UNIVERSITÄT OSNABRÜCK

Beiträge des Instituts für Umweltsystemforschung der Universität Osnabrück

Herausgeber: Prof. Dr. Michael Matthies

Beitrag Nr. 24

Probabilistic Exposure Assessment

Parameter Uncertainties and their Effects on Model Output

Kai Leßmann

November 2002

USF Institut für Umweltsystemforschung Universität Osnabrück

ISSN-Nr. 1433-3805

Beiträge des Instituts für Umweltsystemforschung der Universität Osnabrück

ISSN 1433-3805

Herausgeber

Prof. Dr. Michael Matthies
Universität Osnabrück
Institut für Umweltsystemforschung
Artilleriestr. 34

D-49069 Osnabrück

Tel. 0541/969-2575
Fax. 0541/969-2599

E-Mail: matthies@uos.de
http://www.usf.uni-osnabrueck.de

Abstract

In probabilistic exposure assessment, parameter uncertainties are modeled by probability distributions. This thesis investigates how parameterization strategies for input distributions affect the computed uncertainty. Monte-Carlo simulations of eleven representative chemicals were performed with the multi-media model SimpleBox, part of the European Union System for the Evaluation of Substances (EUSES). This study focuses on its physico-chemical parameters describing aqueous solubility, vapor pressure, and octanol-water partitioning of the substance. A reliable data basis for their parameterization was selected from available literature by applying five selection criteria. The resulting data are scarce and broadly distributed, frequently ranging over several orders of magnitude with an average of less than six values per property.

The influence of the choice of input distribution types was assessed by performing simulations with uniform, triangular, and lognormal distributions, parameterized with identical mean and variance. In particular, the impact on computed mean, variance and distributional shape were assessed. Plots of the functional dependency between parameters and computed values enabled to understand and interpret the resulting differences. The impact on the computed variance was found to exceed the marginal effect on the computed mean by one order of magnitude. Furthermore, the computed variance mirrors the informational content of the parameter distributions, as it is assigned to the distribution types in maximum entropy theory. The uncertainty about the shape of the parameter distribution was quantified by computing an equivalent uncertainty about its location. Compared to the standard error of the mean of the data used in this study, the impact of the shape is significant. But it is marginal compared to the large deviation among values reported in literature. Hence, the choice of a distribution type is only of concern, when the uncertainty about the location is in the same order of magnitude. Effects on the shape of the computed distribution could be identified in case of near-linear functional dependencies. When functional dependencies were extremely non-linear, the distortion they imposed on the computed distributional shape harmonized the differences in parameter distributions. And the effects decreased with the number of probabilistically simulated parameters, as the computed distribution becomes approximately lognormal in agreement with the central limit theorem for multiplicative models.

When data are insufficient for statistical analysis, parameter uncertainties may be derived by expert judgment, e.g. given as default values. Four approaches of different specificity reported in literature, which use generic uncertainties, have been compared. More general approaches were representative rather than conservative in input uncertainties and simulation results. The deviation among the assumed generic coefficients of variability is mostly within the same order of magnitude. But it is large enough to conclude that there is no consensus about default uncertainties.

Four pairs of scenarios, each representing a potential way of parameterizing input distributions, have been compared and analyzed in view of results from this study. Often there was no uniform effect on the target distributions, but some general trends were found, and exceptions to them could be understood. Simulation results support the claim that

most effort should be made to determine the location of the parameter distributions as closely as possible. The lesser impact of spread and shape becomes important once the uncertainty about the location is decreased to a comparable order of magnitude. And results of generic approaches in this setting are similar to more specific approaches and are thus deemed to be sufficient.

Acknowledgements

Ich danke Prof. M. Matthies für die Aufgabenstellung und Begutachtung und Dr. J. Klasmeier für Anregungen und Begutachtung. Für die Finanzierung der Arbeit danke ich der Bayer AG und der BASF AG. Mein besonderer Dank gilt Dr. Andreas Beyer für wesentliche inhaltliche Anregungen und die Betreuung dieser Diplomarbeit.

Für Korrekturvorschläge danke ich Dominik Reusser und Claudia Richter.

Contents

List of Figures

List of Tables

Chapter 1

Introduction

Probabilistic exposure assessment is the application of probabilistic uncertainty analysis to exposure assessment as a part of chemical risk assessment. The aim of uncertainty analysis is to quantify the uncertainty about simulation results, and to identify its causes. The objective of this thesis is to investigate how parameterization strategies for input probability distributions affect the computed uncertainty.

1.1 Risk Assessment

When a new chemical is going to be produced in a member state of the European Union, or if a chemical is newly imported into a member state, the manufacturer or the importer is required to notify the concerning authorities. The authorities are in turn required to carry out an assessment of the risks of the substance to man and environment following the Technical Guidance Document of the European Commission (EC, 1996).

1.1.1 The Risk Assessment Process

Risk assessment consists of four parts: hazard identification, effects assessment, exposure assessment, and risk characterization. Results from the risk assessment are the basis for risk management, which includes drawing conclusions from the results and eventually planning actions to reduce risks. The introduction to the steps of risk assessment in the next sections follows van Leeuwen (1995).

Hazard Identification

Hazard identification seeks to identify any adverse effects that a chemical can possibly have on an exposed individual or ecosystem. It does not consider whether these hazards actually occur, i.e. it ignores the likelihood of exposure.

Effects Assessment

Effects assessment is concerned with estimating dose-response relationships, i.e. the dependency of the extent of effects that a substance has, and the dose or level of exposure. Human health risk assessment concentrates solely on possible effects on human beings. Environmental risk assessment, which is the scope of this work, deals with potential effects on ecosystems, i.e. adverse effects on communities of species in habitats exposed to toxic substances (Solomon and Takacs, 2002, p. 285).

The output of a standard effects assessment is a set of predicted no-effect concentrations (PNEC), which estimate concentrations at which individuals of a certain species are not affected by the substance. To cope with the great diversity of species in ecosystems, usually a simplified approach is taken by deriving PNEC for different environmental compartments: water, sediment, soil and air.

Exposure Assessment

In contrast, exposure assessment seeks to quantify substance concentrations in potentially affected organisms or in environmental compartments. This can either be done by collecting field data of substance concentrations, or by estimating the predicted environmental concentration (PEC) from knowledge about the substance and the environment. Multimedia exposure models are frequently used to derive PEC.

Risk Characterization

Risk characterization integrates the results of effects assessment and exposure assessment and tries to measure the likelihood and severity of adverse effects in the environmental compartments. A common approach is to combine PNEC and PEC to a risk characterization ratio (RCR) defined as the ratio PEC/PNEC, again, for each of the compartments. An RCR value significantly less than one indicates that according to the estimates, the risk of adverse effects is small, and no actions to reduce the risk are necessary. If, in contrast, the RCR exceeds one, then a substantial risk is indicated, and either action must be taken or the risk assessment process may be repeated in greater detail, hoping that the previous assessment only overestimated the risk.

1.1.2 Shortcomings of Deterministic Risk Assessment

A shortcoming of this approach is that existing uncertainties in neither the PEC nor the PNEC are explicitly considered. It is common practice to compensate for this by computing worst case scenarios on the exposure side, i.e. wherever uncertain, conservative estimates are made. On the effects side so-called uncertainty factors (extrapolation factors) are applied. For each extrapolation, e.g. between trophic levels, from laboratory to field, or from acute effects to chronic effects, the PNEC is increased by a factor, e.g. one order of magnitude for each extrapolation step. Usually extrapolation factors range from 10 to 10 000 (van Leeuwen, 1995).

Such procedures are not consistent with the scientific method[1] and may often lead to unrealistically large upper limits (Seiler and Alvarez, 1996). RCR derived in such a fashion only indicate whether the threshold value of one is exceeded. The amount by which it is exceeded (or stays below) cannot be interpreted when the dose-response relationship is unknown, which frequently is the case (Jager et al., 2001).[2] It is then only possible to compare chemicals in a relative risk ranking (van Leeuwen, 1995). However Jager et al. (2001) show that such a ranking may fail when uncertainties of the PEC/PNEC ratios differ.

1.1.3 Probabilistic Risk Assessment

Jager et al. (2001) suggest several possible improvements of the status quo (deterministic risk assessment). Ideally, both sides of the risk assessment procedure should be treated probabilistically. In ecological effects assessment this would mean producing explicit dose-response relationships. A dose-response relationship could be the response of one species as a function of the substance concentration it is exposed to (dose), or a species sensitivity distributions (SSD). An SSD describes the variation of effects of a chemical over a set of species as a statistical distribution, e.g. what percentage of the species is affected given a certain concentration of the chemical. SSD are commonly derived from laboratory testing using selected representative species. On the exposure side, a probabilistic exposure assessment would produce not a deterministic PEC, but a probability distribution of PEC. Same as the deterministic PEC, such a distribution can either be derived from field measurements, or from a quantitative uncertainty analysis.

In quantitative uncertainty analysis, uncertainties are attached to all inputs of a model. These uncertainties are then propagated through the model yielding uncertainties for every output value of the model. In probabilistic uncertainty analysis, uncertainties are represented by probability distributions. There are analytical as well as numerical methods to propagate input distributions (or characteristics of these) through the model, e.g. analytical variance propagation (Slob, 1994), first-order analytical methods (MacLeod et al., 2002) or the first-order reliability method (Hamed and Bedient, 1997). A comprehensive overview can be found in Cullen and Frey (1999, Ch. 7). Among the numerical methods, Monte-Carlo simulation has become the most commonly used (Cullen and Frey, 1999, p. 196).

In the risk characterization step, SSD and the PEC distribution may then be combined into a joint distribution of effects. Results of the probabilistic approach can be presented in statements such as "there is a x percent chance of affecting y percent of the species" or

[1] The scientific method applied to making models with predictive capabilities is summarized in Seiler and Alvarez (2001). Five preconditions are listed that make hypothesis testing "the final and decisive step of the scientific method." The five preconditions are sufficiency of the information (data set) used (e.g. to determine model parameters), replicability and comprehensiveness of the data set, sound logic in the way the model is derived, and honesty in the sense that arguments for and against the model should be considered. Only then is verification of a model or hypothesis meaningful.

[2] Even though PNEC or other effective concentrations (EC) are often derived from parts of a dose-response relationship, additional information about the dose-response relationship is rarely published (Steinbach, 1999, p. 8).

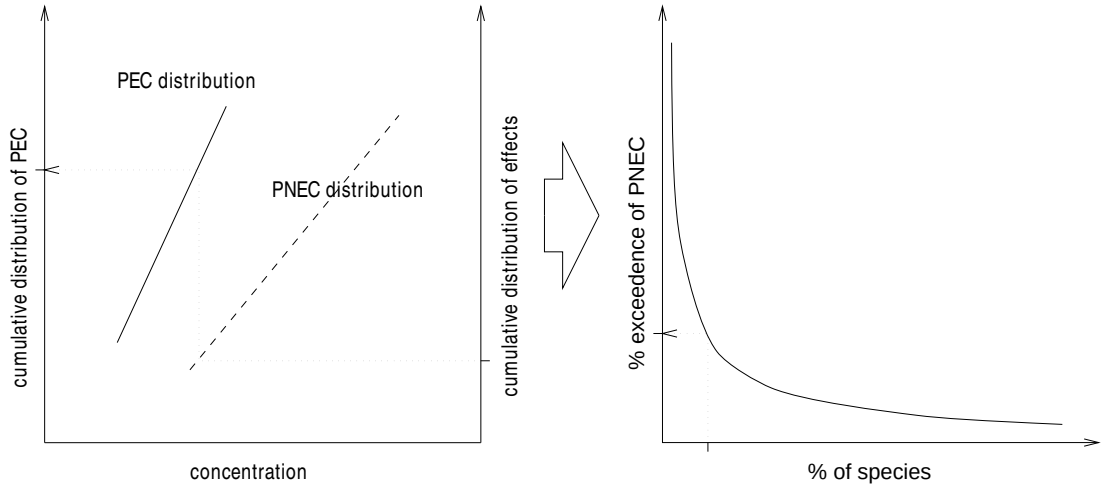

Figure 1.1: Distribution of effects.
Distribution of effects as a result of probabilistic risk assessment, according to Steinbach (1999) and Solomon and Takacs (2002). The effects assessment produces a PNEC distribution, and the exposure assessment produces a probability distribution of PEC. Both are integrated into a distribution of effects, i.e. the exceedence of the PNEC as a function of the percentage of species that are affected.

more generally, as exceedence plots giving the exceedence of the PNEC for any percentage of species (Figure 1.1).

In contrast to deterministic risk assessment, probabilistic risk assessment makes the uncertainties explicit. Uncertainties are dealt with in a transparent and more scientific way, and more information about the risk is passed on. Therefore, a sounder basis for decision making is provided. However, in the risk characterization step, two distributions of significantly different nature need to be combined. While the simulation that produces the PEC distribution may be adapted to miscellaneous specific situations, SSD are derived in laboratory testing. They are neither specific nor can they be adapted to new situations. Uncertainties of extrapolating a laboratory SSD to the field may be accounted for by applying extrapolation factors, yet regional specifics are still ignored.

As an alternative to treating both sides probabilistically, Jager et al. (1997) suggest to leave the effects assessment as it is, and improve only exposure assessment by utilization of probabilistic uncertainty analysis. The PEC distribution is then compared with the "best-guess" PNEC from deterministic assessment, and a probability to exceed this PNEC characterizes the risk. While the advantage of this option is that it is easy to perform and more acceptable for decision makers (Jager et al., 2001), it should be noted that variance and uncertainty about a toxicological factor (i.e. effects assessment) frequently dominate the overall variance (Cullen and Frey, 1999, p. 2), hence the larger share of the overall uncertainty may be ignored.

The following sections provide a short introduction to parameter uncertainties.

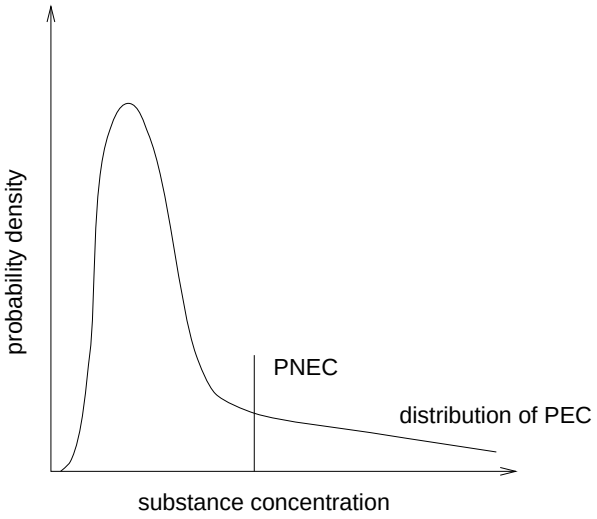

Figure 1.2: Distribution of PEC.
When only a fixed PNEC is available, a probability to exceed the PNEC can be derived by comparing the PNEC with results from probabilistic exposure assessment, namely the probability distribution of the substance concentrations.

1.2 Parameter Uncertainty

Uncertainty of the model output is defined as the possible error or actual variability of the output value as a result of parameter uncertainty or model simplifications (Beyer and Matthies, 2001). Berding et al. (2000) add one more cause of uncertainty to this list when they distinguish three kinds of uncertainty: model uncertainty, scenario uncertainty and parameter uncertainty.

- Model uncertainty (also structural uncertainty) refers to uncertainties about the accuracy of the model, which are caused either by lack of knowledge about the modeled system or by necessary simplifications. Model uncertainty can only be assessed qualitatively, and is addressed by checking model structure, assumptions and its mathematics for correctness.
- Scenario uncertainty occurs when the available data are incomplete for properly parameterizing the model.
- Parameter uncertainty subsumes uncertainties in input parameters, e.g. due to given variability of the quantity, or imperfect measurement of it. The latter two may be subject to quantitative analysis.

Within quantitative uncertainty analysis, i.e. the analysis of parameter uncertainty, two types of uncertainty are frequently distinguished: uncertainty due to lack of knowledge, also referred to as true uncertainty, and variability of the quantity.

1.2.1 Variability, True Uncertainty, and Measurement Error

Variability refers to given heterogeneity or diversity among individuals or in a property (Anderson and Hattis, 1999). It causes uncertainty in the model output, when its dimension is not explicit in the model, e.g. when averages over space, time, or temperature are taken. Variability is not reducible through further study (USEPA, 1997). True uncertainty, sometimes simply referred to as uncertainty, stems from partial ignorance or lack of perfect knowledge (Anderson and Hattis, 1999). It is often a result of measurement errors.

The error of a measurement has two complementary sources, random error and systematic error (Seiler and Alvarez, 1995). Random error is random deviation from the true value. It is assumed to be normally distributed about the true values. Hence, the true value can be approximated by the mean of the measurements, and its uncertainty may theoretically be reduced by conducting additional measurements. The random error of a measurement is usually reported along with the measured value. Systematic error affects all measurements in the same manner, and can therefore not be decreased by further measurements. Causes for systematic errors are numerous, e.g. poorly calibrated measuring equipment. In fact, any error that is not random is systematic by definition.

1.2.2 Uncertainty of Literature Values

Reported values from measurements of physico-chemical properties performed in different laboratories frequently differ by several orders of magnitude (Mackay et al., 1999). It is known that some properties are extremely difficult to determine at certain ranges of their values, due to the physico-chemical behavior of the substance that they imply. One example is the measurement of a large octanol-water partitioning coefficient (K_{ow}), which describes the tendency of a substance to be lipophilic or hydrophilic, where large values of the K_{ow} indicate hydrophilicity (partitioning coefficients are introduced in Section 2.2). The measurement of the octanol-water partitioning coefficient of a very hydrophilic substance (K_{ow} larger than 10^6, i.e. log K_{ow} greater 6) "requires meticulous technique" (Mackay et al., 1999). To give one example, the nine reported measurements of log K_{ow} of octachloro-dibenzo-*p*-dioxin considered in this study range from 8 to 13. Deviations of such a magnitude are usually beyond the random error estimated for each measurement, and may therefore be assumed to be due to systematic errors.

1.2.3 Distinguishing Uncertainty and Variability

When performing probabilistic risk assessment, it is recommended to distinguish between uncertainty and variability (USEPA, 1997; Anderson and Hattis, 1999). This can be done by performing so-called two-dimensional simulations (Cullen and Frey, 1999, p. 217). A simple approach to perform two-dimensional simulations is to separate "variable" from "uncertain" parameters (Decisioneering Inc., 1999).

Two-dimensional simulation is referred to as double looping because the variability in parameters is simulated in an inner loop, surrounded by an outer loop that simulates

the true uncertainty of parameters. In each repetition of the outer loop, a set of values of the "uncertain" parameters is determined according to their distributions. Then the inner loop is run to determine the variability of the model output by considering the fixed set of values from the outer loop, and the distributions of the "variable" parameters. Hence the result of a two-dimensional simulations is a set of output distributions, each representing the variability of the output value for a specific choice of values for the uncertain parameters. Summary statistics can be applied to the result to estimate its uncertainty, e.g. the deviation among the means and variances of the output distributions.

However in many cases parameters are both variable and uncertain to an extent (Cullen and Frey, 1999, p. 225), take for example physico-chemical substance properties on the one hand, and body weight on the other hand.

Physico-chemical substance properties are often quite uncertain when they are difficult to measure (Mackay et al., 1999), thus one could categorize them as "uncertain" parameters. But they are also variable, e.g. they vary with temperature (Beyer et al., 2002). When an average temperature is assumed (e.g. in SimpleBox), then the temperature dependency adds variability to the physico-chemical substance parameters. Body weight is a quantity that can easily be precisely measured, of course it has a great variability over the individuals of a population. Hence body weight may be thought to be a purely "variable" quantity. But when the variability of body weight is estimated from a collected measurement data, its representativeness and the limited number of the data make the estimated mean, variance, and shape of the body weight distribution uncertain.

Hoffmann and Hammonds (1994) suggest a more sophisticated approach to two-dimensional simulation that allows to deal with parameters that are both variable and uncertain. They suggest to derive parameter distributions that only account for the variability, e.g. by parameterizing a distribution with an estimated mean and an estimated variance. The uncertainty of the parameter can then be modeled by estimating the uncertainties of the distribution parameters of the variability distribution, i.e. the mean and the variance. This way, performing a two-dimensional uncertainty analysis is not merely a different simulation technique to be applied to the same data. It is a different approach, which has different data needs and requires structural changes in the input module of the simulation model.

Hoffmann and Hammonds (1994) also suggest a criterion to determine whether or not two-dimensional simulation is necessary. They consider the *endpoint* of the simulation, i.e. the computed values that will be subject to interpretation, and distinguish two cases for endpoints:

1. fixed but unknown values
2. unknown distributions of values

If the desired endpoint is the distribution of values over e.g. a population, then variability needs to be treated as such, and in the presence of uncertainty, two-dimensional simulation becomes necessary. When the endpoint is assumed to be a fixed value, then the computed distribution represents the uncertainty of the value, and all inputs may be regarded as uncertainty only.

1.3 Parameterization of Probability Distributions

The interface of parameter uncertainty and probabilistic assessment is the selection and parameterization of probability distributions, which correspond to the uncertainty about parameters. Parameter uncertainty arises from true variability of the parameter and true uncertainty, i.e. lack of knowledge, about the correct value of the parameter. Both, variability and true uncertainty, are quantified by assessing the available information on a parameter. Usually, there are different kinds of information:

- measurement data
- theoretical considerations
- expert judgment
- defaults

Corresponding to these types, there are methods of utilizing the information. If a sufficient, representative number of measurement data are available, they can be subjected to statistical analysis. Distribution types can be determined by fitting a distribution to the data, or rejected by applying a goodness-of-fit test. Characteristics of distribution functions can be estimated from a data set (Vose, 2000, Ch. 7+9). In particular the selection of a distribution type can be aided by theoretical considerations, e.g. any distribution ranging over negative values may be excluded for non-negative properties.

When the data basis is insufficient to apply statistical methods, expert judgment may be utilized. According to NCRP (1996) an *expert* has "(1) training and experience in the subject area resulting in superior knowledge in the field, (2) access to relevant information, (3) an ability to process and effectively use the information, and (4) is recognized by his or her peers or those conducting the study as qualified to provide judgments about assumptions, models, and model parameters at the level of detail required." There are various possible ways of utilizing expert judgment and combining it with other information. Expert judgment can be exercised in selecting a representative data basis for further statistical analysis. More weight is put into expert judgment by adopting a distribution type suggested by experts, or selecting one or more characteristic of the distribution, e.g. location and spread, according to an expert. Finally, entire probability distributions can be elicitated from experts (Vose, 2000, Ch. 10). As the main drawback, expert judgment is more subjective compared to statistical analysis, and tends to be less transparent.

The adoption of default values is closely related to expert judgment because defaults are often selected by experts. But they may still heavily rely on data, i.e. in case of default distributions for mainly variable parameters such as body weight (Finley et al., 1994). When defaults are commonly used in studies, their comparability is greatly enhanced. Furthermore, the arduous task of defining distributions from expert opinion, which also depends on the availability of experts, does not need to be repeated redundantly.

> "Clearly, there is a need for a default set of agreed parameter distributions for chemical risk assessment." (Jager et al., 2001)

1.4 Influence of the Distribution Characteristics

The aim of conducting exposure assessment is to derive PEC that are as precise and accurate as possible. The main interest in performing a probabilistic exposure assessment is to incorporate the uncertainty in the estimation of the PEC. The quality of probabilistic analysis depends on the quality of its input data.

Berding et al. (2000) stress, that results from Monte-Carlo analysis are very sensitive for badly chosen parameter distributions because input distributions directly affect the result via Monte-Carlo simulation. Bukowski et al. (1995) studied the relative importance of the choice of input distributions versus the inclusion or exclusion of correlation between parameters. They conclude that the impact of the choice of input distributions is larger than the impact of inclusion or exclusion of parameter correlation. Moreover they note that some combinations of input distribution types resulted in "remarkedly wider distributions" than others. Binkowitz and Wartenberg (2001) performed a literature review of procedures used to derive exposure parameter distributions from data. They report that the choices for input distributions made by investigators may substantially affect the output of their analyses.

Hence in any Monte-Carlo analysis, the sensitivity of the the findings and conclusions to changes in the distributional shape of the parameters should be tested (USEPA, 1997). However, this is rarely done by any author in risk assessment (Binkowitz and Wartenberg, 2001).

This study addresses the question, what the effects of different choices of parameter distributions for partioning data are, and how they compare to other uncertainties in exposure assessment. In particular, the following aspects are investigated:

- How large are the uncertainties based on literature values in case of physico-chemical properties of a set of representative substances?
- How do the main characteristics of parameter distributions affect the computed distributions of PEC? What are the effects of changes in location, spread and shape of the input distributions on location, spread and shape of the output distribution?
- How do the impacts of changes in the different characteristics compare to each other?
- What options for parameterizing input distributions for probabilistic analysis are there in situations of scarce data?

Chapter 2

Data

In probabilistic uncertainty analysis parameters are modeled by probability distributions. This study deals with the uncertainty of physico-chemical properties of chemicals due to a lack of knowledge of the true values. Values of octanol-water partitioning coefficients, aqueous solubility, and vapor pressure reported in literature often vary over several orders of magnitude. Data was collected to provide a basis to parameterize distributions to reflect these uncertainties.

2.1 Substances

In this study, eleven exemplary substances are simulated. The list of substances is taken from Berding et al. (2000). According to Berding et al. these substances are representative for a large number of classes of substances. Properties that were considered in the selection of the substances are hydrophilicity, aqueous solubility, volatility, occurrence in the environment, and the extent of use and degradability (Berding, 2000, p. 23). The selected substances are: the five polychlorinated dibenzo-*p*-dioxins with the highest concentrations measured in the environment, i.e. 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), 1,2,3,4,7-pentachloro-dibenzo-*p*-dioxin (PeCDD), 1,2,3,4,7,8-hexachloro-dibenzo-*p*-dioxin (HxCDD), 1,2,3,4,6,7,8-heptachloro-dibenzo-*p*-dioxin (HpCDD), and octachloro-dibenzo-*p*-dioxin (OCDD), di-(2-ethylhexyl)phthalate (DEHP) being the phthalate produced in the vastest quantities, the polycyclic musk fragrance 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-[g]-2-benzopyrane (HHCB), the typical air pollutants 1,2-dichloroethane (EDC) and benzene, linear alkyl benzene sulfonates (LAS) as a typical water pollutant, and ethylendiaminetetra acetic acid (EDTA) which is similar to LAS yet not as degradable in the environment. Table 2.1 lists all substance abbreviations used, and the corresponding full substance names.

2.2 Parameters

Among the parameters concerning the fate of a substance in the environment, partitioning coefficients are of major importance. Partitioning coefficients between two media, medium

Table 2.1: List of Substances. Abbreviations and full names of the chemicals selected for this study.

Abbr.	Substance Name
TCDD	2,3,7,8-tetrachlorodibenzo-*p*-dioxin
PeCDD	1,2,3,4,7-pentachloro-dibenzo-*p*-dioxin
HxCDD	1,2,3,4,7,8-hexachloro-dibenzo-*p*-dioxin
HpCDD	1,2,3,4,6,7,8-heptachloro-dibenzo-*p*-dioxin
OCDD	octachloro-dibenzo-*p*-dioxin
DEHP	di-(2-ethylhexyl)phthalate
HHCB	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-[g]-2-benzopyrane
EDC	1,2-dichloroethane
benzene	benzene
LAS	linear alkyl benzene sulfonates
EDTA	ethylendiaminetetra acetic acid

i and medium j say, are defined as the ratio of substance concentrations at thermodynamic equilibrium in these media, $K_{ij} = C_i/C_j$. It follows, that an unknown partitioning coefficient can be calculated from two others, e.g. using the equation $K_{i1} = K_{ij}/K_{1j}$ (Trapp and Matthies, 1998, p. 45). Figure 2.1 illustrates how to compute the K_{OW} from K_{AW} and K_{OA}. Hence, only a subset of three partitioning coefficients out of six partitioning coefficients (between the four phases gas (A), aqueous dissolved (W), organic dissolved (O), and pure substance) is needed. Moreover, partitioning coefficients can be computed from solubilities of the substance in media, i.e. solubility in water (aqueous solubility) and vapor pressure, which is closely related to solubility in air[1] (Beyer et al., 2002). Here, the octanol-water partitioning coefficient K_{OW}, vapor pressure P^0, and aqueous solubility S_W are selected. Other partitioning coefficient that are needed can be derived from these.

In addition to the partitioning coefficients, the mode of entry of a substance and its degradation in the environmental compartments have an important impact on the environmental fate of a substance (Berding et al., 2000). In SimpleBox, substances may be emitted into air, industrial soil, surface water, and waste water. The mode of entry is modeled by two groups of four parameters, which describe emission of the substance on regional and continental scale. Values from Berding et al. (2000) are used for these parameters, summary tables are given in the appendix (Tables B.1 and B.2). Data for degradation rates is too scarce to derive probability distributions (Berding et al., 2000, p. 224). Degradation rates are therefore neglected in the probabilistic analysis in this study, i.e. fixed values from Berding et al. (2000) are assumed.

[1]Solubility in air and vapor pressure differ by a factor of temperature times universal gas constant.

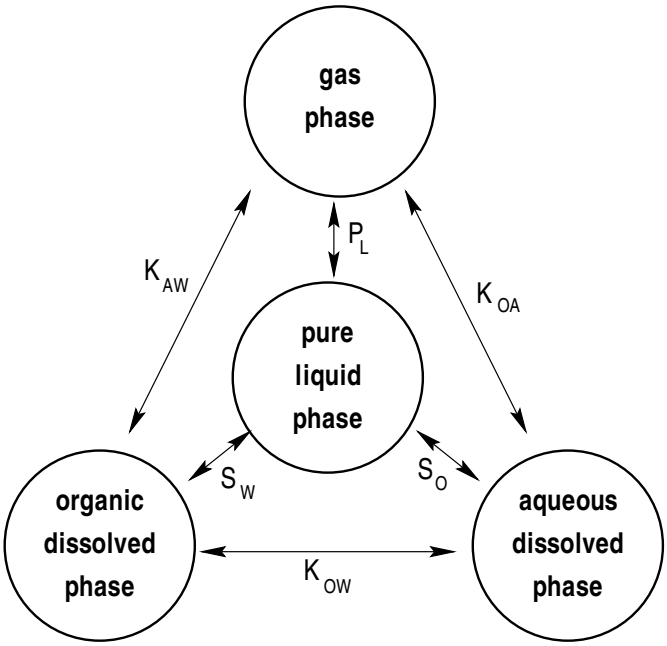

Figure 2.1: Phases and partitioning.
Phases and partitioning coefficients (Illustration adapted from Wania (2002)). An unknown partitioning coefficient can be calculated from two others, here the K_{OW} is computed from from K_{AW} and K_{OA} as $K_{OW} = K_{AW} \times K_{OA}$. S_X denotes solubility in solvent X; P_L is the vapor pressure over liquid phase.

2.3 Sources of Substance Data

Most data are taken from two sources: the handbook of physico-chemical properties by Mackay et al. (1999) and a compilation article by Shiu and Ma (2000). Numerous original articles referenced in these works were consulted to resolve doubts, e.g. in cases where values cited in Mackay et al. (1999) and Shiu and Ma (2000) were contradicting.

It would be preferable to extend the literature search to other handbooks, or even all the original articles referenced in handbooks and compilations. However, necessary resources and time were lacking within this study. Moreover the aim of this work is not to compute precise results, but to discuss the parameter distributions in general, and their parameterization and the sensitivity of their shapes in particular.

2.4 Selecting a Data Basis

The aim of the handbook of Mackay et al. (1999) is to present sufficient experimental data and lists of citations to enable interpretation of the data and the selection of a "best" or "most likely" value. Mackay et al. note that not all reported values are equally reliable. References to the original publication of a measurement in peer reviewed scientific literature are rated over e.g. calculated values, or values from correlations. This implies that only a selection of values from handbooks and compilations ought to be used. Results from Pontolillo and Eganhouse (2001) stress this point.

Pontolillo and Eganhouse (2001) evaluated the quality of available literature values for aqueous solubility and octanol-water partitioning coefficient in case of DDT and DDE. "Egregious errors in reported data and references" were found. In addition to data and citation errors, Pontolillo and Eganhouse point out the vast extent of data duplication. They note that in particular handbooks and compilations suffer from this.

It follows from Pontolillo and Eganhouse (2001) that data taken from handbooks or compilations should always be verified by obtaining the original references. The foremost value of handbooks and compilations would hence be that they provide lists of references. In this study, original references were obtained and used as much as possible.

The following priorities in data selection are recommended in OECD (2002): measured data following OECD guidelines, measured data from other "acceptable" methods, data from quantitative structure activity relationship (QSAR) analysis, and finally default values and expert judgment.

Criteria of Selection Applied in this Study

A subset of the available data is selected for use in this study. The aim is to select only data that are considered reliable. The following set of criteria was derived and applied to the data from Mackay et al. (1999) and Shiu and Ma (2000).

1. *Age of datum:* Data of an older date than 1980 was excluded.
2. *Original references:* Only values reported with reference to the original publication of the datum are adopted.
3. *Measured data:* Only data from experimental measurements are adopted. Values e.g. from calculation, correlation, or summarizing values are rejected.
4. *Temperature of measurement:* Measurements should have been conducted at a temperature of 25°C, however temperatures in the range from 20°C to 30°C were tolerated.
5. *Method of determination:* In rare cases values were rejected because of the method of determination.

Over time, methods of determination have improved, hence values stemming from old experiments may be less precise than values from more recent measurements. It would hence be desirable to assess the precision and consistency[2] of all measurement methods, and to select the measured values accordingly. In lieu of the laborious assessment of all measurement methods, the pragmatic approach of a cut-off date was chosen. The year 1980 was somewhat arbitrarily selected. The cut-off applied to all the dioxin data only in

[2]If the selected data are subjected to statistical analysis, it is required that a homogeneous universe is sampled. Strictly speaking, the measurements of a substance property are only a representative sample of a homogeneous universe if the same measurement method is applied. It is hence desirable that only values are selected that are consistent in the sense that their measurement methods are comparable in accuracy and precision.

case of one value (one K_{OW} value in case of TCDD). The greatest share of values (22 of 79 values, or 28 percent) was omitted due to the cut-off in case of benzene S_W.[3] According to Pontolillo and Eganhouse (2001) the scatter in the reported values for DDT/DDE aqueous solubilities and octanol-water partitioning coefficients has not decreased with time, i.e. they found no indication of the above assumption. However, the four substance/property combinations considered in that study do not suffice to draw general conclusions.

In addition to values reported with references to the original publication, Mackay et al. (1999) reports values quoted from other secondary sources. The available resources and time constraints did not allow to verify these data. They were therefore omitted. As mentioned above, it is necessary to exercise great caution with such citations (Pontolillo and Eganhouse, 2001).

Calculated values are not necessarily less precise than data from experimental measurements. For example values from a regression and interpolation of many precisely measured values of similar chemicals may well possess great precision. Since it is not in the scope of this work to assess the computational methods and their data bases, values from calculations, correlations, or estimations were neglected. According to Pontolillo and Eganhouse (2001) the accuracy and precision of such computational methods is questionable when the data used in their model development and validation is of unknown reliability, as is the case with much of the data they encountered. Furthermore, when calculated values depend on a data basis of measured values, they will be correlated to this data basis. This leads to implicitly using the same measured values twice, giving the data basis a bias towards these values. Selection criterion 3 is in agreement with Shiu and Ma (2000), who list only experimental values in their tables of vapor pressure and aqueous solubility values. Shiu and Ma "believe that it is preferable" to rely on experimental data only.

The method of determination served as a criterion in the works of Shiu and Mackay (1986), Mackay et al. (1999), and USEPA (1994) (according to McKone et al. (1995, p. 10)). Detailed knowledge of the experimental methods is required in order to discriminate the reliability of measured values. In this study, this criterion was only applied in rare cases.

Additional and Alternative Criteria

Some of the studies cited applied still other criteria as the ones conducted here. They are listed in the following.

- Mackay et al. (1999) used information derived from QSAR analyses performed for groups of substances when selecting values to recommend as "best values" as a selection criterion.
- In the same context, Mackay et al. (1999) considered "the perception of the objectives of the authors [...] as an indication of the need of the authors for accurate values." As mentioned above, original references were not consulted for all values, hence no assumptions about the author's objectives could be made.

[3] In case of benzene, 6 of 82 K_{OW} and 22 of 79 S_W were omitted. Likewise, 3 of 42 DEHP K_{OW}, 6 of 32 S_W, and 5 of 23 P^0 and 3 of 28 EDC K_{OW}, 2 of 52 S_W, and 6 of 28 P^0 were omitted.

- Shiu et al. (1988) exploited thermodynamic consistency among the physico-chemical properties as a criterion. Similarly, Beyer et al. (2002) used thermodynamic relationships to derive a set of estimates for partitioning parameters such that these estimates are minimally divergent from the experimental values, yet consistent in the sense of thermodynamics. The relationships from thermodynamics could be exploited here as well to extend the data basis, by converting measurements of related properties to one of the three physico-chemical properties of interest in this study. It was refrained from doing so, because a significant enhancement was not expected and hence the conclusions of this study are not affected by this.

- USEPA (1994) took the reliability of the laboratory which reported the value into account when selecting a data basis to estimate nominal values as well as their uncertainties (as in McKone et al., 1995).

2.5 Resulting Data Set

Application of the above criteria to the data sources Mackay et al. (1999) and Shiu and Ma (2000) lead to a rather small data basis. The number of measurements per physico-chemical property and substance ranges from one to ten. In the exceptional case of octanol-water partitioning coefficient of benzene, there are 22 measurements. 75 percent of the parameters have a data basis of 2–7 values (Figure 2.2).

Table 2.2 shows the numbers of values available in the literature consulted along with the number of values that were selected. From Table 2.2 and Figure 2.2 it is obvious, that the data basis is insufficient for parameter estimation in most cases. Estimation of the mean generally needs to be based on at least 5 values, estimation of the variance requires more than 20 values (see discussion of Tukey's rule in Section 3.1). Only in about half the cases, a mean can be estimated. One should refrain from estimating the variance of any parameter, except the benzene octanol-water partitioning coefficient.

Table 2.2: Numbers of selected values.
Table of data availability. The two numbers given are the number of selected values for each parameter and the total number of values in the consulted literature before selection criteria were applied.

	K_{ow}	S_w	P^0
TCDD	4/28	4/13	7/17
PeCDD	8/17	3/10	1/3
HxCDD	7/19	3/10	2/8
HpCDD	7/23	2/12	2/6
OCDD	9/40	5/13	3/12
DEHP	10/42	6/32	4/23
EDC	5/28	7/52	2/28
benzene	22/82	9/79	4/14

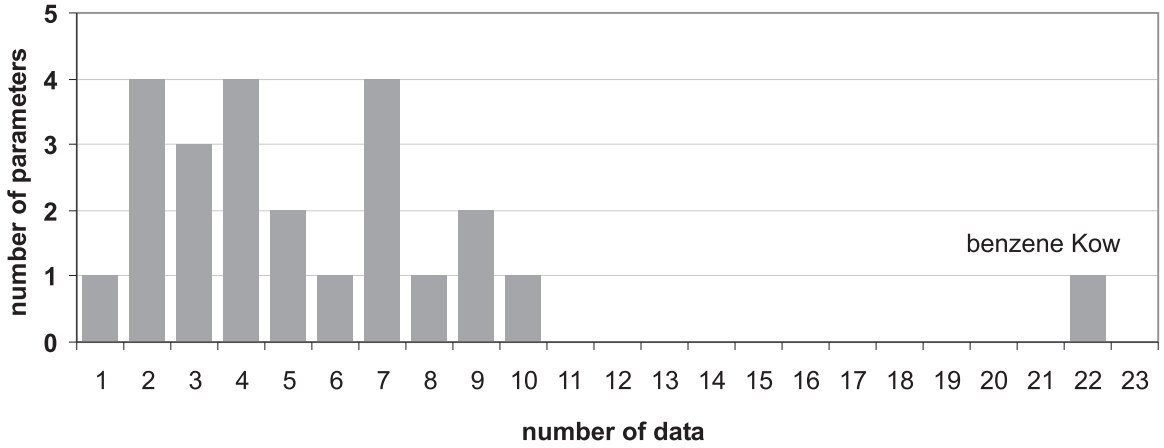

Figure 2.2: Numbers of measurement values.
Histogram of the number of data in the selected data base for each of three physico-chemical parameters and eight substances.

However Monte-Carlo analysis requires probability distributions for the most important input parameters. Scarce data bases are a problem frequently encountered in probabilistic uncertainty analysis. When information in form of data does not merit statistical analysis, it may still be possible to apply methods utilizing additional information, such as expert opinion.

Table 2.3: Summary of parameter means.
Summary of "best estimates" of parameter values. Means estimated in Berding et al. (2000) and in this work, and *selected values* from Mackay et al. (1999) are shown. In the last column, the standard deviation of the mean from this study is given. It is computed from the estimate of the variance, hence the estimates are not very reliable for parameters with few measurements.

Substance	Parameter	*selected value*	*berding* $\bar{x}$	Lessmann $\bar{x}$	$s_{\bar{x}}$ [%]
	S_w [mg/L]	$1.90\text{E}-05$	$1.65\text{E}-04$	$8.92\text{E}-05$	85
TCDD	P^0 [Pa]	$2.00\text{E}-07$	$1.24\text{E}-05$	$7.84\text{E}-07$	79
	K_{ow}	$6.31\text{E}+06$	$3.08\text{E}+07$	$2.17\text{E}+08$	97
	S_w [mg/L]	$1.20\text{E}-04$	$1.18\text{E}-03$	$1.26\text{E}-04$	16
PeCDD	P^0 [Pa]	$5.80\text{E}-08$	$6.96\text{E}-07$	$1.00\text{E}-06$	
	K_{ow}	$2.50\text{E}+07$	$2.84\text{E}+09$	$3.20\text{E}+09$	41
	S_w [mg/L]	$4.40\text{E}-06$	$8.09\text{E}-06$	$5.52\text{E}-06$	11
HxCDD	P^0 [Pa]	$5.10\text{E}-09$	$1.71\text{E}-05$	$1.61\text{E}-05$	98
	K_{ow}	$6.31\text{E}+07$	$1.40\text{E}+10$	$2.39\text{E}+10$	41
	S_w [mg/L]	$2.40\text{E}-06$	$1.12\text{E}-04$	$2.48\text{E}-06$	3
HpCDD	P^0 [Pa]	$7.50\text{E}-10$	$1.71\text{E}-06$	$4.50\text{E}-06$	99
	K_{ow}	$1.00\text{E}+08$	$1.18\text{E}+11$	$3.09\text{E}+11$	44
	S_w [mg/L]	$7.40\text{E}-08$	$1.56\text{E}-05$	$3.65\text{E}-05$	98
OCDD	P^0 [Pa]	$1.10\text{E}-10$	$6.20\text{E}-06$	$3.82\text{E}-06$	67
	K_{ow}	$1.59\text{E}+08$	$8.08\text{E}+11$	$2.06\text{E}+12$	66
	S_w [mg/L]	$2.90\text{E}-02$	$8.65\text{E}+00$	$3.23\text{E}-01$	23
DEHP	P^0 [Pa]	$1.90\text{E}-03$	$2.55\text{E}-04$	$2.25\text{E}-04$	94
	K_{ow}	$3.02\text{E}+07$	$3.51\text{E}+08$	$1.09\text{E}+08$	71
	S_w [mg/L]	$8.60\text{E}+03$	$8.61\text{E}+03$	$8.16\text{E}+03$	2
EDC	P^0 [Pa]	$1.13\text{E}+04$	$1.04\text{E}+04$	$1.05\text{E}+04$	0
	K_{ow}	$2.88\text{E}+01$	$3.02\text{E}+01$	$3.54\text{E}+01$	16
	S_w [mg/L]	$1.76\text{E}+03$	$1.77\text{E}+03$	$1.70\text{E}+03$	2
benzene	P^0 [Pa]	$1.27\text{E}+04$	$1.26\text{E}+04$	$1.26\text{E}+04$	2
	K_{ow}	$1.32\text{E}+02$	$1.52\text{E}+02$	$1.63\text{E}+02$	7
	S_w [mg/L]	$1.10\text{E}+03$	$1.10\text{E}+03$		
LAS	P^0 [Pa]	$1.00\text{E}-06$	$1.00\text{E}-06$		
	K_{ow}	$9.12\text{E}+01$	$9.12\text{E}+01$		
	S_w [mg/L]	$5.00\text{E}+02$	$5.00\text{E}+02$		
EDTA	P^0 [Pa]	$1.00\text{E}-06$	$1.00\text{E}-06$		
	log K_{ow}	$-3.34\text{E}+00$			

Chapter 3

Methods

When performing uncertainty analysis using Monte-Carlo simulation, several issues need to be dealt with. For each important input parameter a probability distribution reflecting the uncertainty about the parameter needs to be determined, i.e. a distribution type and a method of parameterizing it need to be selected. Input distributions then need to be propagated through the model under consideration by Monte-Carlo simulation. In this chapter, the necessary methods in probability theory, parameter estimation, and Monte-Carlo simulation, and the model under consideration are presented.

3.1 Terms from Probability Theory

In the following section, a few terms from probability theory are introduced. More detailed definitions can be found in reference works such as Sachs (1992).

The outcome of a random experiment (such as tossing a coin, determining the weight of a random person, or measuring vapor pressure of benzene) is called an event. A random variable maps events to numbers. Probability distributions assign probabilities to the values of a random variable. In the discrete case, the probability distribution may be tabulated or given through an equation. In the continuous case, the domain of a random variable is a subset of the real line, and the probability of any single value of the random variable is zero.

Probability Distributions

Probability distributions can then be defined by their probability density function (PDF), or their cumulative distribution function (CDF). The PDF assigns a probability density to each event. The probability of a range of values is defined as the integral of the PDF over that range. The CDF $F(x)$ gives the integral of the PDF $f(x)$ with the lower bound at negative infinity: $F(x) = \int_{-\infty}^{x} f(x)\,dx$. Hence $F(x)$ denotes the probability of all values less than x.

While PDF and CDF describe a probability distribution in all detail, there is a variety of summarizing measures that characterize different aspects of a distribution. For example, there are measures of the location, the spread, and the shape.

Measures of Location

The location of a distribution is its central tendency, it describes where the "middle" of the distribution is located. The distribution mean or expected value $E(X) = \int_{-\infty}^{\infty} xf(x)\,dx$ where $f(x)$ is the PDF of X, is the average value of the distribution. Given a random sample $\{x_i\}$ of a distribution, the sample mean $\bar{x} = n^{-1}\sum_{i=1}^{n} x_i$ is an unbiased[1] estimator with minimum variance.[2]

The median is the 50^{th} percentile of a distribution. A percentile marks the value before which the corresponding percentage of probability mass is located, i.e. if x_{50} is the 50^{th} percentile of a random variable X, then $F(x_{50}) = 0.5$ where F is the CDF of X. Hence it is a property of the median, that values both larger and less than the median are equally likely. The mode of a distribution is the most likely value, i.e. the value with maximum probability density.

Measures of Spread

The spread or variation of a distribution is mostly measured by variance and standard deviation, or the coefficient of variation. The variance is defined as the expected square deviation from the mean $\mathrm{Var}(X) = E[(X-\mu)^2] = \int_{-\infty}^{\infty}(x-\mu)^2 f(x)\,dx$ where μ is the mean value of X, and the standard deviation is its square root. The coefficient of variation (CV) is the ratio of standard deviation and mean ($\mathrm{CV} = \sigma/\mu$), hence giving a relative measure of the spread. The sample variance $s^2 = (n-1)^{-1}\sum_{i=1}^{n}(x-\bar{x})^2$ is a minimum variance unbiased estimator of the variance.

Measures of Shape

The shape of a distribution is distinguished after its skewness and its kurtosis. A probability distribution that is not symmetric is said to be skew. The skewness may be measured by the coefficient of skewness. When the right tail of the distribution is flatter then the left tail, the skew of the distribution is positive. The distribution is then said to be skewed to the right. Likewise, negatively skewed distributions are skewed to the left. The coefficient of kurtosis measures how much the shape of the distributions deviates from the bell shape of a normal distribution.

Central Moments

Mean, standard deviation, and coefficients of skewness and kurtosis form a consistent set of measures, because mathematically they are the first, second, third, and forth moment about the mean, respectively.

[1] An estimator is unbiased if its expected value equals the true value of the estimated parameter.

[2] The fact that there is a theoretical lower bound for the variance of an estimator can be exploited to show that some estimators cannot be bettered.

Tukey's 5^k Rule

J.W. Tukey states the following rule of thumb for estimating moments of a distribution: the calculation of the k^{th} moment ought to be based on 5^k observances, i.e. estimates of the mean should be based on more than five measurements, estimates of the variance on 25 measurements or more, and so on (as found in Sachs, 1992, p. 172). Hence when data are scarce, the use of statistics for parameterization becomes particularly problematic for higher order moments such as the variance.

3.2 Selection of Probability Distributions

In probabilistic exposure assessment, uncertainty about input parameters is represented by probability distributions assigned to the parameters. Ideally, distributions are selected and parameterized to reflect the state of knowledge of that particular parameter, in other words, the decision for a distribution type ought to utilize all available information. When only limited information is available the selected distribution type should be the "widest distribution family consistent with the state of knowledge" (USEPA, 1997). Seiler and Alvarez (1996) argue that compliance with the scientific method[3] implies that no distribution is selected "that implies a knowledge that cannot be backed up by theoretical or experimental knowledge."

3.2.1 Maximum Entropy Inference

These thoughts are also in agreement with the maximum entropy principle (MaxEnt). MaxEnt takes its name from the entropy H of a distribution, defined as

$$H = -\int p(x)\log(p(x))dx \tag{3.1}$$

where $p(x)$ is a probability density function. H is a measure of the information contained in $p(x)$. When H is maximized under constraints imposed by the available information about a parameter, a distribution of maximum uncertainty is found, which is consistent with the information given (Theil and Fiebig, 1984).

It is instructive to consider the discrete analog of equation 3.1, following Theil and Fiebig who give a comprehensive introduction to MaxEnt inference. In the discrete case, the entropy H is defined as

$$H = -\sum_{i=1}^{N} p_i \log(p_i)$$

When p_i is considered the probability that event i occurs, then the message that event i has indeed occurred contains information. The amount of information depends on its probability p_i. If event i is likely, e.g. $p_i = 0.95$, then there is little information in the message indicating its occurrence. If, however, the probability of event i is $p_i = 0.01$, say, then the message is a surprise and quite informative. Hence it is sensible to associate

[3]For a definition of the term *scientific method* as used in this work, see footnote 1 on page 17.

high informational content with low probabilities. In statistical information theory the information h of the message that an event with probability p has occurred is $h(p) = -\log(p)$. h is infinite at $p = 0$ and decreases to 0 at $p = 1$.

Furthermore, H then defines the expected information of a message, given a discrete probability distribution p_i of probabilities of all messages. The expected information relates to the uncertainty represented by the distribution as "two sides of the same coin": the higher the expected information of a message, the greater the uncertainty before the message is received.

In Table 3.1 there is a summary of maximum entropy distributions of importance in this study. Vose (2000) and Cullen and Frey (1999) introduce MaxEnt inference as a method to derive parameter distributions for probabilistic analysis.

3.2.2 Other Selection Criteria

Selection of a distribution family[4] is guided by the available information. The available information may differ in its nature, e.g. there may be empirical data, theoretical considerations, or miscellaneous kinds of expert knowledge. In many cases there will be a mixture of different information.

Statistical analysis of empirical data is the most frequently used method (Hamed and Bedient, 1997), and also preferable over eliciting expert opinion to derive subjective distributions (Morgan and Henrion, 1990). However, the required amount of data ("several thousands", Slob, 1994) are not always available.

Among the theoretical considerations to guide a selection are the bounds of the parameter, symmetry or skewness and its direction, and any mechanistic basis of the parameter, e.g. physical, chemical, or biological processes (USEPA, 1997).

Parametric and Non-Parametric Distributions

The information that is available to base the selection of a distribution family on, may differ in the amount of information as well as in the kind of information. The availability of information has an impact on which distribution families are suitable to represent parameter uncertainty. It is useful to divide probability distributions into two classes for this argument.

Probability distributions can be categorized into parametric distributions and non-parametric distributions. The terms "parametric" and "non-parametric" are taken from Vose (2000, p. 272). Parametric distributions are distributions whose shape is a mathematical function of one or more distribution parameters. Often, the shape of a parametric distribution is not intuitive nor obvious from the defining parameters. Examples of parametric distributions are normal and lognormal distributions, and the beta distribution.

[4]The term distribution family is used synonymical with the term distribution type to refer to all distributions defined by one equation and a set of variable parameters.

Table 3.1: Summary of some distribution possessing maximum entropy.

distribution	constraints[1]	source
uniform	lower and upper bound	Vose (2000); Cullen and Frey (1999)
triangular	lower and upper bound, mode	Cullen and Frey (1999)
normal[2]	mean, standard deviation	Cullen and Frey (1999)
beta	lower bound, upper bound, mean, standard deviation	Cullen and Frey (1999)

[1] Constraints are mathematical conditions implied by knowledge of certain facts, e.g. knowledge that a quantity is never negative implies a lower bound of zero.

[2] As a random variable is lognormally distributed when its logarithm is normally distributed, this implies that the lognormal distribution also has maximum entropy in this sense.

Non-parametric distributions have their shape defined by their parameters directly. An example is the uniform distribution, where the two parameters needed specify the lower and the upper bound of the probability density function.

While this classification is helpful, it should be kept in mind that the mathematical parameters of a parametric distribution may be computed from parameter sets that do have an intuitive appeal, and that shape parameters of non-parametric distributions may be computed from mathematical characteristics such as mean and standard deviation. Examples of both of these cases will occur in the following sections.

Statistical Analysis versus Expert Opinion

Whether a parametric distribution may well be used, or whether one ought to select a non-parametric distribution depends on the kind and the amount of information available. The available information determines the possible ways of parameterizing a distribution. Parametric and non-parametric distributions differ in the ease of parameterization.

In cases of large amounts of empirical data, statistical analysis may be used to estimate distribution parameters. For many parametric distributions there are estimators for their parameters, hence a parametric distribution may be parameterized using parameter estimation. This seems to be the ideal approach for numerous reasons. There is mathematical theory to back up parameterization in this case, parameterization is transparent and objective to a high degree. Notice though that there is subjective judgment even beforehand in the selection of the data, the selection of a distribution family, and the estimators of its parameters.

In cases of little or no empirical data, expert opinion is likely to be used for distribution parameterization. Here, non-parametric distributions are apt, because the shape of the distribution is directly and intuitively influenced by the parameters. It is often difficult to get the precise shape right with parametric distributions, i.e. to reflect the expert opinion in an appropriate way.

In the following sections, four distribution families are introduced and discussed that are frequently used in Monte-Carlo analysis: lognormal distribution, triangular distribution, beta distribution, and uniform distribution.

3.2.3 Lognormal Distribution

A random variable is lognormally distributed with parameters μ and σ, if its logarithm follows a normal distribution with the same parameters, i.e. μ is the mean of the logarithms and σ their standard deviation (Figure 3.1). The probability density function (PDF) of the lognormal distribution (denoted $L(\mu, \sigma)$) is given by the following equation (Aitchison and Brown, 1957):

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma x} \exp\left\{\frac{1}{2\sigma^2}(\ln x - \mu)^2\right\}$$

The mean m_L and variance s_L^2 of the lognormal distribution can be computed from the following equations (Sachs, 1992):

$$m_L = e^{\mu + \frac{\sigma^2}{2}} \tag{3.2}$$

$$s_L^2 = e^{2\mu+\sigma^2}\left(e^{\sigma^2} - 1\right) \tag{3.3}$$

The lognormal distribution is one of the most widely used distributions in probabilistic assessment (Cullen and Frey, 1999). There is a number of reasons for this.

First, there are theoretical considerations to use lognormal distributions a priori. Many quantities are restricted to non-negative values, one example are physico-chemical properties of chemicals. The range of lognormal distributions (zero to infinity) is in agreement with this, unlike i.e. the range of normal distributions (-infinity to infinity). Furthermore, it is known from the central limit theorem in probability theory that the product of a large number of random variables has lognormal distribution.[5] Therefore, if one assumes the real world to be roughly multiplicative, the central limit theorem implies that uncertainties about real world quantities will be lognormally distributed (Slob, 1994; Cullen and Frey, 1999). The maximum entropy principle (MaxEnt) provides another theoretical consideration. When the mean μ and the standard deviation σ of a random variable are known, i.e. they are given as constraints for MaxEnt inference, then the normal distribution is the widest distribution still consistent with this knowledge. In this sense, the lognormal distribution with parameters μ and σ is a MaxEnt distribution.

Secondly, there are empirical considerations. Lognormal distributions have often been found to be a good description of data from non-negative physical entities (Slob, 1994). This can also be viewed as evidence to the claim that the real world is roughly multiplicative.

Additionally, the use of lognormal distributions can make the analytical analysis of uncertainty propagation through a model easy. Slob (1994) presents how in purely multiplicative models, the variance of the target distribution can be computed via equations

[5] Originally the central limit theorem states that the distribution of sums of random variables converges to a normal distribution when the number of addents becomes large. When logarithms are taken, the sums of random variables become products of random variables and the resulting normal distribution becomes a lognormal distribution.

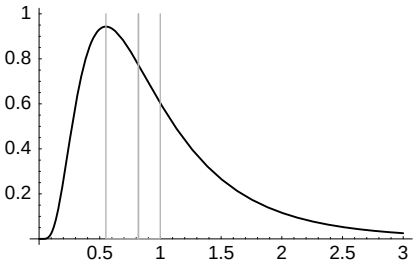

Figure 3.1: Lognormal distribution.
Lognormal distribution $L(\mu = -0.2, \sigma = 0.63)$ with mean $m_L = 1$ and standard deviation $s_L = 0.7$ (Figure 3.1). Vertical lines indicate the mode at $e^{\mu-\sigma^2}$, the median at e^{μ}, and the mean at $e^{\mu+\sigma^2}$. These measures of the distribution location are further apart when σ becomes large, their relative order stays the same.

in closed form that may easily be derived from the model equation. Another example is given in MacLeod et al. (2002). They derive a relationship between input- and output uncertainties by assuming lognormal distributions along with independence of input parameters and linear relationships of inputs and outputs.

Parameterization of the Lognormal Distribution

The lognormal distribution is defined by parameters μ and σ of the normal distribution. The mathematical nature of these parameters puts the lognormal distribution in the class of parametric distributions, apt for parameterization via parameters estimation.

The parameters μ and σ are best estimated as the arithmetic mean and arithmetic standard deviation of the logarithms of the data, $\hat{\mu} = n^{-1} \sum \ln x_i$, where x_i are the available data, and n is their number, and similarly $\hat{\sigma} = (n-1)^{-1} \sum (\ln x_i - \hat{\mu})^2$ (Aitchison and Brown, 1957). Estimators $\hat{\mu}$ and $\hat{\sigma}$ are minimum variance unbiased estimators.[6] It is possible to estimate the mean m_L and the variance s_L^2 of the original data directly. Using the Equations 3.2 and 3.3, the corresponding parameter values μ and σ could then be computed.[7] Crow and Shimizu note that "the parameter estimates resulting from the inverse transformation are biased" (Crow and Shimizu, 1988, p. 2). Therefore, this proceeding should be avoided. When estimates of the mean m_L and standard deviation s_L of the lognormal distribution are needed despite this, special estimators derived by Finney ought to be used (detailed descriptions can be found in Aitchison and Brown, 1957; Crow and Shimizu, 1988). In conclusion, the preferable way to estimate the parameters of the

[6] An estimator with little systematic error (in the sense that its expected value equals the true value of the parameter) is called *unbiased*. A minimum variance unbiased estimator is an unbiased estimator that has the smallest variance theoretically possible.

[7] This proceeding is not recommended, but since these conversions are useful in other situations, the equations are given. Parameters μ and σ of the lognormal distribution can be computed from the mean m_L and standard deviation s_L as follows:

$$\mu = -\frac{1}{2} \ln \frac{s_L^2 + m_L^2}{m_L^4} \qquad \sigma = \sqrt{2 \ln \frac{\sqrt{s_L^2 + m_L^2}}{m_L}}$$

lognormal distribution is the arithmetic mean $\hat{\mu}$ and standard deviation $\hat{\sigma}$ on logarithmic scale, or equivalently, the logarithm of the geometric mean or geometric standard deviation.[8]

More Intuitive Parameterization

Lack of intuitiveness of the parameters μ and σ is a drawback when lognormal distributions are parameterized by utilizing expert knowledge, as opposed to statistical analysis. When logarithms of the data are taken (e.g. when estimating μ and σ) their dimension is lost, which diminishes the meaning and interpretability of the parameters (Slob, 1994). Moreover location and spread of the lognormal distribution depend on both, μ and σ. This is evident from equations 3.2 and 3.3. It makes it difficult to get the shape of the distribution match any expert opinion.

To help this, Slob (1994) proposes to parameterize lognormal distributions via the median M and the coefficient of variation (CV, $\mathrm{CV} = \frac{s_L}{m_L}$) as parameters. Relationships of median and lognormal parameter μ, and CV and lognormal parameter σ are given by the following equations.

$$\mathrm{CV} = \sqrt{e^{\sigma^2} - 1} \tag{3.4}$$

$$M = e^{\mu} \tag{3.5}$$

When μ and σ are computed from the inverse relationships of equations 3.5 and 3.4, respectively, then they only depend on either the median or the CV.

The CV is a relative measure of uncertainty and therefore intuitive. Also relative to the location of the distribution is the dispersion factor k of a distribution. The dispersion factor describes two bounds, M/k and kM, that enclose 95 percent of the probability mass of the distribution.

$$\begin{aligned} P\left(\frac{M}{k} < X < kM\right) &= 0.95 \\ k &= e^{1.96\sqrt{\ln(\mathrm{CV}^2+1)}} \\ &= e^{1.96\sigma} \end{aligned} \tag{3.6}$$

When lognormal distributions are parameterized via the median and either the CV or the dispersion factor, the impact of different parameter values on the distribution shape becomes more obvious and intuitive. Hence these modifications by Slob adjust the lognormal distribution for the use of expert opinion and the parameterization of subjective distributions.

However, some important characteristics of the distribution such as the location of its mode, are not directly specified, and may not accurately reflect expert opinion.

[8] The geometric mean is defined as $(\prod_{i=1}^{n} x_i)^{\frac{1}{n}}$. It follows that $\ln (\prod_{i=1}^{n} x_i)^{\frac{1}{n}} = \frac{1}{n} \ln \prod_{i=1}^{n} x_i = \frac{1}{n} \sum_{i=1}^{n} \ln x_i = \mu_L$.

Keeping the Mean or the Median Fixed

In the literature cited in this study, the approaches taken to parameterize lognormal distributions differ in particular in respect to whether the mean or the median is used to characterize the location of the distribution.

McKone et al. (1995) compute the arithmetic mean to parameterize lognormal distributions. Similarly, Berding (2000, p. 123) parameterizes lognormal distributions using the mean of at least 25 values. Hamed and Bedient (1997) investigate the influence of the shape of input distributions on several characteristics of the computed target distribution. While they are using different distribution types (normal, lognormal, and uniform distributions), they always use the same mean and standard deviation "in order to preserve the probability content of the distributions."

Examples of the use of the median are Slob (1994), Beyer and Matthies (2001), and Jager et al. (1997). In his reference book of applied statistics, Sachs (1992, p. 155) recommends the median in cases of sparse data, unsymmetric distributions, possible outliers, ranked data, and distributions with open classes at the end of their range. The first three indications frequently apply in probabilistic assessment. Unsymmetric distributions are often assumed when a quantity is bounded, e.g. when it cannot be negative. Monte-Carlo analysis is likely to produce some very large values that are few in number and can be considered outliers when input uncertainties are large.

When a distribution is parameterized using expert judgment, either the mean or the median may be used as a parameter. At a fixed mean or median, different uncertainties imply different distributional shapes. The impact of uncertainty on the shape differs depending on the kind of parameter used. Figure 3.2 shows examples where different CV are combined with a fixed mean or a fixed median. In Figure 3.2 four settings of parameterizing lognormal distributions are explored. In all cases, the CV varies from 0.3 to 3.0. For the two plots in the left column a fixed median was used, while in the right column the mean was kept at one value. In the top row median and mean are set to 1.0, in the bottom row, median and mean are set to 100.

The top and the bottom row show the same pattern in the plots, except that plots in the bottom row are stretched by a factor of 100. Notice that the probability density decreased likewise to 100^{th} of the value in the top row. This shows that the results are similar at different orders of magnitude an could hence be extended to all values of mean an median.

For low CV values, the curve of the lognormal PDF is almost bell shaped. Mean and median are close to each other, and there is little difference between using one or the other. When CV increases, the mode of the lognormal distribution shifts towards the left, and in case of a fixed mean a narrow peak is formed close to the y-axis, which can be explained as follows.

When the CV increases at a fixed mean, the standard deviation increases accordingly. The standard deviation is a function of the probability density function, weighted with the distance from the mean.[9] Hence, a large standard deviation implies that much of the probability mass is far away from the mean. At the same time, the mean is the center of

[9] Variance of a continuous random variable $\mathrm{Var}(X) = \int_{-\infty}^{\infty}(x-\mu)^2 f(x)\,dx$ where $f(x)$ is the lognormal PDF

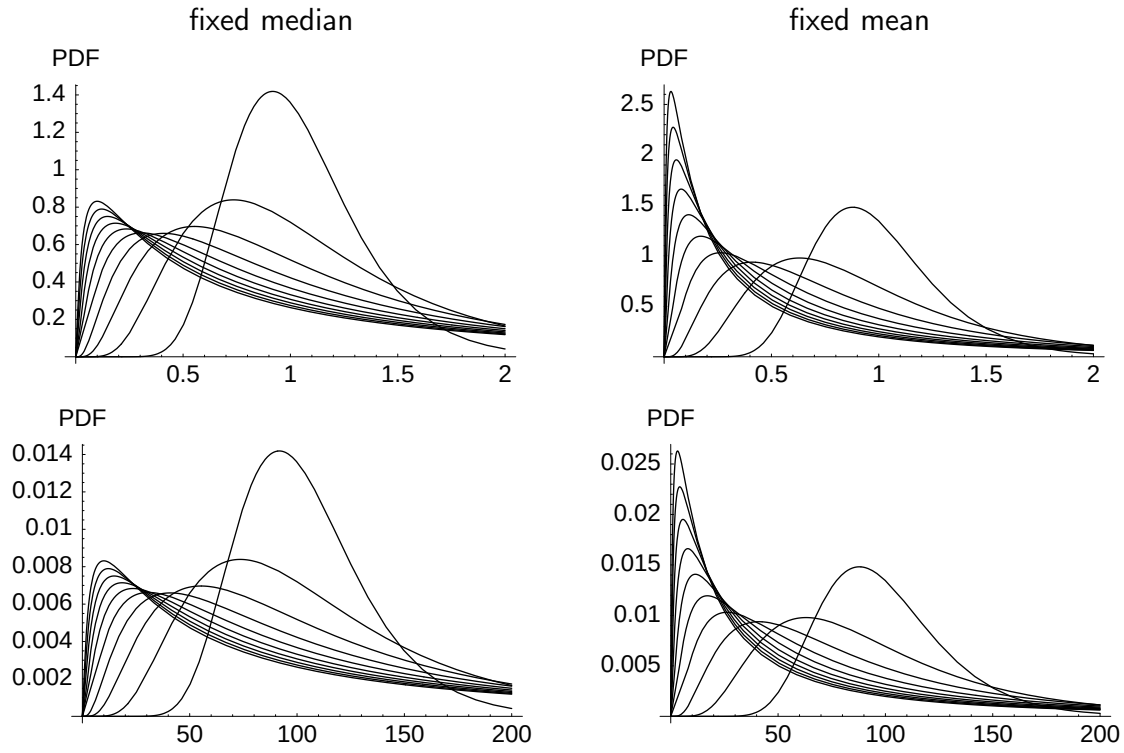

Figure 3.2: Different shapes of lognormal distributions.
Examples of different CV combined with either a fixed mean or a fixed median. Four settings of parameterizing lognormal distributions are explored. In all cases, the CV varies in steps of 0.3 from 0.3 to 3.0. For the two plots in the left column a fixed median was used, while in the right column the mean was kept at one value. In the top row median and mean are set to 1.0, in the bottom row, median and mean are set to 100.

the distribution in the sense that equal amounts of weighted probability mass lie on both sides of it.[10] Since the range of the lognormal distribution is bounded at zero, the distance of the probability mass on the lower side of the mean is also bounded. When the distance of probability mass increases on the upper side of the mean, then an increasing share of the total amount of probability mass is accumulated on its lower side, as far away from the mean as possible, i.e. close to the y-axis, hence creating a narrow peak in the PDF. This argument is not limited to the lognormal distribution, in fact the accumulation of probability mass at the y-axis may be expected for any distribution ranging from zero to infinity.

The percentiles of the distribution in particular will reflect these tendencies, because they indicate points, up to which a certain amount of the total probability mass is spread out. For example, the 50^{th} percentile indicates the point before which half the probability mass is found. When uncertainties become large, all percentiles (with the exception of the 100^{th} percentile) decrease. In fact, their limits are zero when the CV approaches infinity.[11] Figure 3.3 shows two plots of the 90^{th} percentile, the 10^{th} percentile and the

[10] The integral definition of the mean $E(X) = \int_{-\infty}^{\infty} x f(x)\, dx$ shows how the mean is an integral of the PDF, weighted with the x-value

[11] Using a computer algebra system it can easily be verified that $\lim_{s_L \to \infty} x_{99}(m_L, s_L) = 0$, where x_{99} is the 99^{th} percentile, s_L denotes standard deviation, and m_L denotes the mean.

mean of the lognormal distribution as a function of the CV, keeping the mean fixed in one (Figure 3.3A) and keeping the median fixed in the other (Figure 3.3B). The CV is varied from 0 to 20. In Figure 3.3A, there is an increase of the 90^{th} percentile only in the range from 0 to 2. It can be argued that a large uncertainty should be represented by a broad range of the distribution in terms of values that lie inbetween the 10^{th} and 90^{th} percentile. This plot indicates that keeping the mean fixed prohibits such broad ranges. To prevent this, no CV larger than 2 ought to be used in combination with a fixed mean. Furthermore, judging from Figure 3.2 lognormal curves possess an intuitive shape only for CV less than 1.

These kind of problems do not occur when the median is chosen to parameterize the distribution from expert opinion. The resulting shapes of the lognormal PDF, shown in Figure 3.2, left column, do not exhibit a comparable peak at the y-axis, although in this case, too, the mode of the distribution is far to the left of the median.

The plot of the lognormal percentiles, in Figure 3.3, displays a completely different behavior in case of a fixed median (B) as opposed to having a fixed mean (A). The 90^{th} percentile increases monotonic with the CV. In fact the limit of the 90^{th} percentile can be shown to be infinite.

Hence, when the median is used, even at large uncertainties the behavior of the percentiles is more consistent with the expectation that at large uncertainties the bulk of the probability mass is spread out over a large range. Notice though that in Figure 3.3 the mean increases beyond all limits as well. When such distributions are used in Monte-Carlo analysis, this should be kept in mind when analyzing the mean of computed target distributions.

3.2.4 Triangular Distribution

The shape of the triangular distribution is determined by three parameters a, b, and H. Parameters a and b denote the lower and the upper bound, respectively, H sets the position of the mode (Figure 3.4). The distributional shape is determined directly by these parameters, hence the triangular distribution is a non-parametric distribution, suitable to represent expert opinion. In fact, the triangular distribution is the most commonly used distribution to represent expert opinion (Vose, 2000, p. 273).

Reasons for this might be that minimum, maximum, and a most likely value are the most basic information to ask an expert, and correspond directly to the distribution parameters. According to Cullen and Frey (1999), there is also a theoretical foundation: the triangular distribution is the MaxEnt distribution in cases where lower and upper bounds of the distribution range, and the mode are known.

The mean m_T and standard deviation s_T of the triangular distribution are computed from the parameters using the equations

$$m_T = \frac{a + H + b}{3} \tag{3.7}$$

$$s_T^2 = \frac{a^2 + H^2 + b^2 - aH - ab - Hb}{18} \tag{3.8}$$

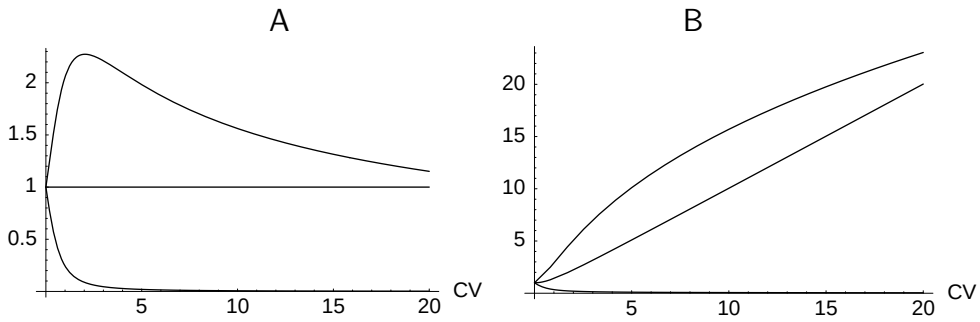

Figure 3.3: Percentiles of lognormal distributions.
Plot of the 90^{th}, the 10^{th} percentile and the mean of the lognormal distribution. The CV is varied from 0 to 20. In plot A, the mean is kept fixed at one, in plot B, the median is kept fixed at one. While in plot B the range encompassed by 10^{th} and 90^{th} percentile increases with the uncertainty represented by the CV, this range decreases in plot A.

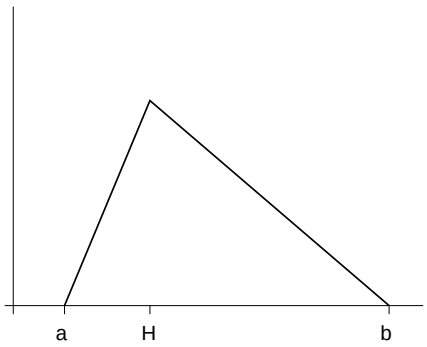

Figure 3.4: Triangular distribution.
Triangular distribution $T(a, H, b)$ where a and b denote the lower and upper bounds, and H is the position of the mode.

The mean m_T always falls in the middle third of the range (a, b). When a and H coincide, then the mean is given by

$$\frac{2a+b}{3} = \frac{3a+b-a}{3} = a + \frac{1}{3}(b-a)$$

Hence the distance of mean and lower border is always at least a third of the total range of the triangular distribution (Figure 3.5). This implies that the mean tends to be large when the upper bound is uncertain (and hence chosen to be large), even if both, the mode and the lower bound are set to low values. As a consequence, the coefficient of variation of the triangular distribution is bounded. When triangular distributions are parameterized with large standard deviations, the large upper bound implies also a large mean value. The maximum CV for triangular distributions is $(\sqrt{2})^{-1} \approx 0.7$.[12] Vose (2000) cautions to use the triangular distributions when maximum values are difficult to determine.

While the triangular distribution may give an accurate description of the state of knowledge about a parameter, it hardly is a realistic estimate of the actual distribution of the uncertainty of a parameter. The sharp edges of this distribution are unlikely to accurately represent any uncertainty from a physical, chemical, or biological process (Cullen

[12] This follows from $\lim_{b\to\infty} CV_{T(a,H,b)} = \frac{1}{\sqrt{2}}$.

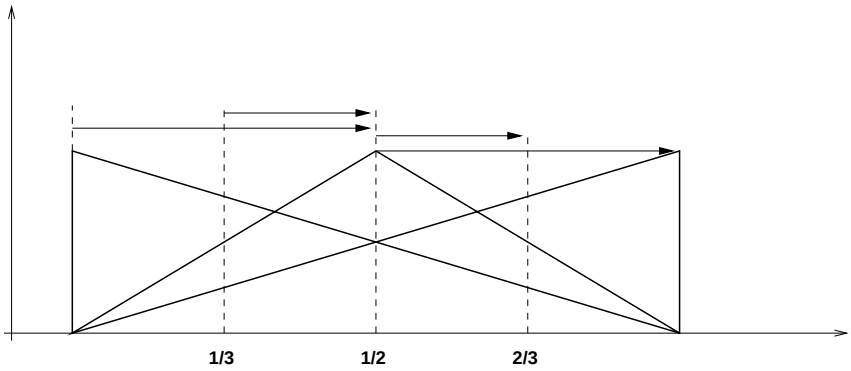

Figure 3.5: Mean and mode of triangular distribution.
Triangular distributions with the mode at the lower bound, at the center, and at the upper bound. The mean of the triangular distribution always falls within the middle third of the range from lower to upper bound, regardless of the location of the mode.

and Frey, 1999). The existence of the three discontinuities at a, b, and H and the the choice of their position need to be backed up by some information, in order to be consistent with the scientific method (Seiler and Alvarez, 1996). A lack of such information would not imply a single most likely value, but rather a trapezoid shape of the distribution. Seiler and Alvarez recommend the beta distribution over the triangular and the uniform distribution (discussed below).

3.2.5 Beta Distribution

The beta distribution is a parametric distribution, it is defined by two so-called shape parameters α_1 and α_2. The PDF is (Cullen and Frey, 1999, p. 69):

$$f(x) = \frac{x^{\alpha_1 - 1}(1-x)^{\alpha_2 - 1}}{B(\alpha_1, \alpha_2)}, \text{ for } 0 \leq x \leq 1, \text{ and } \alpha_1, \alpha_2 > 0$$

where $B(\alpha_1, \alpha_2) = \Gamma(\alpha_1)\Gamma(\alpha_2)\Gamma(\alpha_1 + \alpha_2)^{-1}$, and $\Gamma(x)$ denotes the Gamma function.

Both, Vose (2000) and Cullen and Frey (1999) give equation by which beta distributions can be modified for parameterization from more intuitive parameters than the shape parameters α_1 and α_2. Vose introduces the PERT distribution PERT(a, b, c, γ), where a and c are minimum and maximum of the beta distribution, b is its mode, and γ has an impact on the standard deviation. Using equations for α_1 and α_2 given in Cullen and Frey (1999, p. 164), a beta distribution can be found to fit a lower and upper bound, a given mean and a given standard deviation. Figure 3.6 shows variations of the PERT distribution.

When values for upper and lower bounds, mean and standard deviation are given, the beta distribution possesses maximum entropy. Compared to the triangular distribution, one additional piece of information is needed, the standard deviation. Other than the triangular distribution the beta distribution is smooth, i.e. there are no discontinuities.

When upper and lower bounds are fixed, there is a limit to the spread that a distribution can possibly represent. With increasing standard deviation, the beta distribution converges towards the uniform distribution (Seiler and Alvarez, 1996). Physical properties of

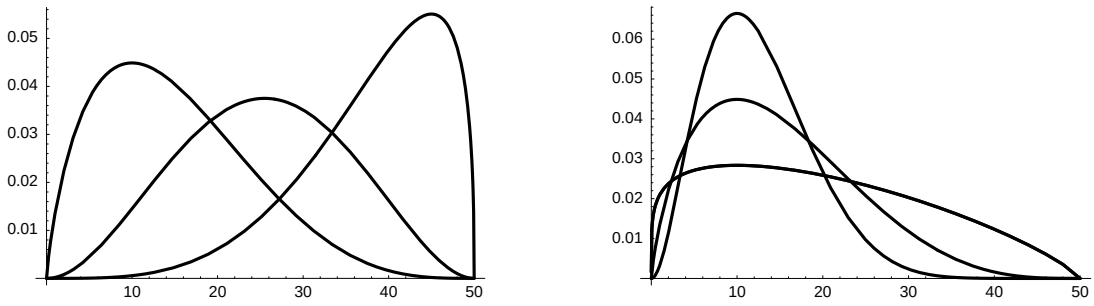

Figure 3.6: Beta and PERT distributions.
The left plot shows PERT distributions with different locations of the mode to illustrate how beta distributions can be used as "smooth triangular" distributions. The right plot shows PERT distributions with the same mode, but different standard deviations, which makes beta distributions more flexible than triangular distributions.

chemicals rarely have no upper limit. The beta distribution is more realistic with respect to this than the lognormal distribution.

3.2.6 Uniform Distribution

The parameters of the uniform distribution, a and b, define the lower and upper bounds of the distribution, respectively. The PDF is:

$$f(x) = (b-1)^{-1} \text{ for } a \leq x \leq b$$

The mean m_U and standard deviation s_U of the uniform distribution are:

$$m_U = \frac{a+b}{2} \tag{3.9}$$

$$s_U = \frac{(b-a)^2}{12} \tag{3.10}$$

It follows from these equations that the lower and upper bounds, a and b, may be set from m_U and s_U as $a = m_U - \sqrt{3}\, s_U$ and $b = m_U + \sqrt{3}\, s_U$.

When the uniform distribution is used to model a non-negative quantity, the lower bound a is non-negative. If this restriction is taken into consideration, a maximum coefficient of variation CV_{max} can be computed:

$$\begin{aligned} m_U - \sqrt{3}\, s_U &> 0 \\ m_U &> \sqrt{3}\, s_U \\ \frac{s_U}{m_U} &< (\sqrt{3})^{-1} \approx 0.58 = \mathrm{CV}_{max} \end{aligned}$$

The existence of such a limiting value should be kept in mind, particularly when comparing different distribution types.

The uniform distribution is the MaxEnt distribution when only minimum and maximum values of a parameter are known. Like the triangular distribution, it is almost exclusively used to model expert opinion, and similar criticism about its sharp edged shape applies.

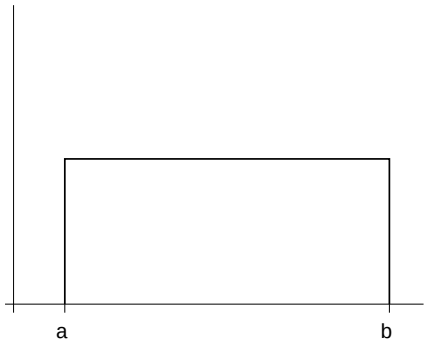

Figure 3.7: Uniform distribution with lower bound a and upper bound b.

3.3 Monte-Carlo Simulation

Monte-Carlo simulation is a numerical method to propagate probability distributions through a model. It is frequently used to perform uncertainty analyses. Its main idea is to estimate the distribution of a target[13] value of the model statistically by sampling the universe of all possible target values.

A possible target value, e.g. soil concentration, can be calculated from a set of model parameters by sampling each probabilistic parameter according to its probability distribution. This is usually referred to as performing a Monte-Carlo *shot* (or *trial* in Crystal Ball® terminology). A random sample of the target distribution of size n is produced by calculating n Monte-Carlo shots.

The resulting random sample of the target value is then subject to statistical analysis, e.g. mean and variance may be estimated from the sample mean and sample variance, respectively. Statements about the shape of the target distribution can be derived by fitting theoretical distributions to the sample and performing goodness-of-fit tests (Decisioneering Inc., 1999, p. 138). Furthermore, target distributions can be characterized and compared via their percentiles.

Sampling from the input distributions is either done by simple random sampling or latin hypercube sampling. The latter guarantees that values from the entire range will be sampled by dividing it up into subranges of equal probability and then drawing from these subranges (Cullen and Frey, 1999, p. 209). Latin hypercube sampling is considered to be more efficient, because a lower number of samples is needed to cover the entire parameter space.

3.4 The SimpleBox Model

SimpleBox is a level 3 model, i.e. it assumes continuous input (emissions) and output (degradation), steady state, and resistances between compartments (hence no thermodynamic equilibrium) (Trapp and Matthies, 1998).

[13]The term *target* refers to the model output of interest.

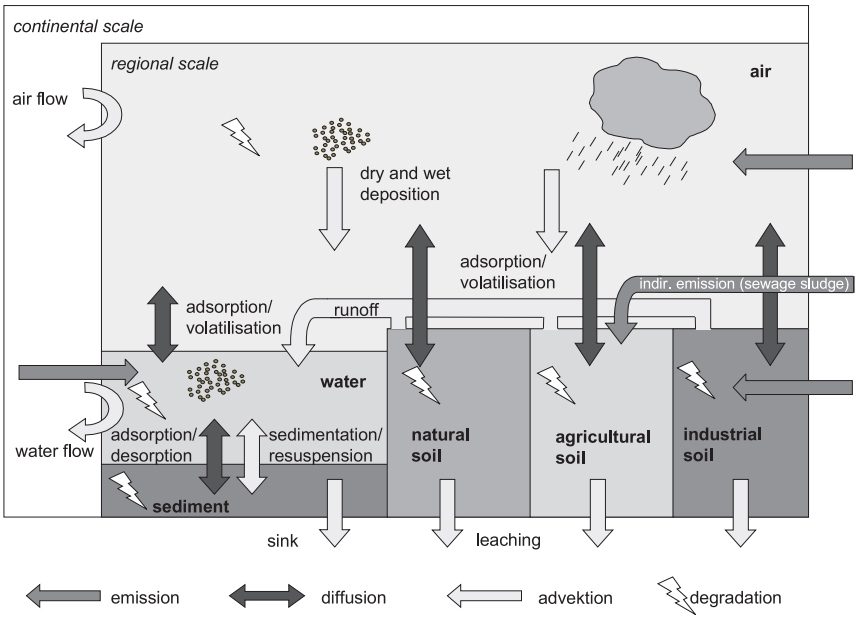

Figure 3.8: SimpleBox flows.
Overview of compartments and processes of the SimpleBox model. Adapted from EC (1996)

Computations in this study are performed with the SimpleBox model (van de Meent, 1993; Brandes et al., 1996) for a number of reasons. The European Union System for the Evaluation of Substances (EUSES) is a model system that covers both sides of the risk assessment process, the effects assessment and the exposure assessment following EC (1996). It incorporates modules for estimating PEC and PNEC, and computes their quotient (RCR) to indicate any existing risks. Descriptions of the individual modules and their interaction can be found in Berding (2000). Within this framework, SimpleBox is the multimedia model that computes background concentrations in air, water, sediment and three sorts of soil: agricultural soil, industrial soil, and natural soil (Figure 3.8). The soils differ in some characteristics, particularly in emissions. There is direct emission into industrial soil, no emission into natural soil and emission via sewage sludge into agricultural soil.

The Excel® spreadsheet version of SimpleBox implemented by Berding (2000) is used in this study with few modifications. The spreadsheet was modified so that care is taken that fractions, e.g. the volume fractions of water and solid matter in sediment, always add up to one.[14] Furthermore, volatilisation rates must not become infinite. The largest modification is a technical one: additional substance data tables enable providing multiple scenarios with different input distributions, in particular different distribution types. The latter were introduced for convenience, but it should be noted that automating the parameterization of the spreadsheet model enables reproducing simulation results. As in Berding et al. (2000), the Crystal Ball® software package is used to perform Monte-Carlo simulations of the spreadsheet model (Decisioneering Inc., 1999).

[14]Fractions can fail to add up to one in probabilistic simulation, when uncertain fractions are set to random, conflicting values. The conflict is solved by normalizing conflicting fractions using their sum.

Chapter 4

Results and Discussion

In a broad sense, sensitivity analysis encompasses all dependencies of computed target[1] distributions on input distributions i.e. parameter distributions. In other words, the effects of varying characteristics of input distributions on characteristics of target distributions are studied. The moments of probability distributions are a set of consistent characteristics, and are chosen here as measures of the location, dispersion and shape of the probability distributions. Table 4.1 summarizes possible dependencies between aspects of input and output distributions in terms of moments, and in which context they are at least partially addressed.

Classical Sensitivity Analysis

Changing an input parameter affects the mean (1. moment), variance (2. moment) and the shape (higher order moments) of the target distribution (Table 4.1). Classical sensitivity analysis investigates the effect on the location of the target distribution by applying deterministic local methods, e.g. differential analysis of the model equations (Saltelli et al., 2000). The dependency of the location of the target distribution on the location of the input distribution is bound to behave similar to the deterministic case. Hence results from sensitivity analysis performed in Berding et al. (2000) give an insight how changes of the

[1] As in the previous sections, the term *target* refers to the target of the computation, i.e. substance concentration in any of the four compartments soil, water, sediment and air.

Table 4.1: Overview of input/output dependencies.
The referenced sections address selected aspects of the dependencies. Section 3.2.3 discusses the effects on the distributions shape in the context of different parameterization approaches.

moment of	moment of target distribution		
input distribution	mean (first moment)	variance (second)	shape (higher order)
mean	classical sensitivity analysis		Section 3.2.3
variance	Section 4.1	Section 4.7	
shape	Section 4.3	Section 4.4	Section 4.5

input distribution's location affect the location of the target distribution. The location of the input distribution also has an impact on the target variance: whether the input location falls within a sensitive or an insensitive region of the parameter space determines the impact of the input variance on the output variance (Beyer and Matthies, 2001).

Thus, by analyzing the local sensitivity for different parameter settings (scenarios) one also gets an idea of how different input mean values relate to the variance of the output (Beyer and Matthies, 2001). The effect of the input distribution's mean on the resulting mean and variance is therefore not further analyzed in this work.

4.1 The Influence of the Dispersion of the Input Distribution on the Location of the Target Distribution

In the simple case of a sum of two random variables X_1 and X_2 with normal probability distributions, the target mean does not depend on anything but the input means. It is computed as follows (Sachs, 1992, p. 144):

$$E(X_1 + X_2) = E(X_1) + E(X_2)$$

Thus in this case, the mean of the distribution of the sum may be calculated deterministically from the mean values of the summands. However this result does not hold in general.

In general, the deterministic output value calculated with the mean values of the input distributions differs from the mean value of the target distribution computed by a full probabilistic assessment. In other words, the input means are not directly mapped to the results, because the resulting mean is affected by other properties of the input distributions. The mean value calculated by propagating the entire probability density function (PDF) can be larger or smaller than the corresponding deterministic result (Figure 4.1). Hence, by performing Monte-Carlo simulations the mean gets "shifted" to the right (positive shift) or to the left (negative shift) of the deterministic calculation.

Positive Shift

Positive shifts in the above sense can be understood analytically in case of a specific situation. Two lognormally distributed input parameters occurring in the numerator and the denominator of a quotient in the model equations result in a positive shift of the mean. Let X_1 and X_2 be two random variables with lognormal distributions, i.e. $X_1 \rightarrow L(\mu_1, \sigma_1^2)$ and $X_2 \rightarrow L(\mu_2, \sigma_2^2)$, where L denotes the lognormal distribution and μ and σ^2 are mean and variance of $\ln X_1$ and $\ln X_2$. Then the distribution of the quotient X_1/X_2 is distributed as (Crow and Shimizu, 1988):

$$\frac{X_1}{X_2} \rightarrow L(\mu_1 - \mu_2, \sigma_1^2 + \sigma_2^2)$$

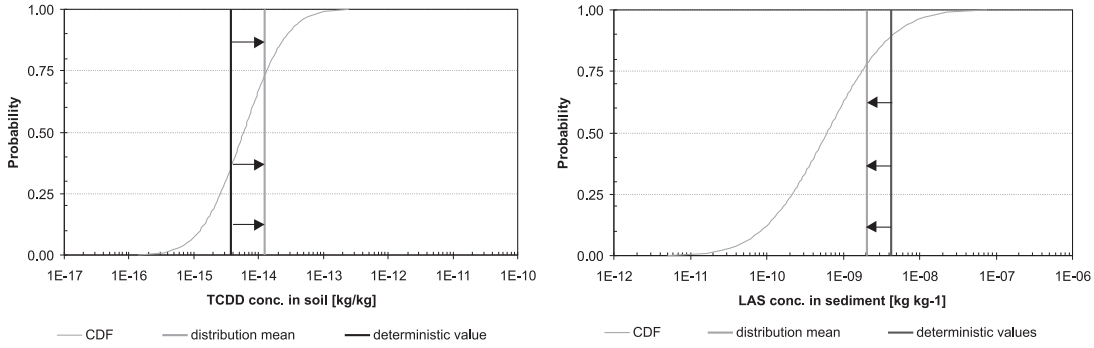

Figure 4.1: Probabilistic means versus deterministic calculation.
Comparative plots of the distribution mean computed via Monte-Carlo simulation, and the deterministic target value computed by taking the distribution means as deterministic model input. In case of TCDD concentration in soil, the deterministic target value is less than the probabilistic mean, while in case of LAS concentration in sediment it is larger. Simulations were performed with scenarios from Berding et al. (2000).

Hence, the expected value of the quotient, which is equivalent to the mean derived by probabilistic calculation, is given by the following equation:

$$E\left(\frac{X_1}{X_2}\right) = e^{\mu_1 - \mu_2 + \frac{\sigma_1^2 + \sigma_2^2}{2}}$$

In contrast, here is the quotient of the input distribution means, which is equivalent to the deterministic calculation:

$$\frac{EX_1}{EX_2} = \frac{e^{\mu_1 + \frac{\sigma_1^2}{2}}}{e^{\mu_2 + \frac{\sigma_2^2}{2}}} = e^{\mu_1 - \mu_2 + \frac{\sigma_1^2}{2} - \frac{\sigma_2^2}{2}}$$

Therefore, the expected value of the quotient $\mathrm{E}(X_1/X_2)$ is larger than the quotient of the means $\mathrm{E}X_1/\mathrm{E}X_2$ by a factor of $e^{\sigma_2^2}$.

Lognormally distributed parameters in quotients are common in SimpleBox scenarios, and hence the effect described above is bound to occur. However the impact of the effect still depends on the relative sensitivity of the concerning parameters and the uncertainty about them.

Negative Shift

In case of LAS concentration in sediment there is a negative shift of the probabilistic result compared to the deterministic calculation with the input distribution means. Analyzing the corresponding SimpleBox model equations is an arduous if not impossible task in this case. However, negative shifts could be reproduced in numeric simulations for several simplified equations.

In particular there was a negative shift in case of two lognormal parameters in the following functional dependency to a model output: $Y = (X_1^{-1} + X_2^{-1})^{-1}$. This kind of functional dependency does occur in the corresponding scenarios.

Conclusion

There are mathematical considerations that imply that the expectation of any target value is not the same as the result of a deterministic calculation using the distribution means. This needs to be kept in mind particularly when comparing results from probabilistic and deterministic simulations.

4.2 Parameterization

Before Monte-Carlo simulation can be performed to assess the impact of different shapes of parameter distributions, suitable scenarios have to be defined. The aim of this section is to parameterize scenarios with input distributions that differ solely in their shapes, and are yet as close to realistic scenarios as possible.

Characteristics of Probability Distributions

Probability distributions are characterized by their location, their dispersion, and the shape of the distribution function. In the following sections, the mean and the standard deviation are selected as measures of the location and the spread, respectively. The mean and the variance are the first and the second moment about the mean. Together with the coefficients of skewness (third moment) and kurtosis (fourth moment) they form a consistent set of measures to characterize probability distributions (Section 3.1). An additional advantage of this choice is that it makes the results of the following sections comparable to theoretical results about moments in probability theory, e.g. theorems about expected values and variance of linear functions of random variables.

Alternative choices for measures of location and spread are the median and the coefficient of variation, respectively. The median is recommended over the mean when the distributions under consideration are skew because it is more robust to the occurrence of small numbers of extraordinarily large values (Sachs, 1992). As lognormal distributions are always skew, and triangular distribution are only symmetric as an exception, the choice of the mean is a trade-off.

Parameter Set

In SimpleBox the necessary physico-chemical properties of a substance are calculated from the three substance parameters octanol-water partition coefficient K_{OW}, aqueous solubility S_W, and vapor pressure P^0. Only these three properties are modeled probabilistically in this section, i.e. their values are varied according to chosen probability distributions. All other parameters are assumed to be fixed. This study focuses on the physico-chemical parameters for the following reasons: When substances are compared, it is useful to concentrate on the parameters that are specific for substances, i.e. physico-chemical parameters, degradation rates, and emissions, thus making the differences between substances more prominent. In case of degradation rates and emissions, the data situation is too poor to derive distribution functions (Berding et al., 2000), which leaves only the physico-chemical parameters.

Scenario Definition

For the physico-chemical properties three common distribution types with distinct shapes are explored, leading to three scenarios:[2]

Scenario *uni* uses uniform distributions $U(a, b)$ for all three parameters, where a is the lower bound, and b is the upper bound.

Scenario *tri* uses triangular distributions $T(a, H, b)$, where a and b are lower and upper bounds, respectively, and H is the mode of the distribution.

Scenario *log* uses lognormal distributions $L(\mu, \sigma^2)$ where μ is the mean of the underlying normal distribution on logarithmic scale, and σ^2 is its variance. Lognormal distributions can alternatively be parameterized, as $L(m, s^2)$ where m and s^2 are mean and variance of the lognormal distribution.

While the distribution shape is varied, both the mean and the variance of the input distributions are kept the same in all these scenarios. Thus, these scenarios separate effects of the shape on the computed target distributions from effects resulting from changes in input distribution mean and/or variance. The same approach has been taken by Hamed and Bedient (1997), who compare normal, lognormal, and uniform distributions, also parameterized with the same mean and standard deviation (in their case to investigate the impact of input distribution shapes on the probability to exceed a given target value). Results from Hamed and Bedient (1997) are discussed in detail in Section 4.5.

Estimating Location and Spread via Triangular Distributions

The comparable scenarios were parameterized following this procedure: The triangular distribution was chosen as the starting point, because it is a three parameter distribution, whereas the uniform and the lognormal distribution are two parameter distributions. While it is easy to derive the two parameters needed for either the uniform or the lognormal distribution from a given triangular distribution, there is no simple way to parameterize a triangular distribution from a given lognormal or uniform distribution, because the third parameter gives the triangular distribution an additional degree of freedom, e.g. the location of the mode, which determines its skewness. Starting out with a uniform distribution, the triangular distribution could be assumed to be symmetrical (as the uniform is) – which would ignore the ability of the triangular distribution to model skew probability densities. Starting out with the lognormal distribution on the other hand, the location of the triangular's mode could be derived from the coefficient of skewness of the lognormal – yet the skewness of the triangular distribution is limited, and the lognormal distribution easily takes on a larger skewness than this limit.

Also the triangular distribution is not as flexible as the lognormal distribution: its mean always falls within the middle third of the range from lower to upper bound (see p. 45). And if a lognormal distribution with a low mean and a high standard deviation was given,

[2]The modified beta or PERT distribution (Section 3.2.5) could be assessed in additional scenarios. This study focuses on the distribution types that are commonly used.

the resulting triangular distributions could be in conflict with the requirement that only positive values must be covered (because K_{ow}, S_w and P^0 are always positive).

Note, that choosing triangular distributions as a starting point has a restricting effect on possible lognormal distributions. The triangular distribution cannot have a coefficient of variation (CV) larger than $(\sqrt{2})^{-1} \approx 0.7$ (Section 3.2.4). Hence, when lognormal and uniform distributions are parameterized with mean and standard deviation from a triangular distribution, their CV is bound to stay below this limit as well.[3]

Nevertheless the triangular distribution is "the most commonly used distribution for modeling expert opinion" (Vose, 2000). In a situation of scarce data it seems a good choice to use a triangular distribution and the following heuristic approach of parameterization.

The triangular distribution's lower bound a and upper bound b were set to the smallest and largest measured literature value available, respectively. The mode H, which represents the most likely value, was set to a value that represents *expert opinion*. For this *expert opinion*, values selected by Mackay et al. (1999) and Shiu and Ma (2000) were used. In some cases, these expert values were not measured values, but e.g. summary values, or values cited without exact reference. When these values were larger than the maximum literature value or less than the minimum literature value, the upper bound b or lower bound a was set to the expert value, which happened eight times (out of 24 parameters).

Similar Approaches in Literature

A similar procedure to this approach is suggested in Taylor and Kuyatt (1994), a technical report that provides guidelines to evaluate uncertainties of measurement results. Taylor and Kuyatt differentiate between *type A* and *type B evaluation of standard uncertainty*. Type A evaluation is done by statistical analysis. If there is no sufficient basis for statistics, type B evaluation is applied which is "usually based on scientific judgment using all relevant information available." In particular Taylor and Kuyatt introduce a method that models the quantity (of which the uncertainty will be estimated) assuming a probability distribution. The distribution is parameterized heuristically, e.g. by giving the interval about the most likely value, which has a 50 percent chance of containing the true value (or a 67 percent or 100 percent chance likewise). A measure for the uncertainty is then derived by taking the standard deviation of this distribution. Suggested distribution shapes are normal distribution, uniform (or rectangular) distribution and triangular distribution. About the choice of distribution shape it is said that "the rectangular distribution is a reasonable default model in the absence of any other information. But if it is known that values of the quantity in question near the center of the limits are more likely than values close to the limits, a triangular or a normal distribution may be a better model." Using this terminology, the above approach uses triangular distributions instead of uniform, because the expert opinion does represent some additional knowledge. The lowest and the highest measurement results are used to set the lower and upper 100 percent limits. According to the National Institute of Standards and Technology (NIST) website, these guidelines are "adopted widely by U.S. industry, companies in other countries, NIST, its sister national

[3]Note that when distributions are shifted (see below), the theoretical lower bound of the CV is further reduced.

metrology institutes throughout the world, and many organizations worldwide" (Taylor and Mohr, 2002).

Parameterizing comparable Lognormal and Uniform Distributions

From these triangular distributions $T(a.H, b)$, distribution means m_T and standard deviations s_T were derived (equations are given Section 3.2.4). Lognormal distributions that are comparable to these initial triangular distributions may then be parameterized using m_T and s_T as the mean m_L and standard deviation m_L of the lognormal distribution. Similarly, comparable uniform distributions can be parameterized using equations from Section 3.2.6.

Avoiding Negative Values

When deriving parameter sets for the uniform distribution by transferring mean and variance from the triangular or the lognormal distribution, the resulting uniform distribution sometimes covers a range that includes negative values. Hence the uniform distribution with the smallest deviation from the desired but impossible case is chosen: a uniform distribution with the lower bound at zero and the given variance. This results in a modified mean value, so that the triangular and the lognormal distribution also have to be shifted to have the new mean. The largest shifts that occurred were 22 percent of the distribution mean. On average, distributions were shifted by 10 percent. In one third of the cases, no shifting was necessary. The variance is independent of the location, and therefore not affected by the shift. The coefficient of variation (CV) however decreases with a shift towards larger parameter values. When the distributions are made comparable to the uniform distributions, the limitation about the CV of a uniform distribution apply to all distribution types, resulting in an upper bound of $(\sqrt{3})^{-1} \approx 0.58$ for the CV. The resulting uniform, triangular, and lognormal distributions constitute the Scenarios *uni*, *tri*, and *log*, respectively. Together, they are also referred to as the *comparable* scenarios.

The parameter distributions used in the *comparable* scenarios (*uni*, *tri*, and *log*) are *not* accurate scenarios to describe the substances. Rather they are technical examples of parameter sets. However they were kept as close to real life substance parameters as possible.

Representative results (sediment compartment) from the Monte-Carlo simulations performed with the Scenarios *uni*, *tri* and *log* are shown in Figure 4.2 (target means) and Figure 4.5 (target means together with associated target standard deviations). Conclusions derived from these representative data apply to the whole set of data. Corresponding figures can be found in the appendix.

4.3 The Influence of the Shape on the Location of the Target Distribution

In Figure 4.2, the mean values of target distributions are shown; the data are grouped by substance, each group consisting of the results from the three scenarios. Values are

given as deviations from the arithmetic mean of the scenarios, which is computed for each substance separately.

The variation of the target mean due to varying shapes of input distributions is relatively small compared to their means. In all cases, the relative deviations are less than 2 percent, when TCDD is set aside, deviations are even less than 1 percent.

Two obvious phenomena in this plot merit further explanation: Switching from one input distribution to another has a different effect on the target mean from substance to substance in the direction it takes; for some substances the mean concentration increases while it decreases for others. Secondly the magnitude of the impact that changes in the shape of the input distribution have, differs in-between substances.

4.3.1 The Direction of the Effect

The direction in which a change in input shape affects the mean differs in-between substances. For example in case of TCDD the target mean increases from scenario to scenario, while it decreases in the cases of HxCDD. The key to understanding these differences lies in two aspects in which the scenarios differ:

1. the functional dependency of input parameter and target values as defined through the model equations
2. the way input parameter distributions cover ranges of parameter values

Functional dependency of parameter and target value is understood to be the behavior of the target value when only one parameter is varied, i.e. while all other parameters are fixed. Here, they are set to the medians of the associated distributions. Hence, the functional dependencies are principally determined through the model equations, but of course the parameter values forming the particular scenario under consideration have an essential impact on it, too, as their values determine the region in parameter space that is varied over. Therefore, functional dependencies of one particular parameter and the concentration in a particular compartment differ from substance to substance.

In combination with the functional dependencies, the range of an input parameter distribution determines the range of possible target values. Naturally, differences in input ranges imply differences in the output. It is therefore helpful to closely consider the differences in ranges.

Figure 4.3 shows the concentrations in sediment for several substances as functions of the three input parameters K_{ow}, aqueous solubility and vapor pressure; all other parameters are set to their deterministic value. The range that is indicated for each of the input parameters is the range covered by the uniform distribution used in Scenario *uni*; the ticks along the x-axis mark percentiles of this uniform distribution. As a property of the uniform distribution, these linear steps in percentiles are equivalent to linear steps in parameter value. The functional dependency curves are therefore undistorted. Percentiles as opposed to the specific units of the parameters allow several functions of different input parameters to be plotted in a single single figure.

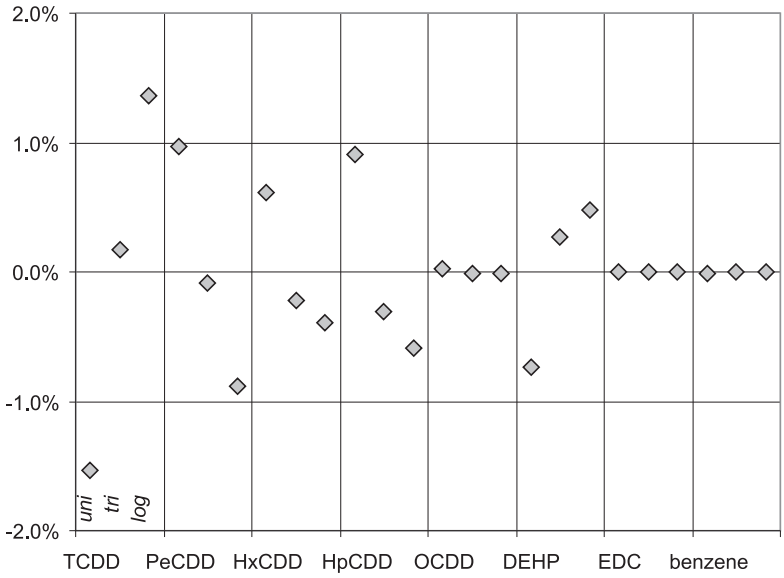

Figure 4.2: Target means in sediment.
Target means from the Scenarios *uni*, *tri*, and *log* for the sediment compartment. Charts with the results in other compartments can be found in the appendix. Data are grouped by substance, each group consisting of the results from the three scenarios. Values are given as relative deviations from the arithmetic mean of the scenarios, which is computed for each substance separately.

To visualize the ranges covered by the different types of input distributions, the actual distribution used in the typical case of vapor pressure of HxCDD are given in Figure 4.4 as an example. The triangular and the lognormal distribution are positively skewed[4] while the uniform distribution is symmetrical. As a consequence, the uniform distributions covers a range of low values of vapor pressure that is not covered by the triangular distribution. The lognormal distribution always covers the entire range from zero to infinity, yet it is evident that the probability of the low values, which are well covered by the uniform distribution, is almost negligible. At the far end of the distributions, the opposite is the case: both the triangular and the lognormal distribution cover a range that includes greater values than the maximum of the uniform distribution.

Comparing the input ranges of the different scenarios from Figure 4.4 with the functional dependencies in Figure 4.3 provides an explanation for the different directions in which target means were affected by different input distribution shapes. It is crucial for the target distribution whether input distributions cover ranges where the sensitivity of the parameter is extraordinarily large (i.e. the slope of the curve is steep), because ranges of great sensitivity have a strong impact on the target distribution. When input ranges and functional dependencies are aligned, differences in ranges become evident. Two examples are used in the following paragraphs for further explanation. The argument that is made applies to other cases in the same way.

Decreasing Target Means HxCDD is one example of a substance where the target mean decreases from *uni* to *tri* and from *tri* to *log*. For sediment concentration of HxCDD,

[4]Also: skewed to the right, i.e. the right tail of the distribution is flatter.

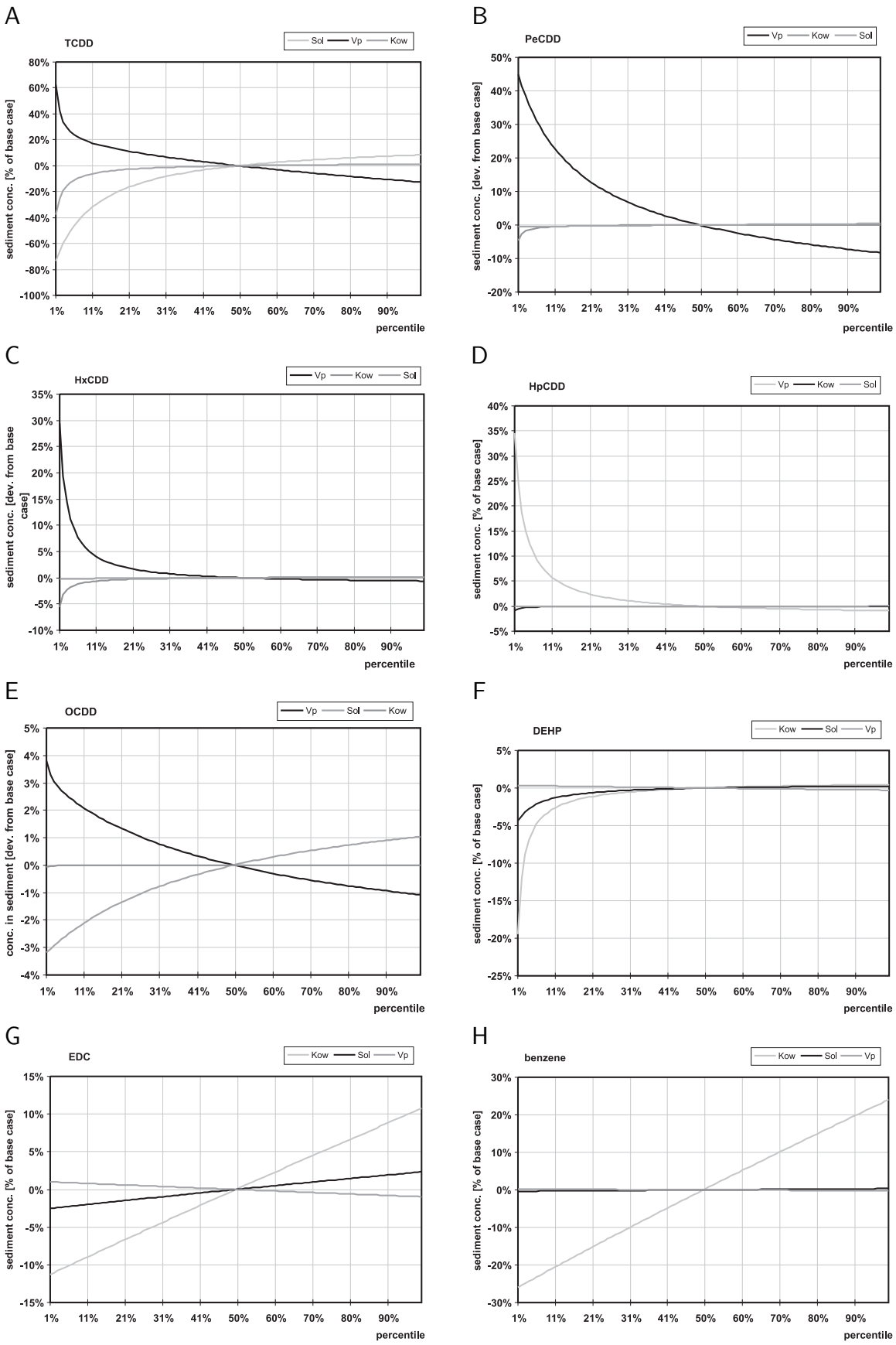

Figure 4.3: Functional dependencies in sediment.
Concentrations in sediment as functions of the input parameters K_{ow}, S_w, and P^0.

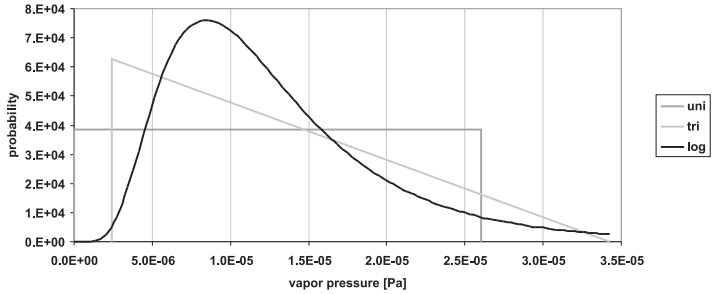

Figure 4.4: Input distributions of parameter P^0 for HxCDD.

vapor pressure is the parameter with the greatest impact on the target value, which is the sediment concentration in this case (its contribution to the total variance of the target distribution is greater than 85 percent). This is visible in Figure 4.3C, because both, the concentration as a function of K_{OW}, and the concentration as a function of aqueous solubilities are nearly constant. In contrast, the variation of the concentration due to changes in vapor pressure are large at low vapor pressures. It is evident that a lower vapor pressure causes a higher concentration of HxCDD. In case of the uniform input distribution there is a much higher probability of low vapor pressures compared to the triangular input distributions. In other words there is more probability mass accumulated at low vapor pressures. Low vapor pressures result in high substance concentrations in sediment. Hence the target distribution in case of uniform input distributions will have more probability mass at high concentrations. The differences in covered ranges at the far end of the input distributions do not have much influence, as the target value takes almost a constant value for these inputs; therefore it is the range close to zero and the effects discussed above that have a dominating influence on the target distribution: A larger share of probability mass at high concentration values leads to a larger mean of the target distribution, which is the observed effect (Figure 4.2). As the lognormal distribution accumulates even less probability mass at low parameter values than both, the triangular and the uniform, this same argument explains why the target mean in case of lognormal input distributions is even smaller.

Increasing Target Means In case of TCDD, the observed effect takes the opposite direction. From Scenario *uni* to Scenario *tri*, and again to Scenario *log*, the target mean increases. The concentration decreases with vapor pressure P^0 and increases with solubility S_W (Figure 4.3A). The impact of the parameters seems to be about equally strong. However, the octanol-water partition coefficient K_{OW} affects the target value in the same way as solubility does. In combination, the impact of S_W and K_{OW} on the target value at low parameter values is greater than the impact of P^0, resulting in low TCDD concentrations. Now, the same considerations as in the previous paragraph apply.

It should be kept in mind, that a "combination" of the impacts of two parameters cannot be estimated in a straightforward way. During Monte-Carlo simulation, all parameters are varied simultaneously, hence low values of S_W and K_{OW} are not guaranteed to coincide. Moreover, when e.g. S_W and K_{OW} are set to values other than the median, the functional

dependency curve of the remaining parameter P^0 will deviate from the curve displayed in Figure 4.3, and vice versa. However statistically Monte-Carlo shots with low S_w or low K_{ow} will occur more frequently than shots with low P^0 values, and it is plausible that functional dependency curves will not be too much distorted, as the model equations are continuous.

In conclusion, whether the target mean increases or decreases depends on whether the ranges, in which the input distributions differ, have a positive or negative effect on the target values. Here, it depends on whether low parameter values imply low or high sediment concentrations.

4.3.2 The Magnitude of the Effect

While the differences in-between the scenarios are overall small, their amount differs significantly from substance to substance. For example, the TCDD means vary by about 3 percent while there is almost no variation of the target means of OCDD, EDC and benzene (less than 0.03 percent) in-between scenarios.

The impact of switching one type of input distribution for another is correlated to the overall sensitivity that the target value shows in case of a particular substance. Classical sensitivity is a *local* property at a specific point in input parameter space. It measures the effect that small deviations from this point have on the target value (Saltelli et al., 2000). Over the course an input range, sensitivity may vary, sometimes to a large extent, e.g. in case of HxCDD, where sediment concentrations depends very sensitively on vapor pressure – but only at low values (Figure 4.3C).

The extent to which the target value varies when the parameter value varies over the entire range may serve as a measure of the overall sensitivity of a target value for a parameter over a range. In the plots of functional dependencies (Figure 4.3) estimates can easily be made: TCDD concentration varies by about 180 percent of the base case,[5] then follow in decreasing order PeCDD (50 percent), HpCDD (35 percent), HxCDD (30 percent), DEHP (20 percent), and OCDD (7 percent). This ranking is in agreement with a ranking of differences of target means in-between substances as it can be estimated from Figure 4.2.

EDC and benzene vary by 20 percent and 50 percent, respectively, although there is almost no inter-scenario variation between their means. This can be explained by the linearity of the functional dependencies (Figures 4.3G and 4.3H). For any linear function Y of a random variable X, i.e. $Y = mX + b$, the resulting mean is independent of the probability distribution of X: $E(Y) = mE(X) + b$ (Sachs, 1992). Therefore, when functional dependencies are near-linear as they are in case of EDC and benzene, changes in parameter distribution will not affect the target mean.

4.3.3 Conclusion

Different choices for the distribution type for the input parameters were found to have an impact on the mean value of the computed target distributions. Whether switching the

[5] The *base case* is the target value computed for all parameters set to their median values.

shape of parameter distributions resulted in an increase or a decrease of the target mean, and the relative magnitude of the impact were explained from the functional dependency of the most influential parameter and the target value. Whether parameter ranges with high sensitivity of the target value were covered by a distribution function is of particular importance.

However, compared to the absolute value of the target means, the impact of changing the distribution type is negligible.

4.4 The Influence of the Shape on the Dispersion

The shape of the parameter distributions also has an influence on the variance of the target distribution (Figure 4.5). In addition to mean values of the target distributions, target variances in sediment are shown as error bars, spanning two standard deviations.

Two aspects of the results in Figure 4.5 will be addressed: The target variances differ in-between substances, and they differ in-between scenarios.

4.4.1 Inter-Substance Differences

To understand the differences of target variance in-between substances, one needs to ask: What are the main differences from substance to substance that have an influence on the variance of the model output? There are two things that have a major impact on the variance of the model output in general:

1. the uncertainty of the input
2. the sensitivity of the model for the input

Especially the combination of a large uncertainty of an input parameter and a great sensitivity of the target value for this parameter will produce a large variance in the target value.

Input uncertainties are summarized in Figure 4.6. They are given as coefficients of variation (CV): For each substance the CV of K_{ow}, S_w, and P^0 are plotted as error bars around a normalized mean. For parameters with the greatest contribution to the target variance, the corresponding bullets are enlarged. As in the previous section, a measure of an overall sensitivity over the entire input range is required. The overall variation about the base case (i.e. all parameters set to the medians of their distributions) is a useful measure (Section 4.3.2)

In the following, the effects of input uncertainty and overall sensitivity on differences of target variance in-between substances will be demonstrated. Two pairs of exemplary substances are chosen: EDC and benzene, and PeCDD and HxCDD.

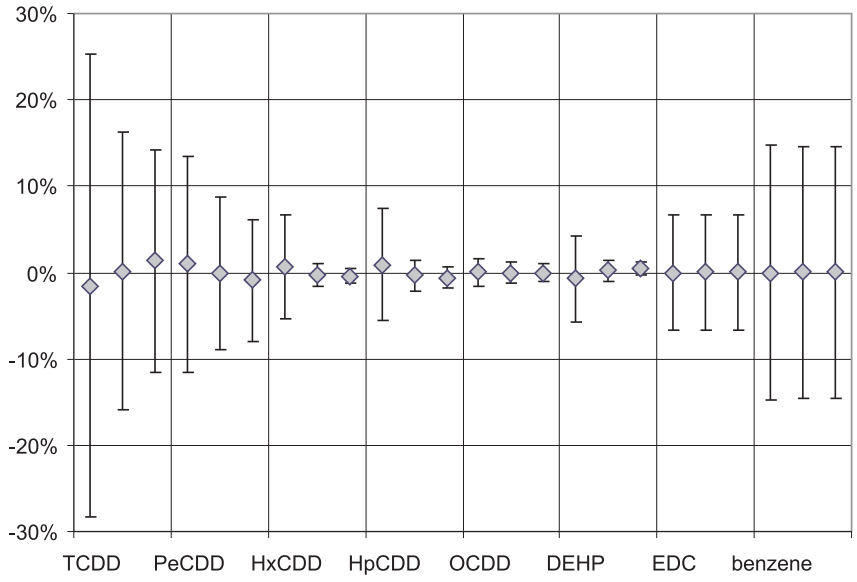

Figure 4.5: Target variances in sediment.
Target means (diamonds) and variances (error bars) from the Scenarios *uni*, *tri*, and *log* in the sediment compartment. Charts with the results for the other compartments can be found in the appendix.

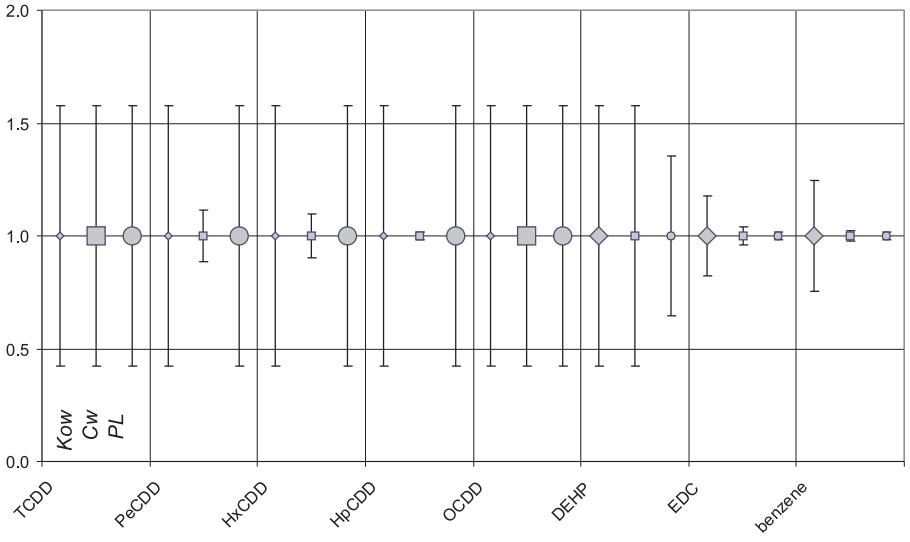

Figure 4.6: Input parameter uncertainties.
The uncertainties of the parameters, given as the CV of the input distributions (error bars). Bullets are enlarged for the most important parameter per substance.

Example EDC and benzene When comparing EDC and benzene, a significantly larger target variance is computed for benzene (15 percent versus 7 percent, see Figure 4.5). This is explained by a larger uncertainty of the input (Figure 4.6). The CV of the K_{ow} is 0.25 in case of benzene versus 0.18 in case of EDC. Furthermore, the overall sensitivity over the input range of K_{ow} is larger in case of benzene: The benzene concentration varies by 50 percent of its base case , while EDC concentrations only vary by 20 percent (see Figure 4.3, p. 58, and discussion on p. 60). The combination of larger sensitivity and

larger input uncertainty result in a larger target variance. The same argument holds in most cases.

Example PeCDD and HxCDD In case of PeCDD and HxCDD, the target variance of PeCDD concentration is larger than the variance of HxCDD concentration. The input uncertainties are the same for both substances and hence do not explain the difference. However, PeCDD concentrations vary over 50 percent of its base case, whereas HxCDD only varies by 30 percent (Figure 4.3). This indicates a larger overall sensitivity in case of PeCDD. Moreover, the slope in case of HxCDD is steep only for a short range of low values of P^0. It is almost zero for the major part of the total range. In the steep part of the curve, the sensitivity is indeed great and comparatively large concentrations will be produced; yet compared to the total range, these large values are too few to have a great impact on the target variance. The almost constant part of the curve with a low sensitivity dominates the target variance. In case of PeCDD, the curve is never as steep as in the former case, but it maintains a decent steepness over the entire range. The high concentration values produced at low vapor pressures may not be as high as in the former case, but they are greater in number. Thus the impact on the target variance is greater.

4.4.2 Inter-Scenario Differences

There are two types of inter-scenario behaviors between target variances in Figure 4.6: those cases where the variance decreases, and those where it stays the same. The difference in the model input in-between scenarios that can explain both, occurrence and direction of this effect, is the sensitivity of the ranges covered by the parameter distributions.

The first class is made up by the dioxins and DEHP. For all substances in this class, the target variance decreases from Scenario *uni* to Scenario *tri*, and decreases further from Scenario *tri* to Scenario *log*. The decrease has a magnitude ranging from 24 percent of the mean variance of two scenarios, to as much as 170 percent.

The second class consists of EDC and benzene. For these substances, the target variance is almost identical no matter which scenario is considered. Differences between two scenarios are less than 2 percent of the mean variance of the concerning scenarios in all cases.

In the following, examples from either class are used to explain how the inter-scenario differences in Figure 4.6 can be explained.

Variance Decreases with Scenarios In case of HxCDD, the vapor pressure P^0 is the parameter with the greatest contribution to the overall variance of the target distribution. Figure 4.7 shows the functional dependency plot of HxCDD concentration in sediment and the vapor pressure, together with the different input distribution shapes used for the parameter P^0.

This plot captures the interaction of different ranges covered by the input distributions, and the sensitivity of the model at points in these ranges. The functional dependency curve reveals a great sensitivity of the sediment concentration at low vapor pressures, indicated by a steep slope. At higher vapor pressures the sensitivity is much lower. From

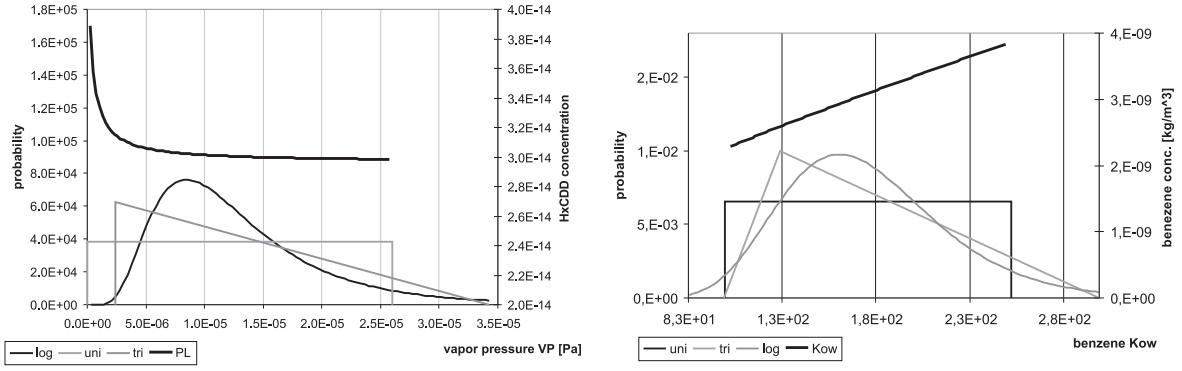

Figure 4.7: Functional dependencies with input distributions.
Functional dependency plots of HxCDD and benzene concentration in sediment, together with the different input distribution shapes used for the parameters P^0 and K_{OW}, respectively.

the probability distribution functions it is evident, that only the uniform distribution covers this range of great sensitivity with a significant share of its probability mass. The triangular distribution does not cover the lowest values at all, and the lognormal distribution, which always covers the range from zero to infinity, assigns only negligibly low probabilities to low vapor pressures. Hence only in case of the Scenario *uni* does the great sensitivity at low values come into effect, leading to a significantly larger variance of the target distribution.

The same argument can be made to distinguish between the triangular and the lognormal distribution. The triangular distribution covers the range from 2.5E-5 Pa to 1.0E-5 Pa with significantly more probability mass than the lognormal distribution. Hence the target variance in case of the *tri* scenario is greater. It is noteworthy that the difference in sensitivity is not as striking as before, which explains why the difference in target variance is smaller from *tri* to *log* than it is from *uni* to *tri*.

The input distributions differ at the upper end of the total range as well. But since the HxCDD concentration is almost constant for parameter values in this range, these differences hardly affect the target variance.

Same Target Variance in all Scenarios In case of benzene, the octanol-water partition coefficient K_{OW} is the parameter with the greatest contribution to the target variance. Plots of functional dependency of benzene concentration in sediment and K_{OW}, along with the input distributions used for K_{OW} in the different scenarios are presented in Figure 4.7.

Similar to the above example of HxCDD, the scenarios differ in the ranges covered by the input distributions. However, the target values are almost identical as Figure 4.5 shows. The difference to the previous example is in the curves of the functional dependency plot. The change of benzene concentration with the K_{OW} is almost linear. Thus the sensitivity measured as the slope of the curve is the same at every point in the total range, and differences in the covering of the range by the different distributions do not matter.

This is in agreement with mathematical theory. A well known property of the variance $\mathrm{Var}(X)$ of a random variable X is that $\mathrm{Var}(mX + b) = m^2\mathrm{Var}(X)$. Moreover

it is known that the variance of a sum of independent random variables is the same as the sum of the variances of the individual random variables, i.e. $\mathrm{Var}(X \pm Y) = \mathrm{Var}(X) + \mathrm{Var}(Y) \pm \mathrm{Cov}(X, Y)$, where $\mathrm{Cov}(X, Y)$ is the covariance. Hence in case of a linear functional dependency the target variance depends on the model and the input variance only, it does not depend on any other characteristics of the input distributions. Therefore, in the case of benzene, the parameter variance is the same for all scenarios.

The argument made for the two examples HxCDD and benzene can be applied to all substances, scenarios, and environmental compartments safe one case: for DEHP in air, variance increases from *uni* to *tri*. However, the parameter distribution is exceptional in this case: the triangular distribution used in *tri* is negatively skew, which makes the triangular distribution cover more sensitive ranges than the uniform and the lognormal distributions (in that order). When this is taken into account, the statement from above applies here as well.

Finally, note that great differences in the target mean often coincide with great differences in variance. It seems plausible that differences in scenarios that have a great impact on either the target mean or the target variance actually have an impact on the target distribution as a whole, hence changing both, the mean and the variance at the same time.

4.4.3 A Word On 90^{th} Percentiles

In the previous sections, input distributions and computed target distributions are characterized by the mean and the standard deviation. In practical risk analysis it is often the mean and the 90^{th} percentile or the 95^{th} percentile that are considered. Standard deviation and location of the 90^{th} percentile are similar to the extent that both describe the spread of the distribution. Often, a distribution possessing a large standard deviation will also have a large 90^{th} percentile. However this need not be the case, as has been shown in Section 3.2.3 in case of the lognormal distribution, where the 90^{th} percentile is shown to decrease with an increasing standard deviation (p. 41). Therefore in this section an effort is made to show that results found for the target standard deviation hold for the 90^{th} percentile as well.

Hamed and Bedient (1997) compare effects of different parameter distribution shapes (normal, lognormal, and uniform distributions) on 50^{th} and 95^{th} percentiles. The model under consideration is from the domain of public health risk assessment and calculates *incremental lifetime cancer risk*. Using first-order reliability method (FORM) as opposed to Monte-Carlo Simulation to propagate distributions through the model, FORM *probabilities of failure* are computed, meaning the probability for the target value to exceed a predefined fixed value. As fixed values the 50^{th} and the 95^{th} percentile of a base case target distribution are chosen.

Their findings are relevant here, as both, the exceedence of the 95^{th} percentile and the 90^{th} percentile itself (as treated in Hamed and Bedient (1997) and in this work, respectively) make statements about the tails of the distribution, while the exceedence of the 50^{th} percentile and the standard deviation describe more central properties of the distribution.

Hamed and Bedient (1997) found that exceedence probabilities for 50^{th} and 95^{th} percentiles are in "excellent agreement", i.e. they behave alike. They argue that this is expected: If the use of certain input distribution shapes results in increased target values, then the probability to exceed a threshold value increases irrespective of the threshold value (the 50^{th} or the 95^{th} percentile in this case). In contrast, it was found that the impact that a change of parameter distribution shape had on the exceedence probability was much greater when the 95^{th} percentile was considered as the threshold value. The impact was measured as the maximum relative change in exceedence probability from a base case.

In this work, a linear regression is performed to establish a correlation of 90^{th} percentiles and standard deviations. If 90^{th} percentiles and standard deviations are correlated, they can be assumed to behave in an analog way, and that results about standard deviations from the previous section also apply to 90^{th} percentiles.

Before a regression can be performed, standard deviations and 90^{th} percentiles of the different substances need to be normalized, because otherwise the enormous differences in-between substances marginalized the differences in-between scenarios. Unlike before, where normalization by the mean has been used to make means and standard deviations comparable, here standard deviations and 90^{th} percentiles are divided by the average median of the scenarios per substance. The median is the 50^{th} percentile, hence it is more compatible to the 90^{th} percentile (the same way, the mean and standard deviation work well together). The decisive difference between mean and standard deviation of a random variable compared to median and 90^{th} percentile, is that the former two are affected by the value of the random variable[6]. In contrast, the median and the 90^{th} percentiles are based on a ranking of the values or, in the continuous case, they are based on the amounts of probability mass to their left and right, regardless of its absolute location. When large standard deviations of the target value coincide with a great skewness of the target distribution, the mean is likely to be large as well. Hence the relative effect of normalization on the 90^{th} percentile is much greater than on the standard deviation. The median is chosen to avoid this.

Despite the difference in their nature noted above, standard deviation and 90^{th} percentile behave in a similar way as measure of the spread of the target distribution. The similarity can be demonstrated with a linear regression that has been performed for 90^{th} percentiles against standard deviations, all normalized by the average of medians as described above. Table 4.2 lists the coefficients of determination of the regression.

The regression of 90^{th} percentiles of the *log* scenario to standard deviations of the *log* scenario fits the data very well, as a coefficient of determination of $R^2 = 0.98$ shows. Figure 4.8 shows this result graphically. The same is true for the regression of 90^{th} percentiles and standard deviations of the *tri* scenario, where the coefficient of determination is $R^2 = 0.97$. R^2 may be interpreted as the extend to which one variable explains the other. Here, the 90^{th} percentile is explained to 98 percent by the standard deviation (or to 97 percent in case of triangular distributions). Hence the same arguments that explained target standard deviations can be used to explain target 90^{th} percentiles.

[6]This is evident from the integral definition of expected value $E(X)$ and variance $\mathrm{Var}(X)$, namely $E(X) = \int_{-\infty}^{\infty} x f(x)\,dx$ and $\mathrm{Var}(X) = E[(X-\mu)^2] = \int_{-\infty}^{\infty} (x-\mu)^2 f(x)\,dx$, which are affected by x and the distance $(x-\mu)$, respectively.

Table 4.2: Coefficients of determination.
Coefficients of determination R^2 of linear regressions of 90^{th} percentiles (rows) against standard deviations (columns). In case of *uni*/*uni* regression determination is raised to 0.83 when an outlier is omitted (TCDD concentration in soil, see text for details). The coefficients of determination are high and indicate a good fit of the regression to the simulation data.

	uni	*tri*	*log*
uni	**0.69**	0.89	0.78
tri	0.51	**0.97**	0.93
log	0.38	0.97	**0.98**

In case of the regression of 90^{th} percentile against standard deviations of the *uni* scenario, the coefficient of determination is just $R^2 = 0.69$, which is significantly lower than in the two previous cases. The data and regression curve are shown in Figure 4.8. TCDD concentration in soil was treated as an outlier. An explanation for this will follow in the next paragraph. By omitting this data point, the determination can be raised to $R^2 = 0.83$; still less than in the cases before.

Both, the outlier and poor determination of the regression in case of the *uni* scenario can be understood by looking at functional dependencies and parameter ranges covered by input distributions. As stated before, in many cases the curve describing the functional dependency of substance concentration in a compartment on an input parameter is particularly steep at values closest to zero, i.e. sensitivity is greatest close to zero. At the same time, it is often this range closest to zero of the parameter that is covered only by the uniform distribution, and not by the other distribution types (see Figures 4.3 and 4.7). Hence, most extreme target values are computed in the *uni* scenario. In case of extreme values, the behavior of standard deviation and 90^{th} percentile differ, as explained before. Therefore the fit of the regression can be expected to be less good in case of the *uni* scenario. In case of TCDD in soil this is taken to an extreme. The functional dependency curve (see appendix) is by far steeper than in any other case, which results in extremely large TCDD concentration values. The same reasons that cause a greater scatter in all the *uni* against *uni* data point, makes TCDD in soil an outlier.

Furthermore regressions of *uni* 90^{th} percentiles to *tri* and *log* standard deviations are better than regression to the *uni* standard deviations (R^2 of 0.89 and 0.78 as opposed to 0.63, see Table 4.2). As the triangular and lognormal distributions mostly do not cover the range closest to zero, it is plausible that their target standard deviations are in better agreement to the 90^{th} percentiles of the *uni* scenario than the standard deviations of the *uni* scenario itself.

Conclusion

In summary, the 90^{th} percentiles and standard deviation of target values showed essentially consistent behavior in case of the considered substances and scenarios. Exceptions occurred when target distributions had long flat tails, i.e. when there were only few very large values generated by Monte-Carlo simulation. In such cases 90^{th} percentiles and standard deviations are not readily comparable anymore, due to their different natures

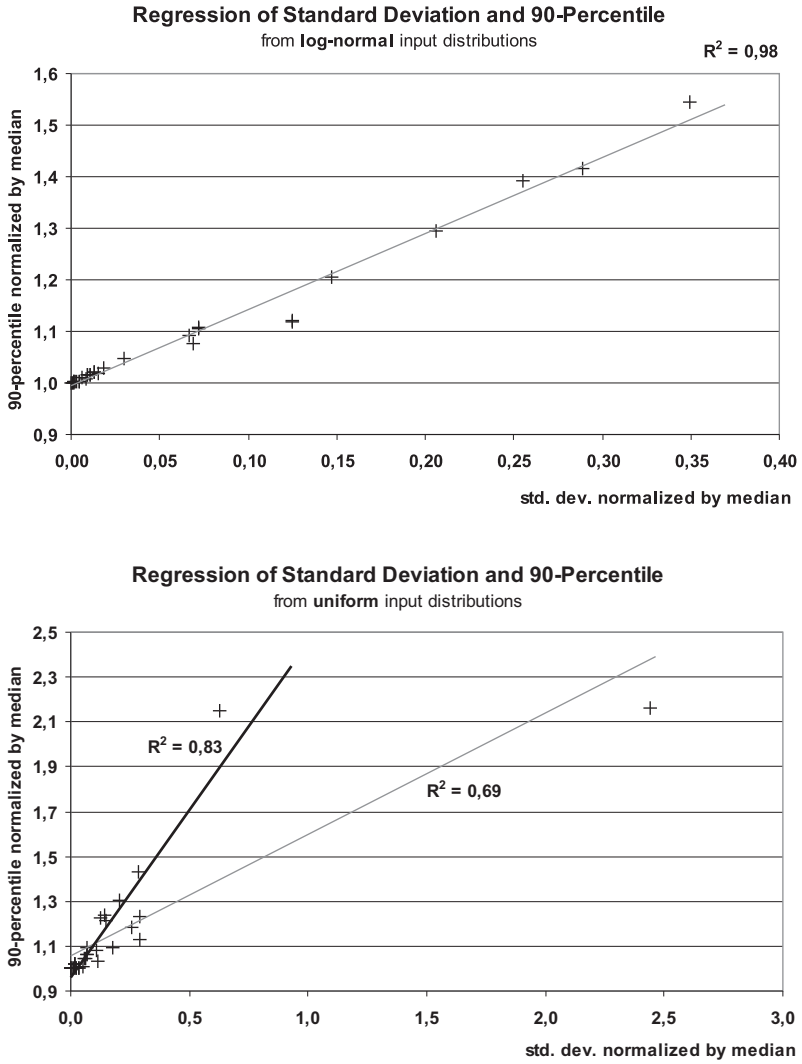

Figure 4.8: Regression of 90^{th} percentile versus standard deviation.
In the bottom plot, two regression curves are shown: the result of regression all data, and the result when the outlier at (2.44, 2.16) is omitted.

(the standard deviation being a weighted measure as opposed to the 90^{th} percentile being based on a ranking). It is in such cases that extra attention should be paid to 90^{th} percentiles.

This result is in agreement with the findings of Hamed and Bedient (1997) as stated above. Additionally, Hamed and Bedient show that in their case, the impact of parameter distribution shapes is greater when considering the 95^{th} percentile as threshold value. An analog trend has not be found in this case. Reasons for this might be, that due to their different natures, standard deviation and 90^{th} percentile do not compare as well as the 50^{th} and 95^{th} percentile as threshold values, and the differences in considering standard deviation and 90^{th} percentile directly as opposed to considering percentiles as threshold values.

4.4.4 Informational Content of the Input and Uncertainty of the Output

In the previous sections, a noteworthy trend was observed: the variance of the computed concentrations decreased from uniform input distributions to triangular distributions and again to lognormal distributions (Figures 4.5 and A.4–A.6). There were cases where the target variance decreased very little or remained about the same, but it did not increase significantly (the sole exception DEHP in air is discussed above). This order (*uni–tri–log*) coincided with the order of increasing informational content of the distribution types: According to the maximum entropy principle (Section 3.2.1), the uniform distribution is appropriate when the only information available are lower and upper bound. The triangular distribution is inferred from upper and lower bound also, and additionally the mode of the distribution. The lognormal distribution is based on arithmetic mean and standard deviation. When estimated from data, the required minimum number of observances are five and 25 observances, respectively, thus more information is contained in mean and standard deviation than in upper bound, lower bound, and mode. Hence, the ranking of the computed target variance mirrors the informational content of the parameter distributions.

A plausible reason for this ranking is the tendency of distribution types that are based on more information to accumulate more of their probability mass closely around their mean. When this is the case, there is a smaller total range. With a smaller total range, there is also a smaller chance to cover additional parameter ranges of large sensitivity, that are not covered by a distribution based on less information.

As explained above in this section, the target variance is influenced by the sensitivity of the range of parameter values that is covered by the parameter distribution. It follows that differences in the parameter ranges are a necessary prerequisite, and the sensitivity must be particularly large over the range covered by one distribution but not the other. Naturally differences in the range that is covered are more likely at the tails of a distributions than in its middle if the distributions are roughly at the same location. Chemical exposure models such as SimpleBox are likely to fulfill these preconditions, because exponential dependencies are common in the model equations, hence sensitivity tends to increase towards one of the distribution's tails.

In this sense, the order in target variance is also a consequence of the information content of the parameter distributions. This result is consistent with Bukowski et al. (1995), who note that addition, multiplication, and division of combinations of uniform and triangular distributions result in remarkedly wider target distributions than combinations of normal and lognormal distributions.

4.4.5 Conclusion of the Influence of the Shape on the Dispersion of the Target Distribution

The effects of different parameter distribution types on the spread of the computed target distributions has been assessed.

The computed target distributions differed in their variance from substance to substance. These differences can be explained by input uncertainty of the parameters and their sensitivity measured as the overall variation. Both have a positive effect on the target spread.

In some cases, uniform, triangular, and lognormal parameter distributions resulted in significantly different target variances. Target variances were almost identical in-between scenarios, when functional dependencies between input parameters and target value were near-linear. Significant differences occurred when the functional dependency between input parameter and target value were non-linear. Then, the impact on the target variance were much larger than the impact on the target mean discussed in Section 4.3. And the differences between scenarios could be explained from case to case by considering the sensitivity of the range of parameter values covered by the parameter distributions.

The variance of a target distribution is a measure of its spread, as is the 90^{th} percentile. The behavior of the 90^{th} percentile was found to be so similar to the behavior of the standard deviation, that results from the analysis in this section may be transfered to the 90^{th} percentile.

Finally, the ranking of parameter distribution type after the variance that they cause mirrors the informational content that is attributed to the distribution types in maximum entropy theory. Hence, in this case, less informational content resulted in a larger uncertainty of the result.

4.5 Shape Influence on Shape

There are three main influences that determine the target distribution shape:

1. the input parameters **shapes**,
2. the **model** (i.e. the form of the function between parameter and target value), and
3. influences from **interaction** with other probabilistic parameters.

The central limit theorem gives an idea of how item 3 influences the shape.

Central Limit Theorem

The central limit theorem (CLT) of probability theory describes how the number of random variables affects the shape of their sums or products. Usually employed in the context of sums of random variables, it states that given a number of independent, positive random variables, the distribution of their sum will be approximately normal, i.e. as their number becomes large, the distribution of the sum converges to a normal distribution (Sachs, 1992). The CLT can also be applied to products of random variables. By taking logarithms this case is reduced to the former case of a sum, now a sums of logarithms of random variables. In consequence, their distribution is then approximately lognormal when the number of random variables in the product is large.

The CLT holds regardless of the distribution type of the factor random variables. If the number of probabilistic parameters is large enough, the shapes of input parameters, and the functions in the model (items 1 and 2) will have no impact on the resulting shape. It can be expected that their influence grows when fewer parameters are varied probabilistically. This section discusses influences on the shape for large numbers of varied parameters, few varied parameters, and the special case of one probabilistic parameter.

4.5.1 Many Probabilistic Parameters

In multiplicative models with large numbers of parameters, the computed target distribution is – according to the CLT – approximately lognormal. The same seems to be true in case of the SimpleBox model: Berding et al. (2000, p. 138) found, that the distribution of concentrations in the environmental compartments are close to lognormal by applying a Kolmogorov-Smirnov test. This result is plausible, because even if the functions between parameters and target values in case of SimpleBox are not solely multiplicative, a great share of the operations are products, and they might dominate the shape of the target distribution (MacLeod et al., 2002).

Obviously, the number of parameters that are varied probabilistically (and hence correspond to independent random variables in the CLT) has a major influence on how well a lognormal distribution fits the target distribution.

Berding et al. applied the Kolmogorov-Smirnov test to the target distributions of three scenarios, varying either substance parameters only (meaning the physico-chemical properties K_{OW}, aqueous solubility, and vapor pressure along with degradation rates and emissions); or the remaining parameters, called model parameters, or, in the third scenario, all parameters. The substance parameters add up to about fifteen parameters (depending on mode of entry), while there are 38 model parameters, and hence an overall number of 53 parameters if both substance and model parameters are varied.

The Kolmogorov-Smirnov test was passed in most cases when 38 or 53 parameters were varied. In case of the fifteen substance parameters it is failed often, the critical value being just missed. This suggests that the more parameters are varied, the closer the target distribution gets to a lognormal shape, just as the CLT states for multiplicative models.

To illustrate that there is no significant difference in the target shape, no matter which distribution type is used for an individual parameter (or a small group of parameters such as the physico-chemical parameters), simulations of the *comparable* Scenarios *uni*, *tri*, and *log* have been performed with a modification: all parameters were modeled probabilistically (whereas before, only the physico-chemical parameters have been varied). Figure 4.9 shows an exemplary plot of the target distribution for soil concentration of benzene. Results for uniform, triangular, and lognormal distributions for physico-chemical parameters are shown in one plot. Even though 50'000 Monte-Carlo shots were performed, the distributions differ somewhat, yet there is no visible trend in the difference from scenario to scenario. The difference seems to be due to the randomness of the Monte-Carlo approach only, and indeed the scatter of several Monte-Carlo simulations of the same parameters scenario can visually not be differentiated from the scatter between the curves in Figure 4.9.

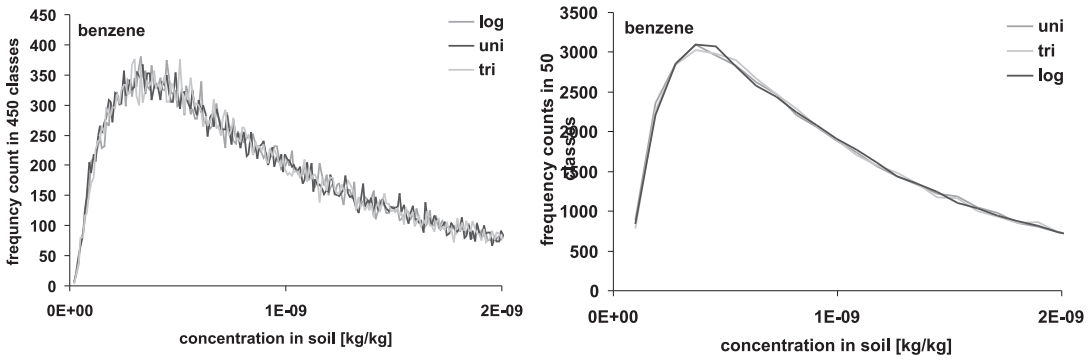

Figure 4.9: Target distributions of soil concentration.
Target distributions of soil concentration using uniform, triangular, or lognormal distributions. For these three scenarios, all parameters were varied probabilistically. The scenarios differ in the distribution types that were assumed for the physic-chemical parameters K_{ow}, aqueous solubility, and vapor pressure. For these three, uniform, triangular, and lognormal distributions were used. In the left plot, the 50 000 shots performed are distributed over 450 equidistant classes. The smoother curve in the right plot is the result of limiting the number of classes to 50. Evidently, the differences in the result among the three scenarios are due to the randomness of the Monte-Carlo simulation rather than the choice of input distributions.

4.5.2 Few Probabilistic Parameters

In case of the *comparable* scenarios, the number of probabilistic parameters is only three. Moreover, in many cases there are probabilistic parameters that have little or no influence on the target distribution, i.e. the target value is insensitive for such parameters. Effectively, this then reduces the number of distributions affecting the shape of the target distribution to two or less.

Consequently, the target distribution shapes are far from lognormal. It has been tried to plot the empirical cumulative density function against the lognormal cumulative derived from mean and median estimated from the simulation results. Any two resulting curves never fit together.

Three cases occurred. Often, the target mean was lower than the target median, indicating that the distribution is negatively skew. This can be due to the input parameter shape and/or the function between parameter and target value. Negatively skew target distributions can easily arise when the input distribution is negatively skew (which does occasionally happen), and also when a positively skew parameter distribution and a decreasing function of parameter and target value coincide, because any decreasing function will map a positively skew distribution to a negatively skew distribution shape and vice versa. A lognormal distribution (which is always positively skew) could in this instance not be plotted. In cases were both, the empirical cumulative, and the cumulative derived from estimated mean and median could be plotted, mostly the empirical cumulative was by far steeper than the derived lognormal cumulative. Figure 4.10 shows TCDD soil concentration as one example for this case. For comparison, a plot of the results for the same substance and compartment, but of a simulation varying all 53 parameters is included in Figure 4.10. It is expected, that the cumulative is steeper when only three parameters are varied (the right plot covers four orders of magnitude, while the plot on the left covers only two), because the 50 additional parameters all contribute to the total uncertainty.

The third case is the one exception to this behavior: in one case, the empirical cumulative was not steeper but flatter than the lognormal cumulative.

4.5.3 One Probabilistic Parameter

If only one parameter is varied, there is no influence from interaction with other probabilistic parameters. If in addition, the function between parameter and target value is linear, then the model will have no influence on the target distribution's shape either, and the shape will only be determined by the parameter distribution – it will be a scaled image of the parameter distribution. Figure 4.11 illustrates this point.

The benzene concentration in soil is a nice example of this case. Here, 100 percent of the contribution to variance are is due to the K_{ow}. As it is know from previous sections, the functions of parameters and concentrations are close to linear (p. 64). As a result, the shape of the target distribution closely resembles the shape of the only input parameter distribution (Figure 4.12). If, on the other hand, the relationship between parameter and target value is non-linear, the input distribution is mapped to a distorted image of itself, the distortion being determined by the functional dependency.

One of the most extreme non-linear functions is that of TCDD vapor pressure and soil concentration (Figure 4.13). The target distributions all show similar shapes despite the fact that vapor pressure has a contribution of about 90 percent to the overall variance, and hence there is almost no other probabilistic parameter to interact with (K_{ow} does not contribute to the variance, hence solubility accounts for the remaining 10 percent). The function dependency of vapor pressure and soil concentration has a very steep slope at low vapor pressures. Its steepness is monotone decreasing. A steep slop results in a wide, spread out target distribution, because even two close input values will be mapped to target values that are relatively far apart. In contrast, a gentle slope focuses the target distribution to a narrow range, just like a constant function would map all values to one single target value. And that is what happens here, especially to the uniform and triangular parameter distributions (Figure 4.13). The long gentle tail of the function concentrates much of the target probability mass in a peak around 4.5E-17 kg/kg, while its steepness at low vapor pressures gives the target distribution a long flat tail. Understandably, the effect is not as strong in case of the *log* scenario, since the lognormal parameter function does not cover the steep ranges of the target value/parameter function very well. However the same effect of concentrating more probability mass in a taller peak and flattening the tail of the distribution is visible.

While in case of benzene and an almost linear model function, the parameter distribution shapes alone determined the target distribution shapes, TCDD is an example of how the model function has a strong impact on the target distribution shape, when it deviates from linearity.

4.6 Sensitivity of Shape versus Sensitivity of the Mean

In Scenarios *uni*, *tri* and *log*, *comparable* input distributions have been used. The distributions in the scenarios are comparable in the sense that their mean values and their

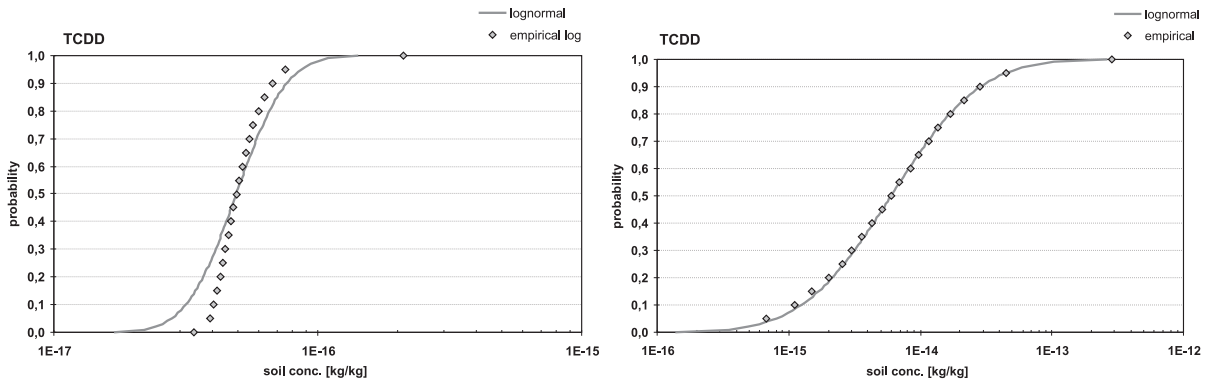

Figure 4.10: Cumulative density functions of TCDD soil concentration.
In cases were both, the empirical, and the derived lognormal cumulative could be plotted, mostly the empirical cumulative was by far steeper than the lognormal cumulative (*left*). When all parameters were varied, it was possible to fit the empirical with lognormal distribution (*right*).

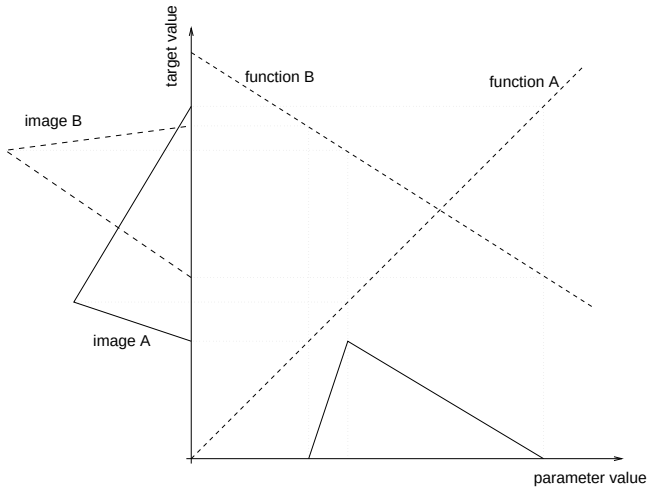

Figure 4.11: Linear model.
If the function between parameter and target value is linear, then the shape will only be determined by the parameter distribution – it will be a scaled image of the parameter distribution. A decreasing function maps to a mirrored image.

standard deviations are equal, and differ only in their shapes. Hence, in Sections 4.3–4.5 it has been shown how the selection of different shapes affect the resulting target distributions.

The selection of different means or different standard deviations can have similar effects on target distributions. Since the data for determining input distributions are often scarce (Chapter 2) it is useful to know whether more effort should be made to determine the "best" shape or the "best" mean (or other measure of location) for a parameter. In other words, it would be useful to know whether target distributions are more sensitive towards uncertainty about the mean or uncertainty about the distribution type.

In order to quantify the difference between selecting another distribution shape and changing the mean, the *equivalence shift* is defined. The equivalence shift is a measure describing how far one distribution needs to be shifted (i.e. by changing its mean) to produce a target

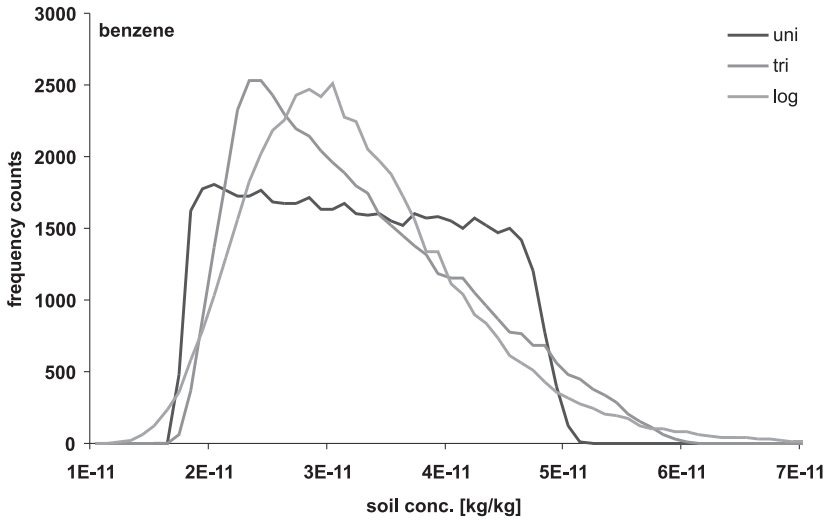

Figure 4.12: Probability density function of benzene in soil.
The plot shows the three different target distributions from the Scenarios *uni*, *tri*, and *log*. As K_{ow} is the only sensitive parameter and the function between soil concentration and K_{ow} is almost linear, the target distributions closely resemble the input distributions. (Input distributions are shown in Figure 4.7 on page 64.)

distribution equivalent to that of a particular other distribution type. Starting point is a situation of comparable locations, e.g. the same means for both distribution types.

Two target distributions are considered equivalent in this section, when they possess the same standard deviation. The other readily available criterion would be equivalence of target means. Standard deviations are preferred, because effects are numerically larger in this case. [7]

4.6.1 Scenario Definition

Based on the *comparable* scenarios (Section 4.2), a series of simulation runs has been performed in which input distributions of one scenario (*uni* or *tri*) are shifted until the target standard deviation equals those from the other scenarios (*tri* and *log*, or *log*, respectively). Standard deviations are kept the same during this procedure. All three substance parameters are shifted simultaneously, since the relative importance of the parameters varies in-between substances and compartments. Thus it is easiest to shift all parameter distributions, which will shift the important ones in any case.

Preliminary tests have shown that a shift of 50 percent of the distributions mean towards larger parameter values was sufficient.[8] In the range from 0 percent to 50 percent, five

[7] Computations with the target mean as the criterion for equivalence were also performed. The results were similar to the results presented, yet there was more scattering and there were more exceptions to the general trend.

[8] In three cases, namely air concentration of DEHP (*tri* and *log*) and sediment concentration of EDC (just *tri*), there were no equivalence shifts possible. Here, standard deviations from Scenario *uni* were lower than in case of *tri* or *log* and only decreased with shifting. Shifts to the opposite direction are not possible as the lower bound of the uniform distribution would become negative in that case.

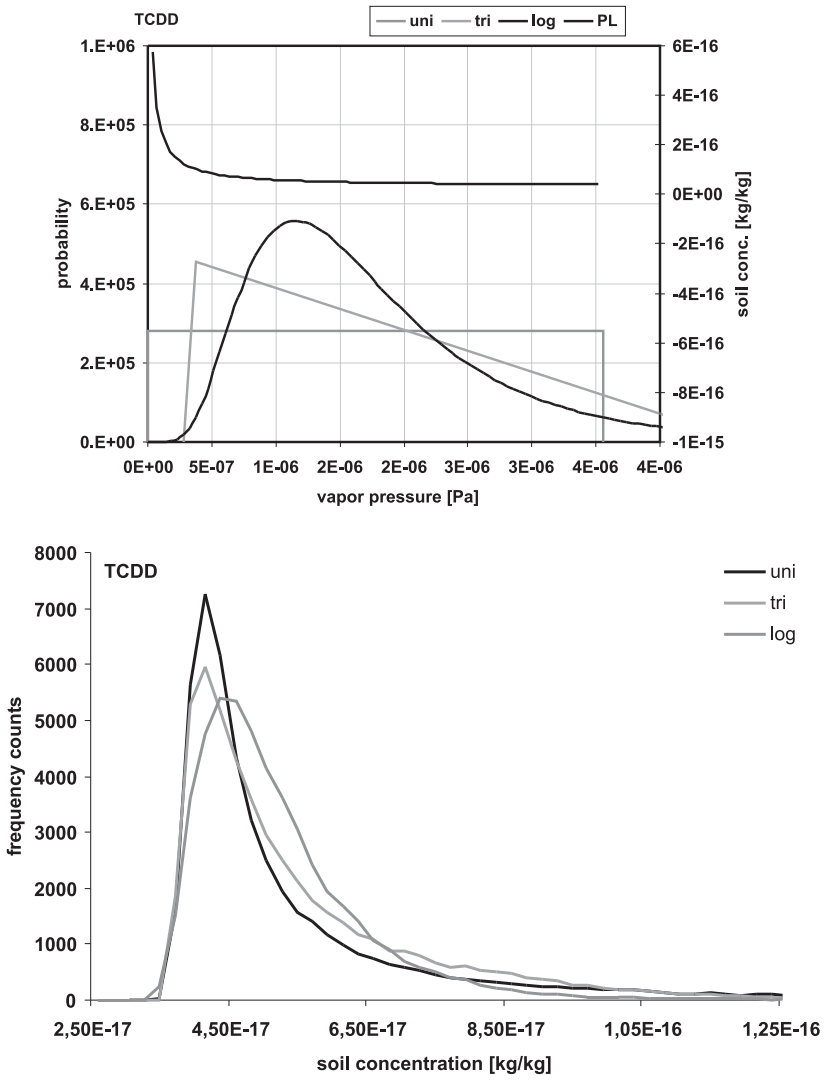

Figure 4.13: Probability density function of TCDD in soil.
The upper plot shows vapor pressure parameter distributions for TCDD along with the curve of the function soil concentration and vapor pressure. Below is a plot of the probability density functions of soil concentration computed for three scenarios (*uni*, *tri*, and *log*).

scenarios have been computed at equidistant steps. At 0 percent shift, the computation is identical to the *comparable* scenarios. Figure 4.14 shows an exemplary result of the simulations. A plot for one substance concentration in a specific compartment is given.

From such plots, equivalence shifts can be estimated. If the target variance changes continuously with the location of the input distribution, then in this case the equivalence shift for *tri* lies in-between 12.5 percent and 25 percent, since standard deviations at 12.5 percent and 25 percent are above and below the standard deviation computed in the *tri* scenario. And then the equivalence shift to match the mean of the lognormal distribution is between 25 percent and 37.5 percent.

To automatize finding these shifts, a regression curve is computed (Figure 4.14). The regression equation used is $y = bx^m$. It was selected from the Excel® built-in regression types, because it visually fits well in many of the cases, and the inverse function is readily

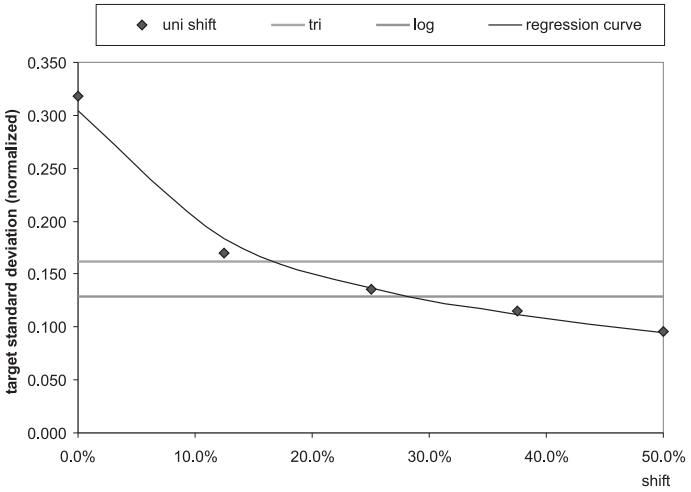

Figure 4.14: Standard deviation from shift scenarios.
Example Plot TCDD in water. In the plot standard deviation values of the concentration are plotted against the percentage of the input mean by which the distribution has been shifted (in this case the uniform distribution). Diamonds indicate simulation results at 0 percent, 12.5 percent, 25 percent, 37.5 percent, and 50 percent, and horizontal lines indicate standard deviations from the *tri* and *log* scenarios.

available. The plot shows that the equivalence shifts estimated from the regression curve are only rough approximations – even though the coefficient of determination is quite high at $R^2 = 0.99$ in this case. In fact, coefficients of determination indicate good fits in almost all cases (the values of R^2 are included in the summary plots, Figure 4.15). Yet the regression curve misses the computed value at 12.5 percent and intersects with the standard deviations from the *tri* scenario at shift values that is probably too large. Such inaccuracy may be tolerated, as the objective is to get only an idea of the shift needed to produce similar results.[9] It should be kept in mind however, that the results from this procedure are just rough approximations.

Two sets of scenarios were computed: in the first set, the triangular distributions from the *tri* scenario were shifted to match the *log* lognormal distributions. In the second set the uniform distributions from *uni* were shifted to match the results from *tri*, and shifted further to match the results from *log*.

4.6.2 Shifted Triangular Input Distributions

The values of R^2 that are indicated in the plot are all larger than 0.88 and on average as high as 0.95 and 0.97 for shifted *tri* scenario distributions and *uni* distributions respectively. Such high values show that the regression performed well for most of the cases considered. Among the estimated shift values, three cases can be distinguished:

[9]To derive a more robust estimate, linear interpolation in-between each two neighboring points could be calculated. Then, intersection points would only be computed when there are simulation results greater and smaller than the fixed values. Graphically this is a readily available feature in Excel®, yet determining the inverse function and intersection point is more arduous.

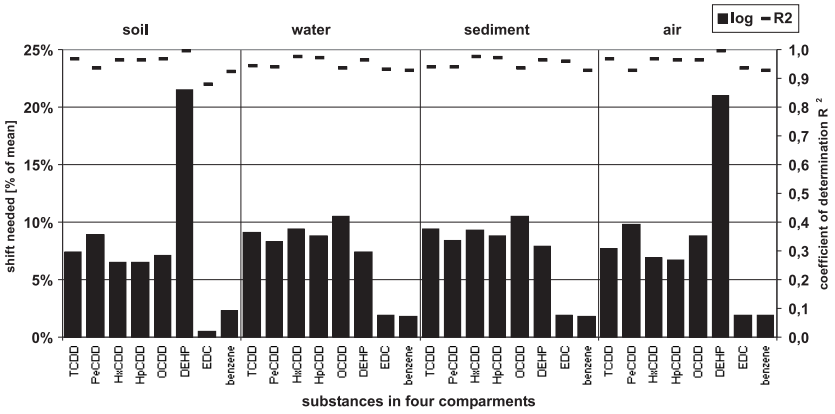

Figure 4.15: Equivalence shifts for triangular distributions.
Summary plot of equivalence shifts for triangular distributions. The bars give the percentage of the mean by which the uniform distribution need to be shifted to produce the same target standard deviation as in case of lognormal distribution shape. Coefficients of determination (R^2) are indicated as points above the bars of the bar chart, their values are on the secondary y-Axis.

1. The equivalence shift for dioxins takes approximately the same value in all compartments and for all dioxins considered,

2. DEHP behaves different from compartment to compartment, i.e. in soil and air the shifts are about twice as large as in the other compartments, and

3. EDC and benzene input distributions need significantly smaller shifts for equivalence to *log* results in all compartments compared to the other substances.

Case 1 The dioxins need an average shift of 8 percent . In Sections 4.3–4.5 the functional dependency plots showed that the dioxins have a range of large sensitivity for input values close to zero. It has been demonstrated that triangular input distributions in *tri* resulted in larger target variances than lognormal distributions in the *log* scenario, because the triangular distributions cover more of this particularly sensitive range. As the triangular distributions are shifted gradually to larger parameter values, i.e. away from the range of greater sensitivity, the target variance will decrease and eventually equal the variance of the *log* scenario. A plot of the lognormal distribution and the shifted triangular distribution computed to be its equivalent (in terms of target standard deviation) stresses this point (Figure 4.16). The parameter ranges that are covered by any such two distributions are in good agreement. This gives further support to the importance of the input parameter distribution for the target distribution.

Case 2 The case of DEHP is special because the equivalence shift differs remarkably from soil and air compartments to the water and sediment compartments: for the former two, the equivalence shift is about 21 percent, whereas it is just 7-8 percent for the latter two compartments. This is easily explained by considering the shapes of input distributions for the dominant parameters. The triangular distributions of K_{OW} and S_W have positive skewness, whereas the P^0 distribution is negatively skew. The skewness of the lognormal

distribution is always positive. A positively skewed triangular distribution is much closer to their lognormal counterparts to begin with, and less shifting is necessary to produce equivalent results. The contributions to variance help to explain the differences: in the compartments soil and air P^0 determines about 50 percent of the target variance, whereas it has only marginal influence in the water and sediment compartments (0 percent and 9 percent, respectively). Figure 4.16 shows DEHP input distributions for K_{ow} and P^0. For each parameter, lognormal and triangular distributions from Scenarios *log* and *tri* are given. In addition, the shifted triangular distribution is given, which is hence equivalent to the lognormal distribution in the target variance it produces. In the top row, the criterion is soil concentration variance to which vapor pressure contributes 50 percent, in the row below the criterion is water concentration variance where vapor pressure has no influence. It is evident, that the negatively skew vapor pressure distribution created a larger shift in case of the top row as opposed to the bottom row.

Case 3 In case of EDC and benzene, the equivalence shifts are significantly lower than in all other cases. This is the same for all compartments. An explanation can be found in the coefficients of variation (CV) of the input parameters. The parameter distributions of EDC and benzene differ from the other parameter distributions in the coefficient of variation. For these two substances, CV for sensitive parameters are significantly lower (Figure 4.6). The CV of the dominant parameters are 0.2 and 0.3 for EDC and benzene, respectively, compared to a CV of about 0.6 for most other substances. Figure 4.17 shows an illustration of the influence the CV has on the distribution shift. The ranges covered by the shifted distribution and the original distribution differ a lot more for smaller CV than for larger CV. In case of small CV only small shifts are needed to cover a parameter range that produces results equivalent to the lognormal distribution, which explains the small equivalence shift in case of EDC and benzene.

4.6.3 Shifted Uniform Input Distributions

When the uniform parameter distributions from Scenario *uni* are shifted towards larger parameter values there are two cases to consider: they can either be shifted until a standard deviation equivalent to the *tri* scenario *or* a standard deviation equivalent to the *log* scenario is reached. Simulations were performed for both cases, and the results are shown in Figure 4.15 Here, the same distinction into three sub-cases as before is made (p. 77).

Case 1 Among the dioxins there is again a fairly common behavior. To equate the *tri* scenario, the uniform distribution needs to be shifted by 18 percent on average; to equate the *log* scenario an average shift of 29 percent is needed. The same explanation as above applies. Note that the difference of the shifts between *tri* and *log* ($29\% - 18\% = 11\%$) is close to the 8 percent equivalence shift of the triangular distribution, and therefore consistent with that earlier result.

Case 2 As before, the results in case of DEHP are different in soil and air opposed to water and sediment. In the latter case, there is a large equivalence shift for the

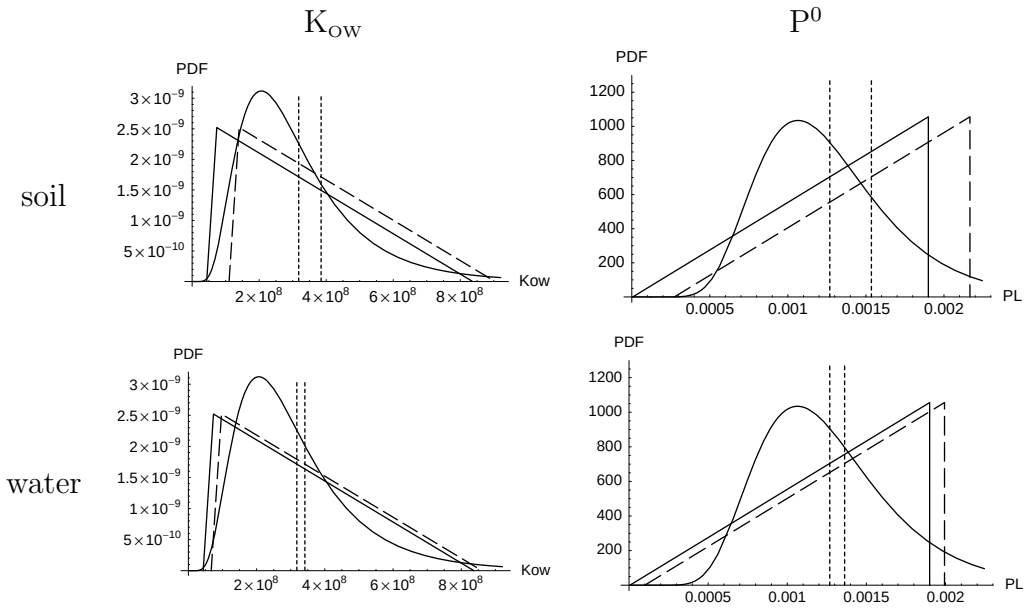

Figure 4.16: Impact of negative skewness (*log* and *tri*).
Plots display DEHP input distributions for K_{OW} (left) and P^0 (right). For each parameter, lognormal and triangular distributions from Scenarios *log* and *tri* are given (solid lines). In addition, the shifted triangular distribution that results in the same target variance than the lognormal distribution is given (dashed lines). In the top row, the criterion is soil concentration variance, to which vapor pressure contributes 50 percent, in the row below the criterion is water concentration variance where vapor pressure has no influence. It is evident, that the negatively skew vapor pressure distribution created a larger shift in case of the top row (soil) as opposed to the bottom row (water). Dash vertical lines indicate the mean values of the distributions.

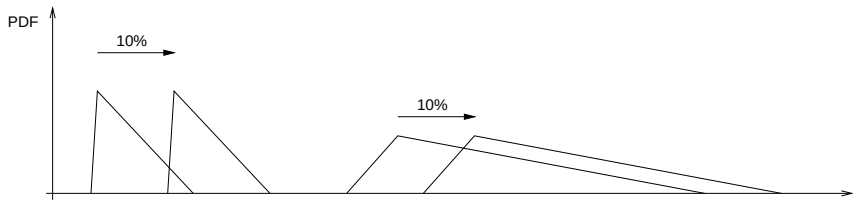

Figure 4.17: Effect of shifting different coefficient of variation (CV).
In case of a smaller CV, the ranges covered by the shifted distribution and the original distribution differ a lot more from each other than in case of a larger CV.

uniform distribution to equate the results of *tri* (20 percent and 18 percent in water and sediment, respectively), and there is a relatively small extra shift necessary to equate *log* (8 percent and 9 percent, respectively). This is understandable, since the triangular and the lognormal distributions are more similar to each other than to the uniform distribution.

The other two compartments soil and air show a different behavior. The equivalence shift to equate *uni* and *tri* is 6 percent in soil. In the air compartment there is no shift necessary, as the results from *uni* and *tri* are already almost identical (less than 0.5 percent difference). In this case the difference between *tri* to *log* is larger than the equivalent shift for *tri*: 18 percent in case of soil, and 19 percent in case of air. Here, as opposed to Case 1, results from the uniform distribution are closer to the results from the triangular distribution. Again, the input distribution shapes provide an explanation. As

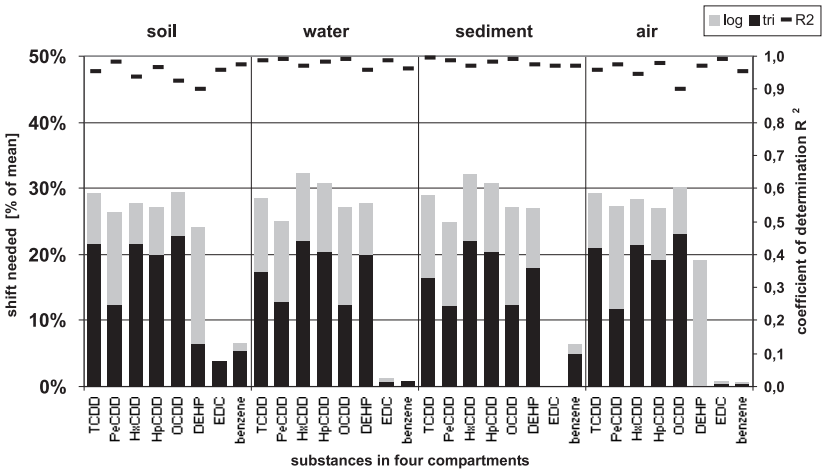

Figure 4.18: Equivalence shifts for uniform distribution.
The bars give the percentage of the mean by which the uniform distributions need to be shifted to produce the same target standard deviation as in case of triangular and lognormal distribution shapes. Coefficients of determination (R^2) are indicated as points above the bars of the bar chart, their values are on the secondary y-Axis. In cases of air concentration of DEHP (*tri* and *log*) and sediment concentration of EDC (just *tri*), no values could be computed (see text for details).

described before, the triangular distribution of vapor pressure is negatively skew whereas the other parameter distributions are positively skew (Figure 4.19). Target variance in case of *uni* is larger than target variance in case of *tri*, because a particularly sensitive parameter range close to zero is covered with more probability mass by the uniform distributions. Shifting the uniform distribution moves it out of this sensitive range. The negatively skew triangular distributions covers the sensitive range less, hence the uniform distribution needs to be removed further than in case of the positively skew triangular distribution.

Case 3 As in the case of shifting triangular distributions, the equivalence shifts for the parameter distributions of EDC and benzene are generally less than for dioxins or DEHP. The same argument holds as above. Compared to the previous results, there is more variation in the equivalence shifts. However, the precision of the method that was used to derive these values is not high enough for these differences to be significant.

4.6.4 Conclusion

The equivalence shifts are summarized in Table 4.3. The relative sensitivity of shape and mean can be assessed by comparing the equivalence shifts to the uncertainties about the mean. In the following, two measures of uncertainty about the mean are considered.

One estimate of the uncertainty about the mean is the standard deviation of the mean $\sigma_{\bar{x}} = \frac{\sigma}{\sqrt{n}}$. The estimate $s_{\bar{x}}$ of $\sigma_{\bar{x}}$ is included in Table 2.3 for the mean values estimated in this study. They range from negligible (0.1 percent in case of EDC vapor pressure) to about 100 percent of the mean (HpCDD vapor pressure), with an average of 46 percent. To

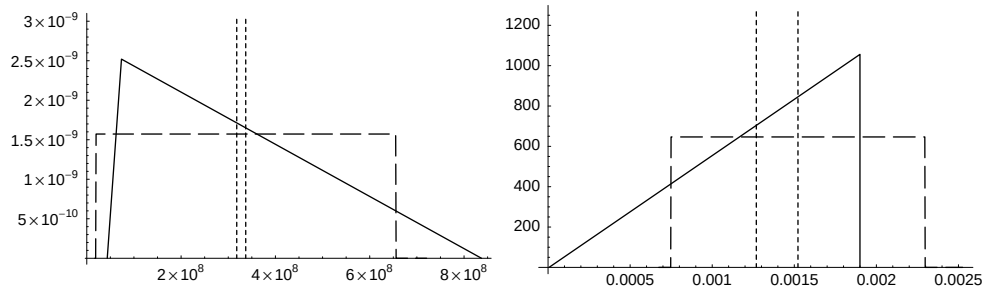

Figure 4.19: Impact of skewness (*tri*).
The impact of skewness on equivalence shifts in case of DEHP. In the left picture, K_{OW} parameter distributions are shown with the necessary shift for the soil compartment, in the right picture, P^0 parameter distributions with the necessary shift for the water compartment are displayed. Vertical lines indicate the distribution means. To equate the P^0 triangular distribution, which is negatively skew, a larger shift is necessary.

Table 4.3: Summary of equivalence shifts.
Percentages are percent of the input mean. In case 1 and in case 2, average values are given.

	equivalence shift [%]		
Case	triangular→lognormal	uniform→triangular	uniform→lognormal
1. Dixions	8	18	29
2. DEHP	7–21	6-20	19-28
3. EDC/benzene	2	2	3

make these standard deviations comparable to the equivalence shifts, it may be necessary to double or triple them. Compared to the largest equivalence shifts (about 30 percent), the uncertainty expressed by the standard deviation of the mean is large. However the uncertainty about the shape is not negligible, and in some cases even in the same order of magnitude (benzene and EDC).

Table 2.3 also lists the means estimated by Berding et al. (2000) and the *selected values* from Mackay et al. (1999). Considering the means estimated in this work, and their standard deviations, the different estimates of the mean are not in agreement, e.g. in case of OCDD vapor pressure there is a difference of four orders of magnitude to the selected value from Mackay et al., in case of TCDD vapor pressures there is a difference of two orders of magnitude to Berding et al. (2000). These differences can be attributed to differences in the data basis as well as to the difference approaches (Section 2.4). Nevertheless do they indicate an uncertainty about a "best estimate" of the parameter that is much greater than the standard error of the mean, estimated in this study. Compared to these differences of "best estimates" from different studies, the uncertainty expressed in the equivalence shifts is marginal.

Hence whether to put more effort into estimating the mean, or into selecting the most appropriate distribution type is determined by the uncertainty about the mean. When the uncertainty about the mean is derived from the difference in literature values of physico-chemical properties, which vary frequently by several orders of magnitude, then

the impact of parameter distribution shape is marginal. However substance concentration have been shown to be sensitive to changes in the input distribution type in some cases. When the location of a parameter distribution is known with some confidence, then the appropriate choice of a distribution type matters.

4.7 Generic Uncertainties

It has been shown in Chapter 2 of this work, that measurement data for K_{ow}, aqueous solubility S_w, and vapor pressure P^0 are scarce. For most substances, there is no sufficient basis for reliable statistics. This is particularly problematic when estimating higher order moments such as the variance and the coefficients of skewness and kurtosis, according to Tukey's 5^k rule (Section 3.1).

In situations of scarce data, deterministic values for parameters are often set based on expert opinion, sometimes collected measurement data are considered in addition. Examples are performing expert elicitation or utilizing so-called selected values in substance handbooks, e.g. Mackay et al. (1999), i.e. values that are recommended by an expert. Care must be taken, because every selection of a recommended value is aimed at a certain use of the selected value, and selected values should not be used out of context.

In probabilistic uncertainty analysis, such expert opinion is a valuable clue on the location of a parameter distribution and can by utilized in different ways to parameterize a probability distribution. For example, it can be used as the median (Beyer and Matthies, 2001), or as the mean value of the distribution (McKone et al., 1995).

Attempts have been made to use a similar approach in regard to parameter uncertainty, i.e. parameterization of the spread of parameter distributions. Default or generic measures of variance have been proposed for substances where available data was insufficient to warrant the use of statistics. In all cases the motivation to use a generic approach was lack of sufficient data. The procedures differ in the degree of detail: the level of generalization ranges from just one uncertainty for all parameters to distinct uncertainties for several ranges of *each* parameter.

In the following sections, approaches used by Beyer and Matthies (2001), McKone et al. (1995), MacLeod et al. (2002), and Jager et al. (1997) are presented and discussed. The four cases share that they all apply to physico-chemical substance properties. The lineup follows the order from the most general approach to more specialized proceedings.

4.7.1 One CV for All Substances

Beyer and Matthies (2001) derive generic input distributions to use with the ELPOS model. ELPOS uses solubilities as physico-chemical properties in all cases, as opposed to partition coefficients. For air, water, and octanol solubilities, lognormal distributions are assumed. All other partitioning data, such as octanol-water partitioning coefficient, are derived from these three solubilities. The medians are set to selected values.

Regarding uncertainties Beyer and Matthies take the most generic approach: *one* uncertainty is assigned to all physico-chemical properties. The standard deviation σ on

logarithmic scale is used to parameterize lognormal distributions. A value of σ=0.77 is chosen to ensure that almost all probability mass of the lognormal distribution lies within a range of plus or minus one order of magnitude; i.e. 99.7 percent lies within the range from μ-3σ to μ+3σ where μ is the mean of the normal distribution on logarithmic scale.

Values of σ can be converted to coefficients of variation (CV) of the lognormal distribution.[10] When applied here, σ=0.77 is found to be equivalent to CV=0.9.

4.7.2 Individual CV for Substance Properties

In the CalTOX model (McKone, 1993) physico-chemical properties of substances are described by octanol-water partitioning coefficient, aqueous solubility, and vapor pressure. For these, lognormal distributions are assumed, and parameterized with mean values and coefficients of variation deduced from literature.

The preferred proceeding is to calculate CV by assessing the standard deviation among the reported values individually for each substance. Highest priority is given to experimental values reported in primary scientific literature (peer reviewed journals). Where such values were insufficient, widely cited secondary references were also used. As a last resort, estimation equations from primary literature (mostly quantitative structure activity relationships, QSAR) were used. From these data, mean and CV were calculated from arithmetic mean and arithmetic standard deviation. In case of estimated input values, means were calculated from the estimation equation. The CV was then derived from the residual error of the estimation equation (McKone et al., 1995).

McKone et al. suggest a generic approach substances where only a few reported values are available. For each parameter, the mean CV value among all substances, for which CV were calculated, is calculated and given as the CalTOX default for that parameter. CalTOX defaults are CV of 1.2 for octanol-water partitioning coefficient, 0.55 for aqueous solubility, and 0.015 in case of vapor pressure.

MacLeod et al. (2002) use a very similar approach to McKone et al. (1995). Lognormal distributions are assumed for aqueous solubility, vapor pressure, and for **log** K_{ow} (as opposed to K_{ow}).

For the ChemCAN model (version 4.0, Trent University, Peterborough, ON, Canada) generic *confidence factors* are recommended to be used "in the absence of site- or situation-specific data." For comparison, the confidence factors 1.1, 1.5, and 1.5 for log K_{ow}, aqueous solubility, and vapor pressure, respectively can be converted to CV 0.05, 0.21, and 0.21.[11]

4.7.3 Several CV for each Substance Property

Jager et al. (1997) discuss the parameterization of the SimpleBox model (van de Meent, 1993; Brandes et al., 1996). Lognormal distributions are assumed for the physico-chemical

[10] $CV = \sqrt{\exp(\sigma^2) - 1}$ (Slob, 1994)

[11] $CV = \sqrt{\exp\left(\frac{\ln^2 k}{1.96^2}\right) - 1}$ (Slob, 1994)

substance properties. The location of the distributions is determined by setting the distribution median to a deterministic value, i.e. a value that is believed to be the best estimate of the true parameter value.

Jager et al. (1997) state that the uncertainty in physico-chemical properties may depend upon the absolute value of the parameter. A possible reason is the difficulty to measure a substance property, which changes with the value of the property (Mackay et al., 1999; Beyer and Matthies, 2001).

When a generic CV is used as a measure of the uncertainty, this is already accounted for: the CV depends on the distribution mean, it is inverse proportional to its value. Hence if a fixed CV is assumed, the actual standard deviation is proportional to the mean (standard deviation = mean$\times$CV). In case of determining K_{ow}, this is in accordance with experience: accurate measurement of very large K_{ow}, i.e. larger than 10^6, is a difficult task (Mackay et al., 1999). But measuring very low vapor pressures is not particularly easy, in fact vapor pressures below 1 Pa are generally difficult to measure. The same is true for very low solubilities. These examples show that it cannot be assumed that uncertainties are simply proportional to the absolute value, and that usage of CV alone is not enough.

Jager et al. address such dependencies by differentiating by parameter and distinguishing two or three separate ranges of different uncertainties for each parameter.

The uncertainties were derived from a regression that uses about 25 representative substances,[12] including TCDD, benzene, and DEHP. For all substances used, log K_{ow} ranged from -1 to 8, log S_w ranged from -5 to 6, and log P^0 from -7 to 6 (for solubility in mg/L, and vapor pressure in Pa).

The residuals of the regression were plotted against the parameter value, and ranges of less or greater scatter were identified using "mainly visual judgment" (Jager et al., 1997). For each of these ranges an uncertainty was then estimated. The estimates of the uncertainty were based on 72 to 581 measurements that fell within the concerning range.

In case of the K_{ow}, three ranges were identified: K_{ow} with a log K_{ow} less than 4 are assigned a CV of 0.57, then up to a log K_{ow} of 5.5 a CV of 2.0 was derived. All K_{ow} with log K_{ow} greater than 5.5 are assigned a CV of 3.59. Aqueous solubility S_w is divided into two ranges, those S_w with log S_w less than zero and those greater than zero, the corresponding CV are 2.0 and 0.47, respectively. Similarly there are two ranges for vapor pressures P^0 for log P^0 less than zero, and greater than zero, here the corresponding CV are 8.8 and 0.34. The trend of these ranges is in agreement with the theoretical considerations made by Beyer and Matthies as mentioned above.

Jager et al. point out, that the quantification of the uncertainty is not based on neither, an extensive literature search nor extensive consultation of experts. The CV are therefore only preliminary but may provide a starting point for future activities.

4.7.4 Comparison of the Different Approaches

Table 4.4 shows a summary of CV used in the different approaches. In the table, the approaches are organized by the level of detail, e.g. Beyer and Matthies is right to McKone

[12] In case of aqueous solubility, only 24 substances were used.

Table 4.4: Different generic coefficients of variation.
Different generic coefficients of variation (CV) used for input parameter distributions for Monte-Carlo Analysis. In case of MacLeod et al. the CV of log K_{ow} is given instead of the CV of the K_{ow}. CV in case of Jager et al. are given in the order of the ranges they apply to i.e. high uncertainties for large K_{ow} and low values of S_w and P^0.

	Jager et al.	McKone et al.	MacLeod et al.	Beyer and Matthies
(log) K_{ow}	0.57, 2.0, 3.59	1.2	(0.05)	0.9
S_w	2.0, 0.47	0.55	0.21	0.9
P^0	8.8, 0.34	0.015	0.21	0.9

et al. because the latter differentiates parameters types.

Discussion of Numerical Values

All approaches yield numerical values in the same order of magnitude; most CV are less than or equal to 2.0. There are two exceptions to this, both are values derived by Jager et al.: Their estimate of uncertainty for K_{ow} with log K_{ow} greater than 5.5 is a CV of 3.59, and their CV for vapor pressures less than 1 Pa is 8.8. In particular the latter value seems to be unrealistically large: with a CV of 8.8, or equivalently an uncertainty factor of 6.0 (Slob, 1994), values as high as six times the median fall into the central 95 percent of the distribution. As noted above, Jager et al. stress that these CV are only preliminary results and not based on an extensive literature search, nor extensive expert consultation.

Another estimate that has a surprising value is the CV from McKone et al. of P^0. At 0.015 it is the lowest estimate among all CV considered here. The CalTOX default CV values are found in the CalTOX spreadsheet[13] (T. E. McKone, personal communication, January 24, 2002). For use as a generic uncertainty, this estimate seems too low – in cases where the P^0 of a substance is known with a certainty that warrants using such a low CV, then a generic assumption should not be necessary. Furthermore, in case of substances with sufficient data, McKone et al. frequently estimate CV much larger than 0.015. Individual CV for P^0 of substances in the CalTOX spreadsheet range from 0.005 to 1.9, with an average of 0.39.

Discussion of the Differences between Approaches

The uncertainty estimate of K_{ow} from MacLeod et al. is excluded from the discussion because estimates on log scales versus linear scales are not comparable.

When the CV from the different approaches are compared, the largest of the CV estimates for each parameter from Jager et al. exceed all other CV. Furthermore, the lowest CV from Jager et al. falls below most of the other CV (with the exception of the very low P^0 values from McKone et al., discussed above). Between McKone et al. and Beyer and Matthies, the "one for all" CV from Beyer and Matthies is larger than the CV for P^0 and S_w from McKone et al. and lower than their CV for K_{ow}.

[13] CalTOX is available at http://www.cwo.com/~herd1/caltox.htm

Therefore, the more general approaches are not always conservative compared to more specific approaches. In order to be conservative, the CV from more general approaches need to exceed all specific uncertainties, e.g. a "one for all" CV had to be larger than 8.8. The different approaches are consistent in another sense though. Rather than being conservative, they are representative to a certain extent, i.e. the more general approaches fall within the ranges set by the more specific estimates (Beyer and Matthies falls within the estimates from McKone et al. for individual parameters, and CV from McKone et al. fall within the ranges from Jager et al.).

The approaches from McKone et al. and MacLeod et al. apply to the same level of detail, i.e. they derive individual uncertainties for substance properties. However, they differ significantly in the numerical values they suggest, e.g. the aqueous solubility CV differ by more than a factor of two. This disagreement is no exception, on the contrary, several values such as the CV for vapor pressure are so far apart across different approaches, that they indicate that there is no consensus within the scientific community about generic uncertainties.

Finally, when data needs of the approaches are compared, a disadvantage that the approach of Jager et al. bears is that its data requirements are greater than those of the other procedures. The uncertainty attached to each range of a parameter is derived statistically from collected measurement data. Since the data falls into as many groups as there are ranges per parameter, only a fraction of the data can be used for each range, as opposed to approaches that do not differentiate this far.

Simulation Results from Generic Approaches

Simulations were performed to evaluate the different approaches of assigning generic uncertainty. Two settings were explored:

1. Three of the above approaches from literature were applied to the eleven substances investigated in this study: Beyer and Matthies (2001); McKone et al. (1995); Jager et al. (1997). As in the original works, lognormal distributions were assumed for all physico-chemical substance parameters. Parameter distributions were parameterized with the CV listed in Table 4.4 and the recommended (*selected*) value from Mackay et al. (1999) as either the mean (in case of McKone et al., 1995) or the median (Beyer and Matthies, 2001; Jager et al., 1997), depending on how the original authors parameterized their distributions.

2. Parameter distributions were parameterized with coefficients of variation (CV) varying from 0.01 to 3.0. To determine the location of the distribution, the recommended value was set either to

   (a) the mean of the lognormal distribution (*fixmean*) or

   (b) the median of the lognormal distribution (*fixmedian*).

   In each scenario, the same CV was used for all physico-chemical substance parameters.

The generic approaches allows to add the substances LAS, EDTA, and HHCB to the set of chemicals considered. While they are treated in Berding et al. (2000) along with the other substances addressed in this study, they were omitted here until now, because the data basis was not sufficient to apply the same procedure of parameterization to these chemicals. Results from simulations 1 are shown in Table 4.5. Results from simulations *fixmean* (2a) and *fixmedian* (2b) can be found in Tables B.3 and B.4, respectively. The latter simulations were carried out in order to have controlled and more abstract scenarios for comparison and interpretation of the former.

A comparison of simulation of the Scenarios *fixmean* and *fixmedian* revealed, that whether the location of the distribution is set via the mean or the median, does make a difference in the variation of the target value. In the majority of cases, the differences from using mean versus median are rather small (less than 0.1) but occasionally they are as large as 1.6. Target CV that result from using the mean are about as often larger than their counterparts, as they are lower than their counterparts. Differences resulting from parameterization via the mean or via the median were also found in the sensitivity of the target CV for changes of the input CV, e.g. raising a CV from 1.5 to 2 can have different effects depending on whether the input distribution's location was determined via the mean or the median. Recall that Jager et al. and Beyer and Matthies use the median, whereas McKone et al. parameterize via the mean, hence differences in target CV may also result from this aspect of parameterization.

In Table 4.5, coefficients of variation (CV) of target distributions computed with the generic approaches range from 0.00 to 1.74 (EDC in soil, Beyer) for the substances considered in the previous sections. In most cases they are considerably larger than the target CV in case of the *comparable* Scenarios *uni*, *tri*, and *log* (Table B.5), which have an upper bound of approximately 0.58 due to the parameterization procedure (Section 4.2). This is explained by differences of the input distributions: the substance specific and parameter specific input CV in case of the *comparable* scenarios are generally lower than the generic CV assumed here (average input CV over all substances are 0.47 in case of K_{ow}, 0.28 for S_w, and 0.38 for P^0). Among the three additional substances in this section (LAS, EDTA and HHCB), CV go up to 28 and even 74. An explanation for these extreme values is the great sensitivity of air concentration to aqueous solubility. The extreme output uncertainty is therefore caused by the large CV suggested by Jager et al. for vapor pressure. The *fixmedian* scenarios have shown larger than average CV for all input CV in these cases, which supports this claim.

The target CV in Table 4.5 also confirm that none of the approaches is generally more conservative than another. Each of the approaches results in the highest, the lowest and the middle target CV in some cases. On the average, the approach by Jager et al. leads to larger uncertainties than McKone et al. and Beyer and Matthies . The latter two result in similar average CV.

To assess the quality of the generic parameterization approaches presented above, one could try verifying the simulation results. It seems impossible to verify the results in Table 4.5 though, because the variation in field measurements of substance concentration is determined by variability in the environmental conditions more than by measurement error. In contrast, the generic input uncertainties represent true uncertainty about the parameters to a large extent. A more apt way to assess the validity of the generic approaches

Table 4.5: Target CV from generic approaches.
Results of simulations with different generic uncertainties. Presented are the coefficients of variation (CV) of environmental concentrations. Only physico-chemical parameters were varied, of those, the most sensitive for every substance and compartment is given, measured in contribution to variance in the Beyer scenario. As the Beyer scenario assumed the same input uncertainties for all parameters, the parameter with largest contribution to variance the Beyer scenario is the most sensitive parameter for all scenarios.

	most		**soil**		most		**water**	
	sensitive	**Jager**	**McKone**	**Beyer**	sensitive	**Jager**	**McKone**	**Beyer**
TCDD	P^0	1.29	0.04	0.59	P^0	0.87	0.24	0.36
PeCDD	P^0	0.48	0.02	0.22	K_{ow}	0.48	0.25	0.19
HxCDD	P^0	0.30	0.00	0.12	K_{ow}	0.49	0.22	0.14
HpCDD	P^0	0.13	0.00	0.02	K_{ow}	0.39	0.18	0.10
OCDD	P^0	0.06	0.00	0.01	K_{ow}	0.29	0.14	0.07
DEHP	K_{ow}	0.05	0.01	0.01	K_{ow}	0.41	0.15	0.14
EDC	S_w	0.92	1.70	1.74	P^0	0.21	0.20	0.53
benzene	K_{ow}	0.84	1.57	1.42	P^0	0.05	0.05	0.12
LAS	K_{ow}	0.46	0.91	0.70	K_{ow}	0.00	0.00	0.00
EDTA	K_{ow}	6.77	0.57	0.75	S_w	0.00	0.00	0.00
HHCB	K_{ow}	1.15	0.83	0.76	P^0	1.03	0.38	0.70
average		*1.13*	*0.51*	*0.58*		*0.38*	*0.16*	*0.21*

	most		**sediment**		most		**air**	
	sensitive	**Jager**	**McKone**	**Beyer**	sensitive	**Jager**	**McKone**	**Beyer**
TCDD	P^0	0.72	0.35	0.36	P^0	0.11	0.00	0.36
PeCDD	P^0	0.30	0.12	0.12	P^0	0.21	0.01	0.12
HxCDD	P^0	0.20	0.05	0.06	P^0	0.19	0.00	0.06
HpCDD	K_{ow}	0.11	0.03	0.02	P^0	0.11	0.00	0.02
OCDD	K_{ow}	0.10	0.03	0.02	P^0	0.10	0.00	0.02
DEHP	K_{ow}	0.26	0.19	0.13	K_{ow}	0.03	0.01	0.13
EDC	S_w	0.28	0.39	0.64	P^0	0.00	0.00	0.64
benzene	K_{ow}	0.32	0.59	0.52	P^0	0.01	0.01	0.52
LAS	K_{ow}	0.05	0.08	0.07	S_w	28.33	1.40	0.07
EDTA	K_{ow}	0.00	0.00	0.00	S_w	73.63	1.32	0.00
HHCB	S_w	1.14	0.77	0.83	S_w	0.47	0.12	0.83
average		*0.32*	*0.24*	*0.25*		*9.38*	*0.26*	*0.25*

would be to compare the generic assumptions with substance specific uncertainties determined with more sophisticated approaches. For example, the average of the eight estimated uncertainties from this work (average CV of 0.49, 0.25 and 0.41 for parameters K_{ow}, S_w and P^0) or averages over all 78 substances in the CalTOX data spreadsheet (average CV of 0.38, 0.39 and 0.38 for parameters K_{ow}, S_w and P^0) could be used.

Compared to the CalTOX averages, the "one for all" approach from Beyer and Matthies is conservative since those CV are more than twice as large. Furthermore, the average values are similar for all parameters, which is in agreement with this approach. The parameter specific estimates from McKone et al. and MacLeod et al. vary around the CalTOX averages, but they remain within the same order of magnitude. The exception is the very low P^0 (0.015), that is critical in this aspect. The lowest CV for each parameter from Jager et al. (0.57, 0.47 and 0.34) are in good agreement, while the larger estimates deviate by one order of magnitude and more from the CalTOX averages, which may be interpreted as conservative. A certain degree of conservatism is appropriate for generic approaches, especially in comparison to average values, since averages underestimate some of the specific values by their nature. When these deviations from the reference case of CalTOX averages are used to rank the quality of the approaches, care must be taken whether the reference data are representative for the chemicals that the generic approach will be applied to.

4.8 Comparing Different Parameterization Strategies

Results from the previous section were often of a technical nature, in particular the *comparable* scenarios, which are not realistic but technical examples. Therefore, in this section additional scenarios are computed to put results from this study into perspective with realistic strategies and evaluate results from this study in that context. The parameterization strategies discussed in this section are in part from real life examples, e.g. *berding* is taken from Berding et al. (2000). Others are parameterization strategies that were discussed or derived in this study.

Scenario *berding* This scenario is taken from Berding et al. (2000). Lognormal distribution shapes are assumed for physico-chemical parameters, and parameterized through a statistical analysis of literature data. The resulting parameters of the lognormal distribution are summarized in Table 2.3 (means) and in Table 4.6 (CV).

Scenario *lognormal* In a mixed approach, lognormal distributions are parameterized using expert values for means, and statistical analysis for the variance. Means are set to *selected values* from Mackay et al. (1999) (Table 2.3), and the variance is derived from the coefficient of variation estimated on the data basis of this study (Chapter 2). The resulting CV are presented in Table 4.6.

Scenario *triangular* It is questionable whether the data basis of this study is sufficient for statistical estimations as they were performed for the previous scenario. Scenario *triangular* presents an alternative to the use of statistics. Similar to Scenario *tri* (Section 4.2), triangular distributions are parameterized from a selected value

(Mackay et al., 1999) as the mode, and minimum and maximum literature values for lower and upper bounds. In contrast to Scenario *tri*, here the distributions were not shifted to allow for the comparable *uni* and *log* scenarios to be constructed.

Scenario *generic* All the above scenarios exploit literature data to estimate the parameter uncertainty. Section 4.7 explored approaches that rely on generic assumptions as opposed to measured data. The approach suggested by Beyer and Matthies (2001) is implemented in the *generic* scenario by parameterizing lognormal distributions with mean values as selected in Mackay et al. (1999) and a common CV of 0.9.

Examples of the parameter distributions are presented in Figure 4.20. Both, the lognormal distribution from Scenarios *berding* and *lognormal* are very skewed, with the mean at the same location as the 77^{th} percentile and the 74^{th} percentile, respectively. In the remainder of this section, four combinations of these scenarios are explored.

1. Scenarios *berding* and *lognormal*, which differ in the selection of the mean, and the data basis used (Section 4.8.1)
2. Scenarios *lognormal* and *triangular*, which are based on the same data, but derive different uncertainties and distribution types from the data (Section 4.8.2)
3. Scenario *generic* is compared to all of the above (Section 4.8.3)
4. While only the physico-chemical parameters are varied in the above combinations, simulations varying all parameters were performed for all four scenarios (Section 4.8.4)

4.8.1 Different Parameterization Based on the Same Literature Data

In the Scenarios *berding* and *lognormal*, parameter distributions are set to the same distribution type, i.e. to lognormal probability distributions. The parameter distributions differ between the scenarios in their means (Table 2.3) and the CV (Table 4.6). In Scenario *berding*, the means are estimated, while the selected values from Mackay et al. (1999) are used in Scenario *lognormal*. The CV are estimated in both parameterization approaches, yet the data bases are different even though they are derived from similar literature sources (Chapter 2). These differences cause in turn differences in the location and the CV of the computed target distributions. Comparing these two scenarios helps to understand how an improved data selection process might change the result.

Simulation Results

Cumulative distribution functions (CDF) were compared for all target values, Figure 4.21 shows two examples. The resulting CDF differ in two aspects, namely the location of the curves (e.g. measured by the distance of the medians), and the uncertainty represented by the slope and spread of the CDF. For example, the CDF of benzene in Figure 4.21 show a large difference of their medians, while the CDF are almost parallel, which indicates that

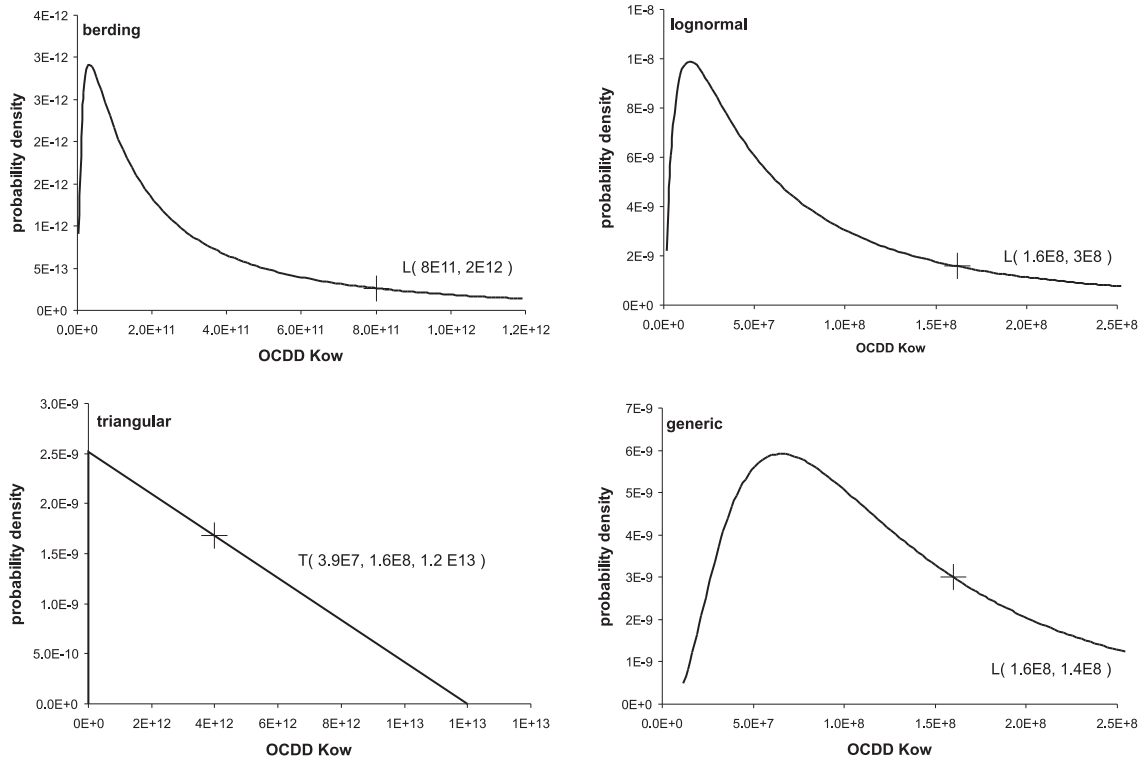

Figure 4.20: Exemplary parameter distributions.
Example parameter distributions from the Scenarios *berding*, *lognormal*, *triangular*, and *generic*. All distributions range from the 0.001 quantile to the 0.85 quantile (i.e. the 85^{th} percentile) except for the triangular distribution, which is shown in totality. For each distribution, the mean value is indicated. The mean and the mode deviate the most in Scenario *berding*, then *lognormal*, *generic*, and finally *triangular*, and the distributions are less skewed in the same order.

Table 4.6: Coefficients of variation.
Coefficients of variation (CV) used in the Scenarios *berding* and *lognormal*. Scenario *generic* uses a CV of 0.9 in all cases, and Scenario *triangular* has CV lower than 0.6 for theoretical reasons (Section 3.2.6).

CV	*berding*		
substance	K_{ow}	S_w	P^0
TCDD	4.09	0.76	2.47
PeCDD	1.19	2.22	0.76
HxCDD	1.50	0.95	2.55
HpCDD	1.80	2.31	1.92
OCDD	2.77	2.98	1.48
DEHP	3.16	3.00	2.55
EDC	0.29	0.03	0.09
benzene	0.40	0.31	0.07
average	*1.90*	*1.57*	*1.49*

CV	*lognormal*		
substance	K_{ow}	S_w	P^0
TCDD	1.95	1.70	2.09
PeCDD	1.16	0.28	2.09
HxCDD	1.09	0.18	1.39
HpCDD	1.17	0.05	1.40
OCDD	1.99	2.20	1.17
DEHP	2.23	0.57	1.89
EDC	0.36	0.06	0.00
benzene	0.32	0.05	0.03
average	*1.28*	*0.64*	*1.26*

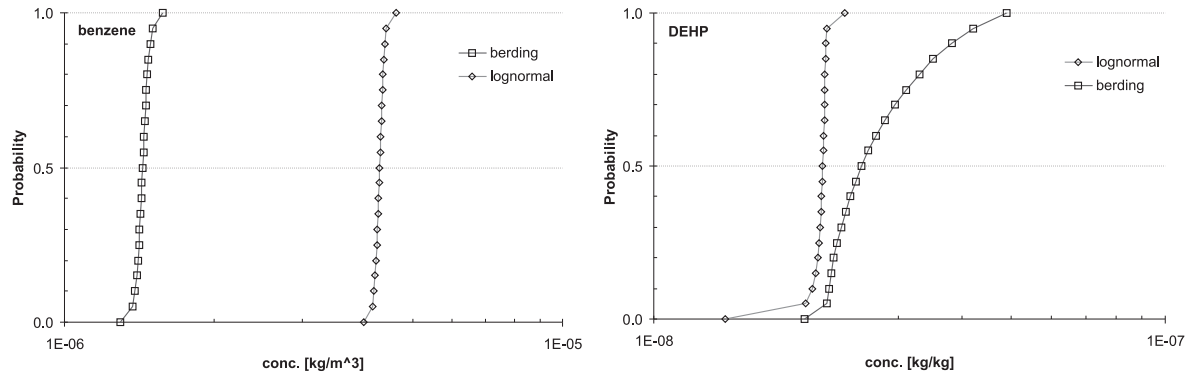

Figure 4.21: Cumulative Distribution Functions.
Example cumulative distribution function (CDF) of Scenarios *berding* and *lognormal*: benzene concentration in water and DEHP concentration in soil. The benzene plot illustrates how differences in uncertainty, i.e. the spread of the CDF, are exceeded by differences in the location of the CDF, particularly the medians. The CDF of DEHP concentration show an exception to that typical case: a large difference in uncertainty of the input distributions results in CDF that are both different in slope and different in location. Here, the difference in shape exceed the deviation of the medians.

the variation of the target values is similar. The medians in case of DEHP are relatively close, compared to the deviation of the shape of the CDF.

Whether a difference in input means has an impact on the target mean depends on the specific importance of the parameter, e.g. the difference of benzene K_{OW} (1.32E+2 versus 1.52E+2, Table 2.3) has an effect, as the K_{OW} is the most influential parameter for benzene concentration in water (Figure 4.21). In contrast, a similar difference in case of EDC (2.88E+1 versus 3.02E+1) has no effect because here the K_{OW} is not sensitive. In this case, there is almost no deviation between sensitive input means (S_W and P^0), and the target CDF are also almost identical in all compartments (not displayed).

DEHP concentration in soil is an example of a target value where both mean and CV of the prominent parameter K_{OW} differ significantly (input CV are 3.16 and 2.23, and input means are 3.0E+7 and 3.5E+8, in case of *berding* and *lognormal*, respectively). Consequently, the target CDF (Figure 4.21) differ in location and in spread.

Overall, the differences in target location exceed the differences in target variation in most cases. From visual judgment of the CDF plots, the deviation of the shapes is larger than the difference of their locations only in the one case of DEHP. In all other cases the two aspects were at least similarly important, in more than half of the cases the difference in location is clearly larger than the difference in the shape of the CDF. Thus a different selection process for the input data has a smaller effect on the result than a different way of parameterizing a distributions location.

4.8.2 A Statistical versus a Subjective Approach

The two parameterization approaches compared in this section (*lognormal* versus *triangular*) rely on the same data, namely the data basis from Chapter 2 and the selected values. The locations of the parameter distributions are similar in both approaches. However

since the selected values are used as the mean in the lognormal distributions and as the mode in triangular distributions they are not the same. Moreover as discussed earlier, the CV of triangular distributions in the *triangular* scenario is limited to stay below approximately 0.7. The estimated CV used in the *lognormal* scenario are up to three times as large (Table 4.6).

Simulation Results

Interesting aspects of the computed target distribution are their location and spread, and in particular their shape since different distribution types were used for parameter distributions. The computed target distributions were compared on the basis of their frequency distributions. Frequency distributions are histograms of Monte-Carlo shots, thus they provide a very direct way to assess the target distribution's shape.

Figure 4.22 shows four examples of frequency distributions in the sediment compartment, which represent the range of different results from the simulation. As the plot of HpCDD indicates, the differences between Scenarios *lognormal* and *triangular* can be dramatic. Explanations for the differences between substances are provided by the functional dependencies of input parameters and computed concentrations (Figure 4.3). The curves in Figure 4.3 apply to the *tri* scenario, which is the *triangular* scenario, but shifted. Thus the actual curves for the *triangular* scenario might differ slightly. In the following, these explanations are applied to the four typical cases in Figure 4.22.

1. EDC is an example for near-linear functional dependencies (Figure 4.3G). Hence the triangular and the lognormal input distribution shapes are mapped to target distributions of similar shape to their input distributions: the target distribution of Scenario *triangular* resembles a triangular distribution, and the target distribution of Scenario *lognormal* resembles a lognormal distribution. The triangular distribution for the most influential parameter in sediment, K_{ow}, is positively skewed. Hence its mode is left of its mean. Since the mode of the triangular distribution and the mean of the lognormal distribution are set to the same value, the location of the triangular input distribution is to the right of the lognormal distribution. This, too, is reflected in the target distributions.

2. In case of DEHP, the lognormal distributions get spread out over a large range, while the triangular distribution has only a small spread. The functional dependency curve in Figure 4.3F changes with larger parameter values from a very steep curve to an almost constant curve. Just like the K_{ow} input distributions for EDC, the triangular input distributions for DEHP are to the right of their lognormal counterparts. The steep part of the curve spreads the lognormal curve out over a wide range of target values, while the triangular distribution covers the almost constant part of it, which maps it to a narrower interval.

3. Similar to the previous case, the slope of the functional dependency curve of P^0 of HpCDD changes from steep to gentle. Unlike the case of DEHP, the curve is decreasing. A decreasing curve mirrors the input distributions (Figure 4.11), thus the target distribution of Scenario *triangular* is found the left of the target distribution

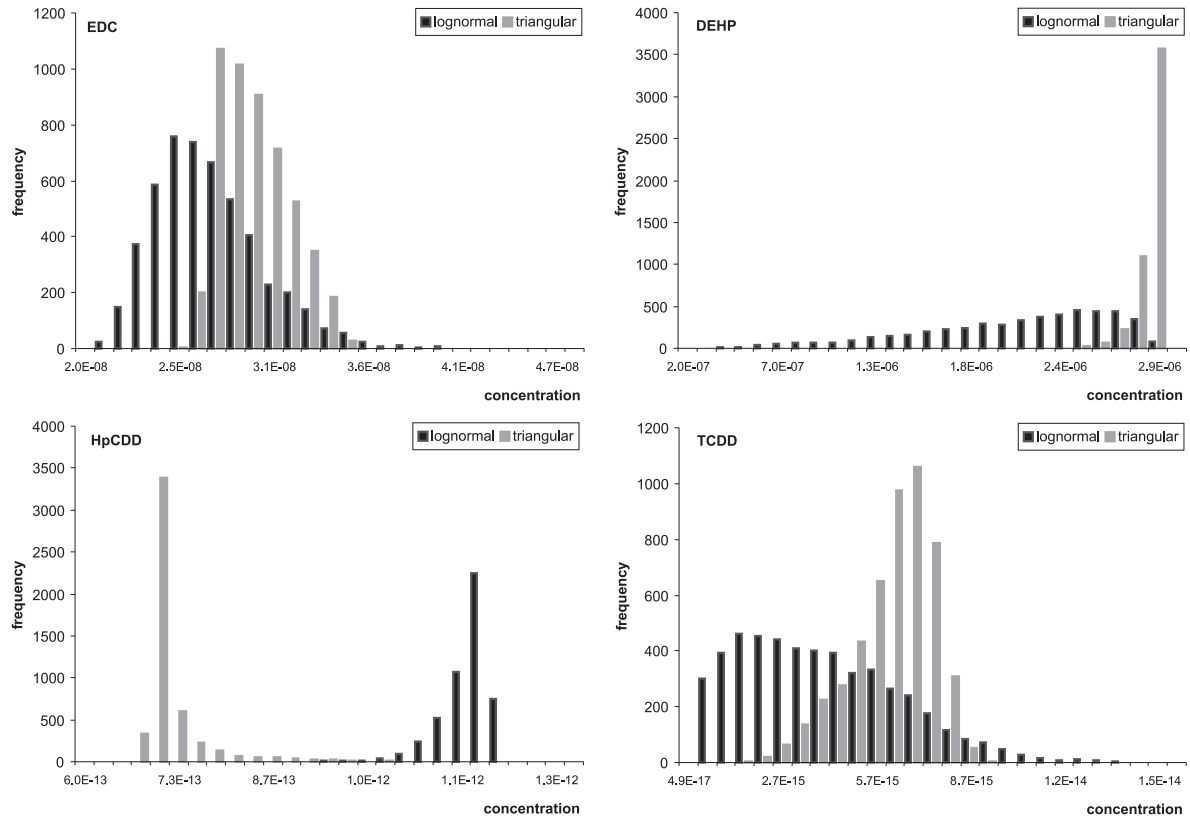

Figure 4.22: Frequency distributions.
Frequency distributions from Scenarios *lognormal* and *triangular* for EDC, DEHP, HpCDD and TCDD in the sediment compartment. The differences between substances can be explained from the functional dependencies (Figure 4.3).

from the *lognormal* scenario. The distance between the target distributions may be due to the larger overall variation in case of HpCDD compared to DEHP (about 30 percent compared to about 15 percent, see the y-axes in Figure 4.3).

4. The target distributions in case of TCDD look similar to the case of EDC, notice though, that they cover ranges of several orders of magnitude unlike the case of EDC. In contrast to the case of EDC, the functional dependency curves of TCDD are very nonlinear (Figure 4.3A). What distinguishes TCDD from the cases of DEHP and HpCDD is that several input parameters are sensitive, and the functional dependencies are almost symmetric about the base case. Hence the distance between input distributions is not stretched when mapped to the distance of the target distributions.

4.8.3 How Realistic is the Generic Approach?

In the generic approach suggested by Beyer and Matthies (2001) parameter uncertainty is represented by a CV of 0.9 regardless of substance and parameter type. Furthermore, the lognormal distribution is selected a priori. In addition to these considerations, Scenario *generic* uses the *selected values* (Mackay et al., 1999) as distribution means, and hence

(as discussed in the previous sections) the location of the input distributions is similar to Scenario *lognormal*, and deviates from Scenarios *berding* and *triangular*.

The generic CV may be considered representative if it is similar to the specific CV from the other scenarios. Compared to the average CV from Scenarios *lognormal* and *berding* (Table 4.6) a generic CV of 0.9 underestimates the parameter uncertainty in most cases, while compared to Scenario *triangular*, where input CV are all less than 0.7, the input uncertainties are overestimated.

Simulation Results

Some comparative plots with CDF from all scenarios are presented in Figure 4.23. Two examples are given, where the *generic* scenario is indeed representative, i.e. the result from the *generic* scenario is an average case compared to the other scenarios (TCDD in water and HxCDD in sediment). In case of HxCDD concentration in sediment, the CDF are far apart in their location. This is due to different locations of the input distributions, hence it is irrelevant when comparing generic uncertainties to specific uncertainties. In the other two examples shown in Figure 4.23, the *generic* scenario underestimates the uncertainty computed in the other scenarios (EDC in soil) or overestimates the target uncertainty (DEHP in soil). Hence no general statement could be made.

4.8.4 Scenarios with many Probabilistic Parameters

The aim of this section is to assess whether the differences between the scenarios that are discussed above prevail when many parameters are varied. Unlike before, now all probabilistic parameters from Berding et al. (2000) are varied (about 50 depending on the mode of entry, Tables B.1 and B.2). Simulations were performed for all of the above scenarios.

Simulation Results

Cumulative density functions (CDF) for all substances and scenarios were compared to the corresponding CDF plots from the previous sections. The effects in the simulation results due to varying many parameters (as opposed to three) are similar for all substances and may be discussed using just one example. The soil concentration of benzene was selected, CDF and frequency plots are shown in Figure 4.24. There are visible effects on the location, spread and shape of the target distributions.

All target distributions appear shifted towards larger values. This effect can be attributed to switching from deterministic values to probability distributions for about 50 additional parameters. For example half lives and emission rates are modeled by positively skew triangular distribution with the mode set to the former deterministic value. These assumptions both result in higher environmental concentrations.

The overall uncertainty represented by the spread of the target distributions has increased significantly, due to the increase in uncertain input parameters. Often the range covered

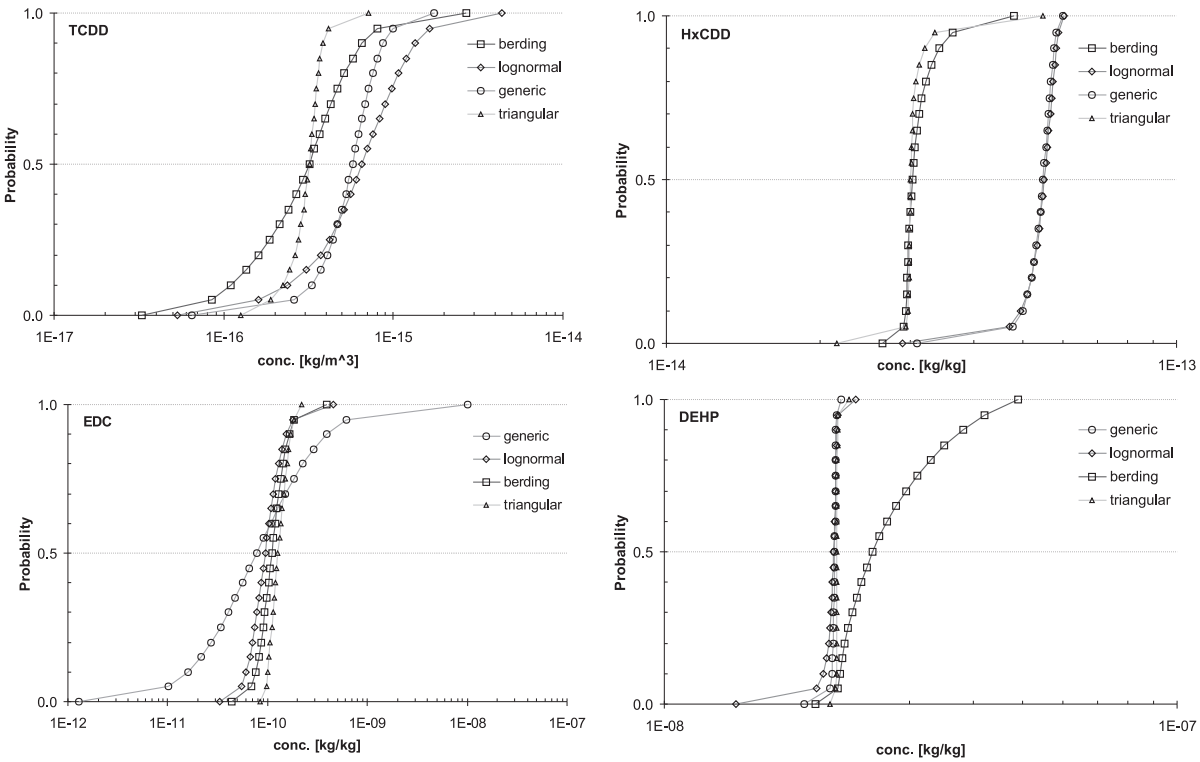

Figure 4.23: Comparison of *generic* scenario to others.
Examples from the comparison of the *generic* scenario to the other scenarios. TCDD concentration in water and HxCDD concentration in sediment in the top row are examples of the representativeness of the *generic* scenario. Here the corresponding CDF fall in-mid the other scenarios. EDC and DEHP concentrations in soil are examples where the assumptions of Scenario *generic* over- or underestimate the uncertainty of one or more of the specific scenarios.

by the target distributions increased by several orders of magnitude. Moreover, the differences between the target uncertainties from the different scenarios has become less. While the benzene CDF from Scenarios *triangular* and *lognormal* are steeper than the CDF from *berding* and *generic*, respectively, in the calculations from the previous sections, the slopes are almost identical now. It can be concluded, that the uncertainty about input CV of the physico-chemical substance parameters have only a marginal influence when many parameters are varied.

The CDF in Figure 4.24 suggest that the shapes of the target distributions are almost identical. Among the displayed CDF, the two from Scenarios *lognormal* and *generic* differ the most. In order to examine their shapes closer, the corresponding frequency distributions have been included in the figure. The resulting shapes are indeed very similar and both resemble lognormal distributions. This is in agreement with the results from Section 4.5, which suggest that the target distributions will converge to lognormal distributions when a large number of input parameters is simulated probabilistically.

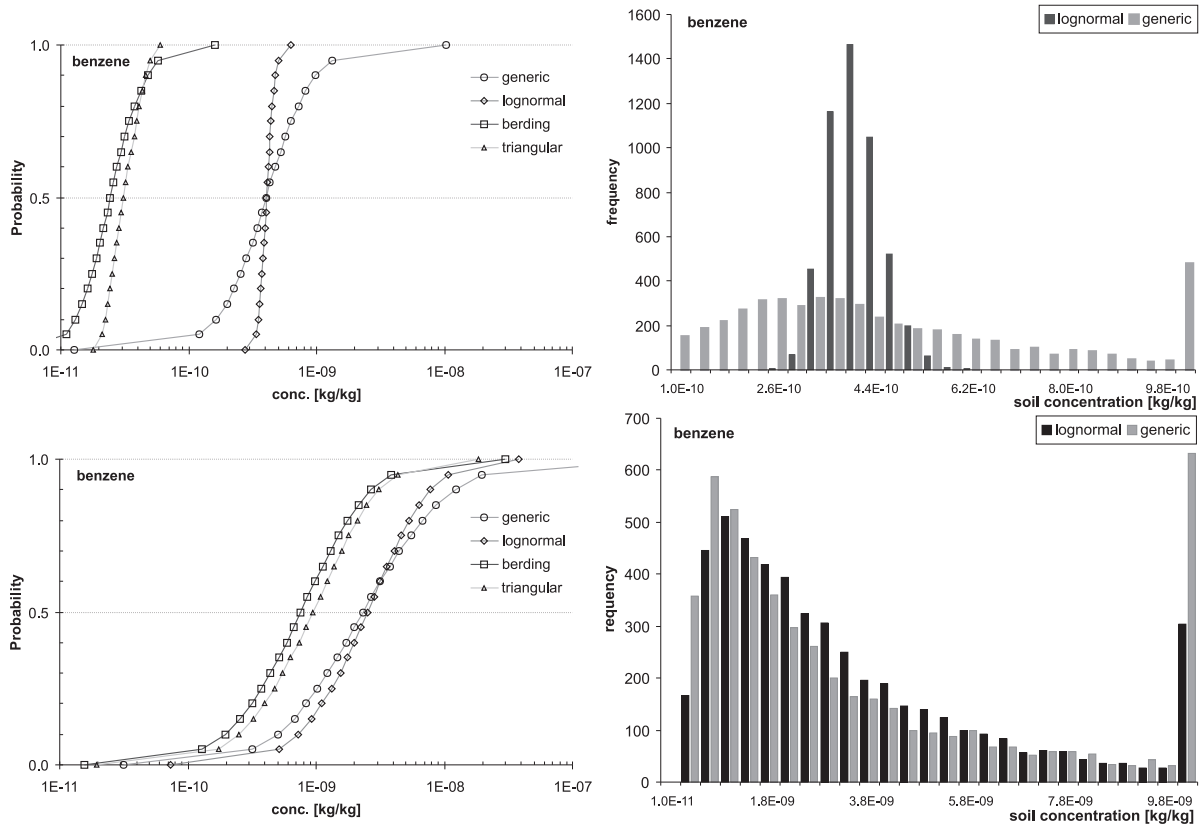

Figure 4.24: Few versus many probabilistic parameters.
Comparison of results from simulations with three (*top*) versus 50 (*bottom*) probabilistic parameters. Soil concentration of benzene is selected as an example.

Chapter 5

Conclusions

Exposure assessment is frequently performed by computing predicted environmental concentrations (PEC) via multimedia models. Multimedia models, e.g. the SimpleBox model, are based on parameters discribing the environment, and parameters describing substance properties, i.e. their emission, degradability and partitioning behavior. Information about the partitioning behavior is often reduced to three physico-chemical properties: the octanol-water partitioning coefficient K_{ow}, aqueous solubility S_w, and vapor pressure P^0. Parameterization of input distributions for K_{ow}, S_w and P^0 for a probabilistic exposure assessment is the main focus of this study.

It was shown in Chapter 2 that measurement data for K_{ow}, S_w, and P^0, are scarce for the chemicals under investigation. A data basis was selected from the available literature values by applying a set of selection criteria to ensure a certain reliability of the data. The resulting data basis is small and for most substances, there are insufficient data for reliable statistics. This is particularly problematic when estimating higher order moments of parameter distributions, such as the variance and the coefficients of skewness and kurtosis. Hence there are large uncertainties about the choice of a distribution type of parameter distributions for a probabilistic assessment.

5.1 Distribution Type

The influence of the choice of different input distribution types was assessed. In particular, the impact on target mean, target variance, and target shape are described and compared.

Informational Content According to Maximum Entropy Theory

The investigated distribution types uniform, triangular, and lognormal represent different states of knowledge or different amounts of information. According to maximum entropy theory, all three distributions can be considered to reflect maximum uncertainty for certain boundary conditions. The information contained in the boundary conditions increases from uniform to triangular and lognormal.

The uncertainties of the target value computed in the scenarios with uniform, triangular, and lognormal parameter distributions conform to this ranking. The variance of the target distributions is never significantly less for parameter distributions of greater informational content.

Functional Dependency Plots

During the discussion and interpretation of the individual simulation results, plots of the local functional dependency of parameters and target values have proven to be very useful to explain inter-scenario and inter-substance differences. Functional dependency plots aid the identification of sensitive parameter ranges and help to understand how different input parameter distributions relate to the results of Monte-Carlo simulations.

Target Mean and Target Variance

The impact of different assumptions about the shape of the parameter distributions on target means is almost negligible, while the impact on target variance is significant. Measured in percent of the target mean, the impact on variance exceeds the impact on target means by about one order of magnitude. The target variance is therefore more sensitive than the target mean, the target mean is almost insensitive to parameter distribution types.

Quantifying the Impact

Uncertainty about the distributional shape of the parameters has been compared to uncertainty about the mean. The impact of assuming different distribution shapes is comparable to a variation of the mean of up to 30 percent. The impact in these terms was relatively large in cases where the parameter ranges covered by two input distributions differed in places with a large local sensitivity. Compared to the uncertainty about the mean value of the data used in this study (standard error of the mean), the impact of the shape is significant. However, compared to the large deviation between locations of the used input distributions, the impact is marginal. Hence, the choice of a distribution type is only of concern, when the uncertainty about the mean is of a comparable magnitude (i.e. about 30 percent or less).

Target Shape

The sensitivity of the target distribution shape to different assumptions about parameter distributions depends on the number of probabilistic parameters. The sensitivity to a single parameter decreases with an increasing number of probabilistic parameters. Simulation results also suggest that the impact of the input shape on the target distribution shape is larger in case of near-linear functional dependencies of parameter and target value, than in case of non-linear functional dependencies. The effect of linear functions is

only to mirror and to scale the input distribution, while non-linear functional dependencies additionally result in a distortion of the input distribution. A distortion caused by the non-linearity might marginalized the differences due to different distributional shapes of parameters and harmonize the target distributions.

Recommendation

The above conclusions indicate that distribution shapes can have a significant impact on the output distributions. In the cases considered, the sensitivity on the input distribution's shape mainly depends on the sensitivity across input parameter ranges, expressed by the functional dependency of parameter and target value. Hence, it is crucial for parameterization of input distributions to be conscious of the parameter range that the distribution covers. Therefore I recommend using intuitive parameterization approaches and visualizing the resulting distributions to double-check whether they are in agreement with the expectations or intentions. Examples following this idea are using median and coefficient of variation to parameterize lognormal distributions (Section 3.2.3), and constructing subjective distributions using modified beta distributions (Section 3.2.5).

5.2 Generic Uncertainties

Another influence on the computed target distribution besides the shape of the parameter distribution is its dispersion. As noted above, less data are required to estimate the variance than characteristics of the shape. Still, the data situation in this study is mostly insufficient for a statistical derivation of the variance. Therefore, the use of default uncertainties has been evaluated.

In situations of scarce data, deterministic values for parameters are often selected based on expert opinion. One example is the selection of "best values" by Mackay et al. (1999). In probabilistic uncertainty analysis, the expert opinion on the deterministic value of a parameter provides a valuable clue on the location of the corresponding parameter distribution. This information can by utilized in different ways to parameterize a probability distribution, e.g. the expert value can be used as mean or median.

Approaches in Literature

Recently, attempts have been made to use a similar approach with parameter uncertainty, i.e. parameterization of the spread of parameter distributions. Default, i.e. generic, measures of variance have been proposed for substances where available data was insufficient to warrant the use of statistics. Four approaches are compared in this study. They differ in the degree of detail: the level of generalization ranges from just one uncertainty for all parameters to distinct uncertainties for several ranges of each parameter.

The input uncertainties assumed in the different approaches were compared, and simulations were performed to assess the effects on target distributions. The numerical values of the input uncertainties were mostly in the same order of magnitude. The more general

input uncertainties are not conservative in the sense that they do not assume larger uncertainties compared to more specific approaches. However the more general approaches are representative in the sense that they assume input uncertainties, which lie mostly within the values suggested in the more specific approaches. This is confirmed by the results of the simulations.

Overall the deviation among the assumed generic uncertainties is large. It is concluded that there is no consensus about default uncertainties. But considering the benefits of generic uncertainties, such as comparability of the results and avoiding statistical analysis on small data sets, the concept of default values for uncertainty should be further pursued. A possible enhancement could be to combine ideas of the approaches presented in this study: To use different CV for different ranges of a parameter, but to determine the ranges and the uncertainties attached to them not from statistics but from expert judgment because statistics have resulted in uncertainties that seem unrealistic. Expert judgment could take into consideration at which values a parameter becomes difficult to measure, e.g. due to measurement methods, as well as the existing literature data.

5.3 Parameterization Strategies in Comparison

Four pairs of scenarios, each representing a potential way of parameterizing input distributions, have been compared and analyzed in view of previous results from this study. Often there was no uniform effect on the target distributions, but some general trends were found, and exceptions to them could be understood.

Reducing the data basis to "reliable" values, and setting the parameter mean to an expert value, as opposed to estimating the mean, both had an impact on the target distribution. Mostly the impact on the location was stronger than the impact on the uncertainty of the target value. Hence, correct parameterization of the mean is more important in this setting than the estimation of the parameter uncertainty.

Two different parameterization strategies using statistics and expert judgment in different ways and to different degrees resulted in visually extremely different parameter distributions. The differences of the computed target distributions are dramatic in some cases.

A generic parameterization strategy resulted in target distributions that were similar to more specific approaches in many cases. However there was no general trend, the generic approach both under- and overestimated the uncertainty in the specific approaches in some cases.

When about 50 parameters were simulated probabilistically, the differences in the uncertainty of the target value decreased, and the shapes of the target distributions became more similar. As it can be expected from theoretical considerations (Section 4.5) the distribution approaches a lognormal distribution as a larger number of input parameters is simulated probabilistically.

It can therefore be concluded that most effort should be made to determine the location of the parameter distributions as closely as possible. The spread of the parameter distributions and their shape are less influential especially when a large number of parameters is

simulated probabilistically. Their lesser impact becomes important once the uncertainty about the location is decreased to a comparable order of magnitude. In the explored settings, generic approaches yield results that are similar to more specific approaches and are thus deemed to be sufficient.

Bibliography

Aitchison, J. and J. A. C. Brown (1957). *The Lognormal Distribution*. Cambride, USA and Melbourne, Australia: Press Syndicate of the University of Cambridge.

Anderson, E. L. F. and D. R. Hattis (1999). Foundations (A. Uncertainty and variability, B. Extremes, extrapolation, and surprise, C. How, when, why to use all of the evidence, D. Decision making). *Risk Analysis 19*, 47–68.

Berding, V. (2000). *Validation of a Regional Distribution Model in Environmental Risk Assessment of Substances*. Ph. D. thesis, University of Osnabrueck.

Berding, V., S. Schwartz, S. Trapp, and M. Matthies (2000). Validierung von Umweltexpositionsmodellen und in Modellen verwendeten Parametern. Final report 20601075, Umweltbundesamt, Berlin.

Beyer, A. and M. Matthies (2001). Criteria for atmospheric long-range transport potential and persistence of pesticides and industrial chemicals. Technical Report FKZ 299 65 402, German Federal Environmental Agency, Berlin, Germany.

Beyer, A., F. Wania, T. Gouin, D. Mackay, and M. Matthies (2002). Selecting internally consistent physical-chemical properties of organic compounds. *Environ. Toxicol. Chem. 21*(5), 941–953.

Binkowitz, B. S. and D. Wartenberg (2001). Disparity in quantitative risk assessment: A review of input distributions. *Risk Analysis 21*, 75–90.

Brandes, L. J., H. den Hollander, and D. van de Ment (1996). SimpleBox 2.0: A nested multimedia fate moel for evaluating the environmental fate of chemicals. RIVM Report 719101029, Rijksinstituut voor Volksgezondheid en Milieu, Bilthoven, The Netherlands.

Bukowski, J., L. Korn, and D. Wartenberg (1995). Correlated inputs in quantitative risk assessment: The effects of distributional shape. *Risk Analysis 15*, 215–219.

Crow, E. L. and K. Shimizu (Eds.) (1988). *Lognormal distributions: theory and application*. New York: Marcel Dekker, Inc.

Cullen, A. C. and H. C. Frey (1999). *Probabilistic Techniques in Exposure Assessment: A Handbook for Dealing with Variability and Uncertainty in Models and Inputs*. New York, NY: Plenum Press.

Decisioneering Inc. (1999). *Crystal Ball 2000 User Manual*. Denver, Colorado: Decisioneering Inc.

EC (1996). *EUSES – Technical Guidance Document in Support of the Commission Directive 93/67/EEC on Risk Assessment for New Notified Substances and the Commission Regulation (EC) 1488/94 on Risk Assessment for Existing Substances, Parts I-IV*. Luxembourg: Office of Official Publications of the European Communities.

Finley, B., D. Proctor, P. Scott, N. Harrington, D. Paustenbach, and P. Price (1994). Recommended distributions for exposure factors frequently used in health risk assessment. *Risk Analysis 14*, 533–553.

Hamed, M. M. and P. B. Bedient (1997). On the effect of probability distributions of input variables in public health risk assessment. *Risk Analysis 17*, 97–105.

Hoffmann, F. O. and J. S. Hammonds (1994). Propagation of uncertainty in risk assessment: The need to distinguish between uncertainty due to lack of knowledge and uncertainty due to variability. *Risk Analysis 14*, 707–712.

Jager, T., H. A. den Hollander, P. Janssen, P. van der Poel, M. G. J. Rikken, and T. Vermeire (2001). Opportunities for a probabilistic risk assessment of chemicals in the European Union. *Chemosphere 43*, 257–264.

Jager, T., M. G. J. Rikken, and P. van der Poel (1997). Uncertainty analysis of EUSES: Improving risk management by probabilistic risk assessment. Report 679102 039, National Institute of Public Health and the Environment (RIVM), Bilthoven, The Netherlands.

Mackay, D., W. Y. Shiu, and K. C. Ma (1999). *Illustrated Handbook of physical-chemical properties and environmental fate for organic chemicals*. CRC Press LLC. CD-Rom Version.

MacLeod, M., A. J. Frazer, and D. Mackay (2002). Evaluating and expressing the propagation of uncertainty in chemical fate and bioaccumulation models. *Environmental Toxicology and Chemistry 21*(4), 700–709.

McKone, T. E. (1993). CalTOX, a multimedia total-exposure model for hazardous waste sites. Technical Report UCRL-CR-111456, Lawrence Livermore National Laboratory, Livermore, CA, USA.

McKone, T. E., R. C. Currie, F. Chiao, and D. P. H. Hsieh (1995). Intermedia transfer factors for contaminants found at hazardous waste sites. Executive report, University of California, Davis.

Morgan, M. G. and M. Henrion (1990). *Uncertainty – A guide to dealing with uncertainty in quantitative risk and policy analysis*. New York, NY: Cambridge University Press.

NCRP (1996). A guide for uncertainty analysis in dose and risk assessments related to environmental contamination. National Committee on Radiation Programs (NCRP), Scientific Committee 64-17, Commentary No. 14.

OECD (2002). *Draft report of the OECD/UNEP Workshop on the Use of Multimedia Models for Estimating Overall Environmental Persistence and Long-range Transport in the Context of PBT/POPs Assessment, Annex 7 "Data Needs"*, Paris, France. OECD.

Pontolillo, J. and R. P. Eganhouse (2001). The search for reliable aqueous solubility (Sw) and octanol-water partition coefficient (Kow) data for hydrophobic organic compounds: DDT and DDE as a case study. Water-Resources Investigation Report 01–4201, U.S. Geological Survey.

Sachs, L. (1992). *Angewandte Statistik: Anwendung statistischer Methoden* (7th ed.). Berlin, Heidelberg, New York, Paris, Tokyo, Hong Kong, Barcelona Budapest: Springer-Verlag.

Saltelli, A., K. Chan, and H. M. Scott (Eds.) (2000). *Sensitivity Analysis*. Chichester, England: John Wiley and Sons, Ltd.

Seiler, F. A. and J. L. Alvarez (1995). Towards a new risk assessment paradigm: Variability, uncertainty, and errors. *Journal of The Franklin Institute 332A*, 221–235.

Seiler, F. A. and J. L. Alvarez (1996). On the selection of distributions for stochastic variables. *Risk Analysis 16*, 5–18.

Seiler, F. A. and J. L. Alvarez (2001). The scientific method and risk management. http://www.wmsym.org/wm98/htmq/sess07/07-01/07-01.html. (06.07.01).

Shiu, W. Y., W. Doucette, F. A. P. C. Gobas, A. Andren, and D. Mackay (1988). Physical-chemical properties of chlorinated dibenzo-p-dioxins. *Environmental Science and Technology 22*, 651–658.

Shiu, W.-Y. and K.-C. Ma (2000). Temperature dependence of physical-chemical properties of selected chemicals of environmental interest. II. chlorobenzenes, polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and dibenzofurans. *J. Phys. Chem. Ref. Data 29*(3), 1–76.

Shiu, W. Y. and D. Mackay (1986). A critical review of aqueous solubilities, vapor pressures, Henry's Law constants, and octanol-water partition coefficients of the polychlorinated biphenyls. *J. Phys. Chem. Ref. Data 15*(2).

Slob, W. (1994). Uncertainty analysis in multiplicative models. *Risk Analysis* (14), 571–576.

Solomon, K. R. and P. Takacs (2002). *Species Sensitivity Distributions in Ecotoxicology*, Chapter 15: Probabilistic Risk Assessment Using Species Sensitivity Distributions, pp. 285–313. Lewis Publishers, CRC Press LLC.

Steinbach, D. (1999). Deterministische und probabilistische Risikobewertung von Methylparathion. Master's thesis, Swiss Federal Institute of Technology, Zurich. ISBN 3-906734-13-7.

Taylor, B. N. and C. E. Kuyatt (1994). Guidelines for evaluating and expressing the uncertainty of NIST measurement results. NIST Technical Note 1297, National Institute of Standards and Technology.

Taylor, B. N. and P. J. Mohr (2002, March). Uncertainty of measurement results from NIST. http://physics.nist.gov/cuu/Uncertainty/.

Theil, H. and D. G. Fiebig (1984). *Exploiting Continuity, Maximum Entropy Estimation of Continuous Distributions*. Cambridge, Massachusetts: Ballinger Publishing Company.

Trapp, S. and M. Matthies (1998). *Chemodynamics and Environmental Modeling*. Berlin Heidelberg: Springer-Verlag.

USEPA (1994). Chemical properties for soil screening levels. Report 5629-240-03D, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina.

USEPA (1997, March). Guiding principles for Monte Carlo analysis. Report EPA/630/R-97/001, U. S. Environmental Protection Agency, Washington, DC 20460.

van de Meent, D. (1993). Simplebox: a generic multimedia fate evaluation model. RIVM Report 672720001, Rijksinstituut voor Volksgezondheid en Milieu, Bilthoven, The Netherlands.

van Leeuwen, C. J. (1995). *Risk Assessment of Chemicals: An Introduction*, Chapter 1: General Introduction, pp. 1–18. Kluwer Academic Press.

Vose, D. (2000). *Risk Analysis, A quantitative guide* (2nd ed.). Chichester, New York; Weinheim; Brisbane; Singapore; Toronto: John Wiley and Sons, Ltd.

Wania, F. (2002). *Fate and Transport of Chemicals in the Environment* (3rd ed.), Volume 17 of *Encylopedia of Physical Science and Technology*, pp. 89–105. Academic Press, San Diego CA.

Appendix A

Additional Figures

A.1 Target Mean

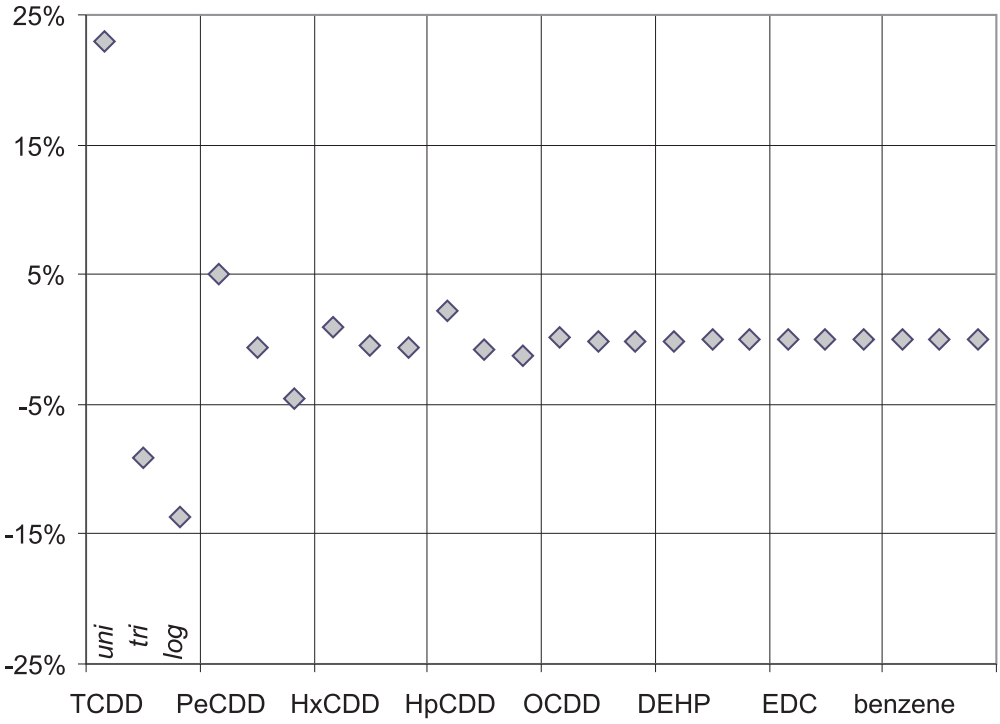

Figure A.1: Target means in soil

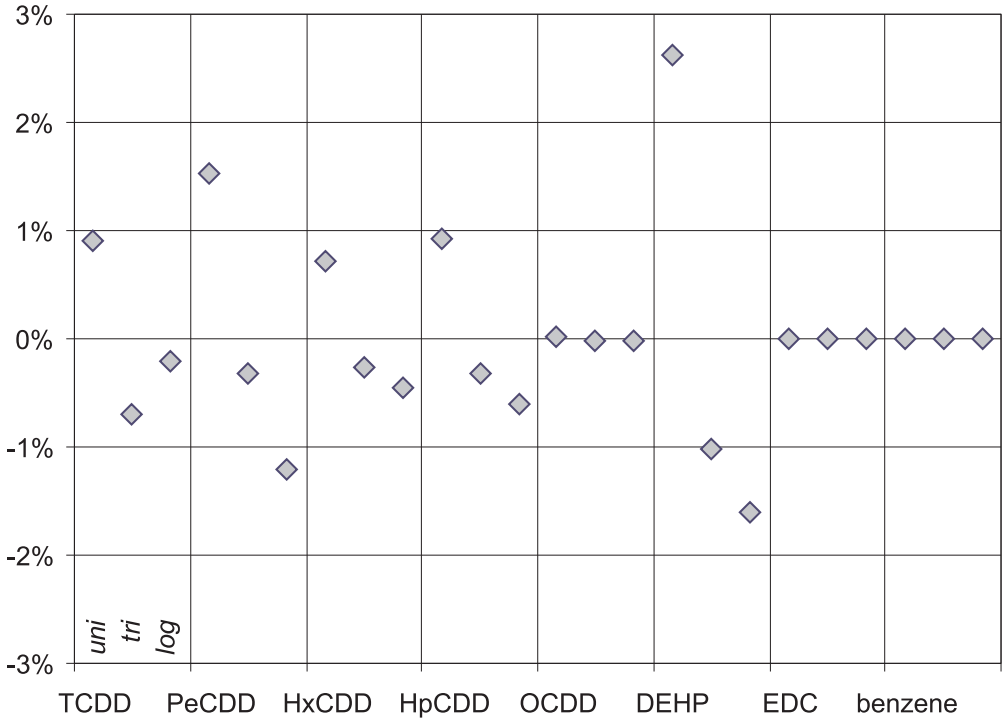

Figure A.2: Target means in water

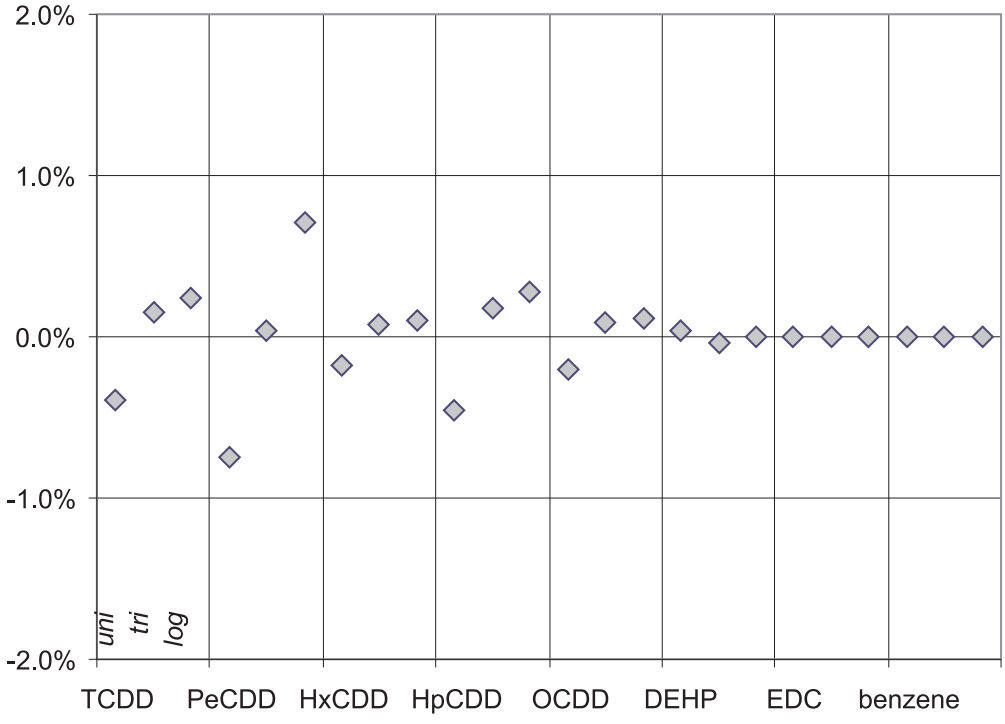

Figure A.3: Target means in air

A.2 Target Variance

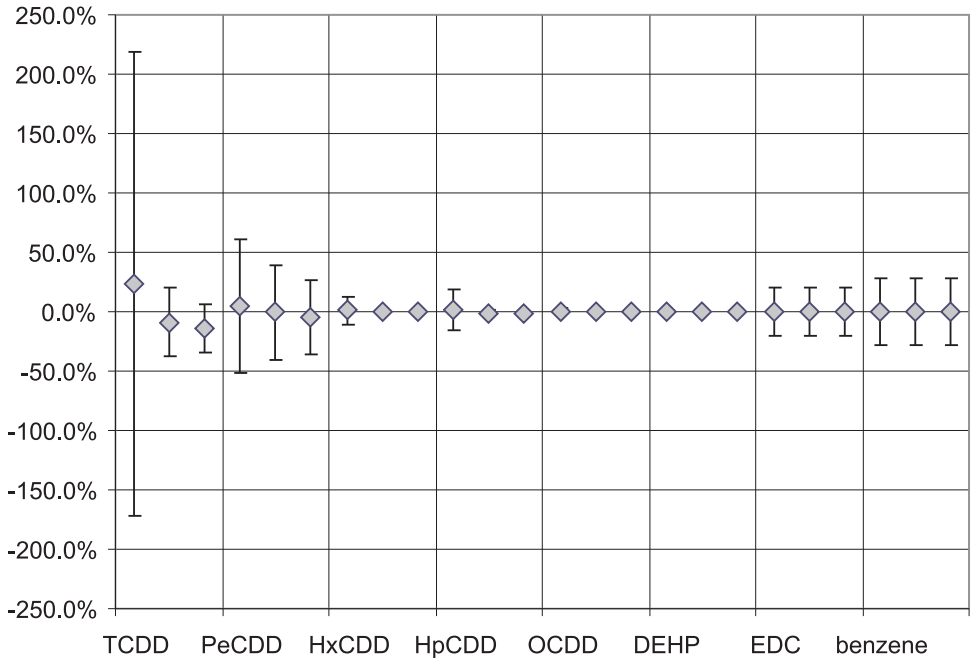

Figure A.4: Target variances in soil

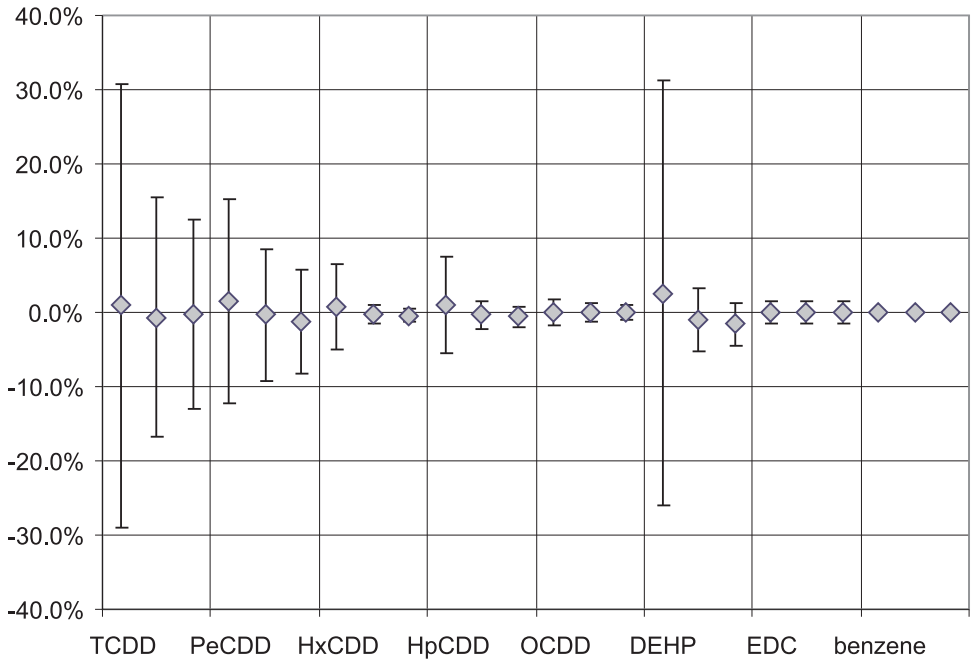

Figure A.5: Target variances in water

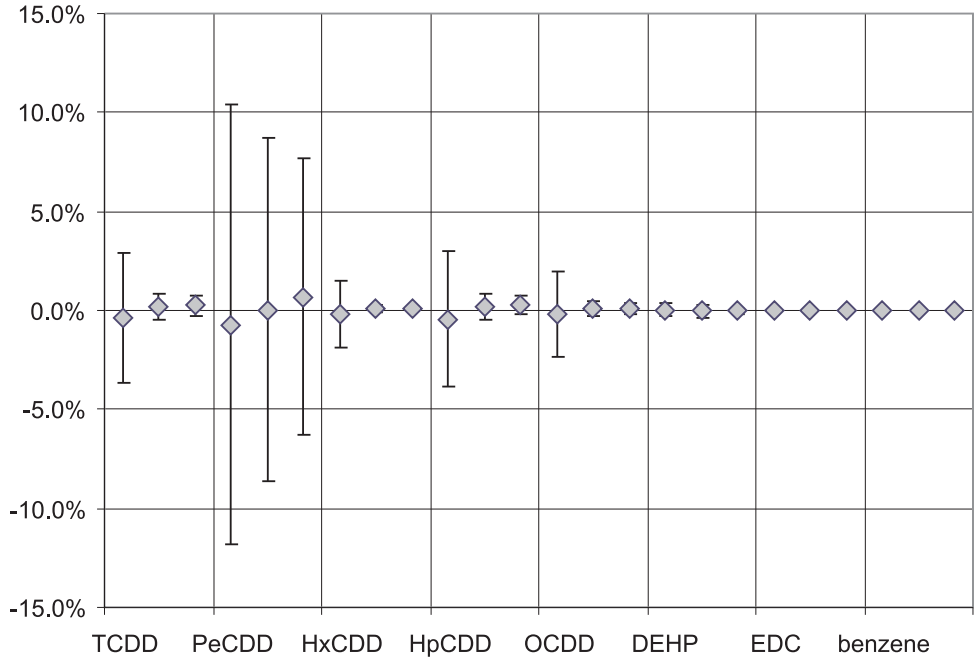

Figure A.6: Target variances in air

Appendix B

Additional Tables

Table B.1: Mode of entry (continental scale)

	emission into			
	air [%]	waste water [%]	surface water [%]	industrial soil [%]
TCDD	100	0	0	0
PeCDD	100	0	0	0
HxCDD	96	4	0	0
HpCDD	95	5	0	0
OCDD	79	21	0	0
DEHP	100	0	0	0
EDC	81	19	0	0
benzene	92	7	0	1
LAS	0	99	0	1
EDTA	0	99	0	1
HHCB	0	100	0	0

Table B.2: Mode of entry (regional scale)

	emission into			
	air [%]	waste water [%]	surface water [%]	soil [%]
TCDD	100	0	0	0
PeCDD	100	0	0	0
HxCDD	96	4	0	0
HpCDD	95	5	0	0
OCDD	79	21	0	0
DEHP	68	32	0	0
EDC	81	19	0	0
benzene	84	9	2	5
LAS	0	99	0	1
EDTA	0	99	0	1
HHCB	0	100	0	0

Table B.3: Target CV of varied input CV. Lognormal distributions are used as parameter distribution, parameterized with the *selected* value as distribution **median**, and the coefficient of variation as indicated in the table columns.

	most	**soil**			most	**water**		
	influent.	**1.0**	**2.0**	**3.0**	influent.	**1.0**	**2.0**	**3.0**
TCDD	P^0	0.65	1.04	1.16	P^0	0.38	0.60	0.72
PeCDD	P^0	0.23	0.34	0.41	K_{ow}	0.21	0.35	0.44
HxCDD	P^0	0.13	0.19	0.23	K_{ow}	0.16	0.28	0.39
HpCDD	P^0	0.03	0.05	0.08	K_{ow}	0.12	0.24	0.31
OCDD	P^0	0.01	0.02	0.03	K_{ow}	0.08	0.19	0.26
DEHP	K_{ow}	0.01	0.02	0.04	K_{ow}	0.15	0.25	0.36
EDC	S_w	1.70	2.71	3.40	S_w	0.58	1.15	1.35
benzene	K_{ow}	1.37	2.13	2.37	S_w	0.14	0.28	0.43
LAS	K_{ow}	0.75	1.24	1.52	K_{ow}	0.00	0.00	0.01
EDTA	K_{ow}	1.01	3.27	2.71	P^0	0.00	0.00	0.00
HHCB	K_{ow}	0.79	1.01	1.14	S_w	0.72	0.93	1.03
average		*0.61*	*1.09*	*1.19*		*0.23*	*0.39*	*0.48*

	most	**sediment**			most	**air**		
	influent.	**1.0**	**2.0**	**3.0**	influent.	**1.0**	**2.0**	**3.0**
TCDD	P^0	0.39	0.55	0.64	P^0	0.03	0.06	0.08
PeCDD	P^0	0.13	0.21	0.27	P^0	0.10	0.15	0.18
HxCDD	P^0	0.07	0.13	0.15	P^0	0.08	0.12	0.14
HpCDD	K_{ow}	0.02	0.05	0.08	P^0	0.02	0.04	0.06
OCDD	K_{ow}	0.02	0.06	0.08	P^0	0.02	0.03	0.06
DEHP	K_{ow}	0.14	0.20	0.24	K_{ow}	0.01	0.01	0.02
EDC	S_w	0.69	1.45	2.78	S_w	0.01	0.02	0.03
benzene	K_{ow}	0.53	1.14	1.71	S_w	0.02	0.02	0.02
LAS	K_{ow}	0.08	0.16	0.22	S_w	4.25	9.20	10.13
EDTA	K_{ow}	0.00	0.00	0.00	S_w	18.83	28.17	10.99
HHCB	K_{ow}	0.87	1.06	1.13	S_w	0.27	0.41	0.47
average		*0.27*	*0.45*	*0.67*		*2.15*	*3.48*	*2.02*

Table B.4: Target CV of varied input CV. Lognormal distributions are used as parameter distribution, parameterized with the *selected* value as distribution **mean**, and the coefficient of variation as indicated in the table columns.

	most	**soil**			most	**water**		
	influent.	**1.0**	**2.0**	**3.0**	influent.	**1.0**	**2.0**	**3.0**
TCDD	P^0	0.67	0.87	0.90	P^0	0.43	0.67	0.79
PeCDD	P^0	0.19	0.23	0.24	K_{ow}	0.22	0.38	0.46
HxCDD	P^0	0.10	0.13	0.14	K_{ow}	0.20	0.42	0.59
HpCDD	P^0	0.02	0.03	0.04	K_{ow}	0.14	0.36	0.56
OCDD	P^0	0.01	0.01	0.02	K_{ow}	0.11	0.24	0.45
DEHP	K_{ow}	0.01	0.04	0.07	K_{ow}	0.18	0.37	0.52
EDC	S_w	1.78	2.80	5.01	S_w	0.57	1.12	1.30
benzene	K_{ow}	1.59	2.36	2.71	S_w	0.13	0.31	0.42
LAS	K_{ow}	0.78	1.30	2.27	K_{ow}	0.00	0.00	0.00
EDTA	K_{ow}	1.02	2.72	5.24	P^0	0.00	0.00	0.00
HHCB	K_{ow}	0.85	1.28	1.45	S_w	0.75	0.98	1.07
average		*0.64*	*1.07*	*1.64*		*0.25*	*0.44*	*0.56*

	most	**sediment**			most	**air**		
	influent.	**1.0**	**2.0**	**3.0**	influent.	**1.0**	**2.0**	**3.0**
TCDD	P^0	0.43	0.65	0.78	P^0	0.04	0.08	0.10
PeCDD	P^0	0.13	0.24	0.32	P^0	0.09	0.12	0.13
HxCDD	P^0	0.07	0.15	0.20	P^0	0.07	0.09	0.10
HpCDD	K_{ow}	0.03	0.08	0.13	P^0	0.01	0.02	0.03
OCDD	K_{ow}	0.03	0.08	0.14	P^0	0.01	0.02	0.03
DEHP	K_{ow}	0.16	0.29	0.38	K_{ow}	0.01	0.02	0.03
EDC	S_w	0.66	1.37	2.64	S_w	0.01	0.02	0.02
benzene	K_{ow}	0.58	1.03	1.16	S_w	0.02	0.02	0.02
LAS	K_{ow}	0.07	0.11	0.18	S_w	4.98	8.95	9.88
EDTA	K_{ow}	0.00	0.00	0.00	S_w	7.14	15.07	17.96
HHCB	K_{ow}	0.90	1.26	1.35	S_w	0.27	0.38	0.42
average		*0.28*	*0.48*	*0.66*		*1.15*	*2.25*	*2.61*

Table B.5: Summary of target CV of *comparable* scenarios. Input distributions were parameterized as described in Section 4.2 (p. 52). There are no target CV for LAS, EDTA and HHCB because data was too scarce for the parameterization approach. In case of the *comparable* scenarios, CV have an upper bound of approximately 0.58.

	most	**soil**			most	**water**		
	influent.	*uni*	*tri*	*log*	influent.	*uni*	*tri*	*log*
TCDD	P^0	1.59	0.32	0.24	P^0	0.30	0.16	0.13
PeCDD	P^0	0.53	0.40	0.33	P^0	0.14	0.09	0.07
HxCDD	P^0	0.11	0.01	0.01	P^0	0.06	0.01	0.01
HpCDD	P^0	0.17	0.03	0.02	P^0	0.06	0.02	0.01
OCDD	P^0	0.02	0.00	0.00	P^0	0.02	0.01	0.01
DEHP	P^0	0.01	0.00	0.00	K_{ow}	0.28	0.04	0.03
EDC	K_{ow}	0.20	0.20	0.20	S_w	0.02	0.02	0.02
benzene	K_{ow}	0.27	0.28	0.28	S_w	0.00	0.00	0.00
LAS	P^0	—	—	—	P^0	—	—	—
EDTA	P^0	—	—	—	P^0	—	—	—
HHCB	P^0	—	—	—	P^0	—	—	—
average		*0.36*	*0.16*	*0.13*		*0.11*	*0.04*	*0.03*

	most	**sediment**			most	**air**		
	influent.	*uni*	*tri*	*log*	influent.	*uni*	*tri*	*log*
TCDD	P^0	0.27	0.16	0.13	P^0	0.03	0.01	0.13
PeCDD	P^0	0.12	0.09	0.07	P^0	0.11	0.09	0.07
HxCDD	P^0	0.06	0.01	0.01	P^0	0.02	0.00	0.01
HpCDD	P^0	0.06	0.02	0.01	P^0	0.03	0.01	0.01
OCDD	P^0	0.02	0.01	0.01	P^0	0.02	0.00	0.01
DEHP	K_{ow}	0.05	0.01	0.01	P^0	0.00	0.00	0.01
EDC	K_{ow}	0.07	0.07	0.07	S_w	0.00	0.00	0.07
benzene	K_{ow}	0.15	0.15	0.15	S_w	0.00	0.00	0.15
LAS	P^0	—	—	—	P^0	—	—	—
EDTA	P^0	—	—	—	P^0	—	—	—
HHCB	P^0	—	—	—	P^0	—	—	—
average		*0.10*	*0.06*	*0.06*		*0.03*	*0.01*	*0.06*

Beiträge des Instituts für Umweltsystemforschung der Universität Osnabrück

Nr. 1: Eberhard Umbach: Umweltverträgliches Wirtschaftssystem in den Bereichen Abfall und Emissionen. März 1997.

Nr. 2: Stefan Trapp, Bernhard Reiter, Michael Matthies: Überprüfung und Fortentwicklung der Bodenwerte für den Boden-Pflanze-Pfad - Teilprojekt Transferfaktoren Boden-Pflanze. August 1997.

Nr. 3: Michael Matthies (Hrsg.): Stoffstromanalyse und Bewertung. September 1997.

Nr. 4: Dirk Melcher: Quantifizierung, Klassifizierung und Modellierung der Phytotoxizität organischer Chemikalien. Oktober 1997.

Nr. 5: Stefan Schwartz: Organische Schadstoffe in der Nahrungskette - Vorstudie zur Validierung von Expositionsmodellen. November 1997.

Nr. 6: Volker Berding: Private Hausbrunnen - Vergleichende Bewertung von Maßnahmen zur Verbesserung der Trinkwasserqualität. Oktober 1997.

Nr. 7: Horst Malchow (Hrsg.): Modellbildung und -anwendung in den Wissenschaften I. Januar 1998.

Nr. 8: Birgit Radtke: Bifurkationen in einem Modell mariner Planktondynamik. Januar 1998.

Nr. 9: Werner Berens: Konzeption eines Umweltinformationssystems für die Universität Osnabrück. Juni 1998.

Nr. 10: Michael Matthies (Hrsg.): Studienprojekte 1998. September 1998.

Nr. 11: Michael Matthies (Hrsg.): Globaler Wandel. September 1998.

Nr. 12: Klaus Brauer (Hrsg.): Institutsbericht. September 1998.

Nr. 13: Klaus Brauer, Horst Malchow, Michael Matthies, Eberhard Umbach (Hrsg.): Materialien des Arbeitstreffens Systemwissenschaft in der Lehre, Universität Osnabrück, 29./30.9.1998. Dezember 1998.

Nr. 14: Horst Malchow (Hrsg.): Modellbildung und -anwendung in den Wissenschaften II. Dezember 1998.

Nr. 15: Horst Malchow (Hrsg.): Modellbildung und -anwendung in den Wissenschaften III. August 1999.

Nr. 16: Michael Matthies (Hrsg.): Regionale Nachhaltigkeit. September 2000.

Nr. 17: Markus Klein: Langjähriger Wasserhaushalt von Gras- und Waldbeständen. Entwicklung, Kalibrierung und Anwendung des Modells LYFE am Groß-Lysimeter St. Arnold. Juni 2000.

Nr. 18: Markus Brune: Multimediale Umweltmodellierung mit Fuzzy-Mengen. Juli 2000.

Nr. 19: Michael Matthies (Hrsg.): Fraktale in Hydrologie und Biologie. Oktober 2000.

Nr. 20: Stefan Fuest (Dissertation): Regionale Grundwassergefährdung durch Nitrat. Dezember 2000.

Nr. 21: Carsten Schulze (Dissertation): Modelling and evaluating the aquatic fate of detergents.
Januar 2001.

Nr. 22: Horst Malchow (Hrsg.): Modellbildung und -anwendung in den Wissenschaften IV. Januar 2001 (download at http://www.usf.uos.de/usf/beitraege/).

Nr. 23: Horst Malchow (Hrsg.): Modellbildung und -anwendung in den Wissenschaften V. August 2001 (download at http://www.usf.uos.de/usf/beitraege/).

Nr. 24: Kai Leßmann: Probabilistic Exposure Assessment, Parameter Uncertainties and their Effects on Model Output
November 2002 (download at http://www.usf.uos.de/usf/beitraege/).

ISSN 1433-3805

Die Beiträge können gegen einen Selbstkostenpreis (ca. 10 – 20 DM pro Exemplar) beim Institut für Umweltsystemforschung, Universität Osnabrück, 49069 Osnabrück bestellt werden.