76	see K _{OW}
kdegair	Total degradation rate air	d	T*(22.92)		MACKAY ET AL. (1991-1997)
kdegwater	Total degradation rate water	d	T*(22.92)		see kdegair
kdegسد	Total degradation rate bulk sediment	d	T*(2292)		see kdegair
kdegsoil	Total degradation rate bulk soil	d	T*(708.3)		see kdegair
ERegAir	Total emission to regional air	kg/d	T*(2.65E-4)		NRW (1996)
ERegFirstWater	Total direct emission to regional surface water	kg/d	T*(3.17E-11)		HORSTMANN AND MCLACHLAN (1994), JONES AND STEWARD (1997)
ERegFirstWastewater	Total emission to regional waste water (before division into treated/untreated water)	kg/d	T*(3.44E-7)		see ERegFirstWater
ERegInd	Total emission to regional industrial soil	kg/d	0		
EContAir	Total emission to continental air	kg/d	T*(2.38E-3)		calculated from regional emission
EContFirstWater	Total direct emission to continental surface water	kg/d	T*(1.74E-10)		calculated from regional emission
EContFirstWastewater	Total emission to continental waste water (before division into treated/untreated water)	kg/d	T*(3.10E-6)		calculated from regional emission
EContInd	Total emission to continental industrial soil	kg/d	0		calculated from regional emission

[#] Probabilistic distributions taken from 1,2,3,4,7-PeCDD.

Table 34 HxCDD.

Parameter	Description	Unit	Realistic	CV	Reference
K _{OW}	Octanol-water partition coefficient	-	6.31E7 L(1.40E10, 2.10E10)	1.50	SHIU ET AL. (1988) for realistic value, MACKAY ET AL. (1991-1997) for distribution
Sol	Water solubility	mg/l	4.4E-6 L(8.09E-6, 7.69E-6)	0.95	see K _{OW}
VP	Vapour pressure	Pa	5.10E-9 L(1.71E-5, 4.37E-5)	2.55	see K _{OW}
kdegair	Total degradation rate air	d	T*(22.92)		MACKAY ET AL. (1991-1997)
kdegwater	Total degradation rate water	d	T*(70.83)		see kdegair
kdegسد	Total degradation rate bulk sediment	d	T*(2292)		see kdegair
kdegsoil	Total degradation rate bulk soil	d	T*(2292)		see kdegair
ERegAir	Total emission to regional air	kg/d	T*(1.18E-4)		NRW (1996)
ERegFirstWater	Total direct emission to regional surface water	kg/d	0		HORSTMANN AND MCLACHLAN (1994), JONES AND STEWARD (1997)
ERegFirstWastewater	Total emission to regional waste water (before division into treated/untreated water)	kg/d	T*(4.57E-6)		see ERegFirstWater
ERegInd	Total emission to regional industrial soil	kg/d	0		
EContAir	Total emission to continental air	kg/d	T*(1.06E-3)		calculated from regional emission
EContFirstWater	Total direct emission to continental surface water	kg/d	T*(3.04E-9)		calculated from regional emission
EContFirstWastewater	Total emission to continental waste water (before division into treated/untreated water)	kg/d	T*(4.12E-5)		calculated from regional emission
EContInd	Total emission to continental industrial soil	kg/d	0		calculated from regional emission

Table 35 HpCDD.

Parameter	Description	Unit	Realistic	CV	Reference
K _{OW}	Octanol-water partition coefficient	-	1E8 L(1.177E11, 2.12E11)	1.81	SHIU ET AL. (1988) for realistic value, MACKAY ET AL. (1991-1997) for distribution
Sol	Water solubility	mg/l	2.40E-6 L(1.12E-4, 2.60E-4)	2.31	see K _{OW}
VP	Vapour pressure	Pa	7.5E-10 L(1.71E-6, 3.29E-6)	1.92	see K _{OW}
kdegair	Total degradation rate air	d	T*(22.92)		MACKAY ET AL. (1991-1997)
kdegwater	Total degradation rate water	d	T*(70.83)		see kdegair
kdegscd	Total degradation rate bulk sedi- ment	d	T*(2292)		see kdegair
kdegsoil	Total degradation rate bulk soil	d	T*(2292)		see kdegair
ERegAir	Total emission to regional air	kg/d	T*(2.04E-3)		NRW (1996)
ERegFirstWater	Total direct emission to regional surface water	kg/d	0		HORSTMANN AND MCLACHLAN (1994), JONES AND STEWART (1997)
ERegFirstWastewater	Total emission to regional waste water (before division into treated/untreated water)	kg/d	T*(1.04E-4)		see ERegFirstWater
ERegInd	Total emission to regional indus- trial soil	kg/d	0		
EContAir	Total emission to continental air	kg/d	T*(1.83E-2)		calculated from regional emission
EContFirstWater	Total direct emission to conti- nental surface water	kg/d	T*(3.04E-8)		calculated from regional emission
EContFirstWastewater	Total emission to continental waste water (before division into treated/untreated water)	kg/d	T*(9.36E-4)		calculated from regional emission
EContInd	Total emission to continental industrial soil	kg/d	0		calculated from regional emission

Table 36 OCDD.

Parameter	Description	Unit	Realistic	CV	Reference
K _{OW}	Octanol-water partition coefficient	-	1.59E8 L(8.08E11, 2.24E12)	2.77	SHIU ET AL. (1988) for realistic value, MACKAY ET AL. (1991-1997) for distribution
Sol	Water solubility	mg/l	7.4E-8 L(1.56E-5, 4.67E-5)	2.98	see K _{OW}
VP	Vapour pressure	Pa	1.1E-10 L(6.20E-6, 9.19E-6)	1.48	see K _{OW}
kdegair	Total degradation rate air	d	T*(22.92)		MACKAY ET AL. (1991-1997)
kdegwater	Total degradation rate water	d	T*(229.2)		see kdegair
kdegscd	Total degradation rate bulk sedi- ment	d	T*(2292)		see kdegair
kdegsoil	Total degradation rate bulk soil	d	T*(2292)		see kdegair
ERegAir	Total emission to regional air	kg/d	T*(2.96E-3)		NRW (1996)
ERegFirstWater	Total direct emission to regional surface water	kg/d	0		HORSTMANN AND MCLACHLAN (1994), JONES AND STEWART (1997)
ERegFirstWastewater	Total emission to regional waste water (before division into treated/untreated water)	kg/d	T*(7.86E-4)		see ERegFirstWater
ERegInd	Total emission to regional indus- trial soil	kg/d	0		
EContAir	Total emission to continental air	kg/d	T*(2.67E-2)		calculated from regional emission
EContFirstWater	Total direct emission to conti- nental surface water	kg/d	0		calculated from regional emission
EContFirstWastewater	Total emission to continental waste water (before division into treated/untreated water)	kg/d	T*(7.08E-3)		calculated from regional emission
EContInd	Total emission to continental industrial soil	kg/d	0		calculated from regional emission

Table 37 DEHP.

Parameter	Description	Unit	Realistic	CV	Reference
K _{ow}	Octanol-water partition coefficient	-	3.02E7 L(3.51E8, 1.11E9)	3.15	RIPPEN (1996) for realistic value, MACKAY ET AL. (1991-1997) for distribution
Sol	Water solubility	mg/l	0.029 L(8.61, 25.95)	3.00	see K _{ow}
VP	Vapour pressure	Pa	1.9E-3 L(2.55E-4, 6.49E-4)	2.55	see K _{ow}
kdegair	Total degradation rate air	d	T*(7.29E-1)		calculated with SRC-AOP (1998) from molecular structure
kdegwater	Total degradation rate water	d	T*(15.2)		EU (1997)
kdegسد	Total degradation rate bulk sediment	d	T*(300)		see kdegwater
kdegsoil	Total degradation rate bulk soil	d	T*(68)		see kdegwater
ERegAir	Total emission to regional air	kg/d	T*(3300)		UBA (1996)
ERegFirstWater	Total direct emission to regional surface water	kg/d	0		see ERegAir
ERegFirstWastewater	Total emission to regional waste water (before division into treated/untreated water)	kg/d	T*(1576)		see kdegwater
ERegInd	Total emission to regional industrial soil	kg/d	0		see kdegwater
EContAir	Total emission to continental air	kg/d	T*(3000)		default value
EContFirstWater	Total direct emission to continental surface water	kg/d	T*(8.70E-1)		default value
EContFirstWastewater	Total emission to continental waste water (before division into treated/untreated water)	kg/d	T*(1.42E-4)		default value
EContInd	Total emission to continental industrial soil	kg/d	0		default value

Table 38 HHCb.

Parameter	Description	Unit	Realistic	CV	Reference
K _{ow}	Octanol-water partition coefficient	-	7.94E6 U(7.94E6, 1.8E6)		PLASSCHE AND BALK (1997)
Sol	Water solubility	mg/l	1.75 U(1.5, 2.0)		see K _{ow}
VP	Vapour pressure	Pa	0.0727		see K _{ow}
kdegair	Total degradation rate air	d	T*(1.34E-1)		see K _{ow}
kdegwater	Total degradation rate water	d	T*(5E5)		see K _{ow}
kdegسد	Total degradation rate bulk sediment	d	T*(1E7)		default value
kdegsoil	Total degradation rate bulk soil	d	T*(1E6)		default value
ERegAir	Total emission to regional air	kg/d	0		see K _{ow}
ERegFirstWater	Total direct emission to regional surface water	kg/d	T*(4.78E-2)		see K _{ow}
ERegFirstWastewater	Total emission to regional waste water (before division into treated/untreated water)	kg/d	T*(3.21E2)		see K _{ow}
ERegInd	Total emission to regional industrial soil	kg/d	0		see K _{ow}
EContAir	Total emission to continental air	kg/d	0		see K _{ow}
EContFirstWater	Total direct emission to continental surface water	kg/d	0		see K _{ow}
EContFirstWastewater	Total emission to continental waste water (before division into treated/untreated water)	kg/d	T*(6.25E3)		see K _{ow}
EContInd	Total emission to continental industrial soil	kg/d	0		see K _{ow}

Table 39 EDC.

Parameter	Description	Unit	Realistic	CV	Reference
K _{ow}	Octanol-water partition coefficient	-	28.84 L(30.2, 8.73)	0.27	BUA (1995) for realistic value, MACKAY ET AL. (1991-1997) for distribution
Sol	Water solubility	mg/l	8.61E3	0.03	see K _{ow}

Parameter	Description	Unit	Realistic	CV	Reference
VP	Vapour pressure	Pa	L(8.61E3, 2.26E2) 1.13E4 L(1.04E4, 9.33E2)	0.09	see K_{OW}
kdegair	Total degradation rate air	d	T*(115)		BUA (1995)
kdegwater	Total degradation rate water	d	T*(9.92E4)		see kdegair
kdegscd	Total degradation rate bulk sediment	d	T*(1E7)		default value
kdegsoil	Total degradation rate bulk soil	d	T*(90)		see kdegair
ERegAir	Total emission to regional air	kg/d	T*(1.28E5)		default value
ERegFirstWater	Total direct emission to regional surface water	kg/d	T*(73.9)		default value
ERegFirstWastewater	Total emission to regional waste water (before division into treated/untreated water)	kg/d	T*(2.98E4)		default value
ERegInd	Total emission to regional industrial soil	kg/d	T*(69.2)		default value
EContAir	Total emission to continental air	kg/d	T*(1.15E6)		default value
EContFirstWater	Total direct emission to continental surface water	kg/d	T*(21.7)		default value
EContFirstWastewater	Total emission to continental waste water (before division into treated/untreated water)	kg/d	T*(2.69E5)		default value
EContInd	Total emission to continental industrial soil	kg/d	T*(6.23E3)		default value

Table 40 BENZ (Benzene).

Parameter	Description	Unit	Realistic	CV	Reference
K_{OW}	Octanol-water partition coefficient	-	131.83 L(151.84, 60.71)	0.4	RIPPEN (1996) for realistic value, MACKAY ET AL. (1991-1997) for distribution
Sol	Water solubility	mg/l	1760 L(1767.73, 511.62)		see K_{OW}
VP	Vapour pressure	Pa	1.27E4 L(1.26E4, 824.9)	0.066	RIPPEN (1995)
kdegair	Total degradation rate air	d	T*(10)		see VP
kdegwater	Total degradation rate water	d	T*(7.95)		see VP
kdegscd	Total degradation rate bulk sediment	d	T*(300)		default value
kdegsoil	Total degradation rate bulk soil	d	T*(30)		default value
ERegAir	Total emission to regional air	kg/d	T*(3.43E4)		UBA (1996A)
ERegFirstWater	Total direct emission to regional surface water	kg/d	T*(792)		estimated
ERegFirstWastewater	Total emission to regional waste water (before division into treated/untreated water)	kg/d	T*(3722)		estimated
ERegInd	Total emission to regional industrial soil	kg/d	T*(2120)		estimated
EContAir	Total emission to continental air	kg/d	T*(1.37E6)		default value
EContFirstWater	Total direct emission to continental surface water	kg/d	T*(1.46E3)		default value
EContFirstWastewater	Total emission to continental waste water (before division into treated/untreated water)	kg/d	T*(1.05E5)		default value
EContInd	Total emission to continental industrial soil	kg/d	T*(1.91E4)		default value

Table 41 LAS.

Parameter	Description	Unit	Realistic	CV	Reference
K_{OW}	Octanol-water partition coefficient	-	T*(91.2)		LWA (1994); value for C12-LAS
Sol	Water solubility	mg/l	T*(1.1E3)		RIPPEN (1995)
VP	Vapour pressure	Pa	T*(1E-6)		minimal value allowed in EUSES
kdegair	Total degradation rate air	d	T*(1.1)		EU (1996)
kdegwater	Total degradation rate water	d	T*(0.5)		GROB (1996)
kdegscd	Total degradation rate bulk sediment	d	T*(1)		WOLTERING ET AL. (1988)
kdegsoil	Total degradation rate bulk soil	d	T*(14)		JENSEN (1999)
ERegAir	Total emission to regional air	kg/d	0 ^a		estimated
ERegFirstWater	Total direct emission to regional surface water	kg/d	3.91 T*(3.91) ^a		estimated

Parameter	Description	Unit	Realistic	CV	Reference
ERegFirstWastewater	Total emission to regional waste water (before division into treated/untreated water)	kg/d	6.78E4 T*(6.78E4) ^a		estimated
ERegInd	Total emission to regional industrial soil	kg/d	6.95E2 T*(6.95E2) ^a		estimated
EContAir	Total emission to continental air	kg/d	0		estimated
EContFirstWater	Total direct emission to continental surface water	kg/d	0		estimated
EContFirstWastewater	Total emission to continental waste water (before division into treated/untreated water)	kg/d	T*(1.29E6)		default value
EContInd	Total emission to continental industrial soil	kg/d	T*(1.32E4)		default value

^a Regional emissions are estimated too high; based on the per-capita use of 3.8 g/d (BUA 1986), the factor 0.05 instead of 0.1 of the EU-production volume is used for the region; thus all emissions are halved; besides, it is assumed that no emissions to air take place.

Table 42 EDTA (acid).

Parameter	Description	Unit	Realistic	CV	Reference
K _{ow}	Octanol-water partition coefficient	-	log: -3.34 log: U(-5.01, -3.34)		BUA (1996)
Sol	Water solubility	mg/l	T*(500)		EU (1996D)
VP	Vapour pressure	Pa	T*(1E-6)		minimal value allowed in EUSES
kdegair	Total degradation rate air	d	0		default value
kdegwater	Total degradation rate water	d	T*(4.81E2)		default value
kdegسد	Total degradation rate bulk sediment	d	T*(1E7)		default value
kdegsoil	Total degradation rate bulk soil	d	T*(1E6)		default value
ERegAir	Total emission to regional air	kg/d	0		estimated
ERegFirstWater	Total direct emission to regional surface water	kg/d	T*(10.4)		default value
ERegFirstWastewater	Total emission to regional waste water (before division into treated/untreated water)	kg/d	T*(4.78E3)		default value
ERegInd	Total emission to regional industrial soil	kg/d	T*(49.2)		default value
EContAir	Total emission to continental air	kg/d	0		estimated
EContFirstWater	Total direct emission to continental surface water	kg/d	T*(1.04E2)		default value
EContFirstWastewater	Total emission to continental waste water (before division into treated/untreated water)	kg/d	T*(4.45E4)		default value
EContInd	Total emission to continental industrial soil	kg/d	T*(4.5E2)		default value

A.4 Substance concentrations

In this section we present a selection of collected concentrations that were used as comparative values for the scenario analyses. The presentation comprises the measured values used and some comparative values. In column *M* the mean is listed if not otherwise stated.

Table 43 Concentrations in surface waters [mg/l].

Substance	Min	Max	M	Comment	Reference
TCDD			2.2E-11	Representative total concentrations in rivers/GB	DUARTE-DAVIDSON ET AL. (1997b)
PeCDD			3.0E-11	see TCDD	see TCDD
HxCDD I			2.7E-11	see TCDD	see TCDD
HxCDD II			6.0E-11	see TCDD	see TCDD
HxCDD III			3.8E-11	see TCDD	see TCDD
HpCDD			2.3E-10	see TCDD	see TCDD
OCDD			1.4E-09	see TCDD	see TCDD
DEHP	5.4E-07	4.9E-04	1.1E-05	River Rhine between Honnef and Bimmen 1991-92, M=Median, estimated from total concentration	NRW (1993)
	1.1E-04	1.0E-02	5.2E-04	Total concentrations of the values above	NRW (1993)
	1.0E-07	3.0E-01		Concentration ranges in surface waters	NRW (1993)
HHCB	1.0E-04	1.2E-03	5.0E-04	30 measured values river Ruhr, 1994/95	ESCHKE ET AL. (1994, 1995)
EDTA	1.0E-03	5.4E-02		River Rhine and tributaries 1980-81, Rhine and Main are highly polluted, Min is detection limit	BUA (1996)
	1.3E-03	4.4E-03		Bodensee 1989-90	BUA (1996)
		4.2E00		Maximal value, Thames/GB	WOLF ET AL. (1992)
LAS	1.0E-03	6.0E-01	1.0E-02	River Rhine	RIPPEN (1995)
	1.0E-03	2.7E00		Concentrations in surface waters	Rippen (1995)
EDC	1.0E-05	1.0E-03		River Rhine at Lobith 1987-1992; Min is detection limit	BUA (1995)
		3.6E-01		Maximal value, river Rhine 1994	BUA (1995)
BENZ	1.0E-05	8.0E-04		River Rhine, values mainly under detection limit	RIPPEN (1995)
		2.0E-01		Maximal value for rivers	BUA (1988)

Table 44 Concentrations in air [mg/m³].

Substance	Min	Max	M	Comment	Reference
TCDD	6.0E-13	3.6E-12	1.4E-12	"Chloraromaten"-measurement campaign 1990, measurement during the whole year; M=median	NRW (1991a)
PeCDD	1.8E-12	4.0E-11	3.4E-12	see TCDD	see TCDD
HxCDD I	2.7E-12	3.3E-11	4.4E-12	see TCDD	see TCDD
HxCDD II	6.3E-12	6.7E-11	1.1E-11	see TCDD	see TCDD
HxCDD III	6.5E-12	5.9E-11	1.1E-11	see TCDD	see TCDD
HpCDD	8.0E-11	8.1E-10	1.7E-10	see TCDD	see TCDD
OCDD	3.1E-10	2.8E-09	6.7E-10	see TCDD	see TCDD
TCDD	1.0E-11	5.7E-10		Big cities in GB, minimum is detection limit	DUARTE-DAVIDSON ET AL. (1997A)
PeCDD	1.0E-11	4.0E-10		see TCDD	see TCDD
HxCDD I	1.0E-11	6.7E-10		see TCDD	see TCDD
HxCDD II	1.0E-11	6.7E-10		see TCDD	see TCDD
HxCDD III	1.0E-11	6.7E-10		see TCDD	see TCDD
HpCDD	1.0E-11	1.1E-08		see TCDD	see TCDD
OCDD	1.0E-11	6.2E-08		see TCDD	see TCDD
DEHP	3.0E-07	1.9E-06	1.1E-06	Clean air 1985	RIPPEN (1995)
	3.0E-05	1.3E-04		Antwerpen/B 1985	RIPPEN (1995)
	1.5E-01	2.6E-01		Highly polluted interiors	EU (1996c)
		6.6E01		Industrial conurbations, maximal values	EU (1996c)
HHCB	1.1E-07	2.2E-07	1.2E-07	Norway, 5 measurements	KALLENBORN ET AL. (1999)
EDC	2.0E-04	1.2E-01		Hamburg	Rippen (1995)
	2.1E-02	3.7E-02		Typical concentrations in industrial areas	BUA (1995)
	4.0E-05	1.8E-04		Tural areas, Germany	BUA (1995)
		1.6E00		Maximal value, city, high traffic	BUA (1995)
			2.5E-04	M=median for 455 cities	RIPPEN (1995)
			1.0E-04	Global background concentration	BUA (1995)
BENZ	2.0E-04	8.4E-02	2.0E-04	Tural areas in Germany, Min is detection limit	BUA (1988)
	5.0E-03	1.0E-02		Conurbations	BUA (1993)
	5.0E-04	1.6E00		Industrial areas and fuel stations	BUA (1988)

Table 45 Concentrations in sediment [mg/kg WWT]

Substance	Min	Max	M	Comment	Reference
TCDD	2.4E-05	2.7E-05		DWT; river Rhine 1987	UBA (1995)
PeCDD	8.0E-06	1.1E-05	1.0E-06	see TCDD	see TCDD
HxCDD I	1.0E-05	1.1E-05		see TCDD	see TCDD
HxCDD II	1.0E-05	2.6E-05	0.0E00	see TCDD	see TCDD
HxCDD III	1.0E-05	1.7E-05		see TCDD	see TCDD
HpCDD	6.8E-05	1.6E-04	4.0E-06	see TCDD	see TCDD
OCDD	5.0E-04	1.3E-03		see TCDD	see TCDD
TCDD	0.0E00	6.0E-06	3.0E-05	DWT; river Elbe, M=median of 8 values	UBA (1995)
PeCDD	0.0E00	1.0E-05		see TCDD	see TCDD
HxCDD I	2.0E-06	1.0E-05	2.0E-05	see TCDD	see TCDD
HxCDD II	2.0E-06	4.0E-05		see TCDD	see TCDD
HxCDD III	3.0E-06	5.0E-05	7.1E-04	see TCDD	see TCDD
HpCDD	3.0E-05	1.6E-03		see TCDD	see TCDD
OCDD	3.4E-04	8.5E-03	3.3E-03	see TCDD	see TCDD
DEHP	2.5E00	5.3E01		Bottom sediment NL (Ijssel) 1977	EC (1999)
	2.0E01	2.0E01		River Rhine NL, DWT	RIPPEN (1995)
	1.3E00	9.4E00		River Necker D, DWT	RIPPEN (1995)
	1.0E-03	1.5E03		Range of measured concentrations	LWA (1993)
EDTA	2.3E-03	1.3E-02		Japan 1979	EC (1999)
LAS			1.1E00	River Rhine, DWT	HENNES AND RAPAPORT (1989)
			5.4E-02	see above	see above
	3.0E-02	3.2E-01	5.0E-02	River Lippe	SCHÖBERL AND SPILKER (1996)
BENZ	1.5E-03	5.0E-03		USA and Japan	RIPPEN (1995)

Table 46 Concentrations in soil [mg/kg WWT] (conversion factor DWT/WWT: 1.13).

Substance	Min	Max	M	Comment	Reference
TCDD	3.5E-07	2.1E-06	5.8E-07	"Chloraromaten"-measurement campaign 1990, from DW, M=median	NRW (1991b)
PeCDD	2.7E-07	2.7E-06	4.9E-07	see TCDD	see TCDD
HxCDD I	1.8E-07	2.6E-06	1.1E-06	see TCDD	see TCDD
HxCDD II	5.3E-07	6.7E-06	1.8E-06	see TCDD	see TCDD
HxCDD III	3.5E-07	4.9E-06	1.2E-06	see TCDD	see TCDD
HpCDD	1.1E-05	1.2E-04	1.8E-05	see TCDD	see TCDD
OCDD	4.0E-05	1.5E-03	7.6E-05	see TCDD	see TCDD
DEHP	3.5E-02	2.7E-01	2.1E-01	Soils in Germany, from DWT, M=mean for soils of meadows	MÜLLER AND KÖRDEL (1995)
		4.5E00		After sudge application, from DWT	see above
EDTA	2.0E-02	1.0E-01		Possible after fertiliser application (estimated)	BUA (1996)
LAS		2.2E03		Maximal value after sludge application	RIPPEN (1995)
		1.4E00		Maximal value without sludge application	RIPPEN (1995)
BENZ	2.0E-03	2.0E-01		Contaminated soil, but mostly under detection limit of 1E-5 to 1E-4	HOWARD (1990)

A.5 Results of the sensitivity analyses

In this section we list the single calculated sensitivities for the concentrations in air, water (total), water (dissolved), sediment, agricultural soil, pore-water of agricultural soil, natural soil, industrial/urban soil. The sensitivity analyses were performed using a parameter set which is the combination of different point scenarios. This *NRW base Scenario* is based on the scenario *NRW realistic* (i.e. the regional parameter of North Rhine-Westphalia using as many measured values as possible). But parameters that can be estimated by EUSES were not replaced. Thus, this scenario does not correspond exactly to the scenario that is used later for the uncertainty analyses.

Table 47 Sensitivities of PECs in air.

Type	Parameter	TCDD	PeCDD	HxCDD	HpCDD	OCDD	DEHP	HHCB	EDC	BENZ	LAS	EDTA	
Degradation parameters	kdegair	-0.2					-0.5	-0.8		-0.3			
	kdegsoil							-0.1			-0.8		
<i>Negligible influence: kdegsoil, kdegwater</i>													
Emissions	EContAir	0.3	0.2	0.2	0.2	0.2	0.1		0.4	0.7			
	EContfirstwastewater							0.1	0.1			0.1	
	ERegAir	0.7	0.8	0.8	0.8	0.8	0.9		0.5	0.3			
	ERegfirstwastewater							0.9	0.1		0.1	0.4	
	ERegInd										0.9	0.5	
<i>Negligible influence: EContfirstwater, EContInd, ERegfirstwater</i>													
PC data	K _{ow}							-0.1			-0.5		
	Molw							0.2			2.0	2.0	
	Sol							-0.2			-2.0	-2.0	
	TempMelt	0.5	0.3	0.2								-0.8	
	Vp	0.1	0.1					0.2			1.0	1.9	
<i>Negligible influence: kein Parameter</i>													
Process parameters	CollEffAer	-0.1	-0.3	-0.3	-0.3	-0.3							
	DepRateAer		-0.1	-0.1	-0.1	-0.1							
	FFlowOut Reg							-0.1				-0.2	
	FrunoffSoil							-0.1			-0.1	-0.6	
	kasl air									1.0		0.5	
	kasl soilair							0.2					
	kawAir							0.1				0.5	
	Rainrate	0.7	0.5	0.5	0.5	0.5	0.8				-0.2		-1.0
	windspeed	-0.8	-0.7	-0.6	-0.6	-0.6	-0.5	-0.2		-1.0	-0.7		
	<i>Negligible influence: Erosion, kasl soilwater, kwsSed, kwsWater, SETTLEvelocity</i>												
Volumetric parameters	area Reg	-0.4	-0.5	-0.5	-0.5	-0.5	-0.6	-0.8	-0.3	-0.2	-1.0	-0.7	
	areaEU	-0.3	-0.2	-0.2	-0.2	-0.2	-0.1	-0.1	-0.3	-0.5		-0.3	
	depthAgric							-0.1					
	depthInd										-0.7		
	fAgric Cont											-0.1	
	fAgric Reg		-0.1	-0.1	-0.1	-0.1					-0.5	-0.6	
	fInd Reg										-0.2	-0.2	
	fNatural Cont		-0.1	-0.1	-0.1	-0.1						-0.2	
	fNatural Reg			-0.1	-0.1	-0.1					-0.3	-0.3	
	fWater Reg							0.1				0.4	
	heightAir	-0.9	-0.7	-0.7	-0.7	-0.6	-1.0	-1.0	-1.0	-1.0			
<i>Negligible influence: depthNat, depthSed, depthWater Cont, depthWater Reg, fInd Cont, fWater Cont</i>													
Other model parameters	ConJunge	-0.1	-0.1								1.0	0.1	
	FconnectSTP						-0.1				0.1		
	FInfSoil							-0.1			-0.1	-0.3	
	FocSoil							-0.1			-0.7		
	FSolidSoil							-0.1			-0.7		
	FWaterSed							0.1					
	FWaterSoil										-0.1		
	RhoSolid							-0.1			-0.7		
	SurfAer	-0.1	-0.1								1.0	0.1	
	<i>Negligible influence: BIOwater, FAirSoil, FocSed, FocSusp, FSolidSed, NReg, NEU, OHConcair, RHOAir, RhoWater, SuspEff, SuspWaterReg, SuspWaterCont, Temperatur</i>												
STP parameters	<i>Negligible influence: alle Parameter</i>												

Table 48 Sensitivities of PECs in water (total).

Type	Parameter	TCCD	PeCDD	HxCDD	HpCDD	OCDD	DEHP	HHCB	EDC	BENZ	LAS	EDTA
Degradation parameters	kdegair	-0.2										
	kdegsew	-0.1	-0.2	-0.2	-0.2	-0.2	-0.2					
	kdegsoil		-0.1	-0.1	-0.1							
	kdegwater	-0.2	-0.2				-0.1			-0.2	-1.0	-0.1
<i>Negligible influence: kdegair, kdegsew</i>												
Emissions	EContAir	0.3	0.2	0.1	0.1							
	EContfirstwastewater											0.2
	ERegAir	0.5	0.7	0.4	0.3	0.1						
	ERegfirstwastewater	0.2		0.5	0.6	0.9	1.0	1.0	1.0	0.4	1.0	0.8
	ERegfirstwater									0.6		
<i>Negligible influence: EContfirstwater, EContInd, ERegInd</i>												
PC data	Kow	-0.2	-0.2	-0.1	-0.1	-0.1	-0.1	-0.1				
	Molw	-0.2					-0.1	-0.7	-0.3	-0.1		
	Sol	0.2					0.1	0.7	0.3	0.1		
	TempMelt	-1.0	-0.3	-0.1								
	Vp	-0.4	-0.1				-0.1	-0.7	-0.3	-0.1		
<i>Negligible influence: none</i>												
Process parameters	CollEffAer	0.2	0.5	0.2	0.2	0.1						
	DepRateAer		0.1	0.1								
	Erosion	-0.3	-0.4	-0.4	-0.4	-0.5	-0.1					
	FFlowOut Reg	-0.1	-0.1	-0.1	-0.1	-0.2	-0.1	-0.2	-0.1	-0.1		-0.5
	FrunoffSoil	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1					-0.8
	kasl soilair							-0.2				
	kawAir	0.3	0.1				-0.1	-0.5	-0.1			
	kawWater						-0.1	-0.2	-0.8	-0.7		
	Rainrate	0.7	0.5	0.4	0.4	0.2		-0.3			-0.1	-1.5
	SETTLEvelocity	-0.1	-0.1	-0.1	-0.1	-0.1	-0.3					
	windspeed	-0.6	-0.6	-0.3	-0.3	-0.1						
<i>Negligible influence: kasl air, kasl soilwater, kwsSed</i>												
Volumetric parameters	area Reg	-0.3	-0.3	-0.6	-0.6	-0.8	-0.9	-0.8	-0.9	-0.9	-1.0	-0.2
	areaEU	-0.4	-0.3	-0.3	-0.2	-0.2	-0.1	-0.2	-0.1	-0.1		-0.7
	depthSed	-0.1	-0.2	-0.2	-0.2	-0.2						
	depthWater Reg	-0.2	-0.1				-0.1			-0.2	-1.0	
	fAgric Cont		-0.1	-0.1	-0.1							-0.2
	fAgric Reg	-0.2	-0.3	-0.3	-0.3	-0.3	-0.1	-0.1				-0.1
	fInd Cont											-0.1
	fInd Reg	-0.1	-0.1	-0.1	-0.1	-0.1						
	fNatural Cont	-0.1	-0.2	-0.1	-0.1	-0.1			-0.1			-0.4
	fNatural Reg	-0.1	-0.1	-0.1	-0.1	-0.1						-0.1
	fWater Cont											-0.1
	fWater Reg	0.2	0.4			-0.2	-0.8	-0.7	-0.9	-0.9	-1.0	
	heightAir	-0.8	-0.6	-0.3	-0.3	-0.1						
<i>Negligible influence: depthAgric, depthInd, depthNat, depthWater Cont</i>												
Other model parameters	ConJunge	0.1	0.1									
	FconnectSTP	-0.8	-0.2	-2.7	-3.1	-4.7	-5.2	-1.8	-0.5	-2.2	-4.1	
	FocSoil							0.1				
	FocSusp	-0.2	-0.2	-0.2	-0.1	-0.1	-0.1					
	FSolidSed	0.3	0.4	0.5	0.5	0.5	0.1	0.1				
	FSolidSoil	-0.3	-0.4	-0.5	-0.5	-0.5	-0.1					
	FWaterSed	1.9	2.8	3.3	3.3	3.4	1.6	0.4				
	Qstp	0.1	0.2	0.2	0.3	0.3	0.4	0.3	0.2	0.2	0.5	-0.1
	RhoSolid	-0.4	-0.6	-0.7	-0.7	-0.7	-0.4					
	SurfAer	0.1	0.1									
	SuspEff	0.1		0.2	0.2	0.4	0.4	0.1				
	SuspWater Reg	0.2	0.5	0.7	0.7	0.8	0.3	0.1				
	SuspWaterCont	-0.1	-0.1	-0.1	-0.1	-0.1						
Temperatur	0.1											
<i>Negligible influence: BIOwater, FAirSoil, FInfSoil, FocSed, FWaterSoil, N Reg, NEU, OHconcair, RHOair, RhoWater</i>												
STP parameters	BOD						0.1	0.1	0.2			0.2
	C activated sludge											
	Density solids activated sludge								0.1			0.1
	Density solids PS								0.1	0.2	0.3	0.1
	Density solids raw sewage								-0.1	-0.1	-0.3	-0.1
	Density solids SLS								-0.1			-0.1
	Fraction oc activated sludge							0.1	0.1			0.1
	Fraction oc raw sewage								0.4	0.5	0.9	0.3
Input solids in raw sewage								0.4	0.5	0.9	0.3	
<i>Negligible influence: Aeration rate, C activated sludge, Depth aerator, Depth PS, Depth SLS, Factor Blackburn et al., Factor Hsieh et al. (1993b), Fraction oc solids PS, Fraction oc solids SLS, Height air column, HRTPS, HRTSLS, K airM, K pore waterM, K waterM, kGa/kLa, Oxygen concentration, Psi, Sludge loading rate, t1/2 aeration, t1/2 PS, t1/2 SLS, TempSTP</i>												

Table 49 Sensitivities of PECs in water (dissolved).

Type	Parameter	TcDD	PeCDD	HxCDD	HpCDD	OCDD	DEHP	HHCB	EDC	BENZ	LAS	EDTA
Degradation parameters	kdegair	-0.2										
	kdegsed	-0.1	-0.2	-0.2	-0.2	-0.2	-0.2					
	kdegsoil		-0.1	-0.1	-0.1							
	kdegwater	-0.2	-0.2				-0.1			-0.2	-1.0	-0.1
	<i>Negligible influence: none</i>											
Emissions	EContAir	0.3	0.2	0.1	0.1							
	EContfirstwastewater											0.2
	ERegAir	0.5	0.7	0.4	0.3	0.1						
	ERegfirstwastewater	0.2		0.5	0.6	0.9	1.0	1.0	1.0	0.4	1.0	0.8
	ERegfirstwater									0.6		
<i>Negligible influence: EContfirstwater, EContInd, ERegInd</i>												
PC data	Kow	-0.5	-0.7	-0.8	-0.8	-0.8	-0.7	-0.2				
	Molw	-0.2					-0.1	-0.7	-0.3	-0.1		
	Sol	0.2					0.1	0.7	0.3	0.1		
	TempMeit	-1.0	-0.3	-0.1								
	Vp	-0.4	-0.1					-0.1	-0.7	-0.3	-0.1	
<i>Negligible influence: none</i>												
Process parameters	CollEffAer	0.2	0.5	0.2	0.2	0.1						
	DepRateAer		0.1	0.1								
	Erosion	-0.3	-0.4	-0.4	-0.4	-0.5	-0.1					
	FFlowOut Reg	-0.1	-0.1	-0.1	-0.1	-0.2	-0.1	-0.2	-0.1	-0.1		-0.5
	FrunoffSoil	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1			-0.1	-0.1	-0.8
	kasl soilair								-0.2			
	kawAir	0.3	0.1				-0.1	-0.5	-0.1			
	kawWater						-0.1	-0.2	-0.8	-0.7		
	Rainrate		0.3	0.1	0.1	-0.1	-0.1		-0.1	-0.1		-0.9
	SETTLVelocity	-0.1	-0.1	-0.1	-0.1	-0.1	-0.3					
	windspeed	-0.6	-0.6	-0.3	-0.3	-0.1						
<i>Negligible influence: kasl air, kasl soilwater, kwsSed, kwsWater</i>												
Volumetric parameters	area Reg	-0.3	-0.3	-0.6	-0.6	-0.8	-0.9	-0.8	-0.9	-0.9	-1.0	-0.2
	areaEU	-0.4	-0.3	-0.3	-0.2	-0.2	-0.1	-0.2	-0.1	-0.1		-0.7
	depthSed	-0.1	-0.2	-0.2	-0.2	-0.2	-0.2					
	depthWater Reg	-0.2	-0.1				-0.1			-0.2	-1.0	
	fAgric Cont		-0.1	-0.1	-0.1							-0.2
	fAgric Reg	-0.2	-0.3	-0.3	-0.3	-0.3	-0.1	-0.1				-0.1
	fInd Cont											-0.1
	fInd Reg	-0.1	-0.1	-0.1	-0.1	-0.1						
	fNatural Cont	-0.1	-0.2	-0.1	-0.1	-0.1			-0.1			-0.4
	fNatural Reg	-0.1	-0.1	-0.1	-0.1	-0.1						-0.1
	fWater Cont											-0.1
	fWater Reg	0.2	0.4			-0.2	-0.8	-0.7	-0.9	-0.9	-1.0	
	heightAir	-0.8	-0.6	-0.3	-0.3	-0.1						
<i>Negligible influence: depthAgric, depthInd, depthNat, depthWater Cont</i>												
Other model parameters	ConJunge	0.1	0.1									
	FconnectSTP	-0.8	-0.2	-2.7	-3.1	-4.7	-5.2	-1.8	-0.5	-2.2	-4.1	
	FocSoil							0.1				
	FocSusp	-0.6	-0.9	-1.0	-1.0	-1.0	-0.8	-0.1				
	FSolidSed	0.3	0.4	0.5	0.5	0.5	0.1	0.1				
	FSolidSoil	-0.3	-0.4	-0.5	-0.5	-0.5	-0.1					
	FWaterSed	1.9	2.8	3.3	3.3	3.4	1.6	0.4				
	Qstp	0.1		0.2	0.2	0.3	0.4	0.3	0.2	0.2	0.5	-0.1
	RhoSolid	-0.4	-0.6	-0.7	-0.7	-0.7	-0.4					
	SurfAer	0.1	0.1									
	SuspEff	0.1		0.2	0.2	0.4	0.4	0.1				
	SuspWater Reg	0.2	0.5	0.7	0.7	0.8	0.3	0.1				
	SuspWaterCont	-0.1	-0.1	-0.1	-0.1	-0.1						
Temperatur	0.1											
<i>Negligible influence: BIOWater, FAirSoil, FlntSoil, FocSed, FWaterSoil, N Reg, NEU, OHconcair, RHOair, RhoWater</i>												
STP parameters	Aeration rate											-0.1
	BOD	-0.1		-0.2	-0.2	-0.4	-0.4	-0.2	-0.1	-0.1	-0.5	
	C activated sludge									0.1	0.5	
	Depth aerator									0.2		
	Depth SLS									0.1		
	Factor Hsieh et al. (1993b)									-0.1		
	Fraction oc activated sludge							-0.1				
	Height air column									-0.1		
	HRTSLS									-0.1		
	K waterM									-0.2		
Sludge loading rate									0.1	0.1	0.5	
<i>Negligible influence: Density solids activated sludge, Density solids PS, Density solids raw sewage, Density solids SLS, Depth PS, Factor Blackburn et al., Fraction oc raw sewage, Fraction oc solids PS, Fraction oc solids SLS, HRTPS, Input solids in raw sewage, K airM, K waterM, kGa/kLa, Oxygen concentration, Psi, t1/2 aeration, t1/2 PS, t1/2 SLS, TempSTP</i>												

Table 50 Sensitivities of PECs in sediment.

Type	Parameter	TCDD	PeCDD	HxCDD	HpCDD	OCDD	DEHP	HHCB	EDC	BENZ	LAS	EDTA
Degradation parameters	kdegair	-0.2										
	kdegsead	-0.3	-0.3	-0.3	-0.3	-0.3	-0.7			-0.1	-1.0	
	kdegsoil		-0.1	-0.1	-0.1							
	kdegwater	-0.2	-0.2				-0.1			-0.2	-1.0	-0.1
<i>Negligible influence: none</i>												
Emissions	EContAir	0.3	0.2	0.1	0.1							
	EContfirstwastewater											0.2
	ERegAir	0.5	0.7	0.4	0.3	0.1						
	ERegfirstwastewater	0.2		0.5	0.6	0.9	1.0	1.0	1.0	0.4	1.0	0.8
ERegfirstwater									0.6			
<i>Negligible influence: EContfirstwater, EContind, ERegInd</i>												
PC data	Kow	0.3	0.1				0.1	0.7	0.3	0.5	0.1	
	Molw	-0.2					-0.1	-0.7	-0.3	-0.1		
	Sol	0.2					0.1	0.7	0.3	0.1		
	TempMelt	-1.0	-0.3	-0.1								
	Vp	-0.4	-0.1				-0.1	-0.7	-0.3	-0.1		
<i>Negligible influence: none</i>												
Process parameters	ColIEffAer	0.2	0.5	0.2	0.2	0.1						
	DepRateAer		0.1	0.1								
	Erosion	-0.3	-0.4	-0.4	-0.4	-0.5	-0.1					
	FFlowOut Reg	-0.1	-0.1	-0.1	-0.1	-0.2	-0.1	-0.2	-0.1	-0.1		-0.5
	FrunoffSoil	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1					-0.8
	kasl soilair							-0.2				
	kawAir	0.3	0.1				-0.1	-0.5	-0.1			
	kawWater						-0.1	-0.2	-0.8	-0.7		
	kwsSed										0.9	
	Rainrate		0.3	0.1	0.1	-0.1	-0.1		-0.1	-0.1		-0.9
	SETTLEvelocity	0.1					0.2				0.1	
	windspeed	-0.6	-0.6	-0.3	-0.3	-0.1						
	<i>Negligible influence: kasl air, kasl soilwater, kwsWater</i>											
Volumetric parameters	area Reg	-0.3	-0.3	-0.6	-0.6	-0.8	-0.9	-0.8	-0.9	-0.9	-1.0	-0.2
	areaEU	-0.4	-0.3	-0.3	-0.2	-0.2	-0.1	-0.2	-0.1	-0.1		-0.7
	depthSed	-0.3	-0.3	-0.3	-0.3	-0.3	-0.7				-1.0	
	depthWater Reg	-0.2	-0.1				-0.1			-0.2	-1.0	
	fAgric Cont		-0.1	-0.1	-0.1							-0.2
	fAgric Reg	-0.2	-0.3	-0.3	-0.3	-0.3	-0.1	-0.1				-0.1
	fInd Cont											-0.1
	fInd Reg	-0.1	-0.1	-0.1	-0.1	-0.1						
	fNatural Cont	-0.1	-0.2	-0.1	-0.1	-0.1			-0.1			-0.4
	fNatural Reg	-0.1	-0.1	-0.1	-0.1	-0.1						-0.1
	fWater Cont											-0.1
fWater Reg	0.2	0.4			-0.2	-0.8	-0.7	-0.9	-0.9	-1.0		
heightAir	-0.8	-0.6	-0.3	-0.3	-0.1							
<i>Negligible influence: depthAgric, depthInd, depthNat, depthWater Cont</i>												
Other model parameters	FconnectSTP	-0.8	-0.2	-2.7	-3.1	-4.7	-5.2	-1.8	-0.5	-2.2	-4.1	
	FocSed								0.4	0.6		
	FocSoil							0.1				
	FocSusp	0.4	0.1				0.2	0.9		0.1	0.1	
	FSolidSed	-0.1	0.1	0.1	0.1	0.1	-0.3	-0.3		0.2	-0.4	-0.4
	FSolidSoil	-0.3	-0.4	-0.5	-0.5	-0.5	-0.1					
	FWaterSed	-2.5	-1.7	-1.3	-1.3	-1.2	-1.3	-4.2	-0.2	-0.6	-0.6	0.2
	Qstp	0.1	0.2	0.2	0.2	0.3	0.4	0.3	0.2	0.2	0.5	-0.1
	RhoSolid	0.1	-0.1	-0.2	-0.2	-0.2	-0.2	0.6		0.3	-0.4	-0.4
	RhoWater	-0.6	-0.6	-0.6	-0.6	-0.6	-0.6	-0.6	-0.6	-0.6	-0.6	-0.6
	SurfAer	0.1	0.1									
	SuspEff	0.1		0.2	0.2	0.4	0.4	0.1				
	SuspWater Reg		-0.1								0.1	
SuspWaterCont	-0.1	-0.1	-0.1	-0.1	-0.1							
Temperatur	0.1											
<i>Negligible influence: BIOwater, ConJunge, FAirSoil, FInfSoil, FWaterSoil, N Reg, NEU, OHconcair, RHOair</i>												
STP parameters	Aeration rate									-0.1		
	BOD	-0.1		-0.2	-0.2	-0.4	-0.4	-0.2	-0.1	-0.1	-0.5	
	C activated sludge								0.1	0.1	0.5	
	Depth aerator								0.2			
	Depth SLS								0.1			
	Factor Hsieh et al. (1993b)								-0.1			
	Fraction oc activated sludge								-0.1			
	Height air column									-0.1		
	HRTSLS									-0.1		
	K waterM									-0.2		
Sludge loading rate								0.1	0.1	0.5		
<i>Negligible influence: Density solids activated sludge, Density solids PS, Density solids raw sewage, Density solids SLS, Depth PS, Factor Blackburn et al., Fraction oc raw sewage, Fraction oc solids PS, Fraction oc solids SLS, HRTPS, Input solids in raw sewage, K airM, K pore waterM, kGa/kLa, Oxygen concentration, Psi, t1/2 aeration, t1/2 PS, t1/2 SLS, TempSTP</i>												

Table 51 Sensitivities of PECs in agricultural soil.

Type	Parameter	TCDD	PeCDD	HxCDD	HpCDD	OCDD	DEHP	HHCB	EDC	BENZ	LAS	EDTA	
Degradation parameters	kdegair	-0.1								-0.1			
	kdegsoil	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-0.1		-0.1	-1.0		
<i>Negligible influence: kdegsoil, kdegwater</i>													
Emissions	EContAir	0.3	0.2	0.1	0.1	0.1			0.2	0.3			
	ERegAir	0.6	0.8	0.7	0.6	0.3			0.2	0.1			
	ERegfirstwastewater	0.1		0.2	0.2	0.6	1.0	1.0	0.6	0.5	1.0	0.7	
	ERegInd											0.3	
<i>Negligible influence: EContfirstwastewater, EContfirstwater, EContInd, ERegfirstwater</i>													
PC data	Kow								0.8	1.0	1.1	0.8	
	Molw								-0.6	-1.0	-0.9	0.4	
	Sol								0.6	1.0	0.9	0.5	
	TempMelt	-5.3	-0.7	-0.3									
Vp	-0.7	-0.1							-0.6	-1.0	-0.9	0.5	
<i>Negligible influence: none</i>													
Process parameters	CollEffAer	0.7	0.5	0.4	0.4	0.2							
	DepRateAer	0.2	0.1	0.1	0.1								
	Erosion								-0.1				
	FFlowOut Reg											-0.1	
	FrunoffSoil											-0.8	
	kasl air											0.3	
	kasl soilair								-0.6	-0.5	-0.4		
	kawAir												0.2
	Rainrate	0.7	0.5	0.4	0.4	0.2			-0.3			-0.1	-1.5
	windspeed	-0.7	-0.6	-0.5	-0.5	-0.2				-0.4	-0.4		
<i>Negligible influence: kasl soilwater, kawAir, kawWater, kwsSed, kwsWater</i>													
Volumetric parameters	area Reg	-0.4	-0.5	-0.6	-0.6	-0.8	-1.0	-1.0	-0.7	-0.6	-1.0	-0.8	
	areaEU	-0.2	-0.2	-0.1	-0.1	-0.1			-0.1	-0.2		-0.2	
	depthAgric	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-0.1		-0.1	-1.0	-0.8	
	fAgric Reg	-0.1	-0.1	-0.3	-0.3	-0.7	-1.0	-1.0	-0.6	-0.5	-1.0	-0.8	
	fInd Reg											-0.1	
	fNatural Cont		-0.1	-0.1	-0.1							-0.1	
	fNatural Reg											-0.2	
	fWater Reg											0.2	
	heightAir	-0.8	-0.7	-0.5	-0.5	-0.2				-0.5	-0.5		
	<i>Negligible influence: depthInd, depthNat, depthSed, depthWater Cont, depthWater Reg, fAgric Cont, fInd Cont, fWater Cont</i>												
Other model parameters	ConJunge	0.7	0.1										
	FconnectSTP	0.1		0.2	0.2	0.6	1.0	1.0	0.6	0.5	1.0	0.5	
	FInfSoil								-0.1			-0.6	
	FocSoil								0.9	0.7	0.8		
	FSolidSoil	-0.9	-0.9	-0.9	-0.9	-0.9	-0.9	-0.9	-0.2	-0.1	-0.8	-0.9	
	FWaterSoil	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	0.1		-0.1	0.9	
	Qstp								-0.1	-0.2	-0.6	-0.5	
	RhoSolid	-0.9	-0.9	-0.9	-0.9	-0.9	-0.9	-0.9	-0.2	-0.1	-0.8	-0.9	
	RhoWater	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	
	SurfAer	0.7	0.1										
	SuspEff							-0.1	-0.1				
	Temperatur	0.4	0.1										
	<i>Negligible influence: BIOwater, FAirSoil, FocSed, FocSusp, FSolidSed, FWaterSed, N Reg, NEU, OHconcair, RHOair, SuspWater Reg, SuspWater-Cont</i>												
STP parameters	BOD						0.1	0.1	0.2			0.2	
	Density solids activated sludge								0.1			0.1	
	Density solids PS								0.1	0.2	0.3	0.1	
	Density solids raw sewage								-0.1	-0.1	-0.3	-0.1	
	Density solids SLS								-0.1			-0.1	
	Fraction oc activated sludge							0.1	0.1			0.1	
	Fraction oc raw sewage								0.4	0.5	0.9	0.3	
	Input solids in raw sewage								0.4	0.5	0.9	0.3	
<i>Negligible influence: Aeration rate, C activated sludge, Depth aerator, Depth PS, Depth SLS, Factor Blackburn et al., Factor Hsieh et al. (1993b), Fraction oc solids PS, Fraction oc solids SLS, Height air column, HRTPS, HRTSLS, K airM, K pore waterM, K waterM, kGa/kLa, Oxygen concentration, Psi, Sludge loading rate, t1/2 aeration, t1/2 PS, t1/2 SLS, TempSTP</i>													

Table 52 Sensitivities of PECs of pore-water in agricultural soil.

Type	Parameter	TcDD	PeCDD	HxCDD	HpCDD	OCDD	DEHP	HHCB	EDC	BENZ	LAS	EDTA	
Degradation parameters	kdegair	-0.1								-0.1			
	kdegsoil	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-0.1		-0.1	-1.0		
<i>Negligible influence: kdegsoil, kdegwater</i>													
Emissions	EContAir	0.3	0.2	0.1	0.1	0.1			0.2	0.3			
	ERegAir	0.6	0.8	0.7	0.6	0.3			0.2	0.1			
	ERegfirstwastewater	0.1		0.2	0.2	0.6	1.0	1.0	0.6	0.5	1.0	0.7	
	ERegInd											0.3	
<i>Negligible influence: EContfirstwastewater, EContfirstwater, EContInd, ERegfirstwater</i>													
PC data	Kow	-0.8	-0.8	-0.8	-0.8	-0.8	-0.8		0.4	0.3	0.1	0.4	
	Molw							-0.6	-1.0	-0.9		0.5	
	Sol							0.6	1.0	0.9		-0.5	
	TempMelt	-5.3	-0.7	-0.3									
	Vp	-0.7	-0.1						-0.6	-1.0	-0.9	0.5	
<i>Negligible influence: none</i>													
Process parameters	CollEffAer	0.7	0.5	0.4	0.4	0.2							
	DepRateAer	0.2	0.1	0.1	0.1								
	Erosion							-0.1					
	FFlowOut Reg											-0.1	
	FrunoffSoil											-0.8	
	kasl air											0.3	
	kasl soilair							-0.6	-0.5	-0.4			
	kawAir												0.2
	Rainrate	-0.1	-0.3	-0.3	-0.3	-0.3		-0.2			-1.2	-2.0	
	windspeed	-0.7	-0.6	-0.5	-0.5	-0.2			-0.4	-0.4			
<i>Negligible influence: kasl soilwater, kawWater, kwsSed, kwsWater, SETTLEvelocity</i>													
Volumetric parameters	area Reg	-0.4	-0.5	-0.6	-0.6	-0.8	-1.0	-1.0	-0.7	-0.6	-1.0	-0.8	
	areaEU	-0.2	-0.2	-0.1	-0.1	-0.1			-0.1	-0.2		-0.2	
	depthAgric	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-0.1	-0.1	-1.0	-0.8	
	fAgric Reg	-0.1	-0.1	-0.3	-0.3	-0.7	-1.0	-1.0	-0.6	-0.5	-1.0	-0.8	
	fInd Reg											-0.1	
	fNatural Cont		-0.1	-0.1	-0.1							-0.1	
	fNatural Reg											-0.2	
	fWater Reg											0.2	
	heightAir	-0.8	-0.7	-0.5	-0.5	-0.2			-0.5	-0.5			
	<i>Negligible influence: depthInd, depthNat, depthSed, depthWater Cont, depthWater Reg, fAgric Cont, fInd Cont, fWater Cont</i>												
Other model parameters	ConJunge	0.7	0.1										
	FconnectSTP	0.1		0.2	0.2	0.6	1.0	1.0	0.6	0.5	1.0	0.5	
	FInfSoil							-0.1				-0.6	
	FocSoil	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-0.1		-0.1	-0.8		
	FSolidSoil	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-0.1		-0.1	-0.8		
	FWaterSoil										-0.1		
	Qstp						-0.1	-0.2	-0.6	-0.5	-1.0	-0.5	
	RhoSolid	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-0.1	-0.1	-0.1	-0.8		
	SurfAer	0.7	0.1										
	SuspEff							-0.1	-0.1				
Temperatur	0.4	0.1											
<i>Negligible influence: BIOwater, FAirSoil, FocSed, FocSusp, FSolidSed, FWaterSed, N Reg, NEU, OHconcair, RHOair, RhoWater, SuspWater Reg, SuspWaterCont</i>													
STP parameters	Fraction oc raw sewage										0.1		
	Input solids in raw sewage										0.1		
<i>Negligible influence: Aeration rate, BOD, C activated sludge, Density solids activated sludge, Density solids PS, Density solids raw sewage, Density solids SLS, Depth aerator, Depth PS, Depth SLS, Factor Blackburn et al., Factor Hsieh et al. (1993b), Fraction oc activated sludge, Fraction oc solids PS, Fraction oc solids SLS, Height air column, HRTPS, HRTSLS, K airM, K pore waterM, K waterM, kGa/kLa, Oxygen concentration, Psi, Sludge loading rate, t1/2 aeration, t1/2 PS, t1/2 SLS, TempSTP</i>													

Table 53 Sensitivities of PECs in natural soil.

Type	Parameter	TCDD	PeCDD	HxCDD	HpCDD	OCDD	DEHP	HHCB	EDC	BENZ	LAS	EDTA
Degradation parameters	kdegair	-0.2					-0.5	-0.8		-0.3		
	kdegsoil	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-0.1			-1.6	
<i>Negligible influence:</i> kdegsoil, kdegwater												
Emissions	EContAir	0.3	0.2	0.2	0.2	0.2	0.1		0.4	0.7		
	EContfirstwastewater							0.1	0.1			0.1
	ERegAir	0.7	0.8	0.8	0.8	0.8	0.9		0.9	0.5	0.3	
	ERegfirstwastewater							0.9	0.1		0.1	0.4
	ERegInd										0.9	0.5
<i>Negligible influence:</i> EContfirstwater, EContInd, ERegfirstwater												
PC data	Kow							0.7	0.6	0.7	-0.4	
	Molw							-0.9	-1.0	-1.0	1.0	1.0
	Sol							0.9	1.0	1.0	-1.0	-1.0
	TempMelt	-5.9	-0.7	-0.4	-0.1	-0.1		-0.1				
	Vp	-0.8	-0.1	-0.1			-0.9	-0.9	-1.0	-1.0	1.0	1.0
<i>Negligible influence:</i> none												
Process parameters	CollEffAer	0.7	0.5	0.5	0.5	0.5	0.8					
	DepRateAer	0.2	0.1	0.1	0.1	0.1	0.2					
	Erosion							-0.1				
	FFlowOut Reg							-0.1				-0.2
	FrunoffSoil							-0.2			-0.2	-1.1
	kasl air										1.0	0.5
	kasl soilair							0.1				
	kawAir							0.1				0.5
	Rainrate		0.3	0.1	0.1	-0.1	-0.1		-0.1	-0.1		-0.9
	windspeed	-0.8	-0.7	-0.6	-0.6	-0.6	-0.5	-0.2	-0.2	-1.0	-0.7	
<i>Negligible influence:</i> kasl soilwater, kawWater, kwsSed, kwsWater, SETTLEvelocity												
Volumetric parameters	area Reg	-0.4	-0.5	-0.5	-0.5	-0.5	-0.6	-0.8	-0.3	-0.2	-1.0	-0.7
	areaEU	-0.3	-0.2	-0.2	-0.2	-0.2	-0.1	-0.1	-0.3	-0.5		-0.3
	depthAgric										-0.1	
	depthInd										-0.7	
	depthNat	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0				-0.8	
	fAgric Cont											-0.1
	fAgric Reg		-0.1	-0.1	-0.1	-0.1					-0.5	-0.6
	fInd Reg										-0.2	-0.2
	fNatural Cont		-0.1	-0.1	-0.1	-0.1						-0.2
	fNatural Reg			-0.1	-0.1	-0.1					-0.3	-0.3
	fWater Reg							0.1				0.4
heightAir	-0.9	-0.7	-0.7	-0.7	-0.6	-1.0	-1.0	-1.0	-1.0			
<i>Negligible influence:</i> depthSed, depthWater Cont, depthWater Reg, flnd Cont, fWater Cont												
Other model parameters	ConJunge	0.8	0.1	0.1			0.9					
	FconnectSTP						-0.1				0.1	
	FInfSoil							-0.2			-0.2	-0.8
	FocSoil							0.9	0.7	0.9	-0.5	
	FSolidSoil	-0.9	-0.9	-0.9	-0.9	-0.9	-0.9	-0.1	-0.2		-1.4	-0.9
	FWaterSed							0.1				
	FWaterSoil	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	0.1		-0.2	0.9
	Qstp										-0.1	
	RhoSolid	-0.9	-0.9	-0.9	-0.9	-0.9	-0.9	-0.1	-0.2		-1.4	-0.9
	RhoWater	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1
SurfAer	0.8	0.1	0.1			0.9						
Temperatur	0.4	0.1										
<i>Negligible influence:</i> BIOWater, FAirSoil, FocSed, FocSusp, FSolidSed, N Reg, NEU, OHconcair, RHOair, SuspEff, SuspWater Reg, SuspWaterCont												
STP parameters	Aeration rate								-0.1			
	BOD	-0.1		-0.2	-0.2	-0.4	-0.4	-0.2		-0.1	-0.5	
	C activated sludge								0.1	0.1	0.5	
	Depth aerator								0.2			
	Depth SLS								0.1			
	Factor Hsieh et al. (1993b)								-0.1			
	Fraction oc activated sludge							-0.1				
	Height air column								-0.1			
	HRTSLS								-0.1			
	K waterM								-0.2			
Sludge loading rate								0.1	0.1	0.5		
<i>Negligible influence:</i> Density solids activated sludge, Density solids PS, Density solids raw sewage, Density solids, LS, Depth PS, Factor Blackburn et al., Fraction oc raw sewage, Fraction oc solids PS, Fraction oc solids SLS, HRTPS, Input solids in raw sewage, K airM, K pore waterM, kGa/kLa, Oxygen concentration, Psi, t1/2 aeration, t1/2 PS, t1/2 SLS, TempSTP												

Table 54 Sensitivities of PECs in industrial/urban soil.

Type	Parameter	TCDD	PeCDD	HxCDD	HpCDD	OCDD	DEHP	HHCB	EDC	BENZ	LAS	EDTA
Degradation parameters	kdegair	-0.2					-0.5	-0.8				
	kdegsoil	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0	-0.1			-0.8	
<i>Negligible influence: kdegwater</i>												
Emissions	EContAir	0.3	0.2	0.2	0.2	0.2	0.1					
	EContfirstwastewater							0.1				
	ERegAir	0.7	0.8	0.8	0.8	0.8	0.9					
	ERegfirstwastewater							0.9				
<i>Negligible influence: EContInd, ERegfirstwater</i>												
PC data	Kow							0.7	0.6	0.7	0.1	
	Molw							-0.9	-1.0	-1.0		
	Sol							0.9	0.9	0.9		
	TempMelt	-5.9	-0.7	-0.4	-0.1	-0.1		-0.1				
	Vp	-0.8	-0.1	-0.1			-0.9		-0.9	-1.0	-1.0	
<i>Negligible influence: none</i>												
Process parameters	ColIEffAer	0.7	0.5	0.5	0.5	0.5	0.8					
	DepRateAer	0.2	0.1	0.1	0.1	0.1	0.2					
	Erosion							-0.1				
	FFlowOut Reg							-0.1				
	FrunoffSoil							-0.2				
	kasl soilair							0.1	-0.9	-1.0	-0.1	-0.5
	kawAir							0.1				
	Rainrate	0.7	0.5	0.5	0.5	0.5	0.8				-0.3	-2.0
	windspeed	-0.8	-0.7	-0.6	-0.6	-0.6	-0.5	-0.2				
	<i>Negligible influence: kasl air, kasl soilwater, kawWater, kwsSed, kwsWater, SETTLEvelocity</i>											
Volumetric parameters	area Reg	-0.4	-0.5	-0.5	-0.5	-0.5	-0.6	-0.8	-1.0	-1.0	-1.0	-1.0
	areaEU	-0.3	-0.2	-0.2	-0.2	-0.2	-0.1	-0.1				
	depthAgric							-0.1				
	depthInd	-1.0	-1.0	-1.0	-1.0	-1.0	-1.0				-0.8	
	fAgric Reg		-0.1	-0.1	-0.1	-0.1						
	fInd Reg								-1.0	-1.0	-1.0	-1.0
	fNatural Cont		-0.1	-0.1	-0.1	-0.1						
	fNatural Reg		-0.1	-0.1	-0.1	-0.1						
	fWater Reg								0.1			
	heightAir	-0.9	-0.7	-0.7	-0.7	-0.6	-1.0	-1.0				
<i>Negligible influence: depthNat, depthSed, depthWater Cont, depthWater Reg, fAgric Cont, fInd Cont, fWater Cont</i>												
Other model parameters	BIOWater											
	ConJunge	0.8	0.1	0.1			0.9					
	FconnectSTP						-0.1					
	FInfSoil							-0.2			-0.1	-0.5
	FocSoil							0.9	0.7	0.9	0.2	-0.7
	FSolidSoil	-0.9	-0.9	-0.9	-0.9	-0.9	-0.9	-0.1	-0.2		-0.7	-0.9
	FWaterSed							0.1				
	FWaterSoil	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	0.1		-0.1	0.9
	RhoSolid	-0.9	-0.9	-0.9	-0.9	-0.9	-0.9	-0.1	-0.2		-0.7	-0.9
	RhoWater	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1	-0.1
SurfAer	0.8	0.1	0.1			0.9						
Temperatur	0.4	0.1										
<i>Negligible influence: FAirSoil, FocSed, FocSusp, FSolidSed, N Reg, NEU, OHconcair, Qstp, RHOair, SuspEff, SuspWater Reg, SuspWaterCont</i>												
STP parameters	Fraction oc raw sewage										0.1	
	Input solids in raw sewage										0.1	
<i>Negligible influence: Aeration rate, BOD, C activated sludge, Density solids activated sludge, Density solids PS, Density solids raw sewage, Density solids SLS, Depth aerator, Depth PS, Depth SLS, Factor Blackburn et al., Factor Hsieh et al. (1993b), Fraction oc activated sludge, Fraction oc solids PS, Fraction oc solids SLS, Height air column, HRTPS, HRTSLS, K airM, K pore waterM, K waterM, kGa/kLa, Oxygen concentration, Psi, Sludge loading rate, t1/2 aeration, t1/2 PS, t1/2 SLS, TempSTP</i>												

A.6 Results of the uncertainty analyses

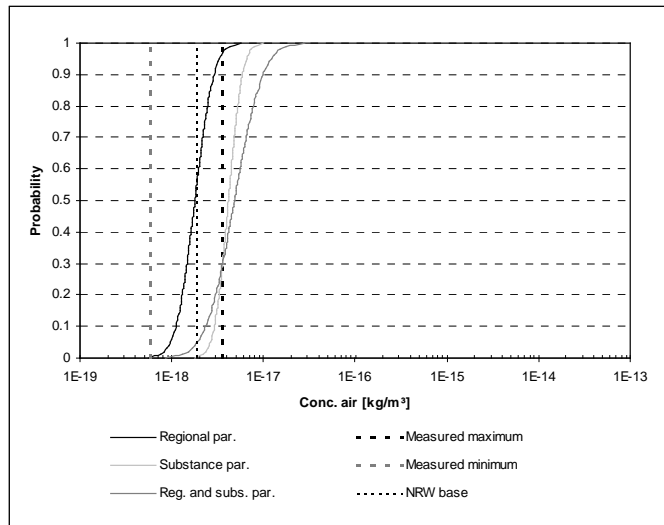


Figure 29 Cumulative distributions of TCDD-concentrations in air.

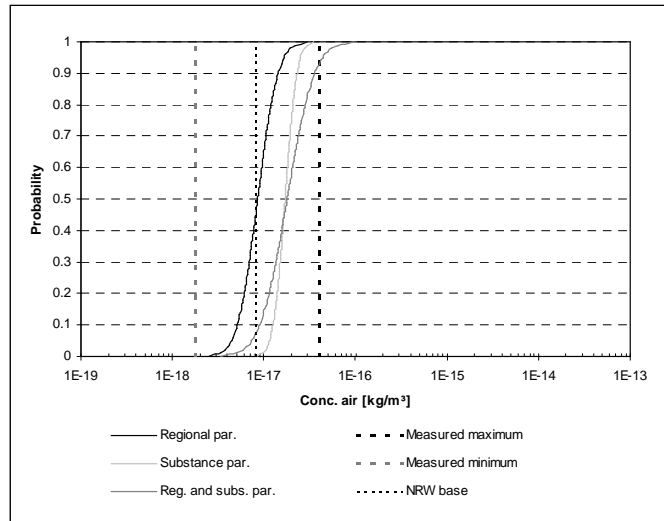


Figure 30 Cumulative distributions of PeCDD-concentrations in air.

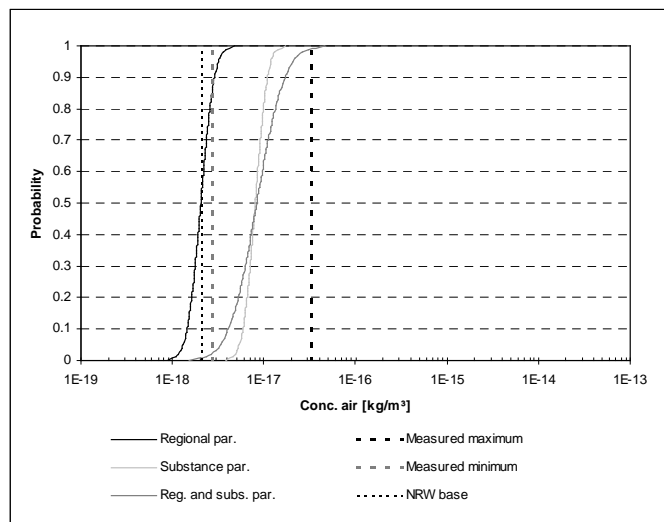


Figure 31 Cumulative distributions of HxCDD-concentrations in air.

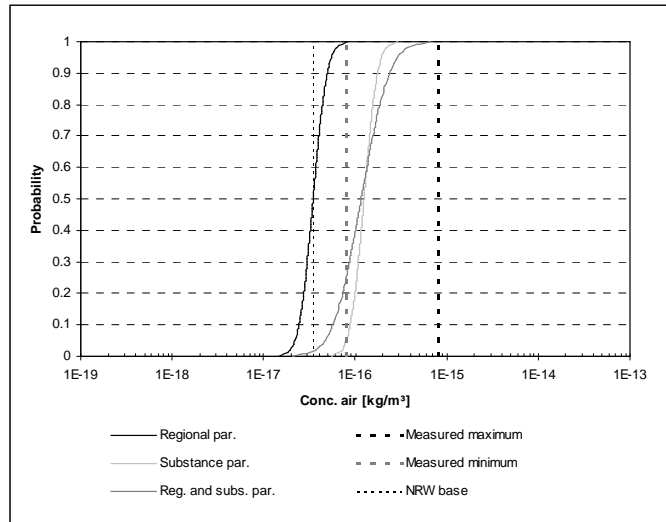


Figure 32 Cumulative distributions of HpCDD-concentrations in air.

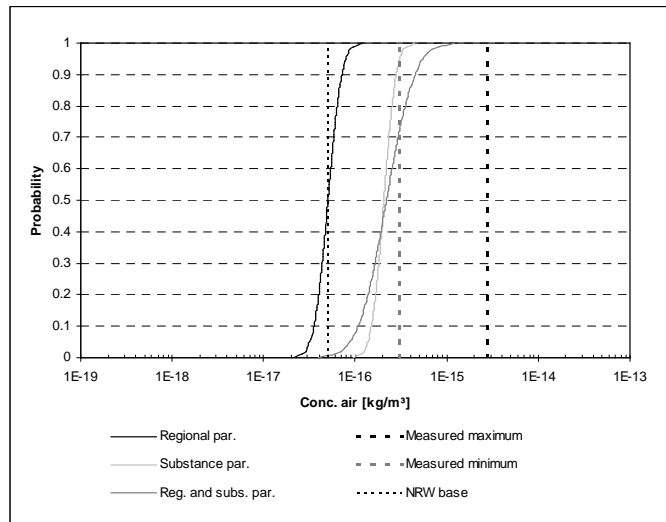


Figure 33 Cumulative distributions of OCDD-concentrations in air.

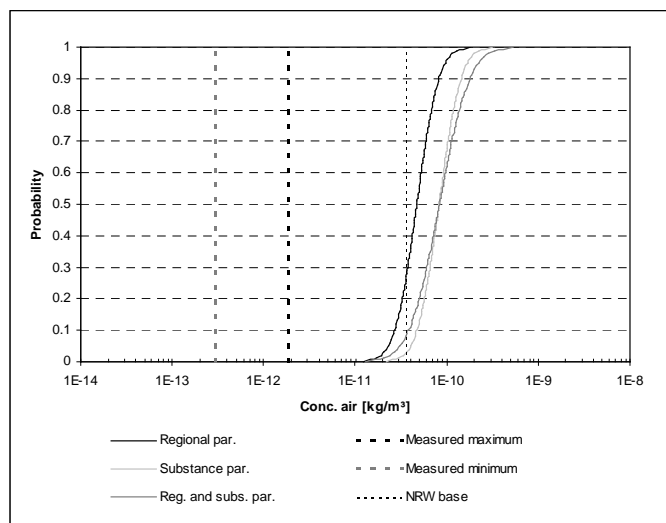


Figure 34 Cumulative distributions of DEHP-concentrations in air.

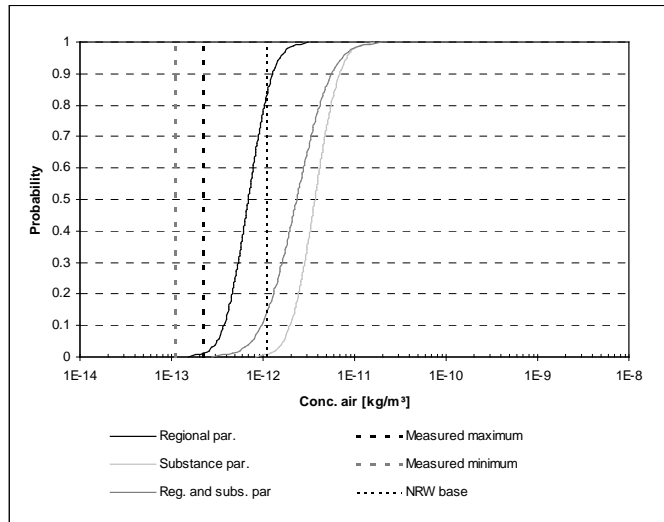


Figure 35 Cumulative distributions of HHCb-concentrations in air.

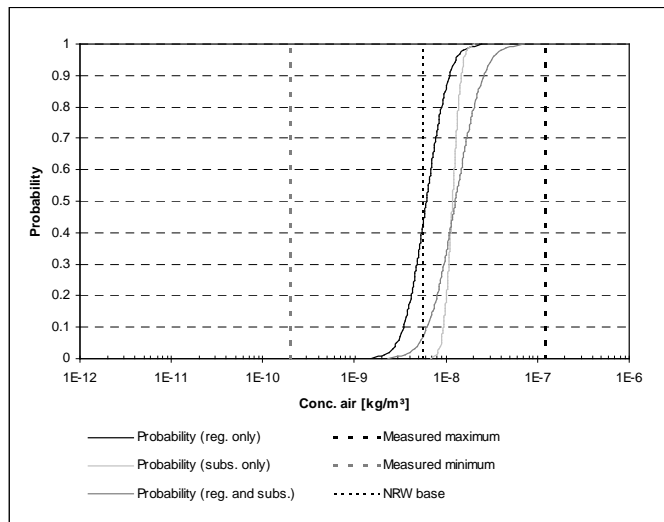


Figure 36 Cumulative distributions of EDC-concentrations in air.

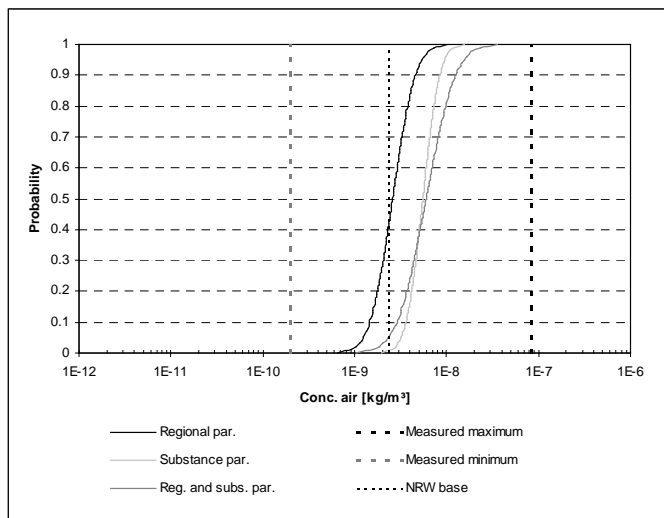


Figure 37 Cumulative distributions of BENZ-concentrations in air.

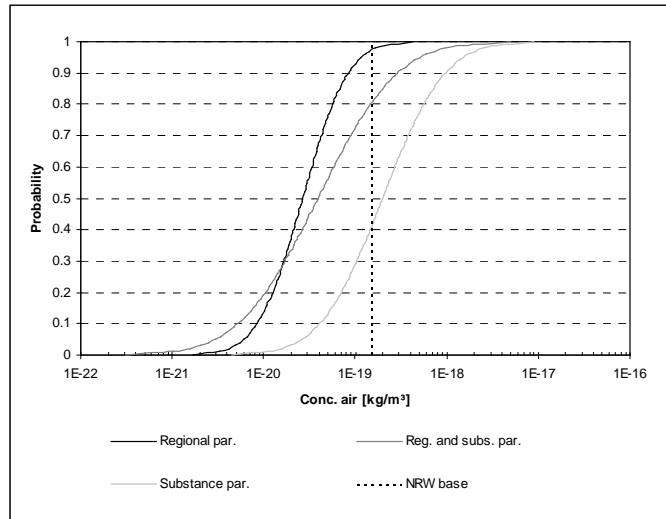


Figure 38 Cumulative distributions of LAS-concentrations in air.

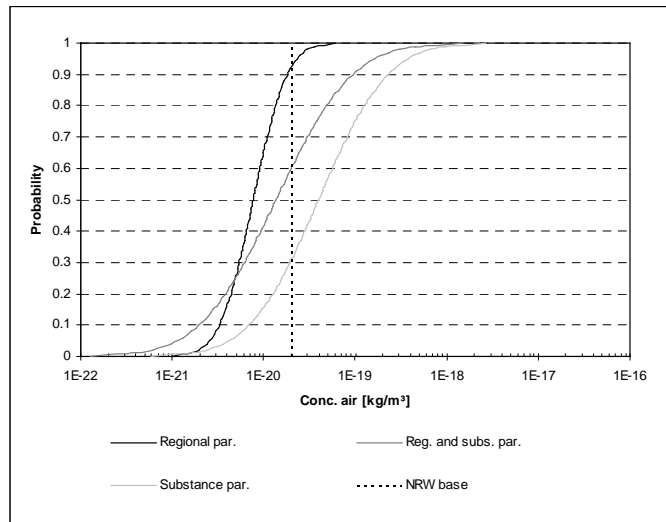


Figure 39 Cumulative distributions of EDTA-concentrations in air.

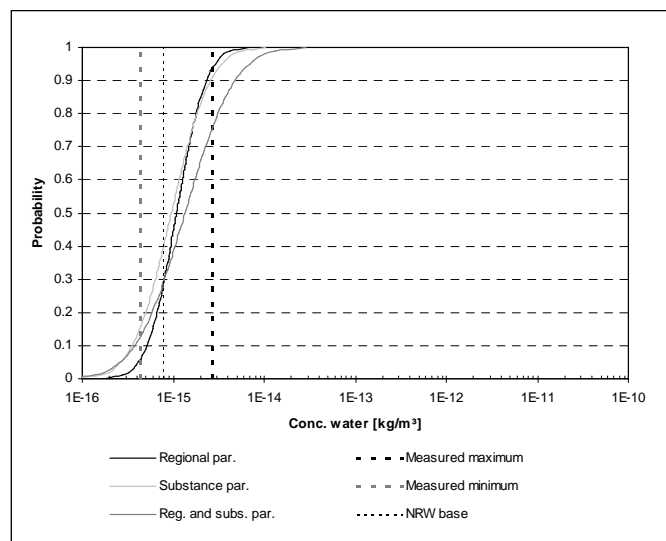


Figure 40 Cumulative distributions of TCDD-concentrations in water.

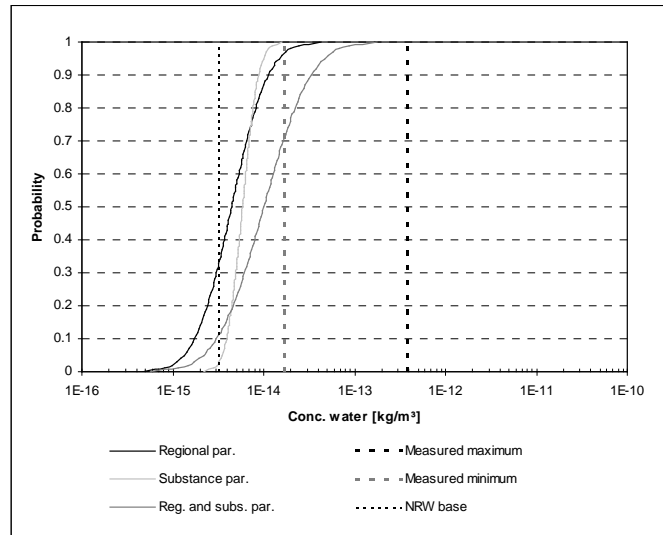


Figure 41 Cumulative distributions of PeCDD-concentrations in water.

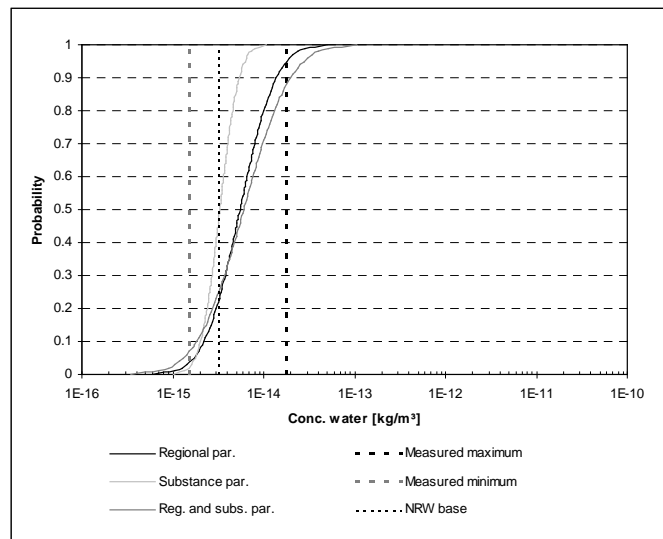


Figure 42 Cumulative distributions of HxCDD-concentrations in water.

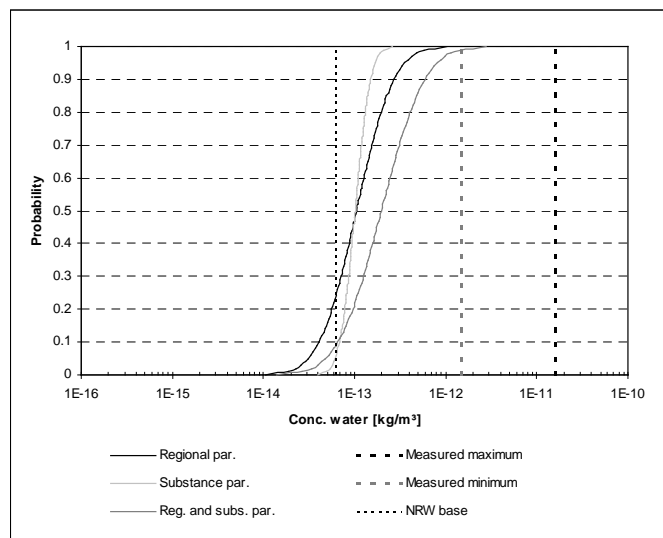


Figure 43 Cumulative distributions of HpCDD-concentrations in water.

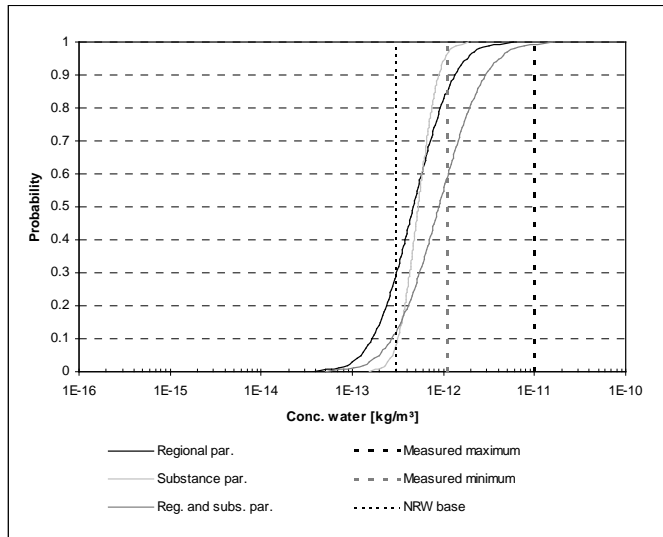


Figure 44 Cumulative distributions of OCDD-concentrations in water.

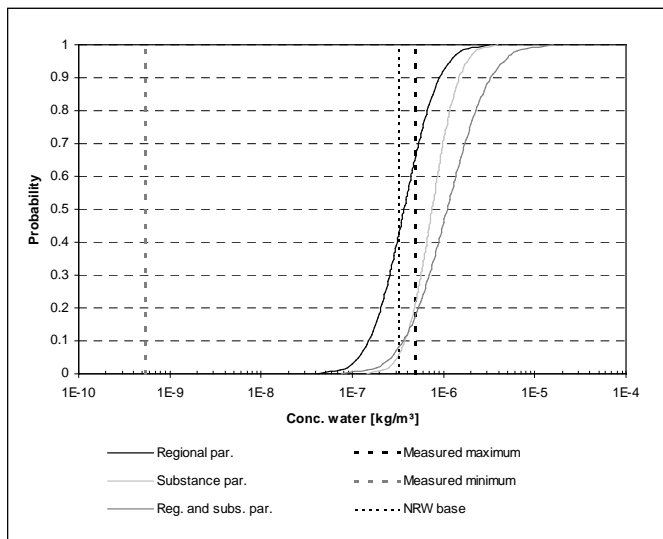


Figure 45 Cumulative distributions of DEHP-concentrations in water.

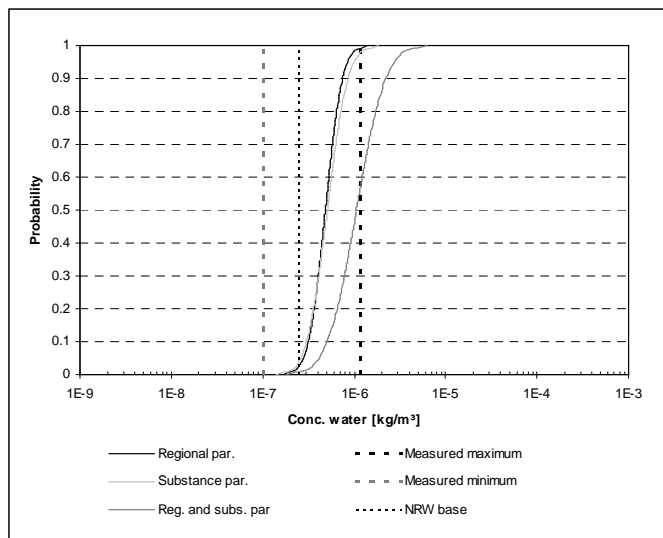


Figure 46 Cumulative distributions of HHCb-concentrations in water.

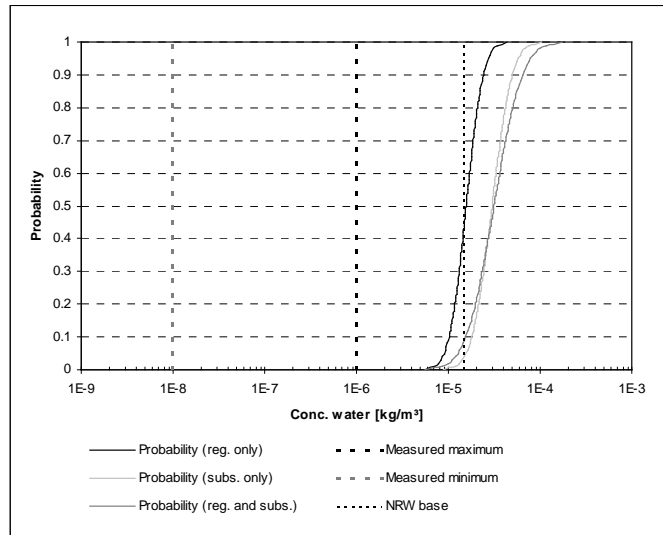


Figure 47 Cumulative distributions of EDC-concentrations in water.

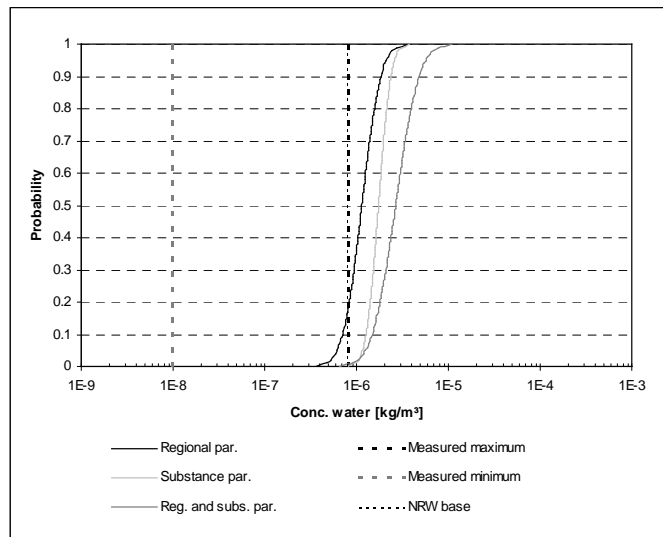


Figure 48 Cumulative distributions of BENZ-concentrations in water.

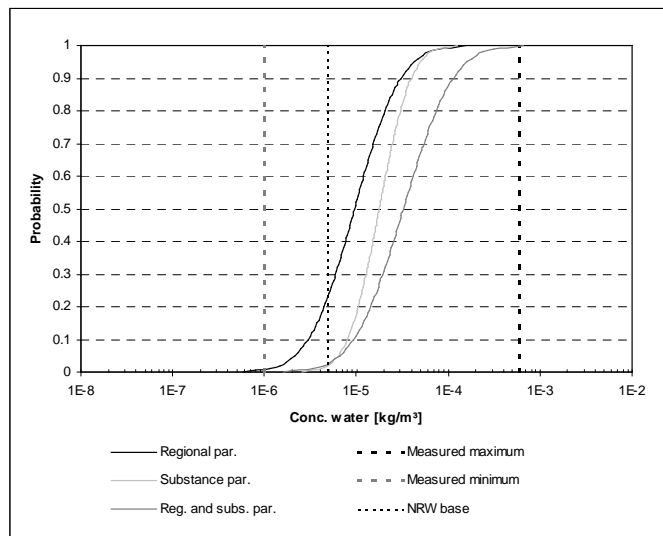


Figure 49 Cumulative distributions of LAS-concentrations in water.

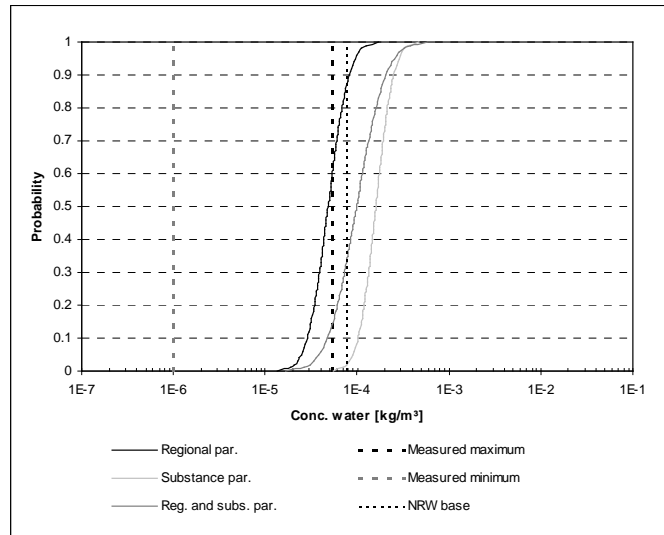


Figure 50 Cumulative distributions of EDTA-concentrations in water.

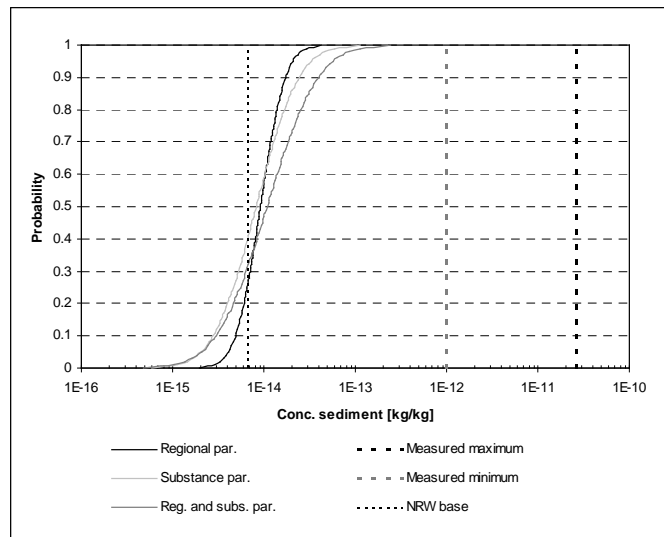


Figure 51 Cumulative distributions of TCDD-concentrations in sediment.

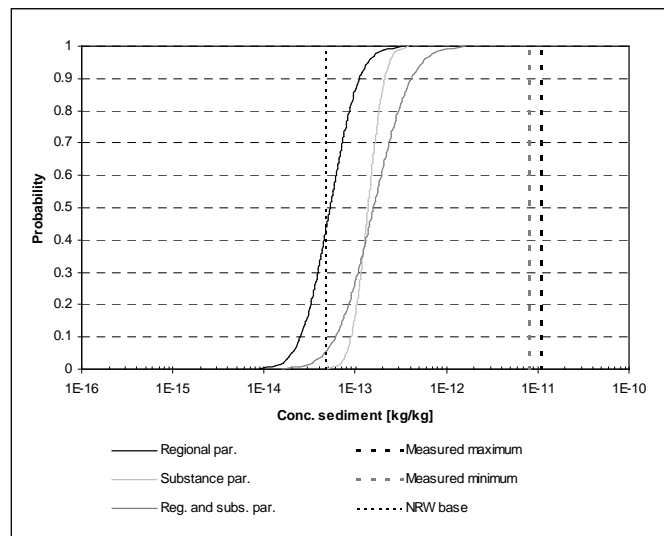


Figure 52 Cumulative distributions of PeCDD-concentrations in sediment.

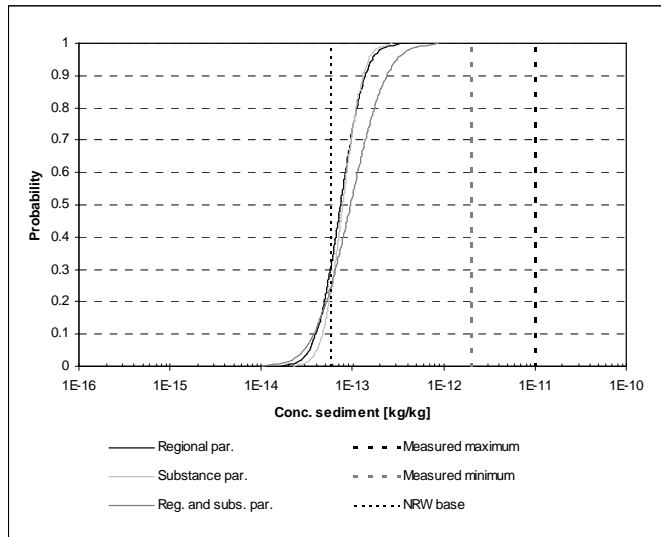


Figure 53 Cumulative distributions of HxCDD-concentrations in sediment.

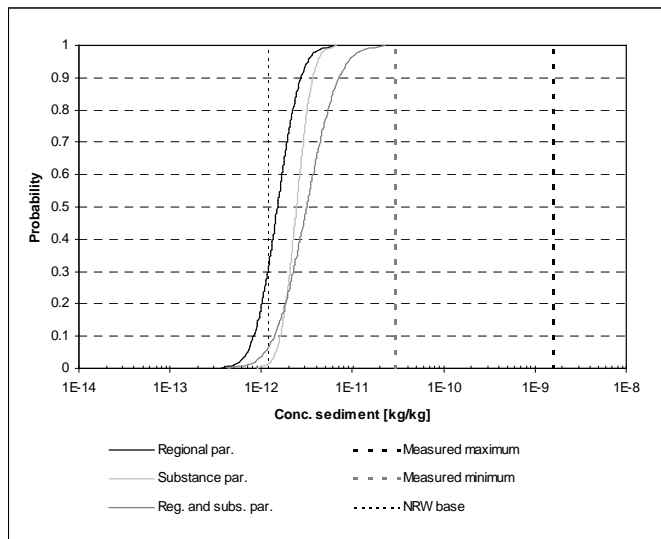


Figure 54 Cumulative distributions of HpCDD-concentrations in sediment.

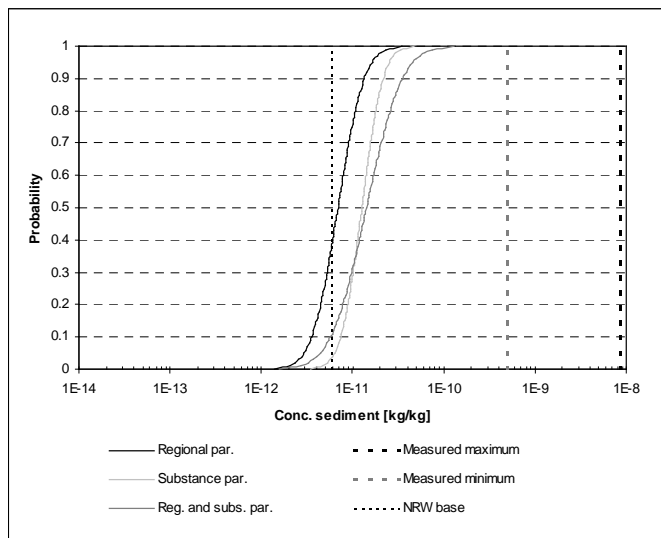


Figure 55 Cumulative distributions of OCDD-concentrations in sediment.

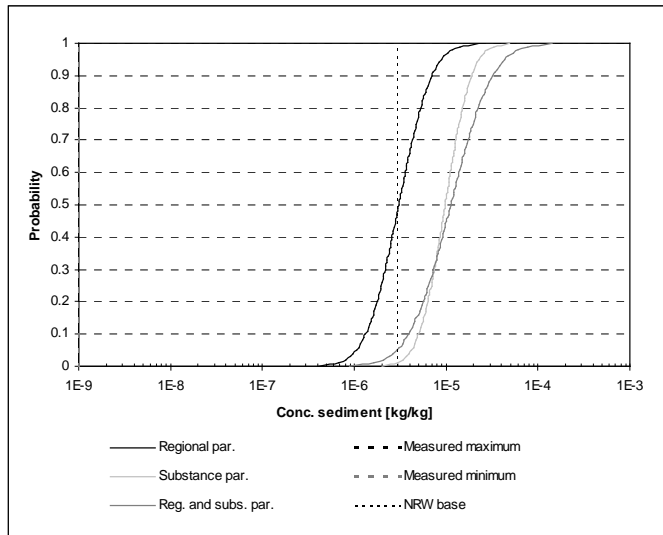


Figure 56 Cumulative distributions of DEHP-concentrations in sediment.

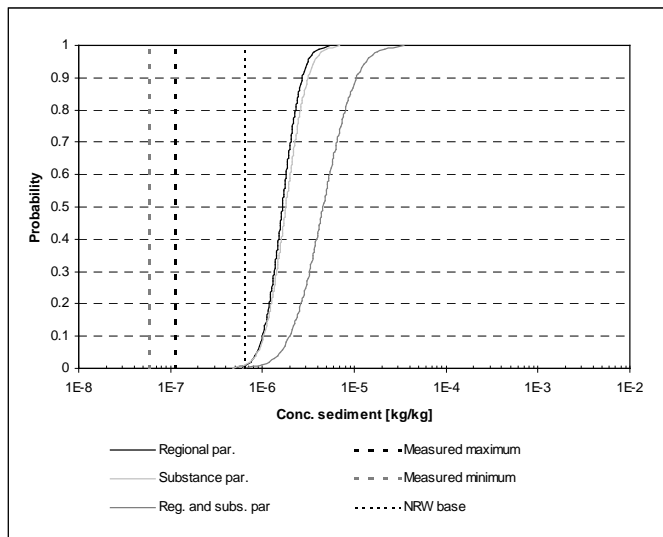


Figure 57 Cumulative distributions of HHCb-concentrations in sediment.

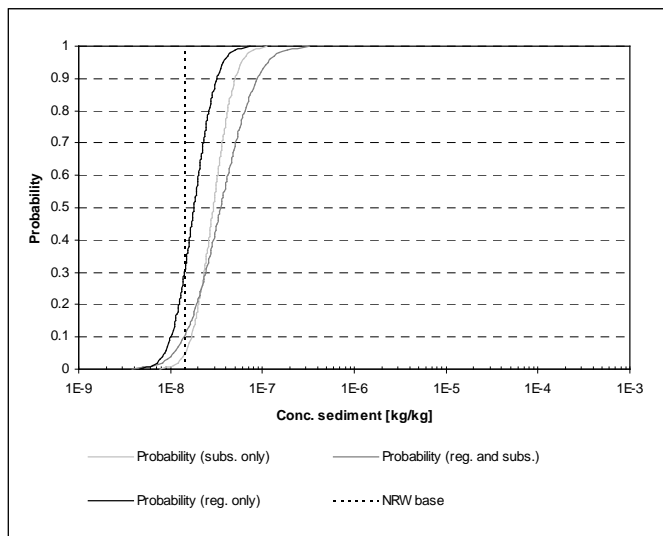


Figure 58 Cumulative distributions of EDC-concentrations in sediment.

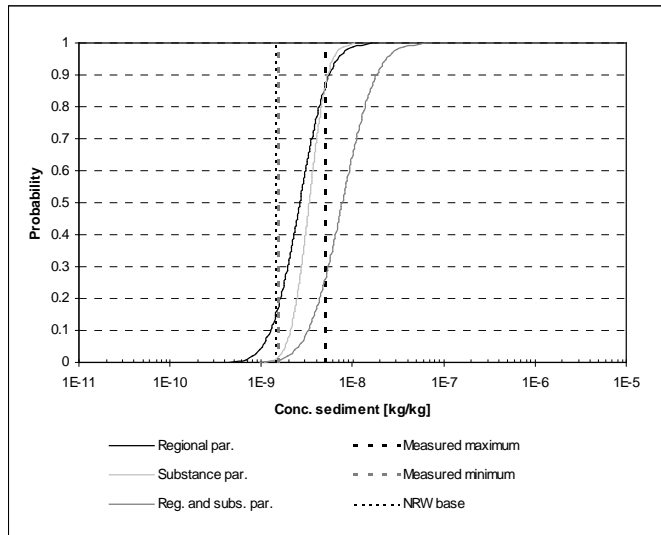


Figure 59 Cumulative distributions of BENZ-concentrations in sediment.

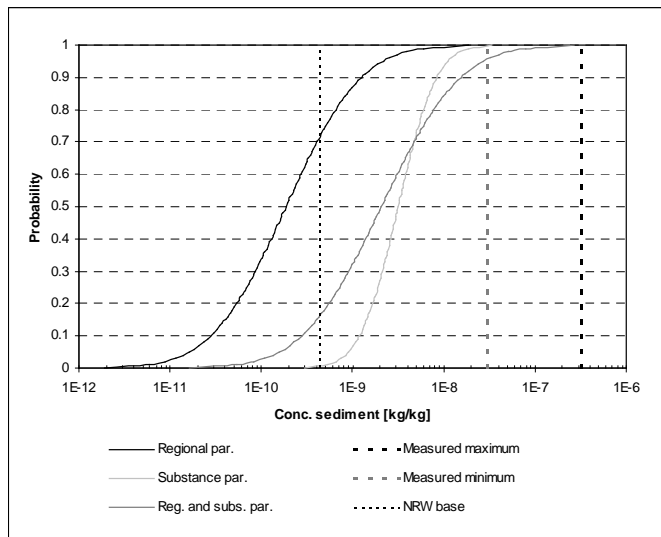


Figure 60 Cumulative distributions of LAS-concentrations in sediment.

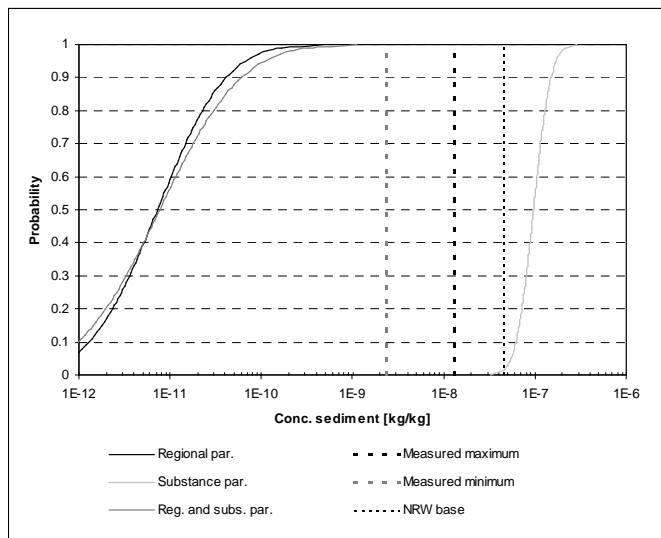


Figure 61 Cumulative distributions of EDTA-concentrations in sediment.

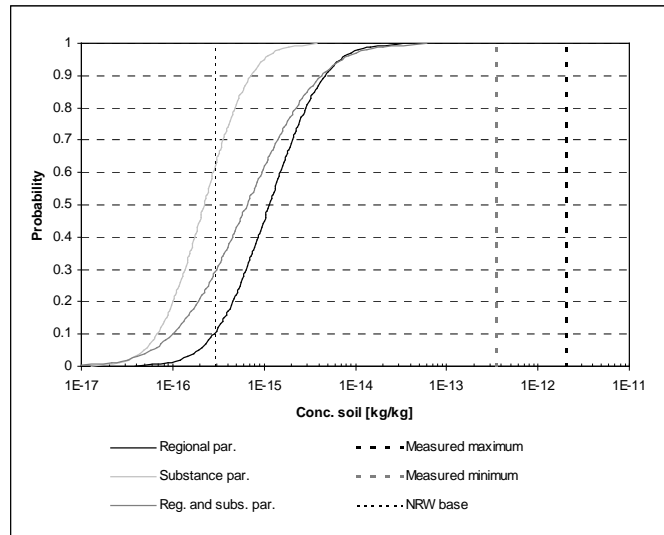


Figure 62 Cumulative distributions of TCDD-concentrations in soil.

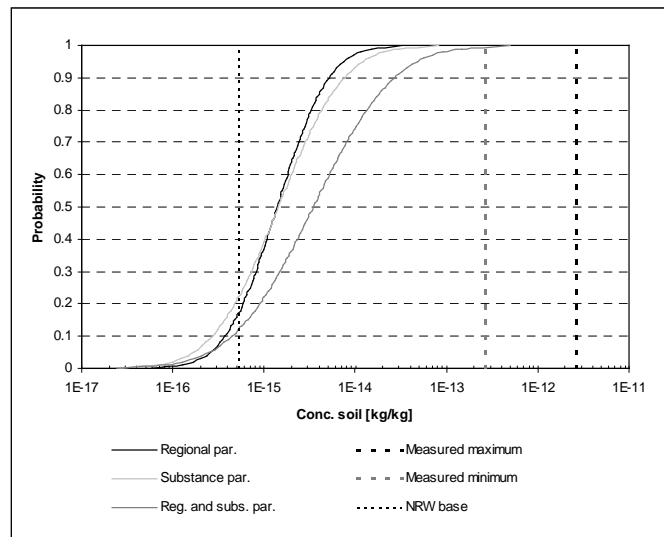


Figure 63 Cumulative distributions of PeCDD-concentrations in soil.

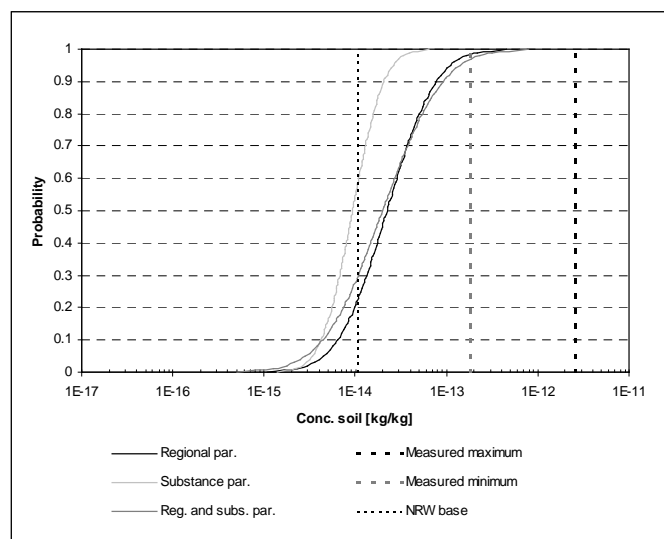


Figure 64 Cumulative distributions of HxCDD-concentrations in soil.

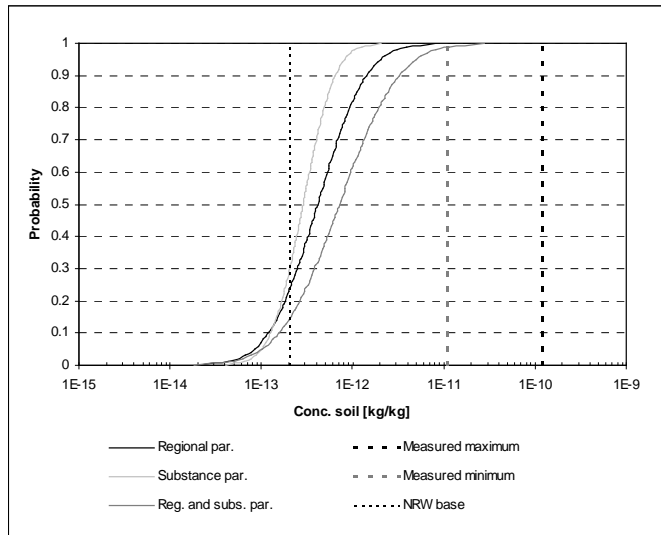


Figure 65 Cumulative distributions of HpCDD-concentrations in soil.

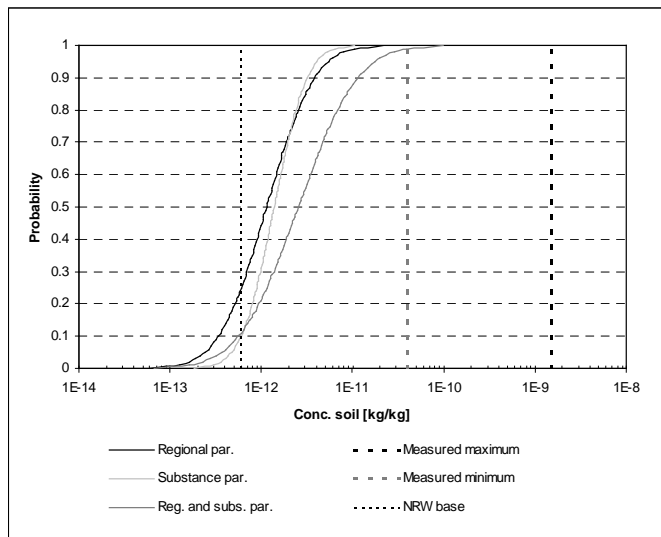


Figure 66 Cumulative distributions of OCDD-concentrations in soil.

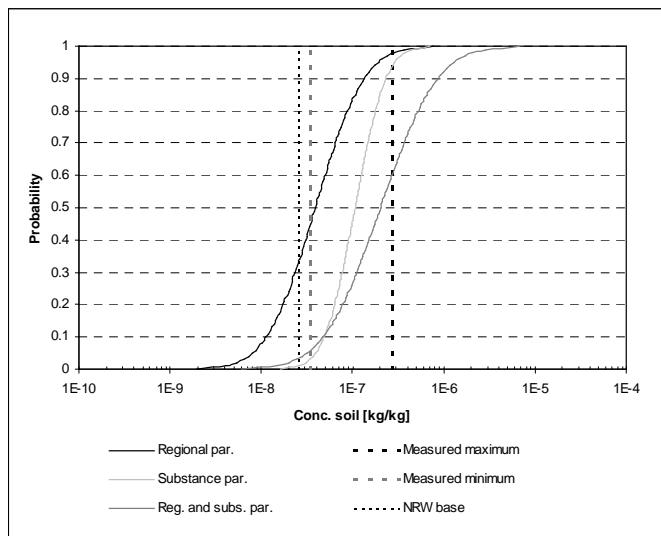


Figure 67 Cumulative distributions of DEHP-concentrations in soil.

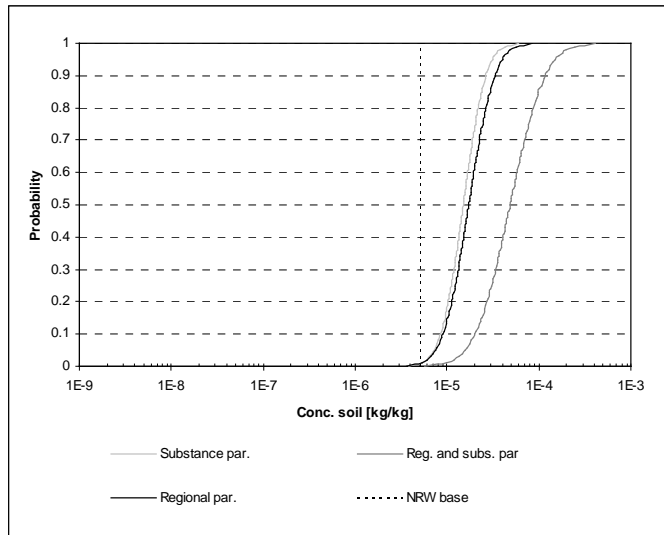


Figure 68 Cumulative distributions of HHCB-concentrations in soil.

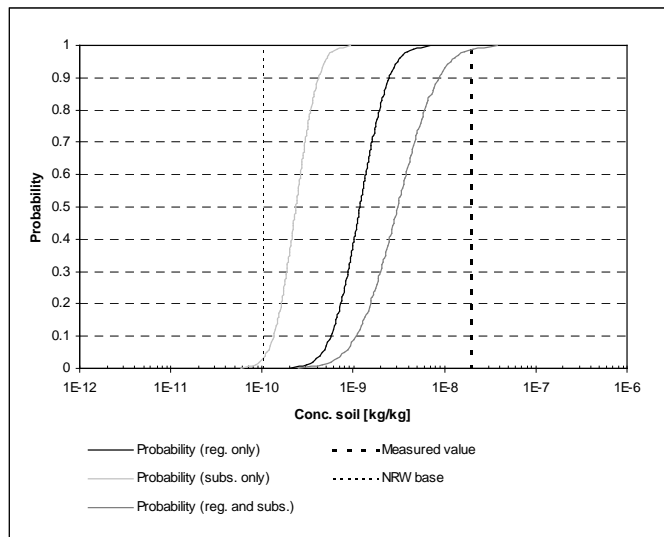


Figure 69 Cumulative distributions of EDC-concentrations in soil.

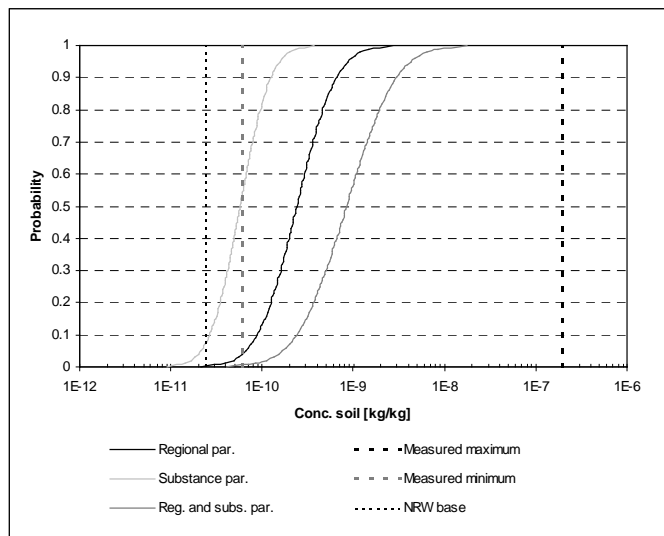


Figure 70 Cumulative distributions of BENZ-concentrations in soil.

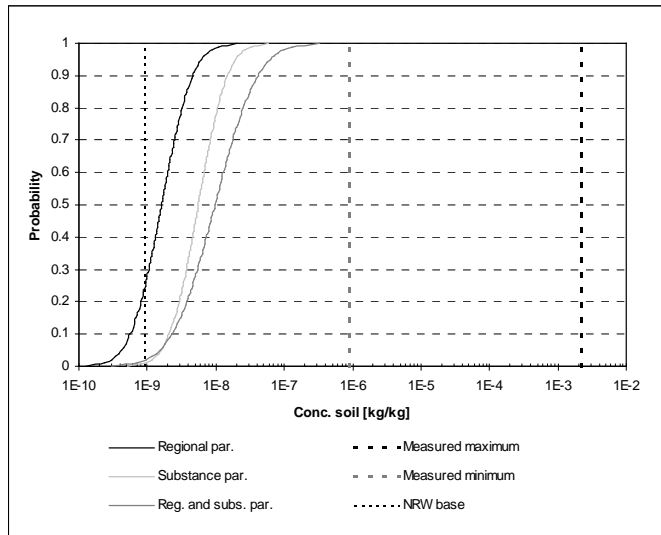


Figure 71 Cumulative distributions of LAS-concentrations in soil.

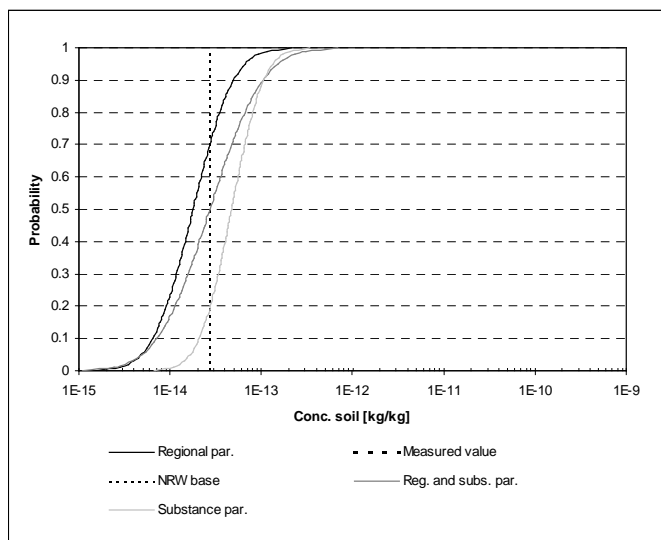


Figure 72 Cumulative distributions of EDTA-concentrations in soil.

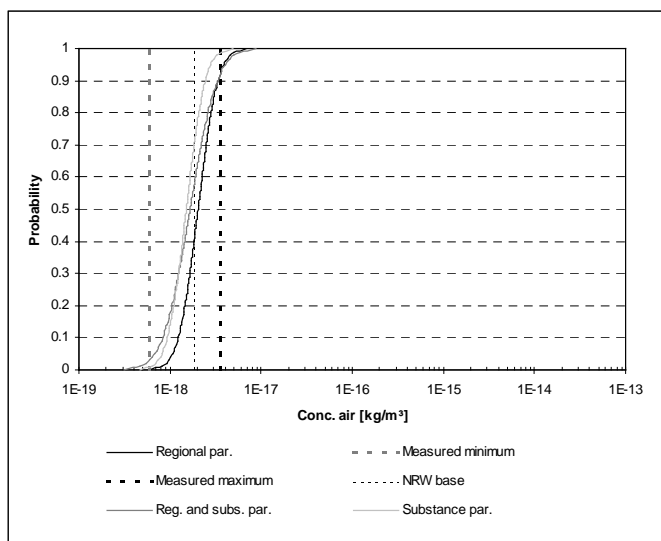


Figure 73 Cumulative distributions of TCDD-concentrations in air with fitted means.

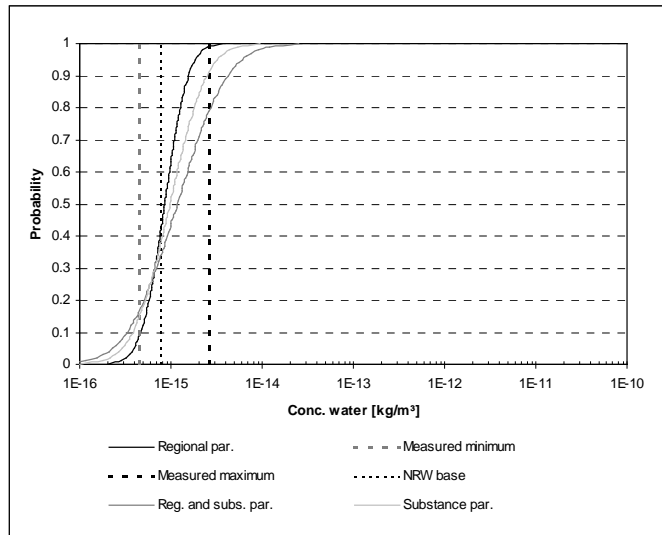


Figure 74 Cumulative distributions of TCDD-concentrations in water with fitted means.

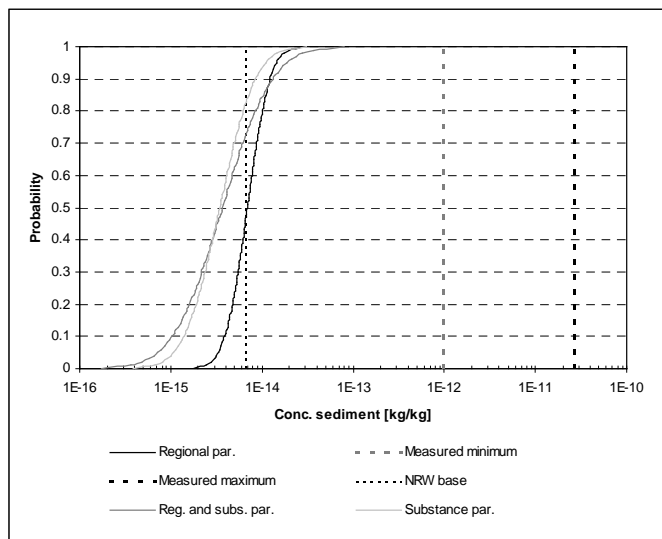


Figure 75 Cumulative distributions of TCDD-concentrations in sediment with fitted means.

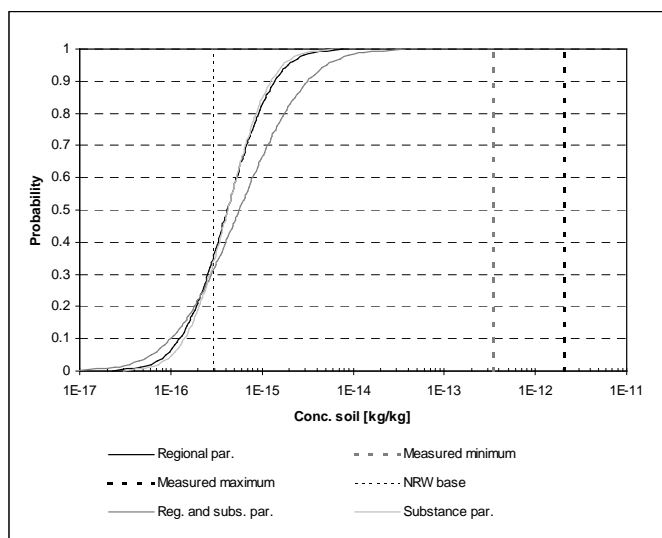


Figure 76 Cumulative distributions of TCDD-concentrations in soil with fitted means.

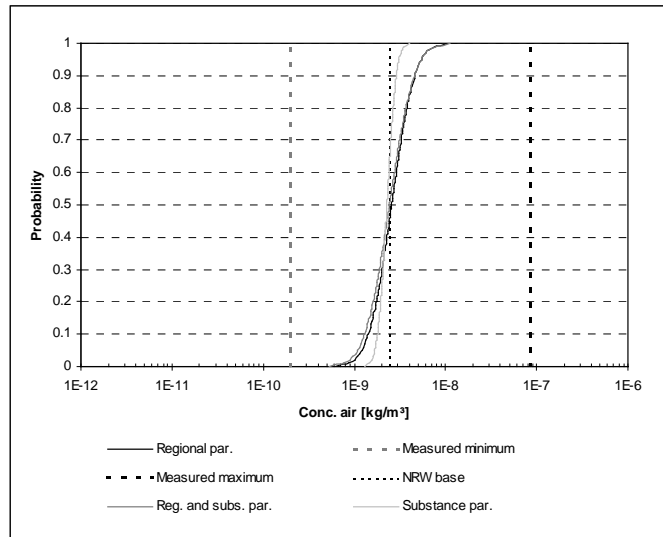


Figure 77 Cumulative distributions of BENZ-concentrations in air with fitted means.

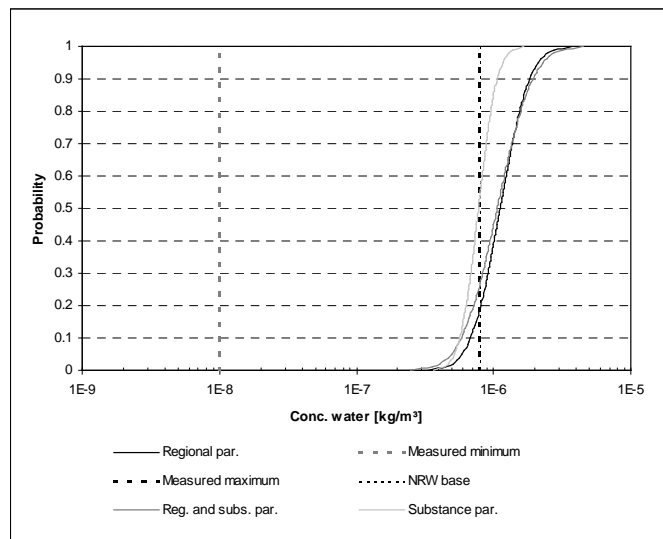


Figure 78 Cumulative distributions of BENZ-concentrations in water with fitted means.

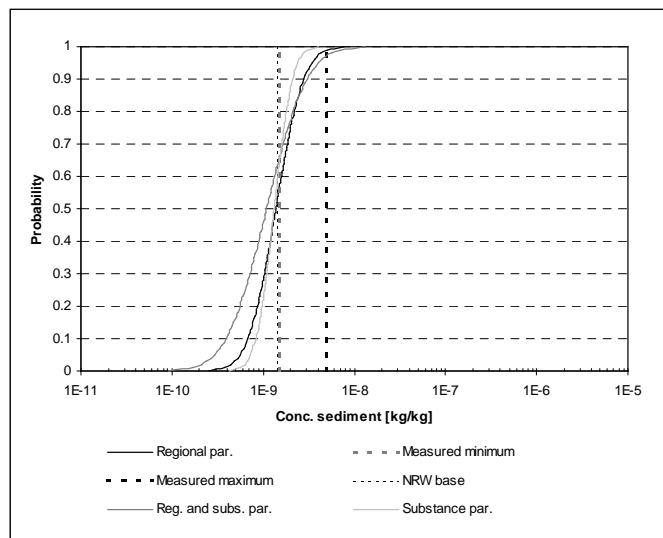


Figure 79 Cumulative distributions of BENZ-concentrations in sediment with fitted means.

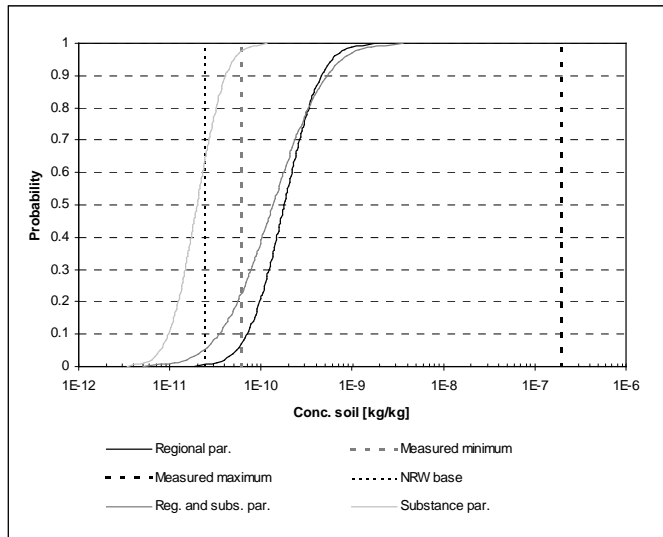


Figure 80 Cumulative distributions of BENZ-concentrations in soil with fitted means.

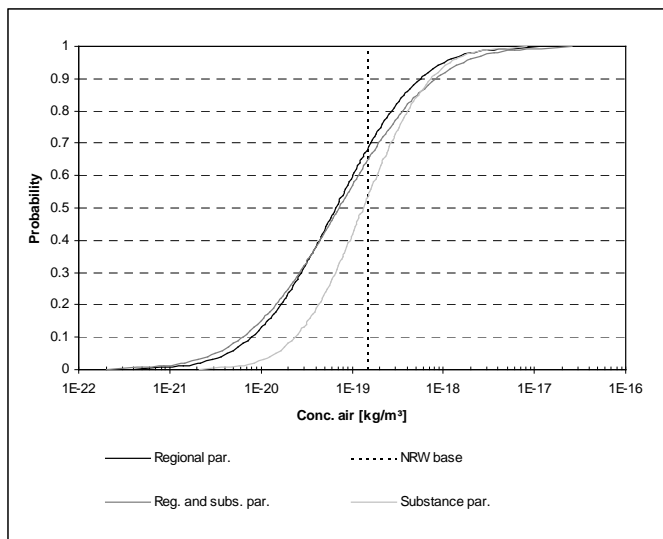


Figure 81 Cumulative distributions of LAS-concentrations in air with fitted means.

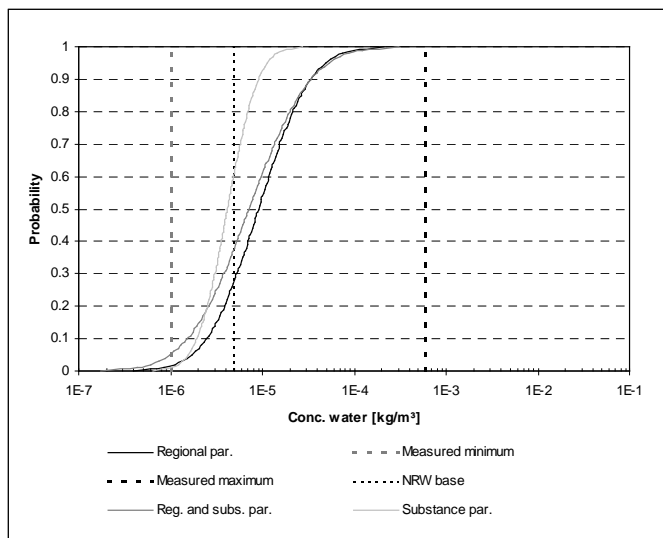


Figure 82 Cumulative distributions of LAS-concentrations in water with fitted means.

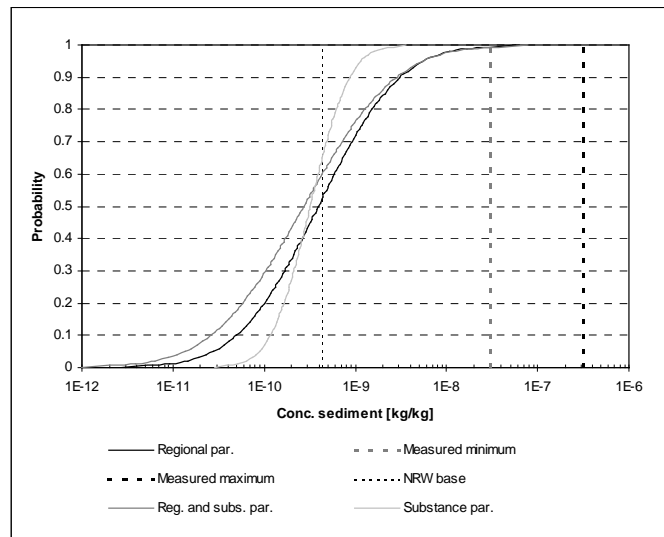


Figure 83 Cumulative distributions of LAS-concentrations in sediment with fitted means.

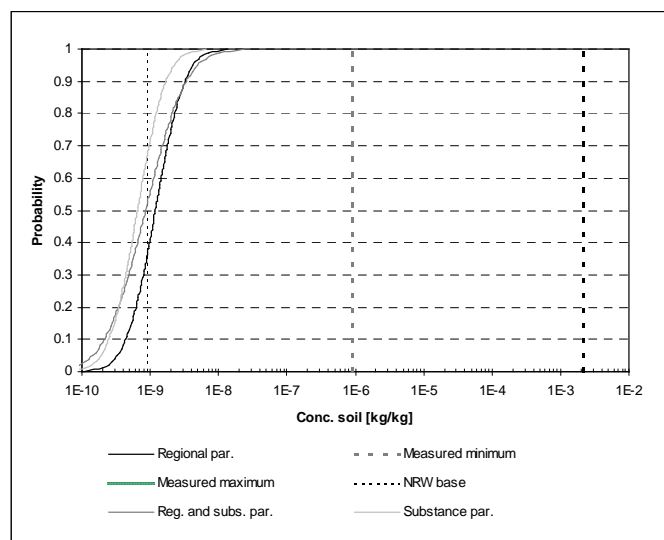


Figure 84 Cumulative distributions of LAS-concentrations in soil with fitted means.